The use of forced oscillations in heterogeneous catalysis

van Neer, F.J.R.

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FORCED OSCILLATIONS IN HETEROGENEOUS CATALYSIS

FRANK VAN NEER

Frank (fränk, fränk; Russ., Ger. fränk), n. 1. Hy, Ya M. (ël yâ’), born 1908, Russian physicist: Nobel prize 1958. 2. Le·on·hard (lâ’ön härt), 1882-1961, German novelist. 3. a boy’s given name.

van (van; Du. vân), prep. (often cap.) from; of (used in Dutch personal names, originally to indicate place of origin). [c. VON]

Neer (när), small village in the south of The Netherlands.
Forced oscillations in heterogeneous catalysis

Chapter 1  General introduction: the use of oscillations in heterogeneous catalysis

Chapter 2  Understanding of oscillation phenomena on a catalyst

Chapter 3  Direct determination of cyclic steady states in periodically forced catalytic reactions

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Franciscus Johannes Robertus van Neer
geboren te Arnhem
Promotor: prof.dr.ir. A. Bliek

Other committee members: dr.ir. H.C.J. Hoefsloot  
prof.dr. P.D. Iedema  
dr. M. Liauw  
prof.dr.ir. G.B. Marin  
dr. E.K. Poels  
prof.dr. A. Renken  
prof.dr. S.M. Verduyn Lunel

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CHAPTER 1

General introduction: the use of forced oscillations in heterogeneous catalysis

PERIODIC OPERATION OF CATALYTIC REACTORS

About 30-40 years ago, the study of unsteady state processes in catalysis was started due to two principal reasons. First, some industrial processes are unavoidably subjected to (small) variations of the reactor conditions such as reactant composition, reactor pressure and temperature. In order to be able to automatically control these processes, the dynamic characteristics of the systems had to be known. A second reason for the research of dynamic properties of catalytic processes was the observation that under unsteady state conditions productivity and/or the selectivity of the process can increase significantly compared to steady state operation (Matros, 1990).

![Diagram of periodic operation](image)

Figure 1.1. The principle of periodic operation. Operating conditions are varied within a certain range. Performance under periodic operation may differ significantly from steady state operation within the range of variation.

The pioneering work on a special type of unsteady state operation, the periodic variation of operating variables, was performed by Douglas in 1967. He showed that the reaction rate of a chemical reaction in a stirred tank can be improved by periodic operation. The principle of periodic operation is illustrated in figure 1.1. When a system variable, the forcing variable, is varied by a so-called forcing function, the time averaged performance, like the reaction rate, may be higher than the highest performance under steady state conditions.
Periodic operation of catalytic reactors may offer also other benefits than reaction rate enhancement. The main categories of possible applications of dynamic reactor operation are summarised below.

Circulating catalysts

The most widespread application of periodic operation is based on the concept of circulating a catalyst between a converter in which the desired reaction takes place and a catalyst regenerator. Catalytic cracking of hydrocarbons is performed in such a system as during this reaction extensive coke deposition takes place and the catalyst rapidly loses activity. This necessitates an on-line regeneration, an oxidation step, to restore the catalyst activity. In principle this type of periodic operation is similar to the type in which reactant concentrations at the inlet of a reactor are varied in time. The variations in the feed concentrations are brought about by circulating the catalyst. The catalyst is moved from one reactor to another with different feed compositions.

In various catalysed oxidations such as the oxidation of n-butane to maleic anhydride, first oxygen penetrates the catalyst and subsequently the oxidation of the hydrocarbons takes place on the surface. In excess of oxygen the hydrocarbons tend to oxidise to CO or CO₂ which has a negative effect on the selectivity. For this reason, oxygen loading and hydrocarbon oxidation are separated and the catalyst is continuously circulated between these two reaction stages. The concept of this type of periodic operation is equal to the previous one. A riser reactor combined with a separate regenerator shows significant improvement for n-butane oxidation compared to conventional reactor systems (Contractor et al., 1987). Other catalytic reactions showing the same effect under periodic operation are oxidative synthesis of aromatic nitriles (Sze and Gelbein, 1976) and oxidation of o-xylenes (Ivanov and Balzhinimaev, 1990).

Periodic flow reversal in order to utilise reaction heat

Since the proposal of Boreskov et al. in 1977 to use periodic flow reversal in fixed bed reactors for efficient heat recovery, much research has been performed in this field. Most of it is done by Matros and coworkers (see for instance the review article written by Matros in 1996). This kind of periodic operation allows autothermal reactor operation even for reactions with a low adiabatic temperature rise. Its principle is simple. Feed having a temperature below where reaction takes off, is introduced in a preheated reactor which is placed in a system as
presented in figure 1.2. Suppose that valve 1 and 4 are open. The feed is rapidly heated by the first part of the bed and the reaction starts. The conversion and temperature rise rapidly and the initial reactor temperature is exceeded. This front of high conversions and temperatures moves towards the end of the reactor while the inlet of the reactor is cooled by the feed. As soon as the heat front has reached the exit of the reactor the flow is reversed (now valve 2 and 3 are open). The heat front is used to preheat the fresh feed and again the reaction takes off. When these switches are periodically imposed, finally the situation will be obtained as presented in figure 1.3. The heat is captured in the catalyst bed which results in an improved performance.

![Figure 1.2. Catalytic fixed bed reactor with periodic flow reversal. Either valve 1 and 4 are open or valve 2 and 3.](image1)

![Figure 1.3. Example of a temperature profile present in the cyclic invariant state during periodic flow reversal. 0 to 3 denote the progress within a half-cycle.](image2)

Implementation of the reversed flow system in industry was realised in various plants. At this moment 10 industrial SO$_2$ oxidation reversed flow units are in use (see for instance Grozev et al., 1994). One full scale reversed flow NO$_x$ reduction plant has been operating in Russia since 1989 (Matros, 1996 and Noskov et al., 1993).

**Periodic flow reversal in order to by-pass the thermodynamic equilibrium limitations**

Reversed flow can also be used for catalytic reactions which are (strongly) equilibrium limited. Vanden Bussche and Froment (1996) worked on methanol synthesis and Kolios (1997) has extensively investigated styrene synthesis out of ethylbenzene. In both cases cocurrent temperature and product concentration slopes along the reactor are favourable for the reaction rate. The equilibrium limited endothermic reaction in which ethylbenzene is dehydrogenated to styrene shows in a conventional industrial adiabatic reactor loaded with an
iron catalyst a conversion of approximately 50% (95% selectivity). By the combination of an endothermic reaction and an adiabatic reactor, the temperature is typically the highest at the reactor inlet whereas the conversion close to the inlet is far from its equilibrium value. Along the reactor the equilibrium conversion is shifted to lower values by the temperature decrease while the conversion increases rapidly by the proceeding reaction. Kolios (1997) showed that by application of the reversed flow concept at least in a part of the reactor an inclining temperature profile (see figure 1.3) goes along with an increasing conversion. This results in a conversion of 80% (90% selectivity) and offers a major improvement in styrene production.

**Variable volume operation**

Stankiewicz and Kuczynski (1995) mentioned in their review article a remarkable type of periodic operation, completely different from those discussed in the previous paragraphs. They suggest to vary the reaction volume of a stirred tank reactor via a forcing function as presented in figure 1.4. The periodic cycle is divided in four parts: the feeding period, the batch period (reaction volume at its maximum), the discharge period and the rest period (reactor volume at its minimum). This mode allows semibatch operation and can be used for two purposes: (i) converting a batch process into a continuous one without losing the benefits of its batch-nature whilst at the same time reducing its typical disadvantages (emission problems) and (ii) manipulating the reactor characteristics over the entire range between CSTR and plug flow reactor. Various types of reactions can be carried out in the same reactor vessel which is particularly important for multi-purpose fine-chemical plants.

![Figure 1.4. The forcing function used during variable volume operation (Stankiewicz and Kuczynski, 1995).](image)

It is shown in the work of Stankiewicz and Kuczynski that for a fine-chemical process the production can be increased by 33% compared to normal operation in a CSTR. In the limiting case where the whole reaction volume is exchanged during one period, the optimum operating point of a three vessel cascade of equal volume can be exceeded by one periodic operated
semi-batch reactor. In addition, variable volume operation can improve the operational flexibility in multipurpose plants.

**Pressure swing reactor**

The pressure swing reactor is developed for carrying out simultaneously reaction and separation of desired products. The reactor is loaded with an admixture of a catalyst and a sorbent in order to selectively remove a reaction by-product. The sorbent is periodically regenerated by a purge gas which is introduced at a pressure lower than the reaction pressure. Using this concept high conversions in an endothermic equilibrium-controlled reaction can be achieved while operating the reactor at a lower temperature compared to a plug-flow reactor packed with a catalyst alone. Carvill *et al.* (1996) showed that the reverse water-gas shift reaction for production of CO, is perfectly suited for this type of periodic operation. At this moment it is investigated by Kodde and Bilek (1997) whether this concept also gains profitable results in case of consecutive reactions like hydrogenation of acetylenes.

**Periodic variation of reactor inlet conditions in order to derive true kinetics**

Surface processes on a heterogeneous catalyst are extremely complex. A good understanding of these processes is useful for catalyst development and reactor optimisation. Often steady state experiments are conducted to model stationary processes. Model parameters obtained under steady state conditions are in general lumped and therefore information concerning the kinetics of the elementary catalytic steps is missing. Information gained from steady state data is therefore not suitable for predicting the behaviour of a catalytic system under transient conditions, for example under periodic operation.

Extra information is obtained when time-resolved data are monitored, like is done in step-response and Temporal Analysis of Products (TAP) experiments. Forced concentration oscillation (FCO) experiments, a type of periodic operation, can be viewed on as an extension of step-response experiments. Instead of imposing one change in reactant concentration to a catalytic system, multiple changes in time are imposed in case of FCO experiments (see figure 1.5). By the complexity of the responses, interpretation of FCO results and modelling of the catalytic reaction is more difficult compared to step-response experiments. However, more information can be obtained from one single experiment. Before the cycle invariant state has been reached, *i.e.* before a response is equal to the response of the previous period, every cycle
starts at different initial catalyst conditions. This is profitable for research into the mechanism of a catalytic reaction, as is demonstrated in Van Neer et al. (1997). Some researchers even state that for certain types of catalytic reactions, discrimination between alternative mechanistic models is only possible on basis of forced concentration oscillation experiments. An example is given by Renken (1990), in which the catalytic addition of acetic acid to ethylene is kinetically described. Other illustrations of kinetic modelling using forced oscillations are the dehydration of ethanol to ethylene on γ-alumina (Golay et al., 1997) and N₂O reduction by CO over Pt (Sadhankar and Lynch, 1994).

![Figure 1.5. Forced concentration oscillation experiments: an extension of step-response experiments.](image)

**Periodic variation of reactor inlet conditions for better selectivity or productivity**

As mentioned before, periodic operation by means of varying reactor inlet conditions may improve the performance of a catalytic reactor. Many examples can be found in literature; a few of them will be brought up here. In the discussion of the various examples the improvements as claimed by the authors will be presented. In view of the discussion which is addressed in the next section concerning the diversity of reference steady state rates which can be used to estimate rate enhancement, some carefulness is advised in the interpretation of the improvements presented below. One did not always use the same type of reference steady state.

One of the first interesting results using periodic variation of inlet conditions, was found during catalytic CO oxidation. Abdul-Kareem et al. (1980) show in their work that on V₂O₅ almost 100% reaction rate improvement can be obtained compared to the steady state reaction rate at the average of the forcing variable. The P₉/P₉₂ ratio was varied with a period of 20
min to achieve this remarkable enhancement. No explanation is given for the observed phenomena, however it is suggested that bulk-surface interactions play an important role as the optimal forcing frequency is low compared to the surface reaction kinetics.

Zhou and coworkers (1986) present one of the highest rate enhancements ever found by periodic operation. During CO oxidation on Pd/Al₂O₃ rates can be improved compared to the "best steady state rate" by a factor of 44. The quotation marks already indicate that this rate enhancement is disputable, as will be explained in the next section. Bang-bang type forcing functions were applied which means that subsequently CO and O₂ were fed to the reactor as demonstrated in figure 1.6. Optimal performance for this system is obtained when the period is approximately twenty seconds and 30% of the cycle time is used for feeding CO and 70% is used for O₂ supply. The large improvement could not be explained by Langmuir-Hinshelwood alike mechanistic models. Zhou and coworkers introduce a mechanism which is based on the existence of islands on the catalyst containing either adsorbed CO or O₂. They propose that under steady state these surface islands are rather large and contain less "energetic" CO and O whereas at periodic operation these islands are numerous but smaller and contain highly energetic CO and O. Reaction is believed to occur at the boundaries of these islands. In view of the above, much higher rates can be expected under periodic operation. Figure 1.7 illustrates the suggested mechanism.

![Figure 1.6. Forcing function of a bang-bang type periodic operation in which the reactor inlet concentrations are varied.](image)

![Figure 1.7. Mechanism as proposed by Zhou et al. (1986) concerning periodic operation of CO oxidation on Pd/Al₂O₃. The catalyst surface filled with islands of CO and O is schematically drawn.](image)

In the work of McNeil and Rinker (1994) methanol synthesis is scrutinised. Commercial methanol synthesis catalysts were subjected to pure component cycling. CO and H₂ were subsequently fed to the reactor in the presence of a small amount of CO₂ (2-3%). The time
averaged rates obtained in this way were compared with the highest rate possible under steady state thereby always using the relation \( y_{CO} + y_{H2}(+y_{CO2}) = 1 \). Steady state reaction rates of the catalytic system in which CO and/or H\(_2\) are diluted, were not analysed for comparison. In this way, the highest rate enhancement achievable is found to be 25\% at commonly applied methanol synthesis conditions. No explanation for the observed phenomena was given by the authors.

An example in which selectivity plays a key role, can be found in partial oxidation of propylene to acrolein and acrylic acid (Saleh-Alhamed et al., 1992). The oxidation to CO\(_2\) is undesired and can be limited by oscillating the inlet propylene concentration. Under commercially applied conditions, selectivity enhancements of 40\% for acrylic acid and 75\% for acrolein are reported when a period of 1-2 min is used. The cycling of propylene keeps the catalyst in a high oxidation state. As lattice oxygen is assumed to be involved in selective oxidation of propylene and radical surface oxygen is responsible for CO\(_2\) formation, a high oxidation state is profitable.

Many other examples can be found in literature. They are listed in the section of this chapter addressing the insides of forced concentration and temperature oscillations in heterogeneous catalysis.

**Vibrational control**

Periodic operation can also be used to modify the kinetic behaviour of a catalytic system in such a way that self-oscillations or instabilities disappear. It may be used in case (chaotic) self-sustained oscillations are undesired and these dynamic responses can not be reduced to an acceptable level by a proportional integral or non-linear feedback control. A sinusoidal vibration on the CO and O\(_2\) flow rates reduces the amplitude of self-sustained CO\(_2\) concentration oscillations on Rh/\(SiO_2\) to one-tenth compared to steady state operation (Qin and Wolf, 1995). Figure 1.8 represents one of the results of Qin and Wolf which clearly shows the effect of periodic operation. The self-oscillations on the Rh catalyst are driven by cooling and reignition processes and the vibrating feed interferes in these surface processes by reducing the extinction and reignition temperatures.
PERIODIC OPERATION: DEFINITIONS AND COMPARISON WITH STEADY STATE OPERATION

Bailey (1977) defined four regions of periodic operation which depend on the period of the oscillations ($T_p$) and the characteristic relaxation time of the system ($T_c$), which in turn is determined by the kinetics of the catalytic reaction steps:

1. **Process-life cycle** ($T_p \gg T_c$). In the long-term operational cycle of many chemical processes deterioration of the catalyst occurs which necessitates shutdown and regeneration of the catalyst. In principle this can also be viewed on as a periodic cycle, however the imposed oscillations are unintentional and their period is very long. Therefore, this class does not fall under the type of periodic operation discussed in this thesis.

2. **Quasi steady state operation** (QSS, $T_p > T_c$). In this case the oscillations are intended and their period is large compared to the response time of the system. Consequently, within a period the reactor operates primarily in the steady state. The performance, the time averaged reaction rate, is just the average of all steady state rates of the conditions passed through.

3. **Intermediate periodic operation** ($T_p = T_c$). The period is in the order of magnitude as the relaxation time of the system and therefore the reactor operates (almost) continuously in a transient state. In this regime the actual reaction rate may vary considerably in time. The performance depends on both the equilibrium and the dynamic properties of the system. Hence, this range of periodic operation is of particular interest.

4. **Relaxed steady state operation** (RSS, $T_p < T_c$). The forcing variables are changed very rapidly compared to the kinetics of the system. The reactor is no longer able to respond to the forced oscillations and consequently it behaves as if the system is operated under steady state. Applying concentration as forcing variable, this will often lead to a relaxed steady state rate equal to the steady state rate obtained at the average of the forcing variable.
As pointed out above, the oscillation frequency (or period) is an important parameter. Often results are presented as time averaged performance versus frequency. When in the trajectory going from quasi steady state at low frequencies to relaxed steady state at high frequencies a non-monotonically ascending or descending development of the time averaged reaction rate is observed, we speak of resonance. The reaction rate at the resonance frequency is often higher than the quasi and relaxed steady state reaction rate. However, this is not a guarantee that the resonance reaction rate is higher than the optimal steady state rate. In this thesis the optimal steady state rate is defined as the highest steady state rate attainable within the range between the upper and lower value of the forcing variable used under periodic operation. This means that when the fraction of one component is forced between 0 and 1 and the fraction of another component is complementary, one should seek for the best steady state condition using all possible combinations of fractions of both components between 0 and 1 (using $\Sigma y_i \leq 1$). An inert third component may be introduced where necessary. Whenever under these circumstances the periodic operation mode results in a better performance, than it is sure that the catalyst produces more of the desired product per unit of time than ever will be possible under steady state conditions. This point of discussion is also addressed in detail by Nowobilski and Takoudis (1986).

An example related to this discussion can be found in work of Zhou et al. (1986). They state in their work that a comparison is made of the reaction rate under FCO with the best steady state reaction rate achievable using the same temperature and flow rate. However, they just used one concentration for CO and O$_2$ for comparison, namely the concentration also used in the FCO experiments. The authors did not investigate the steady state reactions in between the upper and lower values of the forcing variables. Possibly, the tremendous rate enhancement which was found, could partly be explained by the comparison with the non-optimal steady state.

In practise reasons may exist that exclude operation at the optimal steady state. So, there are motives that justify comparison of periodic operation with other steady states. For instance, when the reaction should be performed stoichiometrically in view of separation problems afterwards. It is also possible that the optimal steady state is only found in a very small range of conditions. This means that at these conditions the catalytic system is very sensitive to small perturbations. Periodic operation may assist in remaining close to optimal performance without having a high sensitivity to small changes. The use of periodic operation for this purpose is closely related to vibrational control.
From the above can be concluded that it is important to point out which steady state has been taken for comparison and for what reason.

**FORCED CONCENTRATION AND TEMPERATURE OSCILLATIONS**

The work described in this thesis handles the application of forced concentration and temperature oscillations in heterogeneous catalytic systems. As mentioned before, these types of periodic operation can be used in order to

- enhance the reaction rate
- improve the product selectivity
- control a catalytic system, lower its parametric sensitivity
- elucidate the microkinetic mechanism of a catalytic reaction

In most of the work performed in this field it is aimed to illustrate the first two objectives by means of applying FCO. In addition to the examples given in the first section, many more catalytic reactions were scrutinised and found to show improved performance under imposed concentration oscillations. Table 1.1 gives an overview of catalytic reactions for which rate or selectivity improvement is claimed under forced concentration cycling.

**Table 1.1. An overview of catalytic reactions for which rate or selectivity enhancement is claimed by the researchers under FCO (Silveston, 1995 and Matros, 1996).**

<table>
<thead>
<tr>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol dehydration to diethyl ether</td>
</tr>
<tr>
<td>ethylene oxidation</td>
</tr>
<tr>
<td>SO$_2$ oxidation</td>
</tr>
<tr>
<td>synthesis of ammonia</td>
</tr>
<tr>
<td>Fischer-Tropsch synthesis</td>
</tr>
<tr>
<td>ethylene hydrogenation</td>
</tr>
<tr>
<td>ethylacetate production from acetic acid and</td>
</tr>
<tr>
<td>ethylene</td>
</tr>
<tr>
<td>hydrogenation of butadiene to butane</td>
</tr>
<tr>
<td>CO oxidation</td>
</tr>
<tr>
<td>benzene oxidation to maleic anhydride</td>
</tr>
<tr>
<td>Claus reaction</td>
</tr>
<tr>
<td>methanol synthesis</td>
</tr>
<tr>
<td>styrene polymerisation</td>
</tr>
<tr>
<td>propylene oxidation to acrolein</td>
</tr>
</tbody>
</table>

This list contains a diversity of catalytic reactions. The question rises on what basis these reactions were selected for application of forced oscillations as this information is absent in the publications in which the experimental results are presented. It can be concluded that the reactions listed in table 1.1 are found by coincidence. Apparently, the possibility to a priori determine the feasibility of obtaining favourable results for a given catalytic reaction is still
lacking. This lack of predictability of the behaviour of systems under forced concentration oscillations forms a major drawback in the practical application of this type of periodic operation.

In the field of forced temperature oscillations (FTO) not much work has been performed possibly due to the difficulty in applying this type of periodic operation in real chemical processes. Fast heating and cooling of a catalyst is rather cumbersome. However, recently a promising microstructured reactor was presented which, among others, can be used for rapidly heating and cooling of a catalyst. In figure 1.9 a simplified view is shown of a microstructured reactor which contains channels loaded with catalyst (Von Zech and Hönicke, 1998). One of the advantages of this reactor is the enormously enhanced heat transfer. By changing the heat transfer medium rapidly, fast temperature oscillations of the catalyst can be accomplished. This reactor may initiate further research into the application of temperature oscillations.

Figure 1.9. Schematic view of a microstructured reactor (Von Zech and Hönicke, 1998).

The limited number of articles which are published on temperature oscillation, deal mostly with homogeneous catalytic reactions. Only one article deals with temperature oscillations imposed on a heterogeneous catalyst. Denis and Kabel (1970) investigated dehydration of ethanol to diethyl ether catalysed by cation exchange resin. They used temperature step-response experiments to simulate the response towards FTO. Reaction rate enhancement was found compared to the steady state reaction rate at the average temperature used under FTO. Despite the discussion in their article about the fact that a fair comparison would be accomplished by using the steady state reaction rate which is found at the highest temperature applied in the FTO, they did not calculate the enhancement in this way.
A few researchers have attempted to address the fundamentals underlying resonance, whose existence is a prerequisite for the occurrence of rate enhancement. Feimer et al. (1982) studied Langmuir-Hinshelwood alike mechanistic models in which also Eley-Rideal reaction steps were incorporated. Their general conclusion is that Langmuir-Hinshelwood adsorption-desorption models cannot describe rate enhancement and therefore fail to predict experimental observations. As a reaction to this article Lynch (1984) published results of LH adsorption-desorption models which differ from those used by Feimer as no Eley-Rideal mechanistic steps were included. Dissociative adsorption of one of the reactants was assumed. Lynch stated that reaction rates far beyond steady state rates are obtained. However, he compared the resonance reaction rate with the QSS and RSS reaction rate instead of the optimal steady state (see the discussion in the previous section). Thullie et al. (1987a, 1987b) used Eley-Rideal surface kinetics and concluded that for this type of reactions only reaction rate enhancement compared to the optimal steady state can be obtained when non-linear kinetics are used. Their work is discussed in more detail in chapter 4 of this thesis.

Despite the interesting results obtained by the above mentioned researchers, their work does not enlighten the underlying mechanism of resonance phenomena observed under forced oscillations. As will be concluded in this work, revealing transient phenomena on a catalyst demands an approach in which catalyst surface occupancies are monitored in time under imposed oscillations. Steady state behaviour as well as single component sorption kinetics must be studied thoroughly in order to predict the behaviour of a catalytic system and to generalise its response under transient conditions. The latter is never used in previous work done in this field.

SCOPE OF THIS THESIS

In view of the points discussed above, the aim of the study presented in this thesis is to get insight into the mechanism underlying resonance phenomena, observed under forced concentration and temperature oscillations on a catalyst. In chapter 2 the objective is to formulate conditions for the occurrence of resonance by using a relatively simple Langmuir-Hinshelwood alike model. It is revealed which methodology must be followed in order to find out whether a given catalytic reaction will show resonance under forced concentration and temperature oscillations. As not much research has been performed into the merits of temperature oscillations, the potential of applying this type of periodic operation is presented as well.
The analysis of microkinetic models under forced oscillations, demands numerical integration as analytical solutions of the system equations are often non-existent. Whereas numerical analysis is effective in establishing the nature of response behaviour, it does not easily allow interpretation and often takes much computational effort. A promising method to investigate the response of non-linear systems towards periodic square wave cycling was proposed by Lyberatos and Svoronos (1987) and is based upon Carleman Linearisation. Carleman Linearisation has major advantages, as analytical expressions are derived for the time-averaged performance. It provides a direct method to obtain the periodic steady state, eliminating the necessity of successive numerical integration to convergence to the cycle invariant state. Chapter 3 aims to demonstrate the use of Carleman linearised systems in case of periodically forced catalytic systems. As little attention has been paid so far to limitations of the use of Carleman Linearisation, this issue is addressed as well. The applicability window of CL is discussed and appropriate conditions for its use are formulated.

Chapter 4 can be viewed on as an extension of chapter 2. More complex models are investigated with regard to their behaviour during periodic forcing. Carleman Linearisation is frequently used in the analysis. Emphasis is put on the role of multiplicity, spillover and Eley-Rideal kinetics on the response of heterogeneous catalytic systems under concentration programming. The impact of these mechanistic characteristics on the ability of a system to show resonance is discussed. An underlying purpose of this work is to verify whether reaction rates higher than the optimal steady state reaction rate can be obtained using Langmuir-Hinshelwood alike mechanistic models.

In contrast to the work presented in chapter 2-4, the other chapters in this thesis deal with experimental studies using forced concentration oscillations. Less attention has been paid in literature to other objectives of the use of FCO besides reaction rate and selectivity improvement. These remaining objectives are emphasised by means of chapter 5 and chapter 6.

In chapter 5 the merits of periodic operation in mechanistic studies is underlined. The mechanism of the oxidation of alumina supported Cu during CO oxidation is elucidated by means of using forced concentration oscillations of CO and O₂. In combination with other powerful tools like isotopic labelling and transient FTIR, a proposal for the complete mechanistic scheme is presented which also includes the reduction mechanism based on results of previous research done on this reaction.
Chapter 6 provides insight in the feedback mechanism underlying self-oscillations on supported Pt during CO oxidation. Knowing the fundamentals behind self-oscillations is step 1 in controlling them. To that end, a transient FTIR study is applied to unravel the processes that take place on the catalytic surface. Experiments combined with simulations finally result into a proposal for periodic operation which is able to suppress self-oscillations. It is shown that the suggested mode of concentration forcing stabilizes the catalytic system, thereby demonstrating another goal for the use of forced oscillations in heterogeneous catalysis.

Some overlap between the chapters was inevitable as most chapters have been written in forms suitable for publication in international scientific journals. This may also cause unavoidable differences in the nomenclature.

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CHAPTER 2

Understanding of resonance phenomena on a catalyst under forced concentration and temperature oscillations*

ABSTRACT

Resonance is an interesting phenomenon that may be observed for reactions on catalytic surfaces during periodic forcing of operating variables. Forcing of the variables for non-linear systems may result in substantially changed time averaged behaviour. These resonance phenomena have been observed experimentally by coincidence rather than by systematic analysis. It is not clear for what type of reaction kinetics such behaviour may be expected and predictions are therefore impossible. Clearly, this forms a serious obstacle for any practical application. In this chapter it is set out to analyse the nature of resonance behaviour in heterogeneously catalysed reactions. A Langmuir-Hinshelwood microkinetic model is analysed. It is demonstrated that for weakly non-linear forcing variables, as inlet concentrations, forcing leads to resonance phenomena in terms of the reaction rate only in case high total surface occupancies exist in the steady state. In contrast, forcing of strongly non-linear variables, like temperature, may give rise to resonance phenomena for both low and high surface occupancies. Necessary conditions for resonance to occur are derived.

* This work has been published in: F.J.R. van Neer, A.J. Kodde, H. den Uil and A. Blick, The Canadian Journal of Chemical Engineering 74, 664 (1996).
INTRODUCTION

Improvements in time-averaged production rates and in the selectivity of chemical transformations by unsteady-state periodic operation of non-linear chemical processes have been of interest for more than three decades. Experimental studies demonstrating rate enhancement and selectivity improvement have been carried out on e.g. CO oxidation over noble metals and oxide catalysts (Silveston, 1991), partial oxidation of propylene (Saleh-Alhamed et al., 1992) and methanol synthesis (McNeil et al., 1994). Unsteady state behaviour is interesting for a number of reasons. The possibility of process improvements by periodic operation is now well established on theoretical and experimental grounds. Apart from this, unsteady state analysis has long been used in kinetic studies for model discrimination and parameter estimation. For instance, Renken and Thullie (1990; 1993) showed that forced concentration oscillations may be superior in discriminating between various microkinetic models. As demonstrated by these authors in case of the catalytic addition of acetic acid to ethylene and in case of catalytic elimination reactions, model discrimination is not possible on basis of steady state and step-response experiments only. Interestingly, in a recent study Qin and Wolf (1995) demonstrated for CO oxidation over Rh catalysts that forced periodic oscillations can be used to simultaneously suppress self-oscillations and to obtain an enhancement of the time averaged reaction rate. Whereas numerous studies are now available demonstrating the occurrence of resonance phenomena in case of periodically forced catalytic reactions in case of a known system, the possibility to a priori determine the feasibility of obtaining favourable results for a given catalytic reaction is still lacking. In other words, the generic basis for predicting resonance is absent. Obviously, this lack of predictability of the behaviour of systems under periodic control forms a major drawback in the practical application of resonance phenomena.

One of the problems in analysing the behaviour of a catalytically active system towards forced oscillations is the difficulty in interpreting the response. For this reason we have started with a comparatively simple Langmuir Hinshelwood type reaction mechanism, focusing on both a weakly non-linear and a strongly non-linear forcing variable. Simultaneously, we have investigated the analysis based upon Carleman Linearisation of the governing equations, as proposed by Lyberatos et al. (1987). In principle, Carleman Linearisation has great advantages as now an analytical expression may be derived in the time averaged performance measure in case of square wave input cycling. In view of the large number of system parameters involved, the use of analytical expressions can be far more efficient and enlightening than a numerical analysis.
Resonance behaviour is explained by analysing the surface occupancies of reactive species in time. Generalised rules for its occurrence are given. Finally, some first results obtained using Carleman Linearisation, are compared with numerical integration results and briefly discussed.

**THEORY**

**Kinetic mechanism and mathematical model**

The hypothetical mechanism for the overall reaction $A+B \rightarrow C$, following a relatively simple molecular sorption model, is given by:

\[
\begin{align*}
A + S & \rightleftharpoons AS & k_1, k_{-1} \\
B + S & \rightleftharpoons BS & k_2, k_{-2} \\
AS + BS & \rightarrow C + 2S & k_3
\end{align*}
\]

The dynamic behaviour of the surface species for this model can conventionally be described by the following equations assuming all reactions to be first order in reactive species:

\[
\begin{align*}
\frac{d\theta_A}{dt} = & \quad k_1 \ C_A \ (1-\theta_A - \theta_B) - k_{-1} \ \theta_A - k_3 \ \theta_A \ \theta_B \\
\frac{d\theta_B}{dt} = & \quad k_2 \ C_B \ (1-\theta_A - \theta_B) - k_{-2} \ \theta_B - k_3 \ \theta_A \ \theta_B
\end{align*}
\]

In the analysis we implicitly assume the gas-phase to be of an infinite volume. Thereby limiting ourselves to the phenomena on the catalytic surface and neglecting the impact of sorption and reaction on the gas phase composition. The overall reaction rate is given by:

\[
r = k_3 \ \theta_A \ \theta_B
\]

The forcing variables used in the simulations are the concentration of component A in the gas phase and the temperature of the total system. The concentration was varied by the following square wave forcing function:
The concentration of component B was taken as $0.3 \text{ mol/m}^3$ and is held invariant in the concentration forcing simulations. Temperature waves were generated by:

$$T(t) = 600 \text{ K} + \begin{cases} -100 \text{ K}, & t \in [jP, (j+\frac{1}{2})P] \\ 100 \text{ K}, & t \in [(j+\frac{1}{2})P, (j+1)P] \end{cases}$$

The partial pressures of A and B were 1000 Pa in case of temperature oscillations. The kinetic constants of the model were conventionally taken to be of an Arrhenius-type, thereby rendering temperature a highly non-linear forcing variable:

$$k_i = k_{i,0} \exp \left( -\frac{E_i}{RT} \right)$$

For both under forced concentration oscillations as well as under temperature oscillation, the time averaged rate is given as:

$$\langle r \rangle = \frac{1}{P} \int_{t_{po}}^{t_{po}+P} r(t) \, dt$$

The term resonance is used when the time averaged rate vs. frequency is not a monotonically ascending or descending function when going from quasi steady state at low frequencies to relaxed steady state at high frequencies. Often at resonance frequencies the time averaged rate exceeds the limits of the relaxed steady state and the quasi steady state rate.

Rate enhancement under forced oscillations is understood to indicate a situation where the average rate not only exceeds the quasi and relaxed steady state rate but also the optimal steady state within the boundaries of the forcing parameter. The rate enhancement factor is therefore defined as:
Integration methods

Average rates and surface occupancies in time are presented when two successive cycles of the forcing parameter gave the same simulation results. A proper criterion for this periodically stable situation is difficult to obtain. It is nevertheless highly important in avoiding misinterpretations of the simulation results. Therefore two different integration methods were used in the simulations.

The first method is the commonly applied Runge-Kutta Fehlberg 45 integration algorithm (Sewell, 1988). Calculations with the embedded fourth order method are compared to results of the fifth order Runge-Kutta algorithm and integration time-steps were lowered when the relative difference did not fulfil the required accuracy. Simulation results are assumed to be periodic when the following criterion is met:

\[
\frac{100}{\sum_{j=1}^{100} \left( \frac{\text{rate}(1 + \frac{1}{100} jP) - \text{rate}(1 + \frac{1}{100} (1 + \frac{1}{100} jP))}{\text{rate}(1 + \frac{1}{100} jP)} \right)^2} \leq C
\]

2.9

At high frequencies C equals $10^{-5}$·P and at low frequencies C was set at $10^{-10}$.

Another method to solve the set of non-linear differential equations, is based on a linearisation developed by Carleman (1932). Lyberatos and Svoronos introduced this linearisation in the chemical engineering community (Lyberatos and Svoronos, 1987). It allows explicit, analytical evaluation of the performance behaviour under forced oscillations. The performance measure, in our case the time averaged rate or surface occupancies, can therefore be given as a function of the period, amplitude and cycle split. The advantages compared to numerical integration are that a criterion for sustained oscillations is redundant, the initial conditions for integration are not required and no start-up effects have to be accounted for. Furthermore a major advantage is the explicit analytical expression obtained for the performance measure. However, in some cases this method is not applicable because Lyberatos and Svoronos (1987) assumed in their derivation the eigenvalues of the so-called S-matrices to have negative real parts. Unfortunately this condition is not met for all kinetic models and constants in our study.
Another uncertainty of the Carleman Linearisation method concerns the order of linearisation to be applied. It is not a priori clear what order of linearisation is appropriate and therefore some empiricism is introduced here. In the present work $6^{th}$ order derivatives and higher were neglected, unless noted otherwise. The merits and the appropriateness of Carleman Linearisation used in modelling periodic forcing of catalytic reactions will be further discussed in Van Neer et al. (1999).

**RESULTS AND DISCUSSION**

*Concentration oscillations*

First we will analyse the time averaged reaction rate under forced oscillations for low and high frequencies representing the quasi and relaxed steady state rates. Since the reaction rate depends on the surface occupancy of species A and B, see equation 2.3, the dynamic behaviour of $\theta_A$ and $\theta_B$ at these frequencies should be known.

When considering the sorption of a single component only, the accompanying differential equation can be solved analytically. The time dependence of the surface coverage of reactant A is given by the following expression:

\[
\frac{d \theta_A}{dt} = k_1 C_A (1 - \theta_A) - k_{-1} \theta_A
\]

The steady state solution of $\theta_A$ is given by:

\[
\frac{d \theta_A}{dt} = 0 \quad \Rightarrow \quad \theta_A = \frac{k_1 C_A}{k_1 C_A + k_{-1}}
\]

The general solution of equation 2.10, describing the relaxation after a step change in $C_A$ for a constant temperature and kinetic constants, is:

\[
\theta_A(t) = c \exp\left(-(k_1 C_A + k_{-1}) t\right) + \theta_{A, ss}
\]

Where $c$ is an integration constant and $\theta_{A, ss}$ is the steady state surface coverage of reactant A.
Suppose the forcing parameter is cycling by a square wave with period $P$ and cycle split $\varepsilon$ between configurations denoted by $\delta$ and $\rho$. When $\theta_A(t)$ is assumed to be a continuous function, the solution of the differential equation is given by:

$$t \in [jP, (j+\varepsilon)P]: \quad \theta_A,\delta(t) = c_\delta \exp\left(-(k_1,\delta \cdot C_A,\delta + k_{-1,\delta})(t - j \cdot P)\right) + \theta_A,\delta_{ss}$$

$$t \in [(j+\varepsilon)P, (j+1)P]: \quad \theta_A,\rho(t) = c_\rho \exp\left(-(k_1,\rho \cdot C_A,\rho + k_{-1,\rho})(t - (j+\varepsilon) \cdot P)\right) + \theta_A,\rho_{ss}$$

The integration constants are:

$$c_\delta = \left(\theta_A,\delta_{ss} - \theta_A,\rho_{ss}\right)\frac{(1-Q)}{(1-DQ)}$$

$$c_\rho = \left(\theta_A,\delta_{ss} - \theta_A,\rho_{ss}\right)\frac{(1-D)}{(1-DQ)}$$

in which

$$D = \exp\left(-(k_1,\delta \cdot C_A,\delta + k_{-1,\delta}) \cdot \varepsilon \cdot P\right)$$

$$Q = \exp\left(-(k_1,\rho \cdot C_A,\rho + k_{-1,\rho}) \cdot (1-\varepsilon) \cdot P\right)$$

$\theta_A,\delta_{ss}$ and $\theta_A,\rho_{ss}$ are the steady state occupancies at the high and low value of the forcing parameter.

A general expression for the averaged surface coverage of reactant $A$ can be derived using equations 2.13-2.15:

$$\left< \theta_A \right> = \frac{1}{P} \int_P^P \theta_A(t) \, dt = \varepsilon \cdot \theta_A,\delta_{ss} + (1-\varepsilon) \cdot \theta_A,\rho_{ss}$$

$$\frac{1}{P} \left(\theta_A,\delta_{ss} - \theta_A,\rho_{ss}\right) \frac{(1-Q)(1-D)}{(1-DQ)} \left(\frac{1}{k_1,\delta \cdot C_A,\delta + k_{-1,\delta}} - \frac{1}{k_1,\rho \cdot C_A,\rho + k_{-1,\rho}}\right)$$

Taking the limit of a zero frequency, or $P \to \infty$, with $\varepsilon=0.5$ the average value for $\theta_A$ approaches simply the mean of the steady state occupancy at the low ($\rho$) and high ($\delta$) value of the forcing parameter according to equation 2.16:

$$\lim_{P \to \infty} \left< \theta_A \right> = \frac{\theta_A,\delta + \theta_A,\rho}{2}$$
For high frequencies the period of the cycle approaches zero and hence:

$$\lim_{P \to 0} D = 1 \quad \lim_{P \to 0} Q = 1$$  \hspace{1cm} 2.18

Subsequently the surface coverages during the first and second part of the square wave cycle at high frequencies can be derived using equations 2.13, 2.14 and 2.18, De L'Hôpital's law and the assumption that the functions are periodic:

$$\lim_{P \to 0} \theta_A, \delta(t) = \lim_{P \to 0} \theta_A, \rho(t) = \frac{\theta_A, \delta ss \cdot k_\delta \cdot (1-\varepsilon) + \theta_A, \rho ss \cdot k_\rho \cdot (1-\varepsilon)}{k_\delta \cdot (1-\varepsilon) + k_\rho \cdot (1-\varepsilon)}$$  \hspace{1cm} 2.19

in which

$$k_\delta = k_1, \delta \cdot C_A, \delta + k_{-1}, \delta \quad k_\rho = k_1, \rho \cdot C_A, \rho + k_{-1}, \rho$$  \hspace{1cm} 2.20

So, at high frequencies the surface coverage is constant and has the same value during both parts of the cycle.

For concentration oscillations, $k_{i, \rho} = k_{i, \delta}$. Using the steady state solution equation 2.11, this limit reduces to

$$\lim_{P \to 0} \langle \theta_A \rangle = \frac{k_1 \frac{(C_A, \delta + C_A, \rho)}{2}}{k_1 \frac{(C_A, \delta + C_A, \rho)}{2} + k_{-1}} = \frac{k_1 \langle C_A \rangle}{k_1 \langle C_A \rangle + k_{-1}} = \theta_A \langle C_A \rangle$$  \hspace{1cm} 2.21

The time averaged $\theta_A$ under high frequency concentration oscillations is the steady state value of $\theta_A$ at the average concentration, in the present case 0.4 mol/m$^3$. This result is also valid for a two component system and was used to verify the simulations at the high frequency limit.

The calculations with the Langmuir-Hinshelwood model under forced concentration oscillations either result in positive resonance, in absence of resonance or in negative resonance. Figure 2.1 shows positive resonance behaviour: a maximum is obtained for the time averaged rate vs. frequency of oscillation. Quasi and relaxed steady states are reached at low and high frequencies respectively. In order to explain the response, to check the limits and to estimate the optimal steady state rate, we need to recur to the steady states for the
Understanding of resonance phenomena

concentration range of A between 0.1 and 0.7 mol/m³, as indicated in figure 2.2. The optimal steady state is obtained for C_A = 0.1 mol/m³ and the optimal rate is 0.10 s⁻¹. In this case no rate enhancement is observed under forced oscillations i.e. the time averaged rate in figure 2.1 never exceeds this value. In fact no rate enhancement was found for this model for all the concentration oscillation simulations, as was already noted by Renken (1990).

Figure 2.1. Time averaged rate versus frequency; \( k_1 = 4 \times 10^4 \), \( k_1 = 1 \times 10^5 \), \( k_2 = 3 \times 10^4 \), \( k_2 = 1 \times 10^4 \), \( k_3 = 1 \times 10^6 \) (units as shown in notation); markers denote Carleman results and the line represents the results of numerical integration.

Figure 2.2. Steady state occupancies and rates versus C_A; k_1, k_2, k_3 as in figure 2.1; marker denotes \( \theta_B \) at the average of \( \theta_A, \theta_B \) and \( \theta_A, \theta_p \).

The low frequency limit seems to be the average of the rate at C_A,\_\_\_\_ and C_A,\_P (QSS) and at high frequencies the rate approaches the steady state value at C_A = 0.4 mol/m³ (RSS); both observations agree with the results of the single component adsorption.
In order to explain the resonance observed at a oscillation frequency of approximately 10 Hz, in figure 2.3 the surface occupancy of A and B are plotted versus the dimensionless time (time * frequency) at various oscillation frequencies.

Figure 2.3. Surface occupancies versus the dimensionless time at different oscillation frequencies (Hz); [1]: 10^4, [2]: 10^4, [3]: 10^3, [4]: 10^3.

At low frequencies $\theta_A$ and $\theta_B$ follow the transients in the concentration of A instantaneously. For higher oscillation frequencies $\theta_B$ is the first which cannot keep pace with the changing gas phase concentration as the kinetics of sorption of B are slowest. $\theta_B$ experiences the average of $\theta_A$ in the upper and lower part of the concentration cycle and therefore component B tends to approach the occupancy which is marked by a symbol in figure 2.2. Note that $\theta_B$ at this point is higher than the average of $\theta_B$ at $C_{A,S}$ and $C_{A,P}$ (this is not clearly visible in figure 2.2). In figure 2.3 a significant increase of the average of $\theta_B$ can be observed when $\theta_B$-profile no. 1 is compared with profile no. 2. Although $\theta_A$ is lowered by the increase in $\theta_B$, the net effect on the reaction rate is positive since $\theta_B$ is the limiting component on the surface of the catalyst ($\theta_B<\theta_A$ and $r=\theta_B\theta_A$). Therefore a small change in $\theta_B$ has a relatively stronger impact on the rate than the
same variation in $\theta_A$. Figure 2.3 shows that $\theta_B$ first becomes constant and subsequently declines when $\theta_A$ can no longer keep track of the imposed transients for frequencies in excess of $10^3$ Hz. The time averaged value of $\theta_A$ increases from a mean value at $C_{A_8}$ and $C_{A_0}$ to the steady state value at $C_A=0.4$ mol/m$^3$. The rate of the surface reaction drops as a result of the decline in $\theta_B$. Finally at the highest frequency used both surface occupancies become invariant and the reaction rate tends towards the relaxed steady state limit.

In analogy to positive resonance, a minimum between the low and high frequency limits, denoted as negative resonance, can obviously be observed as well (figure 2.4). Again B is the slowest component but now B is present in excess on the surface at steady state and the situation reverses; the surface occupancy of the limiting component drops and the reaction rate falls off.

![Graph](image)

*Figure 2.4. Time averaged rate versus the oscillation frequency; $k_1=4\cdot10^3$, $k_2=1\cdot10^3$, $k_3=3\cdot10^2$, $k_4=1\cdot10^4$, $k_5=1\cdot10^6$ (units as shown in notation); markers denote Carleman results and the line represents the results of numerical integration.*

It has been found that the following two conditions are sufficient to observe resonance phenomena:

1) The sorption behaviour of the forced component must be at least as fast as the sorption of the other component involved. This means that when $\theta_A$ is the first species that cannot keep up with the changes, no resonance will be found. As outlined before, resonance is due to the ability of one component to follow the transient conditions, whereas the second is not. When $A$ is the species with slow sorption characteristics, this situation won’t occur since $\theta_B$ can only be varied via $\theta_A$ (in case $k_1$ is relatively low). The system will tend to move monotonically from the quasi steady state at low frequencies to the state with invariant surface occupancies for both $A$ and $B$ at high frequencies.
2) The surface has to be almost totally occupied at steady state in the considered concentration window. When this condition is not met both components can adsorb and desorb without any mutual influence. Therefore $\theta_B$ will only slightly change under the cycling of $C_A$ and so at low frequencies already the situation is obtained in which $\theta_B$ is nearly constant. At higher frequencies $\theta_A$ will no longer keep up with the transient concentrations and the time averaged rate tends towards the relaxed steady state value without passing extremes.

In figure 2.5 and 2.6 cases are shown for which these requirements are not fulfilled. In figure 2.5 the sorption dynamics of the forced component (component A) are too slow. The system presented in figure 2.6 does not show any competition between the adsorbed species. The surface reaction rate is high compared to the adsorption rate of B. Every species B that adsorbs, reacts immediately which results in a surface almost completely filled with component A. As expected, for both cases no resonance is observed.

![Figure 2.5](image1.png)  
Figure 2.5. Time averaged rate versus the oscillation frequency; $k_1=10^3$, $k_2=10^5$, $k_3=10^7$, $k_4=10^9$, $k_5=10^{11}$ (units as shown in notation); markers denote Carleman results and the line represents the results of numerical integration.

![Figure 2.6](image2.png)  
Figure 2.6. Time averaged rate versus the oscillation frequency; $k_1=10^3$, $k_2=10^5$, $k_3=10^7$, $k_4=10^9$, $k_5=10^{11}$ (units as shown in notation); markers denote Carleman results and the line represents the results of numerical integration.

An interesting case which differs from the situations discussed so far, is presented in figure 2.7, showing the response towards concentration oscillations when the sorption kinetics of A and B are the same and the surface reaction rate constant is relatively high. In respect of the first requirement this handles a situation which is on the verge of (dis)appearance of resonance phenomena. The second requirement is fulfilled as can be observed in figure 2.8.
A remarkable second resonance peak is observed in figure 2.7. In order to explain this behaviour again the steady state surface occupancies and the development of the surface species in one period under forced oscillations are reviewed. At steady state the surface is either completely occupied by A or by B. A sharp transition between these two situations is observable. The optimal steady state is reached for $\theta_A=\theta_B=0.5$. Since B occupies every site which is not occupied by A and vice versa, the response under forced oscillations may be analysed by observing the behaviour of only one surface species, for which we take A. For low oscillating frequencies, $\theta_A$ initially follows the oscillations almost instantaneously (figure 2.9, no. 1). At moderate frequencies (figure 2.9, no. 2) the highest value of $\theta_A$ is no longer attainable and the time averaged value of $\theta_A$ declines in the upper part of the concentration cycle (figure 2.9, no. 3). $\theta_B$
increases in this part of the cycle and since $\theta_B$ is the limiting species ($\theta_B < \theta_A$) the reaction rate increases. However, when $\theta_A$ gets below 0.5 the rate drops (figure 2.9, no. 4). At higher frequencies (figure 2.9, no. 5) the occupancy has risen in the lower part of the cycle because $\theta_A$ tends to a constant value for both parts of the concentration cycle. The reaction rate is slightly enhanced but a large increase is obtained when the frequency is further raised. The peak in the rate can be understood by means of figure 2.8. The relaxed steady state is approached from a situation in which $\theta_A$ is low, but finally $\theta_A$ must approach the steady state value at $C_A = 0.4$ mol/m$^3$ which is relatively high (see figure 2.8). So, when going from a low to a high average $\theta_A$ a rate maximum is reached as demonstrated in the second maximum in figure 2.7. We are not aware that the sketched situation with a double maximum has ever been described before. It demonstrates that the nature of resonance phenomena may be even more complicated than initially expected.

Figure 2.9. Surface occupancy of $A$ versus the dimensionless time at various frequencies (Hz); [1]: $10^3$, [2]: $10^4$, [3]: $10^5$, [4]: $10^6$, [5]: $10^7$, [6]: $10^8$, [7]: $10^9$, [8]: $10^{10}$.

The question arises why $\theta_A$ is no longer able to reach the high level, whereas it is still able to approach the low level at moderate frequencies (figure 2.9, no. 2-4). In that case, the surface occupancies do no longer follow the transients in the gas concentrations instantaneously and $\theta_A$ deviates first from the high occupation level while $\theta_B$ still reaches a coverage close to 1 (the sum of $\theta_A$ and $\theta_B$ is always close to unity). When it is realised that A and B have identical kinetic constants, differences between their sorption behaviour only arise from gas-phase concentrations. The ratio of the concentrations of A and B indicates therefore whether the surface is filled with A or B. A surface which is covered with equal amounts of A and B exists when this ratio is 1. At periodic oscillations between 0.1 and 0.7 mol/m$^3$ the $C_A/C_B$ ratio varies from 1/3 to 7/3. So in the situation at hand the ratio during a cycle is respectively a factor 3 and 2 $\frac{1}{3}$ away from 1. Figure 2.10 shows that going from low to moderate frequencies at first the
Understanding of resonance phenomena

The system will tend to a situation with predominately species B on the surface as a result of the asymmetry of the logarithm of $C_A/C_B$ around the value at which an equally filled surface exists. The arrows illustrate the range of concentration ratios as experienced by the system.

This theory is verified by a simulation in which $C_A$ was varied between 0.1 and 0.9 mol/m$^3$ whereas, as before, $C_B$ is kept invariant at 0.3 mol/m$^3$. In this case the logarithm of the concentration ratio $C_A/C_B$ for both half cycles is symmetrical (log 9/3 vs. log 1/3) around the point $C_A/C_B$=1 where $\theta_A$ and $\theta_B$ are identical. As expected $\theta_A$ is able to reach the high level at intermediate frequencies, the relaxed steady state is approached from a situation in which $\theta_A$ is relatively high and therefore the second peak is absent. Figure 2.7 shows that in this case only one maximum is obtained in the average rate vs. frequency plot.

So, when the surface reaction is relatively fast ($k_3$ is high) and the kinetic constants of the sorption of A and B are of the same order of magnitude, a sharp transition is obtained in the steady state plot and resonance is found under forced oscillations. The condition for resonance, the sorption kinetics of A must not be slower than those of B, is just met. When the sorption of A is much slower than that of B, also no resonance is found for cases in which the surface reaction is relatively fast (see figure 2.6).

It is worthwhile at this point to verify that the kinetic constants used in our study are physically relevant and to see in what range of oscillating frequencies the described resonance phenomena could in principle be observed. To this end we have compared the kinetic constants used in the simulations to global values which may be derived from Transition State Theory (Zhdanov et al., 1988). Activation energies were obtained from predictions given by

![Figure 2.10. Qualitative picture of the dimensionless concentration ratio $C_A/C_B$ as experienced by the system as a result of finite sorption rates at low to moderate frequencies. Identical sorption kinetics were taken for A and B.](image-url)
Dumesic et al. (1993). In table 2.1 the results of the calculations at 500 K for simple molecules like CO, NO and Cl2 are given. It can be concluded that nearly all the kinetic constants applied in the concentration oscillation simulations are within the boundaries predicted by the Transition State Theory and the phenomena described in this work are therefore in principle prone to experimental validation.

Table 2.1. Kinetic constants at 500 K calculated with the Transition State Theory and the given activation energy, compared with the constants used in the concentration forcing simulations.

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>$E_{act}$ / kJ/mol</th>
<th>Kinetic constants estimated with TST</th>
<th>Kinetic constants used in the simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>molecular adsorption:</td>
<td>A + * $\rightarrow$ A*</td>
<td>$10^1 - 10^5$ m$^3$ / mol·s</td>
<td>$10^1 - 10^5$ m$^3$ / mol·s</td>
</tr>
<tr>
<td>molecular desorption:</td>
<td>A* $\rightarrow$ A + *</td>
<td>$10^1 - 10^8$ s$^{-1}$</td>
<td>$10^6 - 10^8$ s$^{-1}$</td>
</tr>
<tr>
<td>Langmuir-Hinshelwood reactions:</td>
<td>A* + B* $\rightarrow$ C + 2*</td>
<td>$10^1 - 10^6$ s$^{-1}$</td>
<td>$10^2 - 10^6$ s$^{-1}$</td>
</tr>
</tbody>
</table>

*Temperature oscillations*

Temperature oscillations can be expected to produce far more dramatic effects than concentration oscillations, in view of the highly non-linear behaviour of kinetic constants with regard to temperature. In addition, instead of forcing one component, now both components are directly influenced by the forcing variable. This difference is already apparent when considering the relaxed steady state. In analogy to the concentration forcing, first the single component sorption behaviour at high and low temperature oscillation frequencies are analysed. Again equations 2.19-2.20 are used. We assume that

\[
(k_{l,5} C_{A,5} + k_{-l,5}) \gg (k_{l,\rho} C_{A,\rho} + k_{-l,\rho})
\]

on the basis of the normally strong dependence of kinetic constants on temperature (note that $T_5 > T_\rho$). We may now derive:
So, the time averaged surface coverage for high frequencies equals the steady state surface coverage at the highest temperature during square wave temperature cycling. This result was also found for two component systems and is very useful in the understanding of the response of catalytic systems towards temperature oscillations. The quasi steady state occupancy is again simply the mean of the steady state occupancy at the low and high temperature.

\[ \lim_{p \to 0} \langle \theta_A \rangle = \frac{\epsilon (k_{1,0}\, C_{A,0} + k_{-1,0}) \theta_{A,0}}{\epsilon (k_{1,0}\, C_{A,0} + k_{-1,0})} = \theta_{A,0} \]

2.23

Figure 2.11. Steady state occupancies and rate versus the temperature; \( k_{1,0}=1 \times 10^{13}, k_{1,0}=5.8 \times 10^{14}, k_{2,0}=1 \times 10^{14}, k_{2,0}=5.3 \times 10^{28}, k_{3,0}=1 \times 10^{14}, E_1=150, E_1=50, E_2=150, E_3=250, E_3=50 \) (units as shown in notation).

In general two types of parameter sets can be distinguished. As a first case we will look at a situation in which under steady state the surface of the catalyst is not entirely occupied. Figure 2.11 shows the adsorption equilibria and steady state rates for a range of temperatures with the upper and lower temperature of the cycle as boundaries. For the parameter set used here, A is the dominating species on the surface at high temperatures, whereas B is dominating at low temperatures. The maximum catalyst surface coverage is around 50%; the optimal steady state is obtained at a temperature of 650 K and in this situation one of the components is present in minority on the surface. It is clear that the optimal steady state is not necessarily found when both \( \theta_A \) and \( \theta_B \) are at their maximum because the surface reaction constant increases with temperature as well. Since there is room within the considered temperature window for an increase in the surface occupancy for one of the components compared to the optimal steady state occupancy, it may be possible to enhance the reaction rate by periodically changing the temperature. Figure 2.12 (solid curve) shows that this is indeed the case. A maximum rate enhancement (defined in equation 2.8) of a factor of 7 can be reached for a frequency of 1 Hz.
It is clear that reaction rates considerable in excess of the optimal steady state value can be obtained and that rate enhancement is by no means restricted to a narrow frequency window. Again, the explanation of this behaviour can be found by tracing surface occupancies versus time under various frequencies. The profiles of $\theta_A$ and $\theta_B$ during one period are given in figure 2.13. For the sake of clarity this time another way of presenting (compared to the previous section) was chosen for the same kind of results.

At low frequencies $\theta_A$ and $\theta_B$ respond to temperature transients instantaneously. At higher frequencies species A is no longer able to keep track of these transients and the occupancy of A tends to approach its high temperature level. Subsequently the time averaged value of $\theta_A$ rises in the low temperature part without a concomitant, substantial decrease in $\theta_B$. As in this part of the cycle $\theta_A$ is the limiting component, the rate is enhanced. At even higher frequencies (figure 2.13, no. 4) $\theta_A$ becomes constant exactly at its high temperature steady state occupancy and $\theta_B$ starts to deviate from the quasi steady state coverage. Now the rate is decreased by the decline of the time averaged value of $\theta_B$ in the low temperature part of the cycle. Finally at the highest frequency used both occupancies approach the high temperature steady state level and the relaxed steady state is obtained.

An important condition for the occurrence of resonance under temperature oscillations is the dissimilar dynamic behaviour of A and B with respect to the adsorption and desorption on the surface. Under steady state, the component showing the slowest sorption behaviour should occupy more sites with increasing temperature. This is an additional requirement for the
occurrence of rate enhancement for systems with low total surface coverages. In case the surface is fully occupied, other criteria apply as will be shown later on.

![Graph showing surface occupation of A (---) and B (- - -) versus the dimensionless time at different frequencies (Hz); [1]: 10^3, [2]: 10^4, [3]: 10^5, [4]: 10^6, [5]: 10^7, [6]: 10^8, scale of all the graphs: 0 - 1.](image)

The former condition concerning the occurrence of resonance, is illustrated by figure 2.14 in which k_{2,0} and k_{2,0} are varied keeping the ratio k_{2,0}/k_{2,0} constant. Since k_1 is relatively small compared to the other kinetic constants, for a constant ratio k_{2,0}/k_{2,0} the same steady state profiles are obtained. The rate enhancement factor is below 1 for low k_{2,0} values and no significant resonance is seen. With these relatively low values for the pre-exponential factors the two components almost have the same kinetic constants, so they behave quite similarly in attaining the relaxed steady state: the dissimilarity in the dynamic behaviour is absent.
Figure 2.14. Rate enhancement factor at various frequencies for constant $k_{2,0}/k_{-2,0}$; other kinetic constants as in figure 2.11.

In the same figure can be observed that at higher $k_{2,0}$ values an enormous rate enhancement can be obtained which reaches a plateau value. This plateau results from the maximum rate in the lower part of the temperature cycle where $\Theta_A$ is at the steady state value at 700 K and $\Theta_B$ has the value for the steady state occupancy at 500 K. In this case a rate enhancement factor of around 7 was observed. Furthermore it is illustrated that the range of frequencies in which reasonable rate enhancement occurs, widens for higher values of $k_{2,0}$ and $k_{-2,0}$.

As a second case we take a catalyst surface which is almost totally covered under steady state. Under this condition it is not sufficient for predicting rate enhancement to focus just on the steady state cosorption profiles of A and B. In figure 2.15 steady state coverages of a certain parameter set are given for the considered temperature range. When A and B are both present, B is always in minority on the surface. Under forced temperature oscillations a maximum rate enhancement of 3 is found which is shown in figure 2.12 (dashed curve). This can only be explained on the basis of the individual adsorption equilibria of the components. It is apparent from figure 2.15 that B has the potential to occupy much more surface sites when A is absent. When the temperature is oscillated at frequencies which can be followed by B but not by A, the surface occupancy of A becomes invariant at a high temperature level, corresponding to a relatively low occupancy. Free sites are available for B to adsorb and the rate is enhanced. Again, differences in sorption kinetics may give rise to resonance phenomena. Under steady state, the component showing the slowest sorption behaviour should almost completely cover the surface and should occupy less sites with increasing temperature. This is an additional requirement for the occurrence of resonance for systems with high total surface occupancies.
Understanding of resonance phenomena

1.00 — 0.75 • •••

0.50 • •••

0.25 • •••

500 600 T/K

0.004

0.003

0.002

0.001

0.000

700

Figure 2.15. Steady state occupancies and rate versus temperature; $k_{10} = 1 \cdot 10^8$, $k_{210} = 1 \cdot 10^{14}$, $k_{30} = 1 \cdot 10^6$, $k_{40} = 1 \cdot 10^6$, $k_{50} = 1 \cdot 10^6$, $E_1 = 10$, $E_2 = 125$, $E_3 = 10$, $E_4 = 150$, $E_5 = 10$ (units as shown in notation). $B^*$ denotes the steady state surface occupancy of $B$ without the presence of $A$.

The pre-exponential factors used in the temperature oscillation simulations were less realistic as can be seen in table 2.2. The range over which the pre-exponential factors were varied, were too wide. However, the conclusions concerning the analysis of the steady state and the requirements for the occurrence of rate enhancement remain the same when other kinetic constants are applied.

Table 2.2. Comparison of pre-exponential factors calculated with the Transition State Theory and the factors used in the temperature forcing simulations.

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>Pre-exponential factors estimated with TST</th>
<th>Pre-exponential factors used in simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>molecular adsorption: $A + * \rightarrow A^*$</td>
<td>$10^1 - 10^5$ m$^3$/mol·s</td>
<td>$10^5 - 10^9$ m$^3$/mol·s</td>
</tr>
<tr>
<td>molecular desorption: $A^* \rightarrow A + *$</td>
<td>$10^{12} - 10^{19}$ s$^{-1}$</td>
<td>$10^4 - 10^8$ s$^{-1}$</td>
</tr>
<tr>
<td>Langmuir-Hinshelwood reactions: $A^* + B^* \rightarrow C + 2*$</td>
<td>$10^{12} - 10^{19}$ s$^{-1}$</td>
<td>$10^0 - 10^5$ s$^{-1}$</td>
</tr>
</tbody>
</table>

Carleman Linearisation versus numerical integration

Simulations using Carleman Linearisation were performed with MATLAB V4.2 (The MathWorks Inc.) and decreased the computational efforts drastically compared to numerical integration. In the forced concentration simulations shown in the figures 2.1, 2.4, 2.5 and 2.6
the differences with numerical integration results were within 0.1%. However only a part of
the numerical results of the cases shown in figure 2.7 could be reproduced by using Carleman
Linearisation. For frequencies lower than $10^{4.3}$ and $10^{3.6}$ Hz respectively, the discrepancies
between the two methods increased. Carleman Linearisation gave for these frequencies very
high positive and even negative rates.

With respect to the temperature oscillations all computational results presented using
Carleman Linearisation and numerical integration were identical. Even 2\textsuperscript{nd} order Carleman
linearisation produced correct results. Hence, even in the case of a strongly non-linear forcing
variable, Carleman Linearisation may produce the right results.

In Van Neer \textit{et al.} (1999) the appropriateness of Carleman Linearisation is addressed and
conditions for using this method are formulated.

\textbf{CONCLUSIONS}

It was demonstrated for a Langmuir-Hinshelwood microkinetic model that forced oscillations
in the reactant concentration may produce a time averaged behaviour which is substantially
different from steady state behaviour. Resonance phenomena are observed over a reasonably
broad frequency range. The present theoretical analysis of resonance under concentration
forcing showed that such phenomena occur under conditions that are realisable in practice and
therefore the results of the computations are open to experimental verification.

In general resonance phenomena are observable during imposed concentration oscillations on
catalytic surfaces when the forced component has comparatively fast sorption kinetics and the
catalytic surface is almost fully occupied. This can be understood in that the system behaves
more non-linear with respect to the reaction rate when the components are competing for
adsorption on the surface and highly influencing each other. If not, according to equation 2.1
the time derivative of $\theta_A$ becomes linearly dependent on the forced concentration and the time
derivative of $\theta_B$ becomes even close to zero for low surface reaction rates.

Resonance is caused by the inability of the surface species of the non-forced component to
follow the changes in the surface occupancy of the forced component. This leads to a
temporarily invariant surface occupancy of the non-forced component at a level which
deviates both from its relaxed steady state and from its quasi steady state level. Steady state
profiles can be used to predict the type of resonance (positive or negative) as well as the low and high frequency limits.

For the analysed molecular sorption microkinetic model, rate enhancement beyond the optimal steady state level was not observed in case of concentration forcing. In contrast, temperature constitutes a highly non-linear forcing parameter, resulting both in strong resonance effects and in a large value of the rate enhancement factor. This is observed for systems showing both low and high surface occupancies in the steady state. Again, dissimilar dynamic behaviour with respect to sorption kinetics of the components involved is a prerequisite to the occurrence of resonance phenomena. In steady state, the component showing the slowest sorption behaviour should occupy more sites with increasing temperature. This is an additional requirement for the occurrence of rate enhancement for systems with low total surface occupancies. For systems with high surface occupancies, the component showing the slowest sorption behaviour should almost completely cover the surface and should occupy less sites with increasing temperature. Steady state profiles can be used to verify these conditions.

The analysis of the forced system using Carleman Linearisation of the governing equations was found to be adequate in many cases considered and, when applicable, it represents an extremely useful tool to reduce the computational effort drastically. Even in case of strongly non-linear forcing variables, like temperature, Carleman Linearisation produces the right results using a low order of linearisation.

**NOTATION**

- $c$: integration constant; equation 2.12, -
- $C$: constant in criterion for sustained periodic oscillations; equation 2.9, -
- $C_A$: concentration of component A, mol/m$^3$
- $C_B$: concentration of component B, mol/m$^3$
- $\langle C_A \rangle$: average of $C_{A,5}$ and $C_{A,p}$, mol/m$^3$
- $D$: equation 2.15, -
- $E_i$: activation energy of reaction $i$, kJ/mol
- $f$: forcing frequency, Hz
- $k_{1,2}$: kinetic constant, m$^3$/mol·s
- $k_{-1,-2,-3}$: kinetic constant, s$^{-1}$
- $k_{1,0}$: pre-exponential factor, m$^3$/mol·s
\( k_{1,0} \)  pre-exponential factor, \( s^{-1} \)

\( k_\delta \)  equation 2.20, -

\( k_p \)  equation 2.20, -

\( P \)  period, \( s \)

\( Q \)  equation 2.15, -

\( r \)  reaction rate, \( s^{-1} \)

\(<r>\)  time averaged reaction rate under forced oscillations, \( s^{-1} \)

\( R \)  ideal gas constant, \( J/mol \cdot K \)

\( t \)  time, \( s \)

\( T \)  temperature, \( K \)

Greek letters

\( \delta \)  denotes the upper part of the square wave cycle, -

\( \varepsilon \)  cycle split, -

\( \theta_A \)  coverage of surface species A, -

\( \theta_B \)  coverage of surface species B, -

\( \theta_{A,SS} \)  steady state coverage of reactant A, -

\(<\theta_A>\)  time averaged coverage of surface species A, -

\(<\theta_B>\)  time averaged coverage of surface species B, -

\( \rho \)  denotes the lower part of the square wave cycle, -

\( \Psi \)  rate enhancement factor; equation 2.8, -

REFERENCES


REFERENCES

DIRECT DETERMINATION OF CYCLIC STEADY STATES IN PERIODICALLY PERTURBED SORPTION-REACTION SYSTEMS USING CARLEMAN LINEARISATION*

ABSTRACT

An investigation into the merits and pitfalls of the use of Carleman Linearisation in analysing periodic operation of heterogeneous catalytic processes has been conducted. This linearisation technique offers the advantage of direct determination of the cycle invariant state for systems perturbed by square wave cycling. It is shown that the applicability of Carleman Linearisation can be assessed on the basis of its ability to predict the steady state behaviour at the upper and lower limits of the forcing parameter. If this newly developed criterion is not met, critical state variables need to be reviewed to obtain reliable estimations under periodic forcing using Carleman Linearisation. This requires relatively easy steady state calculations. Surpassing of the critical values under forced oscillations results in incorrect Carleman predictions. It is furthermore shown that a closer agreement between numerical calculations and Carleman Linearisation can be obtained by shifting the point of linearisation closer to the extreme of the forcing parameter where Carleman Linearisation fails.

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INTRODUCTION

The dynamics of catalytic reactions have become an important area of research because of the specific information obtained from dynamic response analysis and the practical relevance of these phenomena to, for instance, reactor stability. A special form of dynamic response analysis is the analysis of the transfer functions in case of periodic forcing. Under such conditions, resonance phenomena may be observed, whereby the time averaged behaviour deviates significantly from the steady state behaviour. Periodic forcing is also a powerful tool in discriminating between a variety of possible mechanisms and can thus be used to further shed light on reaction pathways (see e.g. Thullie and Renken, 1993, van Neer et al., 1997a).

Whereas resonance phenomena in principle can be used to enhance the performance of catalytic systems, it is not generally possible to identify a priori what catalytic systems may demonstrate such behaviour. This lack of predictability obviously hampers the implementation of periodic control strategies. In recent work (van Neer et al., 1996) an initial attempt was made to explain resonance behaviour of a relatively simple catalytic system. In view of the large number of system parameters involved, the response of complex, multi-step catalytic reactions is much more difficult to interpret. An efficient analysis is therefore a prerequisite for good interpretation of such systems. Whereas numerical analysis is effective in establishing the nature of response behaviour, it does not easily allow interpretation and in this respect the use of analytical expressions for the time averaged behaviour are preferable. A promising method to investigate the response of non-linear systems towards periodic square wave cycling was proposed by Lyberatos and Svoronos (1987) and is based upon Carleman Linearisation (Carleman, 1932). Carleman Linearisation has major advantages, as analytical expressions are derived for the time-averaged performance. Hence, the analysis of responses towards input programming in catalytic reactions thus becomes more amenable to physical interpretation as compared to numerical methods. Carleman Linearisation provides a direct method to obtain the periodic steady state, eliminating the necessity of successive numerical integration to convergence to the periodic steady state which demands a high computational effort. Carleman Linearisation was proven to be superior to other methods as for instance the Pi criterion (Hatzimanikatis et al., 1993).

Carleman Linearisation (CL) was used earlier in optimal control of non-linear continuous time systems (Svoronos et al., 1994), analysis of Hopf bifurcation (see e.g. Tsiligiani and Lyberatos, 1987) and periodic optimisation of chemical reaction systems (Hatzimanikatis et al., 1993). The present study aims to demonstrate the use of Carleman linearised systems in case of periodically square wave forced catalytic systems. The response of a variety of
Direct determination of cyclic steady states using Carleman Linearisation

microkinetic models towards concentration and temperature oscillations is studied. Both the models used and the forcing variables differ in non-linearity. A simple Langmuir-Hinshelwood model and systems demonstrating complex dynamic behaviour have been studied. As little attention has been paid so far to limitations of the use of Carleman Linearisation, this issue is addressed in detail. The applicability window of CL will be discussed and appropriate conditions for its use are formulated.

THEORY

Carleman Linearisation

The models used in this study are sets of non-linear ordinary differential equations of the general form:

$$\frac{d\theta}{dt} = f(\theta, u(t))$$  \hspace{1cm} (3.1)

where $\theta$ is a vector of state variables and $u(t)$ is a forced control variable like the reactant concentration or system temperature. In the cases to be presented later the state variables invariably are surface occupancies. The vector function $f$ can be Taylor-expanded to the order $m$ around a steady state solution ($\theta_{CL}$) considering $u$ as a constant for a certain time interval:

$$\frac{d\theta}{dt} = A_{10}(u)_{\theta_{CL}} + \sum_{n=1}^{m} A_{1n}(u)_{\theta_{CL}} \theta^{[n]}$$  \hspace{1cm} (3.2)

where $\theta^{[n]} = \theta \otimes \theta \otimes \ldots \otimes \theta$, $\otimes$ denoting Kronecker multiplication (e.g. if $\theta = [\theta_A \theta_B]^T$ then $\theta^{[2]} = [\theta_A \theta_B]^T [\theta_A \theta_B]^T = [\theta_A^2 \theta_A \theta_B \theta_B \theta_A \theta_B]^T$). $A_{10}$ and $A_{1n}$ are matrices containing coefficients from the Taylor-series expansion of system $f$. For a second order expansion of a two variable model the following matrices are derived:

$$A_{10}(u)_{\theta_{CL}} = f = \left[ \begin{array}{c} d(u) \\ g(u) \end{array} \right]_{\theta_{CL}}$$  \hspace{1cm} (3.3)
Carleman Linearisation of a system includes an additional step namely the transition to a system with new state variables (Carleman, 1932). The $m$th order CL of the system in equation 3.1 is obtained by defining the expanded state vector $w$ which contains the new state variables:

$$w = [\theta, \theta^{(1)}, ..., \theta^{(m)}]^T$$  

It was shown by Lyberatos and Svoronos (1987) that the resulting system is linear with respect to the expanded state vector:

$$\dot{w} = \frac{\partial w}{\partial t} = \begin{bmatrix} A_{11} & A_{12} & \cdots & A_{1,m} \\ A_{20} & A_{21} & \cdots & A_{2,m-1} \\ 0 & A_{30} & \cdots & A_{3,m-2} \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & A_{m,0} \end{bmatrix} \begin{bmatrix} w \\ \partial w \\ \vdots \\ \partial w \\ \partial w \\ \vdots \\ \partial w \end{bmatrix} + \begin{bmatrix} A_{0} \\ 0 \\ \vdots \\ 0 \\ \vdots \\ \vdots \\ 0 \end{bmatrix} = S(u)_{\theta_{cl}} \dot{w} + z(u)_{\theta_{cl}}$$  

The newly obtained matrices $(A_{ij})$ can be derived from equation 3.3-3.5 by

$$A_{i,j} = I_n \otimes A_{i-1,j} + A_{i,j} \otimes I_n = A_{i-1,j} \oplus A_{i,j}$$  

in which $i > 1$ and $\otimes$ denotes a Kronecker sum. The function of performance, for example the reaction rate, can be expanded likewise and expressed in Carleman-variables:
Direct determination of cyclic steady states using Carleman Linearisation

\[ r(\theta, u) = r_0(\theta) + k^T(u) \]

The control variable \( u \) is of the form:

\[ u(t) = u_{CL} + \begin{cases} \delta & t \in [jT, (j + \frac{1}{2})T] \\ -\delta & t \in [(j + \frac{1}{2})T, (j + 1)T] \end{cases}, \quad j = 0, 1, 2, \ldots \]

For the sake of clarity the cycle split has been chosen to be 0.5 throughout this study. \( T \) denotes the oscillation period.

According to Lyberatos and Svoronos (1987) the time average performance, in the present study the time average reaction rate \( J \), is given by the following explicit expressions assuming that the eigenvalues of \( S(\delta) \) and \( S(\rho) \) have negative real parts:

\[ J(T) = J_1 + J_2 - J_3 J_4 J_5 \]

where

\[ J_1 = J_{1a} + J_{1b} \]
\[ J_{1a} = \frac{1}{2} \cdot r_0(\delta) \]
\[ J_{1b} = -\frac{1}{2} \cdot k^T(\delta) S^{-1}(\delta) \xi(\delta) \]
\[ J_2 = J_{2a} + J_{2b} \]
\[ J_{2a} = \frac{1}{2} \cdot r_0(\rho) \]
\[ J_{2b} = -\frac{1}{2} \cdot k^T(\rho) S^{-1}(\rho) \xi(\rho) \]
\[ J_3 = k^T(\rho) S^{-1}(\rho) - k^T(\delta) S^{-1}(\delta) \]
\[ J_4 = \frac{(I - R)(I - DR)^{-1}(I - D)}{T} \]
\[ J_5 = S^{-1}(\rho) \xi(\rho) - S^{-1}(\delta) \xi(\delta) \]

where \( I \) represents the identity matrix and
Besides the analysis of the time average performance it is possible to derive analytical expressions for the state variables, in the present cases surface occupancies, within a cycle-period. The microkinetics of surface reactions are more fruitfully studied on the basis of the development of surface occupancies in time, rather than by cycle averaged data (van Neer et al., 1996). The surface occupancy profiles are obtained by integrating

\[ D = \exp\left(\frac{1}{2} S(\delta) T\right) \quad R = \exp\left(\frac{1}{2} S(\rho) T\right) \tag{3.21} \]

which results in the following expressions assuming the solution is periodic (Lyberatos and Svoronos, 1987):

\[
\Theta(t) = \begin{cases} 
\exp\left(S(\delta)(t-jT)\right)\zeta(\delta) - 
\left[1-\exp\left(S(\delta)(t-jT)\right)\right]S^{-1}(\delta)\zeta(\delta) & t \in [jT,(j+\frac{1}{2})T] \\
\exp\left(S(\rho)(t-(j+\frac{1}{2})T)\right)\zeta(\rho) - 
\left[1-\exp\left(S(\rho)(t-(j+\frac{1}{2})T)\right)\right]S^{-1}(\rho)\zeta(\rho) & t \in [(j+\frac{1}{2})T,(j+1)T], j = 0,1,2,\ldots \tag{3.22}
\end{cases}
\]

where

\[ \zeta(\delta) = -[I-RD]^{-1}\left([R-RD]S^{-1}(\delta)\zeta(\delta) + [I-R]S^{-1}(\rho)\zeta(\rho)\right) \tag{3.24} \]

\[ \zeta(\rho) = -[I-DR]^{-1}\left([D-DR]S^{-1}(\rho)\zeta(\rho) + [I-D]S^{-1}(\delta)\zeta(\delta)\right) \tag{3.25} \]

For a catalytic system with two surface species, the first two elements of \( \Theta(t) \) represent the time development of the first and the second species within a period. The values derived in this way are relative and must be added to the steady state values of the point around which the system was Taylor-expanded. In this way the surface occupancies within a cycle-period are obtained.
Direct determination of cyclic steady states using Carleman Linearisation

Numerical integration

To investigate whether the Carleman Linearised system retains the essential dynamic characteristics, a comparison is made with a numerical integration method, for which the commonly applied Runge-Kutta Fehlberg 45 algorithm is taken. Calculations with the embedded fourth order method are compared with the results of the fifth order RK algorithm. Integration time-increments were decreased when the required accuracy was not met. Simulation results were assumed to be periodic when the following criterion is met:

$$\Psi = \sum_{j=1}^{100} \left( \frac{J(\frac{1}{100} jT) - J((1+\frac{1}{100} j)T)}{J((1+\frac{1}{100} j)T)} \right)^2 \leq C$$

At high frequencies ($1/T>10^5$ Hz) C was set at $10^{-5}T$ and at low frequencies C was set at $10^{-10}$.

Application to surface catalytic reactions

The benefits of CL will be demonstrated for a number of conventionally used sorption reaction models. Three hypothetical mechanisms for the overall reaction $A+B \rightarrow C$ were used in the simulations. A first, simple model in which all reactants adsorb molecularly on the catalytic surface, can be formulated as follows (model 1):

$$A + S \leftrightarrow AS \quad k_1, k_2$$
$$B + S \leftrightarrow BS \quad k_3, k_4$$
$$AS + BS \rightarrow C + 2S \quad k_5$$

Here S denotes an active site on a catalytic surface.

Dissociative adsorption of component A is included in model 2. Therefore, the latter system has a more strongly non-linear character.

$$A_2 + 2S \leftrightarrow 2AS \quad k_1, k_2$$
$$B + S \leftrightarrow BS \quad k_3, k_4$$
$$AS + BS \rightarrow C + 2S \quad k_5$$
Finally, model 1 was extended to a more complex scheme (model 3) in which species A on the catalyst can be stored in a so-called buffer and becomes a non-reactive species. Here the system consists out of three state-variables, $\theta_{A1}$, $\theta_{A2}$ and $\theta_{B1}$, representing $AS_1$, $AS_2$ and $BS_i$ respectively.

\[
\begin{align*}
A + S_I & \leftrightarrow AS_I \quad k_1, k_2 \\
B + S_I & \leftrightarrow BS_I \quad k_3, k_4 \\
AS_I + BS_I & \rightarrow C + 2 S_I \quad k_5 \\
AS_I + S_2 & \leftrightarrow AS_2 + S_I \quad k_6, k_7
\end{align*}
\]

In the analysis we implicitly assumed the gas-phase to be of an infinite volume, thereby limiting the analysis to the phenomena on the catalytic surface and neglecting the impact of sorption and reaction on the gas phase composition. Hence, the dynamic behaviour of the surface species can conventionally be described by ordinary differential equations assuming all reactions to be first order in reactive species. The equations of model 3 are given here to serve as an example:

\[
\begin{align*}
\frac{d\theta_{A1}}{dt} &= k_1 C_A (1 - \theta_{A1} - \theta_{B1}) - k_2 \theta_{A1} - k_6 N \theta_{A1} (1 - \theta_{A2}) + k_7 N \theta_{A2} (1 - \theta_{A1} - \theta_{B1}) \\
\frac{d\theta_{A2}}{dt} &= k_6 \theta_{A1} (1 - \theta_{A2}) - k_7 \theta_{A2} (1 - \theta_{A1} - \theta_{B1}) \\
\frac{d\theta_{B1}}{dt} &= k_3 C_B (1 - \theta_{A1} - \theta_{B1}) - k_4 \theta_{B1} - k_5 \theta_{A1} \theta_{B1}
\end{align*}
\]

Here $N$ denotes the number of sites $S_2$ compared to the number of sites $S_I$.

In case of concentration oscillations the concentration of A was varied by a forcing function as given before (equation 3.10). The concentration of component B was held invariant. In the temperature oscillation simulations a similar square wave forcing function was used. Partial pressures of component A and B were kept constant and concentrations are therefore given by:

\[
C_A(t) = C_B(t) = \frac{P_{A,B}}{R T S(t)}
\]
Temperature forcing was investigated in view of its strongly non-linear nature, arising from the Arrhenius type temperature dependence of the reaction rate constants:

\[ k_i(t) = k_{i,0} \exp \left( -\frac{E_i}{R T_s(t)} \right) \]  

\[ \text{3.31} \]

RESULTS AND DISCUSSION

Merits of Carleman Linearisation

In case of periodically forced systems, convergence to the cyclic steady state may be slow and non-monotonic. This is illustrated by a numerical simulation of periodic forcing of a surface reaction, obeying model 2 type kinetics. Convergence to the cyclic steady state is illustrated by plotting the deviation from the cyclic steady state, the periodicity criterion \( \psi \) (equation 3.26), vs. the number of successive forced cycles (figure 3.1). For a low oscillation frequency the number of cycles needed to approach the cycle invariant state is limited, but the numerical evaluation of each cycle is time consuming. The response for a high frequency cycle is estimated reasonably fast, but many cycles are required before the periodicity criterion is met. Hence, the total CPU time required is still high. When the steady state at the average value of the forcing variable is taken as the initial condition, see figure 3.1 (2), the number of cycles decreases only marginally. In addition, a problem arises at intermediate frequencies (not shown here). A stiff model, i.e. large differences between the dynamics of sorption of the components, demands more points per period for an accurate estimation than a model showing a rather smooth response. Unfortunately the steepness of the response is not always predictable and therefore the number of points required for proper evaluation is not known a priori.

Figure 3.1 further illustrates that in periodically forced systems convergence to the cyclic steady state does not necessarily follow a monotonic path. For frequencies of \( 10^3 \) and \( 10^4 \) Hz local minima are obtained. When a less stringent periodicity criterion was chosen, the simulation would stop far before the periodic invariant state.
Figure 3.1. Convergence to the cycle invariant state for model 2 at various frequencies. \( \Psi \) (equation 3.26) is plotted versus the number of imposed cycles. Initial conditions: \((\theta_A, \theta_B) = (0.4, 0.4)\) except for (2) where the steady state has been taken as IC. \( k_1 = 2 \times 10^5 \), \( k_2 = 1 \times 10^5 \), \( k_3 = 2 \times 10^5 \), \( k_4 = 1 \times 10^5 \), \( k_5 = 1 \times 10^5 \) (units as shown in notation). \( C_A^P = 0.1 \), \( C_A^B = 0.7 \) and \( C_B = 0.3 \) mol/m$^3$.

In contrast to successive numerical integration routines, CL allows the direct determination of the time averaged reaction rate under forced oscillations. CPU time is dramatically reduced compared to numerical integration since often second and third order linearisations are sufficient for a close approximation of the original system. CL is faster than numerical integration in most cases up to the 7th order. Beyond this order of linearisation, CL is no longer attractive since inversion of the S-matrices (equation 3.7) becomes too time consuming. The size, $s \times s$, of the S-matrices as function of the order $m$ and the number of state variables $b$ can be estimated by:

\[
s = \sum_{i=1}^{b} t^m \tag{3.32}
\]

A reasonable compromise between calculation time and accuracy is obtained with a fourth order linearisation, which was therefore used in this work unless stated otherwise.

Figure 3.2 illustrates the validity of CL, by comparing numerical integration and CL for model 1. The time averaged rate under square wave cycling of the concentration of reactant A, is given for various cycling frequencies. At low frequencies the reaction rate is equal to the average of the steady state rate at $C_{A,B}$ and $C_{A,P}$ since the imposed transients are closely
followed by the catalytic system. This results in quasi steady state behaviour. In the relaxed steady state, at high oscillation frequencies, the steady state rate at the average value of $C_A$ is approached, as the system can no longer keep pace with the periodically changing value of the forcing variable. A detailed explanation of the obtained resonance phenomena observable particular in the transition region between quasi and relaxed steady state, can be found elsewhere (van Neer et al., 1996). A good agreement is obtained between numerical integration and CL over the entire range of frequencies analysed. The order of linearisation is irrelevant for this simple model (even 2nd order linearisation gave a good approximation) in spite of the fact that resonance behaviour, typical of non-linear systems, is observed. Apparently, the original non-linear character of the system is well maintained by a relatively low order Carleman linearised set of equations.

Carleman Linearisation may be used as an efficient tool for identification of optimal periodic control. This is illustrated in figure 3.3 in the case of concentration oscillations on a model 2 system. Species A is assumed to adsorb dissociatively and its gas phase concentration is used as the forcing variable. The sorption kinetics of species B are varied while the ratio of the adsorption and desorption rate constant is kept constant. The results are obtained using the direct differentiation in cycle-period of equation 3.11 as given by Hatzimanikatis et al. (1993). Optimum periodic control periods were analysed using CL combined with an optimisation algorithm. In the manner sketched the data in figure 3.3 were estimated efficiently while successive integration routines would have taken at least two orders of magnitude more CPU time.

In equation 18 in Hatzimanikatis et al. (1993) a minus sign is missing in front of the first bracket.
Figure 3.3 shows that in case the sorption kinetics of B are much slower than the kinetics of A, i.e. when the rate constant $k_3$ is low, the rate improvement compared to the relaxed steady state rate, the rate at the average concentration of $A^2$, is high. When species A and B have similar sorption kinetics, i.e. for high values of $k_3$ in figure 3.3, no rate improvement is observed. This can be understood by the fact that an optimum in the rate is achieved in case the forced component is able to follow the gas phase concentration transients, whereas the non-forced component is not (van Neer et al., 1996). The cycle-period for which a maximum rate is observed increases for lower values of $k_3$. Due to the slower sorption behaviour, component B is not able to keep up with the transients at longer cycle-periods.

In a similar way all kinds of catalytic reactions can be monitored within a wide range of kinetic constants using CL. It allows us to efficiently identify the optimal forcing strategy. Unfortunately the applicability of CL is restricted. In the following the formulation of sufficient conditions for the use of CL is addressed.

Criteria for validity of Carleman Linearisation

To assess the applicability of CL, first the assumptions used in the derivation of Lyberatos and Svoronos (1987) will be analysed. In the derivation of the analytical expressions for

\footnote{Note that this is not necessarily the optimal steady state.}
periodically forced systems (equation 3.11-3.22), these authors assumed that the eigenvalues of $S(\delta)$ and $S(\rho)$, see equation 3.7, must have a negative real part. Initially, this will be used as a criterion for the validity of the linearisation and it will be referred to it as the S-criterion. As the S-matrices show similarities to the Jacobian matrix of a system, it was analysed whether stability criteria were applicable as conditions for the validity of CL.

The left-upper part of the S-matrix, $A_{11}$ in equation 3.4, has the same size as the Jacobian matrix. $A_{11}$ reflects the behaviour of the S-matrix as it always shows positive real parts in the eigenvalues when these appear in the eigenvalues of the complete S-matrix. The similarity of $A_{11}$ compared to the Jacobian at the point of linearisation becomes clear in equation 3.33. Here, for a forced system that is described by two ordinary differential equations (d, g) with two state variables $(\theta_A, \theta_B)$ the following matrices are constructed:

$$
A_{11}^\delta = \begin{bmatrix}
\frac{\partial d}{\partial \theta_A} & \frac{\partial d}{\partial \theta_B} \\
\frac{\partial d}{\partial g} & \frac{\partial d}{\partial g}
\end{bmatrix}_{C_A^\delta, \theta_{A,CL}, \theta_{B,CL}}
\quad
A_{11}^\rho = \begin{bmatrix}
\frac{\partial d}{\partial \theta_A} & \frac{\partial d}{\partial \theta_B} \\
\frac{\partial d}{\partial g} & \frac{\partial d}{\partial g}
\end{bmatrix}_{C_A^\rho, \theta_{A,CL}, \theta_{B,CL}}
$$

$$
Jac = \begin{bmatrix}
\frac{\partial d}{\partial \theta_A} & \frac{\partial d}{\partial \theta_B} \\
\frac{\partial d}{\partial g} & \frac{\partial d}{\partial g}
\end{bmatrix}_{C_A, \theta_{A,CL}, \theta_{B,CL}}
$$

Note that in the $A_{11}$ matrices $C_A^\delta$ and $C_A^\rho$ are used instead of $C_{A,CL}$, which is used in the determination of the Jacobian. Naturally, Jacobian matrices can also be constructed for $C_A=C_A^\delta$ or $C_A=C_A^\rho$. Despite the close agreement between the matrices in equation 3.33, stability criteria do not reflect the occurrence of positive eigenvalues in $A_{11}$ and consequently also not in the S-matrices. For a simple system like model 1 instabilities are not observed as the eigenvalues of the Jacobian have negative real parts for all parameter sets. In contrast, the eigenvalues of the $A_{11}$ matrices show positive real parts in several cases; local stability is therefore not a proper criterion for the use of CL (assuming the S-criterion to be a valid one).

It may be concluded that the assumption made in the derivation of Lyberatos and Svoronos (1987), is not suited as a measure for the applicability of CL since it does not reflect an easily assessable property of a system. Therefore, the search to a useful criterion for the validity of CL was initiated. In the work presented below, it will even be shown that the S-criterion is neither necessary nor sufficient.
Chapter 3

Figure 3.4 shows a situation in which CL approximates the numerical results very closely. The development of the surface occupancies within one period in the cycle invariant state were calculated using equation 3.23. For a stepwise increase of the concentration at a dimensionless time \( j \), an increase in the surface coverage of A is observed while the surface occupancy of B decreases. In the middle of the cycle (at \( j + \frac{1}{2} \)) the gas phase concentration of A is lowered and the processes are reversed. The S-criterion is violated for the present case as in the \( \rho \)-part of the cycle the eigenvalues of \( S \) contain positive real parts. This becomes clear when the eigenvalues of \( A_{11} \) are reviewed: \((0.24, -2.2 \cdot 10^4)\). Nonetheless, numerical integration and Carleman calculations give identical results. Hence, the S-criterion apparently is not a suitable criterion to identify validity regions for CL.

This is further illustrated in figure 3.5. Surface occupancies are plotted versus the dimensionless time for a system with a different set of kinetic constants as compared to the previous case. Although the eigenvalues of the S-matrices all have negative real parts and thus the S-criterion is fulfilled, a large deviation is obtained between the two methods. In the lower part of the cycle (\( C_A = C_A^0 + \rho, \rho < 0 \)) the approximation using CL deviates significantly from the numerical integration results. For a higher order of linearisation only minor improvements are obtained and a positive real part in the eigenvalues is never observed.

A further analysis of deviations that occur between the linearised and the original system is obviously needed to come to suitable conditions for the application of the CL method. To that end the impact of the various parts of the derivation presented in equation 3.11-3.20 were analysed in situations that showed significant deviations and in situations that did not show
deviations. Table 3.1 shows, for the case presented in figure 3.2 which did not give deviations between the original and the linearized system, the contributions of the different parts of equation 3.11 to the time averaged reaction rate at various frequencies.

Table 3.1. Contributions of the various parts of equation 3.11 in the time averaged rate and the numerically estimated rate for model 1 (all units as shown in notation). $k_{1-5}$ as in figure 3.2. $C_A^0=0.1$, $C_A^\delta=0.7$, $C_B=0.3$ and $C_{A,CL}=0.4$ mol/m$^3$.

<table>
<thead>
<tr>
<th>log (f/Hz)</th>
<th>$J_1 + J_2$</th>
<th>$J_{1a} + J_{2a}$</th>
<th>$J_{1b} + J_{2b}$</th>
<th>$J_{1b}J_{2b}$</th>
<th>$J_{CL}$</th>
<th>$J_{num}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.002378</td>
<td>-4.586e-4</td>
<td>8.368e-8</td>
<td>0.001920</td>
<td>0.001918</td>
</tr>
<tr>
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<td></td>
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<tr>
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<td>-4.586e-4</td>
<td>-4.586e-4</td>
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<td>0.002378</td>
</tr>
</tbody>
</table>

At low frequencies the time average reaction rate is solely determined by the steady state reaction rates at the extremes of the control variable. Obviously, these are represented by $J_1+J_2$ as the term $J_3J_4J_5$ is negligible. The $J_4$ matrix reduces to the identity-matrix multiplied by the frequency of oscillation because the elements of $R$ and $D$ become zero (see equation 3.19 and 3.21). So when the frequency is low, the term $J_3J_4J_5$ becomes small. At higher frequencies the latter term becomes more significant and its influence grows until the term is equal to $J_{1b}+J_{2b}$ in the relaxed steady state. Now the time averaged reaction rate is approximately $J_{1b}+J_{2b}$ which is the steady state rate at the mean value of $C_A$. This is true as long as the point of linearisation is the steady state at the average value of the forcing variable ($C_{A,CL}=C_{A,av}$). At extremely high frequencies, $f > 10^{15}$ Hz, numerical errors occur (not shown here), $J_3J_4J_5$ no longer cancels out $J_{1b}+J_{2b}$ and the calculations fail. This is caused by singularities in the estimation of the inverse of $(I-DR)$.

In table 3.2 the $J$-matrices are given of a system for which CL and numerical integration differ significantly. As the relaxed steady state (determined by $J_{1a}+J_{2a}$; see table 3.1) is correctly predicted where the quasi steady state is not, the error must be due to a deviation in $J_{1a}+J_{2a}$. Further analysis shows that $J_2$ ($J_2=J_{2a}+J_{2b}$) differs from the numerically calculated steady state rate at $C_A=C_{A,CL}+\delta$ (note that $J_2$ has to be multiplied by 2 to make a fair comparison, as the cycle split is 0.5). From these results it must be concluded that $J_{2b}$ is causing the error as the Carleman prediction of the steady state at the upper part, $C_A=C_{A,CL}+\delta$, deviates less than 0.1% from the numerical solution. This demonstrates that if one steady state is predicted...
inaccurately in the sense that the linearised system does not approximate the original system, the other may still be estimated correctly.

Interestingly, a good agreement between the two methods is obtained at intermediate frequencies. The error introduced by $J_{2b}$ is cancelled out by $J_3J_4J_5$ which is most clearly observable in the relaxed steady state at high frequencies.

Table 3.2. Contributions of the various parts of equation 3.11 in the time averaged rate and the numerically estimated rate for model 1. $k_1=1\cdot10^2$, $k_2=1\cdot10^4$, $k_3=1\cdot10^2$, $k_4=1\cdot10^4$, $k_5=1\cdot10^6$ (all units as shown in notation). $C_A^0=0.1$, $C_A^\delta=0.7$, $C_B=0.3$ and $C_{A,CL}=0.4$ mol/m$^2$.

<table>
<thead>
<tr>
<th>$\log (f/Hz)$</th>
<th>$J_1 + J_2$</th>
<th>$J_{1a} + J_{2a}$</th>
<th>$J_{1b} + J_{2b}$</th>
<th>$J_3J_4J_5$</th>
<th>$J_{CL}$</th>
<th>$J_{num}$</th>
</tr>
</thead>
<tbody>
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<td>0.1585</td>
<td>-0.2173</td>
<td>NaN$^3$</td>
<td>NaN$^3$</td>
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</tr>
<tr>
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<td>-9.609e+7</td>
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</tr>
<tr>
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<tr>
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<td></td>
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<td>0.1596</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>-0.2173</td>
<td>0.1585</td>
<td>0.1585</td>
</tr>
<tr>
<td>6</td>
<td>-0.05874</td>
<td>0.1585</td>
<td>-0.2173</td>
<td>-0.2173</td>
<td>0.1585</td>
<td>0.1585</td>
</tr>
</tbody>
</table>

To investigate the impact of the nature of the forcing function on the appropriateness of the CL, two sets of simulations were done. First, for a system with a response that is well described by the linearised set of equations, the amplitude was increased for a constant frequency of oscillation. As of a certain amplitude deviations from numerical calculation become significant (figure 3.6). For even higher amplitudes the surface occupancies as calculated from the Carleman linearised system differ greatly from the original system. It must be noted that the S-criterion is only met for figure 3.6A. So this time the S-criterion, coincidentally, appears to be a proper condition for the use of CL. In the cases shown in figure 3.7, with a variable oscillating frequency and a constant amplitude, the S-criterion is never met. Still, for high frequencies the development of the surface occupancies is in good agreement with numerically calculated profiles. This is in agreement with the results presented in table 3.2.

From all simulation results it is concluded that a sufficient condition for the use of CL is its ability to predict the state variables in the steady state at the extremes of the control variables. This will be referred to as the E (extreme)-criterion. Whenever both the steady state surface coverage at $C_{A,CL}+\delta$ and at $C_{A,CL}+\rho$ ($\rho<0$) are estimated accurately, the transient response

$^3$ NaN: not a number. This indicates a division by zero or (+ or -) infinity.
Direct determination of cyclic steady states using Carleman Linearisation

During imposed oscillations is well predicted at all frequencies. This is clarified below on basis of the results shown above.

As indicated in table 3.2, the deviation between results of Carleman linearised and the original system regarding the prediction of the steady state behaviour at the low value of the forcing variable, causes an incorrect prediction of the transient reaction rate over a broad range of frequencies. At low frequencies the steady state situation is approached in both half-cycles of the oscillation. Obviously, when the steady states ($J_1$ and/or $J_2$) are incorrect, the time averaged rate under forced oscillations is also inaccurate. At high frequencies the relaxed steady state is approached, formed by the point of linearisation. The steady state at the point of linearisation is by definition correct because it is the input given to the linearised system.

The phenomena as presented in figure 3.6 and 3.7 can also be understood when the condition postulated above is adopted. For higher forcing amplitudes the upper and lower part of the cycle are further apart from the point of linearisation and subsequently the steady states are predicted less accurately. When the frequency is increased (figure 3.7) the system is no longer able to follow the transients which entails that the steady states in both parts of the cycle are never reached. This results in a correct prediction of the behaviour during the imposed oscillations. The error introduced by $J_{1b}$ and/or $J_{2b}$ is compensated by $J_3J_4J_5$ as demonstrated in table 3.2.

At first sight it is rather remarkable that the ability to predict steady states is a sufficient condition for the application of CL in a dynamic environment in which square waves are imposed. However, when the linearised system is able to find its path towards the steady state, it must also contain the information of that pathway. As oscillations are in the present work transitions from one state, lying between two extreme steady states, to another state also located between these two extremes, the condition sounds more logical.

The E-criterion offers the possibility to use CL in monitoring forced catalytic reactions since the reference steady states are estimated easily applying numerical or even analytical techniques. In contrast to the S-criterion, the E-criterion represents a sufficient condition for application of the Carleman linearised system, but not a necessary one. This may be illustrated in figure 3.8, where the ratio of the steady state reaction rate estimated using CL and the numerically estimated rate are shown (note that in this part of the work only $J_1$ and $J_2$, steady state rates, are used in view of their importance shown before). This ratio is plotted for values of the forcing variable below the point of linearisation ($C_{A,<CL}=0.4 \text{ mol/m}^3$). The system
analysed equals that used in figure 3.7. At the point where the CL prediction deviates more than 0.1% from the numerically calculated rate, the surface occupancies were taken (see markers). The linearised system is able to predict coverages for A in the part of the cycle where the value of the forcing variable is low, only when the coverages are located above $\theta_{A}^{\text{init}}$ (0.8 in this example). Coverages below this value are not reliable and the latter value is therefore called the critical coverage of A. The critical coverage of B is an upper limit as can be observed in figure 3.8. These critical values may now be used to explain the data in figure 3.7. As long as critical values for the surface coverage of A or B are not passed at the low
value for the forcing variable, the CL system is representative for the original system despite the fact that the E-criterion is not met. At low frequencies, applied in the figures 3.7A and 3.7B, both the occupancy of A is lower than $\theta_A^{\text{crit}}$ and the occupancy of B is higher than $\theta_B^{\text{crit}}$. Hence, the CL profiles deviate from the numerically calculated ones. In conclusion, critical state variables as derived from calculations of the steady states can be used to assess the validity of the Carleman linearised system, in case the E-criterion is not met.

![Figure 3.8. Steady state surface occupancy versus concentration of A (numerically estimated) and the ratio of Carleman Linearisation and numerical integration estimation of the steady state rate for model 1. $k_{1-5}$ as in figure 3.7. $C_A,CL=0.4$ and $C_B=0.3$ mol/m$^3$.](image)

Critical values were also calculated for the case presented in figure 3.6 and the same behaviour is observed. Imposing oscillations with high amplitudes (see figure 3.6B and 3.6C) results in occupancies temporarily located beyond the critical boundaries. In the part of the cycle where the forcing variable is low, $\theta_A$ and $\theta_B$ have passed their critical values and significant deviations are observable. When the Carleman steady state prediction fails at both extremes of the cycle (not shown here), two critical values for each state variable will be required to ensure reliability in case the E-criterion is not met.

In view of the above, it may be of considerable interest to know which region around a point of linearisation can be properly approximated by the Carleman linearised system. To investigate the reason for an incorrect Carleman steady state estimation$^4$ (or the reason why the E-criterion is not met), all catalytic systems which show erroneous steady state predictions were analysed in detail. One aspect in the analysis concerned the reaction rates of the

---

$^4$ The terms incorrect and erroneous prediction/estimation refer to the occurrence of significant deviations between the approximation using Carleman Linearisation and the original system. Theoretically, an estimation based on Carleman Linearisation is always correct.
individual reaction steps in the mechanism. The same ratio as before \((J_{\text{ss,CL}}/J_{\text{ss,num}})\) as well as the rates of the individual steps in the mechanism were plotted versus the concentration of component A. In all cases using relatively simple models like model 1, CL starts to deviate when there is a change in the rate-sequence of the elementary steps compared to the point of linearisation. Figure 3.9 shows that in case of the system presented in figure 3.6.

**Figure 3.9.** Individual steady state rates of the steps in model 1 (numerically estimated) and the ratio of the steady state rate calculated using Carleman Linearisation and the rate calculated by numerical integration. (1): \(J_{\text{ss,ads,A}}=k_1C_A(1-Q_A-Q_B)\), (2): \(J_{\text{ss,ads,B}}=k_2C_B(1-Q_A-Q_B)\), (3): \(J_{\text{ss,reaction}}=k_3\theta_A\theta_B\) (4): \(J_{\text{ss,des,A}}=k_4\theta_A\) (5): \(J_{\text{ss,des,B}}=k_2\theta_B\ k_{1-5}\) as in figure 3.6. \(C_{A,CL}=0.4\) and \(C_{B}=0.3\ \text{mol/m}^3\).

At high concentrations in this graph (near the point of linearisation; \(C_{A,CL}=0.4\ \text{mol/m}^3\)) the desorption of component B forms the slowest step in the mechanism whereas the adsorption of A is the fastest step. At lower concentrations the desorption of A is slowest and the adsorption of B shows the highest rate. Compared to the point of linearisation a change in the rate-sequence has occurred. As of the point where the rate-sequence changes, CL results start to deviate from the numerically calculated steady state rates. Once again figure 3.9 makes clear that the occurrence of positive real parts in the eigenvalues of the S-matrix is not a proper criterion as can be observed from the point where for the first time positive values occur (S-criterion). In case of simple models it was found out that the change in the rate sequence was always the reason for the incorrect prediction of the steady state rates at the extremes of the oscillation. More complex models (e.g. model 3) show similar behaviour, although sometimes just before such a change CL fails in predicting the behaviour of the original system correctly. Drastically changing surface occupancies are noticeable in the latter case. It is important to note that an improvement of the CL prediction can be obtained using a higher order of linearisation or an improvement method, as described in the next section, as long as there is no change in the rate-sequence. In case such a shift is present, improvements
are marginal or absent. This is demonstrated by the example presented in figure 3.10. It is shown that after a change in the rate-sequence no significant improvement is observed using higher orders of linearisation.

![Figure 3.10. The ratio of the steady state rate calculated using Carleman Linearisation at various orders (see legend) and the rate calculated by numerical integration for model 1.](image)

Comparing the data in figure 3.9 and figure 3.6, both obtained with the same parameter set, one would expect that the CL simulations in figure 3.6 fail for an amplitude smaller than the one used in figure 3.6A, given the fact that a change in the rate-sequence of the elementary steps occurs in between the upper and lower value of the control variable. However, the CL system and original system produce identical results. This can be understood by the fact that the frequency of oscillation is (far) above the frequency at which quasi steady state is found. The system is not able to relax to its steady state during each half-cycle, therefore the critical values are not passed and there is no change in the rate-sequence of the elementary steps during square wave cycling.

**Use of Carleman Linearisation for strongly non-linear forcing variables**

Temperature oscillations serve as an illustration of the behaviour of a system in case of strongly non-linear forcing variables. The Arrhenius-type dependence of the reaction rate on temperature creates a highly non-linear system. This non-linearity leads to a strong increase in the number of evaluation points per cycle, required to produce accurate numerical integration.
results. Low frequency temperature oscillations, imposed on a model 1 system, can induce a remarkably steep response, i.e. the occurrence of high reaction rates for short periods within the cycle. Figure 3.11 shows that at least $10^4$ data points per cycle should be used to obtain reliable numerical results. This leads to a considerable increase in the computational effort. For that reason it is interesting to notice that even a 2nd order CL produces correct results.

![Figure 3.11. Influence of number of points per cycle on the numerically integrated time average rate at a oscillation frequency of $10^2$ Hz for model 1.](image)

The highly non-linear nature of temperature as the forcing variable appears to influence the relaxed steady state results. As demonstrated in van Neer et al. (1996), at high frequencies the average surface occupancy for both components equals the steady state coverage at the highest temperature used during the cycling. This means that the reaction rate in the relaxed steady state is

$$J_{rss} = k_5(T_{s,av}) \cdot \theta_A^\delta \cdot \theta_B^\delta$$

and not just the steady state rate at the mean value for the forcing variable. This behaviour must also follow from the J-matrices in case of a proper CL estimation; see table 3.3. For low frequencies the time average rate is determined by $J_1 + J_2$ and $J_3J_4J_5$ is negligible, like before. In the relaxed steady state $J_1 + J_2$ is no longer cancelled out by $J_3J_4J_5$ as was observed in all simulations with concentration forcing. Hence the performance under periodic conditions, expressed as the time averaged reaction rate, is not exclusively estimated on the basis of $J_1 + J_2$ as was the case in the tables 3.1 and 3.2. Consequently in case of a failure in the CL calculation of the steady states at the extremes of the cycle, it is not certain that the relaxed...
steady state is well predicted in contrast to the results of the concentration forcing simulations. When CL is able to predict the steady state coverages well at the highest temperature, there is no doubt on the accuracy of the estimated relaxed steady state.

Table 3.3. Contributions of the various parts of equation 3.11 in the time average rate and the numerically estimated rate for model 1. $k_{1,0}=1\times10^{16}$, $k_{2,0}=1\times10^{4}$, $k_{3,0}=1\times10^{5}$, $k_{4,0}=1\times10^{3}$, $k_{5,0}=1\times10^{3}$, $E_1=1.5\times10^{3}$, $E_2=1\times10^{4}$, $E_3=1.25\times10^{4}$, $E_4=1\times10^{4}$, $E_5=1\times10^{4}$ (all units as shown in notation). $T_{s_p}=500$, $T_{s_s}=700$ and $T_{s_{CL}}=600$ K.

<table>
<thead>
<tr>
<th>log $(f/\text{Hz})$</th>
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<th>$J_{ha} + J_{2a}$</th>
<th>$J_{ib} + J_{2b}$</th>
<th>$J_3 J_4 J_5$</th>
<th>$J_{CL}$</th>
<th>$J_{num}$</th>
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<td>3.862e-4</td>
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<td>0.001189</td>
<td>0.001189</td>
</tr>
<tr>
<td>0</td>
<td>:</td>
<td>:</td>
<td>:</td>
<td>-9.874e-5</td>
<td>0.001287</td>
<td>0.001281</td>
</tr>
<tr>
<td>5</td>
<td>0.001189</td>
<td>8.024e-4</td>
<td>3.862e-4</td>
<td>-5.876e-4</td>
<td>0.001776</td>
<td>0.001776</td>
</tr>
</tbody>
</table>

Figure 3.12. The ratio of the steady state rate calculated using Carleman Linearisation and the rate calculated by numerical integration vs. temperatures using various orders of linearisation for model 1 (see labels). $k_{1,0}=1\times10^3$, $k_{2,0}=1\times10^4$, $k_{3,0}=7\times10^2$, $k_{4,0}=1\times10^4$, $k_{5,0}=1\times10^3$, $E_1=1\times10^3$, $E_2=1\times10^4$, $E_3=1\times10^4$, $E_4=1\times10^4$, $E_5=1\times10^4$ (units as shown in notation), $P_A=P_B=1000$ Pa and $T_{s_{CL}}=600$ K.

For a stronger non-linear input variable such as temperature, it may be necessary to increase the order of linearisation. 4th order CL may still produce results that deviate from numerical calculations (see table 3.3: compare $J_{num}$ and $J_{CL}$ at $f=10^4$ Hz). As stated before, when a shift in the rate-sequence does not occur, improved CL results can be obtained by increasing the order of linearisation. Figure 3.12 demonstrates this in case of a temperature oscillation around 600 K. The amplitude is varied in the simulations and the ratio of the CL steady state
rate and the numerically calculated rate at the extremes of the forcing variable is given. Within the temperature window shown in the graph a change in the rate-sequence of the elementary steps does not occur. In case of 2\textsuperscript{nd} order linearisation a deviation is obtained at both low and high temperatures where higher orders only fail at the high temperatures. Unfortunately, upon increasing order of linearisation the improvement becomes less.

Also here, it is possible to estimate critical values for the state variables of the dynamic system. In the first two cases presented in figure 3.13 (A and B) the development of the surface occupancies within one cycle is estimated using a linearisation around the average temperature. Proper predictions (deviation < 0.1 %) are obtained when the surface occupancy of A is below and the occupancy of B is above its critical value (dotted lines) at the upper part of the cycle. As observable from figure 3.13 at high frequencies the critical values are not exceeded and the simulation results are adequate. At lower frequencies (figure 3.13B) the critical boundaries are passed in the first half-cycle. Clearly, CL predictions are incorrect. Higher orders of linearisation may not produce satisfactory results: in figure 3.12 even an order of 8 still gave significant deviation from the numerical estimation and higher orders only result in marginal improvement. A rather unexpected remedy is depicted in figure 3.13C. Instead of using the average of the forcing variable as point of linearisation, another point closer to the steady state that could not be approximated properly by CL, was taken. Subsequently, δ and ρ, the amplitudes of the oscillation, were changed in such a way that the same situation was obtained as before. For the example in figure 3.13 this works out as follows. Initially the linearisation was performed around $T_{S_{CL}}$=600 K as oscillations between $T_{S_{δ}}$=300 and $T_{S_{δ}}$=900 K were imposed. As the higher part of the oscillation gave no good approximation, $T_{S_{CL}}$=800 K is used as new point of linearisation. The amplitude in the lower part (ρ) becomes 500 K and the amplitude in the upper part (δ) 100 K to obtain the same oscillations. It can be concluded from the response that now the CL estimation is very good and critical values are absent. The linearisation is performed near the steady state which could not be approximated accurately, which results in an improvement of the estimation under dynamic conditions. This method of improvement can be used in all cases in which the rate-sequence of the elementary steps does not change. It is not merely applicable in situations where temperature is the forcing variable; good results are also obtained in concentration forcing simulations for weakly and strongly non-linear systems.

The example given above shows that the estimation of the steady state that is poorly approximated by CL, may be improved by shifting the point of linearisation. This necessarily leads to a poorer approach of the other steady state. However, this latter may not be observable due to the fact that the impact is only very small. So, a less accurate estimation of
one steady state does not necessarily undo the advantages gained by the improvement of the other steady state.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3_13.png}
\caption{Surface occupancy during one period in the cyclic steady state at various frequencies and points of linearisation for model 1. $k_{1,0.5,0}$ and $E_{1,5}$ as in figure 3.11. $T_{S^p}=300$ and $T_{S^o}=900$ K.}
\end{figure}

**Use of Carleman Linearisation for complex and strongly non-linear systems**

Model 2 assumes dissociative adsorption and associative desorption of one of the reactants. This results in an increase in non-linear character as compared to model 1 and multiple steady states may now arise. Under forced oscillations the cyclic steady state response of such a system may depend on the initial condition of the catalyst (van Neer et al., 1997b). Since CL does not require initial conditions it is interesting to focus on its use in such systems.
In figure 3.14 the time average reaction rate under forced concentration oscillations is given for a system which exhibits bi-stability within the window of concentrations that are imposed. Table 3.4 shows the stationary states for this system at the average value of the forcing variable (used as point of linearisation) and in figure 3.15 the steady state coverages are given as function of the concentration of A between the upper and lower value of this forcing variable.

The simplest response in figure 3.14 is the so-called negative resonance: a minimum is observed in the time average rate versus frequency plot. Numerical simulation using the initial condition of a surface that is completely filled with component B (1) and CL performed at steady state 1 (table 3.4), the points denoted with a circle in figure 3.15 at the average of the forcing variable $C_A$, produce identical results. At all frequencies applied the same type of attractor governs the relaxation to the two states $C_A^0$ and $C_A^8$ (0.1 and 0.7 mol/m$^3$ respectively in the present case). Both steady states as well as the point of linearisation are located on the same steady state branch (denoted with $A_1$ and $B_1$). The system does not exhibit a rate-sequence shift, the surface occupancies remain approximately constant at the level of steady state 1 and so CL produces correct results.

For a forced system with different initial conditions, for instance a surface that is fully occupied by component A, a deviating behaviour is observed. The non-linearised catalytic system shows a maximum reaction rate between the relaxed and quasi steady state, termed "positive resonance". Much higher rates compared to the previous situation are obtained. The system starts at the steady state branch denoted by $A_3$ and $B_3$ due to the different initial condition. At high forcing-frequencies the system variables do not respond instantaneously to the state variables and the point at which the system shifts from one branch to the other is not reached. At low frequencies in the part of the cycle with a low value for the forcing variable, the system has to undergo a steady state branch transition; there are no steady states denoted with a square at low concentrations of component A (figure 3.15). The use of steady state 3 (table 3.4 and figure 3.15, square) in the CL gives correct results at high frequencies since the surface occupancies during the oscillations are located on one and the same steady state branch and near the values of the occupancies used in the linearisation. As, at low frequencies, the system has to undergo the branch transition and in addition there is a shift in the rate-sequence of the elementary steps, CL fails. When steady state 2 (table 3.4 and figure 3.15, triangle) is taken as point of linearisation a response is obtained which has no physical meaning. It gives unrealistic results since an unstable trajectory is followed which will never become stable. Apparently, the linearised system cannot cope with a transition from one
steady state branch to another and therefore CL is not suited for use in systems that exhibit multiple steady states.

Figure 3.14. Carleman Linearisation (markers) and numerical integration estimation (lines) of the time average rate versus frequency for model 2. Various points of linearisation (s.s. 1 - s.s. 3; see table 3.4) and two initial conditions were used: (1) \( (\theta_A, \theta_B) = (0, 1) \) and (2) \( (\theta_A, \theta_B) = (1, 0) \). \( k_{1.5} \) as in table 3.4. \( C_A^0 = 0.1 \), \( C_A^1 = 0.7 \) and \( C_B = 0.3 \text{ mol/m}^3 \).

Figure 3.15. Steady state surface occupancies (numerical integration result) at various concentrations of A for model 2. \( k_{1.5} \) as in table 3.4 and \( C_B = 0.3 \text{ mol/m}^3 \). Solid lines represent \( \theta_A \) and dashed lines \( \theta_B \). Markers: see text.

Table 3.4. Stationary states at \( C_A = 0.4 \) and \( C_B = 0.3 \text{ mol/m}^3 \) for model 2. \( k_1 = 1 \cdot 10^4 \), \( k_2 = 1 \cdot 10^6 \), \( k_3 = 1 \cdot 10^5 \), \( k_4 = 1 \cdot 10^9 \), \( k_5 = 1 \cdot 10^7 \) (all units as shown in notation).

<table>
<thead>
<tr>
<th>type of steady state</th>
<th>steady state 1</th>
<th>steady state 2</th>
<th>steady state 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta_A )</td>
<td>stable node</td>
<td>saddle point</td>
<td>stable node</td>
</tr>
<tr>
<td>( \theta_B )</td>
<td>0.0011</td>
<td>0.11</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>0.99</td>
<td>0.85</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Finally a system that contains three state variables, will be analysed (model 3). In this model component A can be stored, for instance by spillover from the reactive sites of A to a site which is not reactive. This introduces an additional state variable. The E-condition as formulated before still can be used: when the steady states at the boundaries of the oscillations are correctly predicted, CL is applicable for prediction of the dynamic response. Hence in figure 3.16 the steady state estimations of CL and numerical integration are compared for a model 3 system. Two different points of linearisation were applied. In case the average value of the concentrations \((C_A=0.4 \text{ mol/m}^3)\) is taken as base for the linearisation even second order linearisation gives good results when the concentration of A remains relatively high \((C_A>0.1 \text{ mol/m}^3)\). Thus, in principle CL will be able to predict responses on square wave forcing for this complex system with three state variables, as long as \(C_{A,P}>0.1 \text{ mol/m}^3\) (assuming no problems at \(C_{A,5}>C_{A,CL}\)). At low concentrations CL deviates significantly from the numerical value. Higher order linearisations do not improve the result. Better estimations are obtained when the point of linearisation is chosen closer to the point where the deviation starts \((C_{A,CL}=0.04 \text{ mol/m}^3)\). Unfortunately the accuracy at higher concentrations becomes worse which implicates the existence of an optimal point of linearisation. For instance for the simulation of concentration oscillations between 0.05 and 0.75 \text{ mol/m}^3\) the optimal point of linearisation is found to be 0.25 \text{ mol/m}^3\) for the present case. The reason for the difficulty in the approximation of this system by CL lies in the fact that there is a rate-sequence shift in the window of concentrations shown in figure 3.16. At the marked concentration radical changes in the surface occupancies are observed.

![Figure 3.16. Carleman Linearisation (markers) and numerical integration estimation (lines) of steady state rates at various concentrations of A for model 3. Two points of linearisation were used (see legend). \(k_1=1\cdot10^5, k_2=1\cdot10^5, k_3=1\cdot10^5, k_4=1\cdot10^5, k_5=1\cdot10^6, k_6=1\cdot10^2, k_7=1\cdot10^3, N=1\cdot10^2\) (units as shown in notation) and \(C_B=0.3 \text{ mol/m}^3\).](image-url)
Direct determination of cyclic steady states using Carleman Linearisation

CONCLUSIONS

Carleman Linearisation is a useful and particularly efficient tool in understanding the response of heterogeneous catalytic systems towards forced square wave oscillations and in the a priori prediction of rate resonance phenomena. Analytical expressions derived from the Carleman Linearised system give both the time averaged performance of the system and the development of the state variables in case of cycling one forcing variable. Whereas successive numerical integration may be very time consuming to reach the cycle invariant state, CL results in direct determination of this state.

Carleman Linearisation can be used in case the system can be described by a set of ordinary differential equations. A fair agreement is observed between numerical and Carleman simulations for a number of conventionally used microkinetic sorption-reaction models. The response to periodic forcing of relatively complex systems, i.e. with more than two state variables or high non-linear systems, as well as relatively simple systems with both weakly and strongly non-linear forcing variables, can be well described. A sufficient condition for the use of CL is that the steady states at the extremes of the forcing variable must be predicted accurately. This is a new condition for the use of CL for the analysis of square wave programming than used up to now, as to this time it was assumed that the real parts of the eigenvalues of the S-matrices need to be negative. The latter requirement is neither sufficient nor necessary.

Steady states at the upper and/or lower value of the forcing variable cannot be estimated with CL when the sequence of the rates of the elementary steps in the microkinetic mechanism changes compared to the point around which the system was linearised. In the vicinity of such a shift failures arise. For a correct prediction of steady states in systems that exhibit multiplicities the type of attractor at the lower and upper part of the cycle must be the same as the one at the point of linearisation. Carleman Linearised systems cannot handle transitions from one steady state branch to another.

The prediction of the steady states at the extremes of the forcing variable can be improved when there is no change of the rate-sequence. Two remedies result in more accurate estimations. First the order of linearisation can be increased up to the point where the size of the matrices become excessive. Alternatively, it is possible to improve the CL predictions by shifting the point around which the linearisation is performed closer to the erroneously predicted steady state, without losing accuracy in the estimation of the other steady state. This remedy has often much more effect than an increase of the order.
Whereas the correct prediction of the steady state behaviour at the extremes of the forcing parameter provides a sufficient condition for CL to be applicable, in some cases where these steady states are not well estimated still good approximations for the variables of interest can be obtained. This is due to the fact that during periodic operation the steady states are not necessarily reached. As long as the state variables stay within the window of states that can be approached by the Carleman Linearised system, no failures occur. Such boundaries can be easily estimated using a comparison of the steady state calculations of the Carleman Linearised system with numerical integration or analytical results. Whenever under periodic operation the surface occupancies surpass these boundaries, CL will no longer be a reliable tool.

**NOTATION**

- **A**: amplitude of oscillation with regard to $C_{i,v}$ or $T_{s,v}$, mol/m$^3$ or K
- **$A_{ij}$**: matrices defined by equation 3.8
- **$b$**: number of state variables
- **$c$**: vector defined in equation 3.24 and 3.25
- **$C$**: constant in criterion for cyclic steady state, equation 3.26
- **$C_i$**: concentration of component $i$, mol/m$^3$
- **$C_{i,v}$**: average concentration of component $i$, mol/m$^3$
- **$C_{i,p}$**: concentration in the upper part of the cycle, mol/m$^3$
- **$C_{i,p}$**: concentration in the lower part of the cycle, mol/m$^3$
- **$C_{i,CL}$**: concentration at which Carleman Linearisation is performed, mol/m$^3$
- **$D$**: matrix defined in equation 3.21
- **$E_i$**: activation energy of reaction step $i$, J/mol
- **$f$**: vector function in equation 3.1
- **$f$**: oscillation frequency, Hz
- **$J$**: time average rate under forced oscillations, s$^{-1}$
- **$J_{i}$**: defined in equation 3.12-3.20
- **$J_{num}$**: numerically calculated time average rate
- **$J_{ss}$**: time average rate in the relaxed steady state, s$^{-1}$
- **$J_{ss}$**: steady state reaction rate, s$^{-1}$
- **$I$**: identity matrix
- **$J_{ss,i}$**: steady state reaction rate of step $i$, s$^{-1}$
**Greek Letters**

- $\delta$  \( \text{amplitude of control variable in the upper part of the cycle} \)
- $\theta$  \( \text{vector of surface occupancies} \)
- $\theta_{\text{CL}}$  \( \text{steady state occupancy in the point at which the linearisation is performed} \)
- $\theta_{i}$  \( \text{steady state occupancy at } T_s = T_s^{\delta} \)
- $\rho$  \( \text{amplitude of control variable in the lower part of the cycle} \)
- $\psi$  \( \text{criterion for cyclic steady state, defined in equation 3.26} \)
REFERENCES

- Neer, F.J.R. van, B. van der Linden and A. Bliek. Forced concentration oscillations of CO and O₂ in CO oxidation over Cu/Al₂O₃, Catalysis Today 38, 115 (1997a) or chapter 5 of this thesis.
CHAPTER 4

Concentration programming of catalytic reactions*

ABSTRACT

In this chapter the role of multiplicity, spillover and Eley-Rideal kinetics is investigated with regard to behaviour of a catalytic reaction during square wave concentration programming. This work can be viewed upon as a continuation of chapter 2 where a Langmuir-Hinshelwood molecular adsorption/desorption model was analysed in detail. It is demonstrated that dissociative adsorption of the forced component does not lead to stronger resonance phenomena on the surface of the catalyst compared to molecular sorption. When the non-forced component shows dissociative adsorption, sharper resonance peaks will be observed. Dissociative adsorption combined with high surface reaction rates may lead to multiplicity under steady state conditions. In that case, complex behaviour under concentration programming may also be observed in the sense that the response towards concentration oscillations depends on the initial conditions of the catalyst. The complex behaviour can be understood when the phase planes of the surface occupancies are investigated. It is shown that a large storage capacity on the catalyst influences the response towards concentration programming such that the relaxed steady state is shifted to much lower oscillation frequencies. Cases are presented where this shift leads to higher reaction rates as well as cases where rates are decreased. The generality of the observed phenomena is emphasised by an example in which spillover terms are included in a mechanism based on Eley-Rideal kinetics: the shift of the relaxed steady state to lower frequencies also appears in case of systems obeying Eley-Rideal kinetics. In contrast to the statements of Feimer et al. (1982), rate enhancement could be simulated using adsorption/desorption models.

INTRODUCTION

Periodic operation of chemical processes may contribute to more selective manufacturing processes since it has been proven that selectivity and activity of catalytic reactions can be significantly improved by programming of input parameters in time (see e.g. Stankiewicz and Kuczinsky, 1994). Numerous studies are available demonstrating occurrence of resonance and reaction rate enhancement compared to steady state operation in case of periodically forced catalytic reactions, as is shown in chapter 1 of this thesis. It is not a priori possible to predict whether cycle averaged performance under cyclic programmed conditions is favourable for a given catalytic reaction. This lack of predictability forms a major drawback in the practical application of periodic operation. To understand the response of a catalytic reaction towards input programming a sound fundamental approach is required. In recent work (van Neer et al., 1996) resonance phenomena for relatively simple catalytic systems was set out to analyse. From this study an understanding of the phenomena that occur on a catalytic surface in case of resonance was gained.

With the present work multiple objectives are met. First of all more complex models will be investigated with regard to their behaviour during periodic forcing. Emphasis is put on the role of multiplicity, spillover capacity and Eley-Rideal kinetics on the response of heterogeneous catalytic systems under concentration programming. The impact of these mechanistic characteristics on the ability of a system to show resonance is discussed. Another purpose is to verify whether rate enhancement can be predicted on basis of more extended adsorption/desorption models, as relatively simple molecular adsorption models (see van Neer et al., 1996) does not show reaction rate enhancement beyond the optimal steady state.

MODELS, FORCING FUNCTION AND ALGORITHMS

The models used in this study were all derived from the base molecular adsorption/desorption model used in chapter 2. In the next sections the differences compared to this model, the so-called characteristics of the catalytic reaction mechanism, will be emphasised.

The applied forcing function in the concentration of a reactant A is a square wave. This function was chosen because in most experimental work described in literature, square waves were used. By its simplicity, the interpretation of results of square wave forced systems is easier compared to systems where other forcing functions are used. As not much is known on the underlying principles of resonance, a simple forcing function is favourable. Furthermore,
Feimer et al. (1982) compared square wave forcing with sinusoidal waves and concluded that the former is a better form since it represents the largest possible variation from a mean value and therefore will induce the greatest resonance. Only in exceptional cases where at the extremes of the forcing variables the output variable is very low, this statement may not be true.

Except for one model, the concentration of reactant A was varied between 0.1 and 0.7 mol/m$^3$. These upper limit and lower concentration limits were chosen rather arbitrary. The lower limit of 0.1 mol/m$^3$ was used instead of zero because in reality concentrations above a catalytic surface will not easily approach zero very fast. Imposed concentration oscillations are attenuated in a reactor thereby preventing concentrations to become zero, especially when the forcing frequency is high. The concentration of a second reactant B was kept constant at 0.3 mol/m$^3$ and a cycle split of 0.5 was used unless noted otherwise. The forcing function is visualised in figure 4.1.

![Figure 4.1. The forcing function as used in the simulations. The cycle split is denoted by $\epsilon$.](image)

In the next section the following model characteristics will be addressed with respect to its impact on the response during concentration programming: dissociative adsorption of the forced component instead of molecular adsorption (model 1), dissociative adsorption of the non-forced component (model 2), reactant storage capacity of a catalyst (model 3) and Eley-Rideal reaction in combination with reactant storage (model 4). An example of a model 2 catalytic reaction is CO oxidation on Pt. It will be investigated in view of the experimentally observed rate enhancement compared to the optimal steady state reaction rate by using the specific kinetic constants of this reaction.
Simulation results are mostly presented as the time averaged reaction rate versus oscillation frequency. In a few cases frequencies were applied which are unrealistic in the sense that in practise never such high frequencies could be generated. Results of catalytic reaction systems demonstrating resonance for high frequencies can be translated to systems obeying slower kinetics. Resonance phenomena will shift towards lower frequencies which can be estimated simply by using the factor by which the kinetics of the system has been lowered.

Examples of ordinary differential equations which describe the dynamics of catalytic systems, can be found in chapter 2 and chapter 3. These equations were also used in the present study. The time averaged rate and surface coverages in the cycle invariant state were obtained using Carleman Linearisation whenever this method was applicable (van Neer et al., 1999). In the other cases the ODE's were integrated using the Runge-Kutta-Fehlberg 45 algorithm, a numerical technique. Whenever Carleman Linearisation is not applicable, this will be noted in the captions of the specific figures and RK45 is used instead. The same criterion for the approach of the cyclic steady state is used as in chapter 2.

RESULTS AND DISCUSSION

**Model 1: dissociative adsorption of the forced component**

In this model one of the components is assumed to adsorb dissociatively. For a single surface reaction step, this model may be represented as:

\[
\begin{align*}
A_2 + 2S & \leftrightarrow 2AS \\
B + S & \leftrightarrow BS \\
AS + BS & \rightarrow C + 2S
\end{align*}
\]

Like in case of molecular adsorption models, the response to forced oscillations depends on the ratio of the surface reaction rate and the sorption rates of component A and B.

In case the rate of the reaction between the adsorbed species, the surface reaction rate, is lower than the other reaction steps, i.e. the adsorption and desorption of component A and B, no qualitative differences are observed compared to the molecular sorption model. In the following this is demonstrated for a case in which a minor positive resonance was found. Steady state surface occupancies are given versus the forcing variable in figure 4.2 and the
time averaged rate in the cyclic steady state is given as a function of the forcing frequency in figure 4.3.

Figure 4.2. Steady state reaction rate and surface occupancies for model 1. \( k_1 = 2 \cdot 10^3 \), \( k_2 = 1 \cdot 10^4 \), \( k_3 = 2 \cdot 10^7 \), \( k_4 = 1 \cdot 10^4 \), \( k_5 = 1 \) (units as shown in notation). Marker: see text.

Figure 4.3. Time averaged rate versus frequency for model 1. Kinetic constants as in figure 4.2.

The profiles of the surface species during one period in the cyclic steady state are not shown as the behaviour of the species is similar to what has been observed before (chapter 2). The principle of the occurrence of resonance is the same. At the resonance frequencies component B is no longer able to follow the forced transients of the concentrations of reactant A, as desorption of reactant B is slow. The time averaged rate is slightly increased since \( \theta_B \) experiences the average of \( \theta_A \) and figure 4.2 shows that this results in a higher average \( \theta_B \) (see marker). A more detailed explanation for these phenomena can be found in chapter 2. As the response is similar to that of the molecular sorption model, this sets the conditions for the occurrence of resonance:

- The sorption behaviour of the forced component must be at least as fast as the sorption of the other component involved. This means that when \( \theta_A \) cannot keep up with the concentration variations, no resonance will be found.
- The surface has to be almost completely occupied in the concentration window applied during concentration programming.

In the presented case, the rate under forced concentration oscillations does not exceed the optimal steady state rate as can be concluded from a comparison of the maximum reaction rate presented in figure 4.2 and in figure 4.3. This is observed for various sets of kinetic constants and strongly suggests that rate enhancement can not be obtained with the present model and forcing function. This and the fact that the response on concentration programming is similar to that of the molecular sorption model, is rather remarkable. Many authors claimed stronger
resonance when the non-linearity of a system increases (see for instance Thullie et al., 1987). Focusing on single component sorption, sheds a light on the obtained results.

It is useful to compare the equations that describe the dynamics of single component sorption in case of molecular and in case of dissociative adsorption. For a change in concentration $A$, the mass balance equations and the solution in time for molecular adsorption are respectively

$$\frac{\partial \theta_A}{\partial t} = k_1 C_A (1 - \theta_A) - k_2 \theta_A \quad 4.1$$

$$\theta_A(t) = \theta_{A,SS} + (\theta_{A,0} - \theta_{A,SS}) \exp(-\lambda t) \quad 4.2$$

where $\theta_{A,0}$ is the initial surface coverage and $\theta_{A,SS}$ the final steady state surface coverage at the imposed concentration. The time constant $\lambda$ is:

$$\lambda = k_1 C_A + k_2 \quad 4.3$$

The balance for dissociative adsorption including the reversed step reads:

$$\frac{\partial \theta_A}{\partial t} = 2k_1 C_A (1 - \theta_A)^2 - k_2 \theta_A^2 \quad 4.4$$

The surface coverage $\theta_A$ can be obtained as

$$\theta_A(t) = \frac{-B - \sqrt{Q} + (B - \sqrt{Q})D \exp(-\sqrt{Q}t)}{2A(1 - D \exp(-\sqrt{Q}t))} \quad 4.5$$

where

$$A = 2(k_1 C_A - k_2) \quad 4.6$$

$$B = -4k_1 C_A \quad 4.7$$

$$Q = 16k_1 k_2 C_A \quad 4.8$$
Concentration programming of catalytic reactions

and D is the integration constant governing the steady state surface occupancy. For this case the time constant can be derived as:

\[ \lambda = \sqrt{Q} = 4\sqrt{k_1 k_2 C_A} \]  

When the two cases are compared the time constant (relaxation constant) \( \lambda \) differs in its dependence on the kinetic constants. Furthermore, the molecular adsorption model relaxes exponentially to the steady state (equation 4.2) whilst the dissociative adsorption model shows a quotient of natural exponents (equation 4.5). When the time constants are assumed to be equal, both models give similar relaxation times going from one steady state to another, as can be concluded from figure 4.4. This implies that the time constant determines the relaxation time. Equation 4.3 and equation 4.9 show that in case of molecular sorption the time constant is equal to or higher than the time constant of the dissociative adsorption model (using the same value for \( k_1, k_2 \) and \( C_A \)). The relaxation time constant will therefore be similar or higher using dissociative adsorption of component A.

Figure 4.4. Comparison of molecular adsorption/desorption model (continuous line) and dissociative adsorption/desorption model (dashed line) during the relaxation from one steady state to another.

As a consequence of this, for the present case using dissociative adsorption the relaxation of component A will be retarded as compared to the case using molecular sorption. Component A, being the forced component, and resonance is merely observed when the surface occupancy of the forced component is able to follow the changes whereas the non-forced is not. In this respect the retardation of the sorption dynamics of component A is not likely to intensify the resonance phenomena; on the contrary, it is more likely that resonance will be less pronounced.
The surface occupancy under steady state conditions is another important aspect in the occurrence of resonance. The molecular sorption model results in higher surface occupancies compared to the dissociative adsorption model at the same ratio for $k_{\text{out}}/k_{\text{des}}$ (except for a very low ratio). This means that using the same kinetic constants, the catalytic surface of a dissociative adsorption system probably shows more empty sites. As noted before, high surface occupancies are required to obtain resonance phenomena. This forms another explanation for the absence of stronger resonance for the present model compared to the molecular sorption model.

The case discussed so far, handled a situation in which the surface reaction is the slowest elementary step of the complete system. As mentioned before, the molecular sorption model shows other dynamic behaviour when the surface reaction rate is relatively fast. In analogy to this model, the dissociative adsorption model shows in similar situations other behaviour as well. This difference is already observable from steady state behaviour. High surface reaction rates may induce multiple steady states as is shown in figure 4.5, which are not observed when the surface reaction rate is low.

Steady state reaction rates and surface occupancies are shown in figure 4.5 and 4.6 for a specific set of kinetic parameters between the boundaries of the concentration window of the forced reactant, component A. Multiplicity is observed for concentrations higher than 0.21 mol/m$^3$; two stable nodes and one saddle point are found from this concentration$^1$.

Figure 4.5. Steady state reaction rates for model 1. $k_1=1\cdot10^4$, $k_2=1$, $k_3=1\cdot10^3$, $k_4=1$, $k_5=1\cdot10^2$ (units as shown in notation).

Figure 4.6. Steady state surface occupancies for model 1. Kinetic constants as in figure 4.5. Dotted lines denote unstable steady states.

$^1$ The same set of parameters is used in chapter 3 to explain the applicability of Carleman Linearisation.
In the analysis of the response on forced concentration oscillations of systems that exhibit multiplicity, it was noticed that the response depends strongly on initial conditions, in contrast to the response of a model without steady state multiplicities. In figure 4.7 the dependence of the time averaged rate on initial catalyst occupancies is shown for model 1 using a (relatively) high value for the kinetic constant of the surface reaction. In case of a start-up with a catalyst almost completely filled with component B negative resonance is obtained: there is a minimum observed in the time averaged rate versus the frequency. In addition, the reaction rate is low. When a catalyst almost fully occupied by component A is chosen as the initial condition, high rates are observed and the system shows a positive resonance. At the resonance frequency a reaction rate 30% higher than the steady state rate at the average value of the forced component is obtained. Note that the time averaged rate is still lower than the optimal steady state rate (see in figure 4.5 the optimal steady state rate at $C_A=0.21$ mol/m$^3$).

![Figure 4.7](image)

**Figure 4.7. Time averaged rate versus frequency of oscillation for model 1. Kinetic constants as in figure 4.5. Initial condition (I.C.) of the catalyst is denoted as $(\theta_A, \theta_B)$. All results are obtained using numerical integration.**

Although it is not clearly observable in figure 4.7, the reaction rates at low frequencies are equal in both cases. Both responses are stable; in numerical simulations of dynamic systems unstable reaction rates will never be found.

The explanation of the development of the time averaged rate at various frequencies is similar to that of a molecular sorption model, except for the dependence on the initial condition of the catalyst. The sensibility of the response for various initial conditions can only be explained when the phase planes of this system are investigated.
In figure 4.8 and 4.9 the relaxation to the different stable states is visualised at the two extremes of the forcing parameter ($C_A=0.1$ and $C_A=0.7$ mol/m$^3$). As follows from figure 4.6 at $C_A=0.1$ mol/m$^3$ one attractors is found (• in figure 4.8) and at $C_A=0.7$ mol/m$^3$ two attractors are found (□ and ■ in figure 4.9). The influence of the initial condition of the catalyst can now be understood. At $C_A=0.1$ mol/m$^3$ the system relaxes to the steady state indicated by •. The initial situation determines the starting point in figure 4.8. When $\theta_A=1$ and $\theta_B=0$, the starting point is far away from the end point (•). However, with $\theta_A=0$ and $\theta_B=1$ the distance is much shorter. At relatively high frequencies, i.e. when the time available to approach the steady state is short, the stable point will be reached before the switch is made to the high concentration only when the latter initial condition is used, I.C.=(0,1).

In that case, the starting point in figure 4.9 is near □ and the system will relax to this point. However in the other case, starting with $\theta_A=1$ and $\theta_B=0$, • is not reached and therefore after the concentration switch the initial point in figure 4.9 will be different: the system relaxes to ■. So, depending on the initial state of the catalyst, at high frequencies the system oscillates between • and either □ or ■. At low frequencies, i.e. when there is enough time to reach the steady state at the low concentration (•), the system is able to approach □ for both cases and the periodic behaviour is equal.

This example shows that analysis of the phase planes is a prerequisite in understanding the phenomena on a catalyst under forced oscillations for a system that exhibits multiplicity. In addition, it has been demonstrated once more that the optimal steady state is not exceeded using a dissociative adsorption model and the applied forcing function.
Model 2: dissociative adsorption of the non-forced component

For the previous model it was concluded that dissociative adsorption of the forced component leads to slower sorption relaxation of the surface species of this component and therefore no sharp resonance peak is obtained. However, slower sorption dynamics of component B can be favourable with respect to the occurrence of significant resonance phenomena. In all cases discussed, B forms the non-forced component and therefore dissociative adsorption of B, which results in slower relaxation, may give rise to a more pronounced resonance. In the next case where B adsorbs dissociatively (model 2; figure 4.10), other kinetic constants were used as in figure 4.2 (model 2) otherwise no resonance could be obtained. This hinders a fair comparison between the two models. However, the rather sharp resonance observable in figure 4.10 was found several times for a system with dissociative adsorption of reactant B, whereas the previous system with dissociative adsorption of reactant A has never shown this behaviour. This is in agreement with the conclusion as drawn from the analysis in the previous section concerning the single component sorption.

Figure 4.10. Time averaged rate versus frequency for model 2; reactant B adsorbs dissociatively. \( k_1 = 1 \cdot 10^4, k_2 = 1 \cdot 10^7, k_3 = 1 \cdot 10^9, k_4 = 1 \cdot 10^7, k_5 = 1 \cdot 10^9 \) (units as shown in notation).

The systems described in this chapter and in chapter 2, do not show reaction rates above the optimal steady state rate under the concentration programmed conditions. This casts some doubt on the applicability of this type of forced concentration oscillations and on the ability to simulate rate enhancement using the applied microkinetic sorption/reaction models. Despite the results of the simulations, it is not 100% certain that a specific case might not show rate enhancement. A specific case is CO oxidation on Pt as many authors claim rate enhancement for this reaction (e.g. Barshad and Gulari, 1985; Zhou et al., 1986). They sometimes (wrongly) use the term rate enhancement to denote higher average rates compared to the steady state rate at the average of the forced concentration (see the discussion in chapter 1), however in a few
cases reaction rates in excess of the optimal steady state have indeed been measured. Despite the fact that the reaction simply obeys the mechanism represented by model 2, this case is special for two reasons: there is no reversed reaction for the adsorption of oxygen and the kinetics of the elementary steps show large differences.

CO oxidation on Pt has the potential of showing resonance phenomena in view of the conditions for occurrence of resonance. First of all CO inhibits the reaction on the surface by strong adsorption, resulting in a competition for empty adsorption sites. Secondly, the sorption kinetics of CO and O₂ differ by an order of magnitude.

The most accepted mechanism for this reaction is given by

$$
\begin{align*}
\text{CO} + S & \leftrightarrow \text{CO}S \quad k_1, k_2 \\
\text{O}_2 + 2S & \rightarrow 2\text{O}S \quad k_3 \\
\text{CO}S + \text{O}S & \rightarrow \text{CO}_2 + 2S \quad k_5
\end{align*}
$$

Pre-exponential factors and activation energy, from which the kinetic constants were estimated for a temperature of 325°C, were adopted from Kaul et al. (1987). The temperature was selected from a pre-study in which several temperatures were screened to find one for which rate enhancement can be observed under forced oscillations. The concentration of CO is chosen as the forcing variable. This reaction is therefore an example of a case in which the non-forced component shows dissociative adsorption (model 2).

In figure 4.11 the steady state reaction rate (in mol CO₂ produced per mol active sites per second) is given versus the concentration of CO. At the optimal steady state, obtained at very low CO concentrations, the CO and O surface coverage are almost equal at 0.48 (-). When this optimal steady state lies within the window of concentrations applied under forced oscillations, little benefit can be expected from periodic operation as the highest possible rate is obtained when both coverages are 0.5 (-). The reaction rate enhancement will therefore never exceed 8%.

In the following 4 examples forced concentration oscillation cases will be discussed for the model presented above. Various upper and lower values for the CO concentration and the cycle split are applied. The concentrations and the cycle split differ from the standard one as used in the other case studies in this chapter. To avoid that the optimal steady state rate is one of the reference rates, first a simulation is done using a relatively low amplitude and a symmetric square wave as forcing function (case 1 in table 4.1). Figure 4.12 shows that this
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results in very low reaction rates. Obviously, the reference steady state rates are also low, but these rates are never exceeded. The two attractors during the forced oscillations are both steady states with high CO occupancies on the surface and in between these steady states there are no extreme surface occupancy changes. Switching between these two CO inhibited steady states does not result in a profitable time averaged reaction rate.

Case 2 shows a situation in which the optimal steady state lies within the applied concentrations under periodic forcing by an increase of the amplitude of the oscillation. A first observation is that the time averaged reaction rate is significantly higher compared to the previous case. However, the maximum reaction rate is still lower than the optimal steady state rate. It was found out that in order to exceed the highest rate possible under steady state, the cycle split has to be changed. The part of the cycle in which CO inhibits the reaction, at high CO concentrations, should be kept short. In case 3 and 4 this is accomplished by using a low value for the cycle split. To maintain the same average CO concentration the upper value of the oscillation was adjusted. The result of this concentration programming can be observed in figure 4.12. A short period with a high concentration of CO in combination with a long period with a low amount of CO results in a high time averaged reaction rate using an oscillation period of $10^5$ Hz. The maximum reaction rate under forced oscillations even exceeds the optimal steady state rate. Although the improvement is very small (0.6% and 0.5% respectively for case 3 and 4), it has been identified as real rate enhancement. Both 8th order Carleman Linearisation and numerical integration indicate that there is a significant difference between optimal steady state and the maximum rate under forced oscillations. When the cycle split is further decreased, finally the situation is obtained as denoted by case 5 in figure 4.12. The system responds only to the part of the cycle with a low concentration of CO as the other part of the cycle is too short and the corresponding steady state rate will be obtained at every oscillation frequency.

**Table 4.1. Forcing functions as used in the cases shown in figure 4.12.**

<table>
<thead>
<tr>
<th>case</th>
<th>upper value $C_{CO}$ / mol/m$^3$</th>
<th>lower value $C_{CO}$ / mol/m$^3$</th>
<th>average $C_{CO}$ / mol/m$^3$</th>
<th>$C_{O_2}$ / mol/m$^3$</th>
<th>cycle split</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.60</td>
<td>0.20</td>
<td>0.40</td>
<td>0.20</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.78</td>
<td>0.020</td>
<td>0.40</td>
<td>0.20</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>1.54</td>
<td>0.020</td>
<td>0.40</td>
<td>0.20</td>
<td>0.25</td>
</tr>
<tr>
<td>4</td>
<td>3.82</td>
<td>0.020</td>
<td>0.40</td>
<td>0.20</td>
<td>0.1</td>
</tr>
</tbody>
</table>
To understand the underlying mechanism of this rate enhancement, two cases will be explored with respect to the surface occupancies in the cycle invariant state at a frequency of $10^2$ Hz. Figure 4.13 and 4.14 show the development in surface coverages for the cases 2 and 4. At a cycle split of 0.5 CO dominates the surface during the entire period whereas at a cycle split of 0.1 $\theta_{CO}$ and $\theta_O$ are almost equally distributed. This influences the product $\theta_{CO}\times\theta_O$, which governs the reaction rate. For case 2 this product remains below the optimal steady state value whereas in case 4 during part of the cycle a higher value of $\theta_{CO}\times\theta_O$ is observed. When the area below and above the optimal steady state line are compared (figure 4.14), it becomes clear that the reaction rate under forced oscillations is higher than the best steady state operation. The short period with a high concentration of CO is sufficient to supply enough CO for the whole period. This is due to the faster adsorption kinetics of CO compared to $O_2$. During the second part of the cycle, oxygen adsorbs and reacts with CO, thereby creating empty sites which then can be occupied by $O_2$. A slight increase of $\theta_O$ is observed. In the first part of the cycle empty sites are preferentially occupied by CO.

This example shows that it is possible to obtain rate enhancement using forced concentration oscillations and adsorption/desorption models, in contrast to what is concluded by Feimer et al. (1982). It shows in addition that this enhancement is not easily achieved and that its value is rather low. This is due to one of the conditions for the occurrence of resonance which is a necessity to obtain rate enhancement: there must be a competition between the components for adsorption on the surface. This implies that the surface is almost fully occupied (see
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chapter 2 of this thesis). To get radical changes on the surface, the system should be forced using oscillations within a concentration window that also contains the optimal steady state, as shown in the CO oxidation example. The optimal steady state in case of fully occupied surfaces, will be obtained when both components occupy almost 50% of the catalytic surface. This means that there is not much left for improvement under periodic operation.

Figure 4.13. Case 2 (see table 4.1). $\theta_{\text{CO}}$, $\theta_0$ and the product $\theta_{\text{CO}} \theta_0$ are shown within one period in the cycle invariant state under forced oscillations (f.o.) at a frequency of $10^2$ Hz. $\theta_{\text{CO}} \theta_0$ at the optimal steady state is given for comparison.

It must be noted that the conditions at which rate enhancement is found do not correspond to those found in literature (see e.g. Barshad and Gulari, 1985). The simulations show that very high frequencies must be used in order to obtain resonance phenomena. These differences compared to experimental studies may either be due to the fact that only one forcing variable has been used in the simulations, in contrast to the experimental work, or that more sophisticated models should be used. The latter is also suggested by Zhou and coworkers (1986) for CO oxidation on Pd.

Model 3: spillover terms

In model 3 reversible spillover (or diffusion) of an adsorbed species A from a reactive surface site ($S_1$) to a non-reactive buffer site ($S_2$) has been taken into account:
The ratio of the number of sites $S_2$ to $S_1$ is denoted as N. It was found that the conclusions drawn from this model also apply to systems in which the non-forced component B is stored in a buffer.

The buffer capacity of a catalyst acts to store reactants during high gas concentrations and release them for reaction under low concentrations. Spillover or diffusion to and from inactive sites may give rise to surface occupancies that are not feasible under steady state conditions. For this reason first a case was taken that does not show resonance in situations without buffer capabilities to explore whether resonance could be induced by inclusion of spillover terms. In the next example this absence of resonance can be ascribed both to the fact that component A shows slower sorption kinetics than B and to the fact that under steady state conditions the surface is not fully occupied (average surface occupancy is 70%). Figure 4.15 shows the response of such a system on forced concentration oscillations using various values for $k_6$ and $k_7$ (in all simulations $k_6 = k_7$). For low values of $k_6$, for slow spillover kinetics, the case without spillover terms is approximated and indeed no resonance is observed; a smoothly rising time averaged rate is observed with increasing oscillation frequency. Resonance phenomena occur for faster spillover kinetics. A plateau value is obtained for the reaction rate between quasi and relaxed steady state using intermediate spillover kinetics. Compared to the model without buffer, the reaction rate is enhanced by the presence of storage capacities; resonance is

\[
\begin{align*}
A + S_1 & \leftrightarrow A S_1 & k_1, k_2 \\
B + S_1 & \leftrightarrow B S_1 & k_3, k_4 \\
A S_1 + B S_1 & \rightarrow C + 2 S_1 & k_5 \\
A S_1 + S_2 & \leftrightarrow A S_2 + S_1 & k_6, k_7
\end{align*}
\]

Figure 4.15. Time averaged rate versus frequency for model 3 at various values for $k_6$. Kinetic constants: $k_1 = 1 \cdot 10^2$, $k_2 = 1 \cdot 10^4$, $k_3 = 1 \cdot 10^4$, $k_4 = 1 \cdot 10^4$, $k_5 = 1 \cdot 10^5$, $k_7 = k_6$ and $N = 100$ (units as shown in notation).
induced by the introduction of spillover terms. The use of very fast spillover kinetics results again in a smoothly ascending rate without plateau. Remarkably, the relaxed steady state is shifted towards lower frequencies by a factor of $10^3$.

Under steady state conditions the influence of the buffer is absent since the net flux to and from the non-reactive sites is zero. The quasi and relaxed steady state rate are therefore the same for all cases in figure 4.15.

Explanations for the observed behaviour in the resonance regime will be given in the next example where different kinetics are used for the same model. In that case the molecular sorption model without spillover shows resonance (figure 4.16). For high values of the kinetic constants of the spillover step, when the adsorbed component is able to switch very fast between active and inactive buffer sites, resonance phenomena disappear. Again the relaxed steady state is approached at much lower frequencies, which in this particular case is not favourable compared to a catalyst without buffer capacity. In fact, the inclusion of a storage term into the microkinetic model always works out negatively for the present example, as at each frequency the time averaged rate is lower for the this model compared to the model without spillover terms.

Figure 4.18 and 4.19 give insight into the response upon concentration oscillations for the catalytic system with storage capabilities presented in figure 4.16. The occupancies of A and B on active sites ($\theta_{A1}$ and $\theta_{B1}$) and the buffer sites ($\theta_{A2}$) are shown during one period of oscillation in the cycle invariant state. At $f=10^{-2}$ Hz all species follow the changes instantaneously and quasi steady state behaviour is observable. Periodic operation at slightly higher frequencies ($10^{1.5}$ Hz) shows that slow spillover delays the response of the surface occupancy $\theta_{A1}$ in each half-cycle (notice the kink in the profile). $\theta_{B}$ is affected by the fact that $\theta_{A1}$ and $\theta_{B}$ are almost complementary. The time averaged rate decreases since the average value of $\theta_{A1}$ increases at the expense of $\theta_{B}$ (note that $\theta_{A1} > \theta_{B}$ and $\theta_{B}^< = \theta_{A1} \cdot \theta_{B}$). This increase of the average value of $\theta_{A1}$ can be understood as follows. For $f=10^{0.5}$ Hz, $\theta_{A2}$ is no longer able to follow the changes in $\theta_{A1}$ induced by the concentration oscillations of component A.

In this case $\theta_{A2}$ tends to stabilise at a level which is higher than the average value at the quasi steady state (see for instance the average at $f=10^{-2}$ Hz). This is caused by the fact that $\theta_{A2}$ experiences the average of $\theta_{A1}$ at $C_A=0.1$ and 0.7 mol/m$^3$ and tends to approach the corresponding steady state value as denoted in figure 4.17 by the square. Subsequently, the higher buffer occupancy leads to an increase of supply of A to the active sites in the second
part of the cycle. Finally this results in a higher $\theta_{A_1}$ which is clearly observable in figure 4.18. $\theta_{A_2}$ tends to increase when it cannot keep track of the fast surface changes, so its impact in the first part of the cycle is less compared to the second part of the cycle. The quasi steady state value of $\theta_{A_2}$ is already high in the first part of cycle.

When further increasing the oscillation frequency the rate of spillover to and from the buffer becomes insufficient to follow the changes and the variation in the effectively used buffer capacity drops to zero. This becomes clear from the horizontal profile of $\theta_{A_2}$. At this point $\theta_{A_2}$ is far from its quasi steady state value. As a result the attractors of the other species shift and
\( \theta_A \) and \( \theta_B \) relax to another value within the half-cycles. As of a frequency of \( 10^{1.5} \) Hz \( \theta_B \) is no longer able to follow the transients instantaneously and finally stabilises. At a frequency between \( 10^1 - 10^2 \) Hz a local maximum in the time averaged rate is obtained by an increase of the average value of \( \theta_B \) (figure 4.16). However this maximum is lower than in systems without buffers, as the change in the rate by the increase of \( \theta_B \) tends to be neutralised by the change caused by the buffer as described in the previous paragraph. In the relaxed steady state (\( f = 10^{3.5} \) Hz) all surface species are invariant in time; the steady state level at the average of \( C_A \) is attained for \( \theta_{A1}, \theta_{A2} \) and \( \theta_B \).

Generally spoken, in catalytic systems with large buffers the attractors for the active surface species are changed under forced concentration programming compared to systems without buffer capacity. Furthermore, the relaxed steady state is approached at much lower frequencies. This may either have a positive or a negative effect on the time averaged rate. In case the relaxed steady state rate is higher than the quasi steady state rate, buffer terms will enhance the rate (figure 4.15) except for systems showing positive resonance without buffer capacity. This is caused by the tendency of spillover terms to dampen existing positive resonance behaviour which lowers the rate at the resonance frequencies. When the relaxed steady state rate is lower than the quasi steady state, spillover terms will reduce the time averaged rate (see for instance figure 4.16) except for systems showing negative resonance. Similar to the above, negative resonance phenomena are dampened which results in higher rates at resonance frequencies.

Remarkably, the spillover models investigated up to this point, do not show more pronounced resonance effects than observed for models without spillover terms. However, in literature examples are given of systems that without buffer do not show rate enhancement but in which inclusion of buffer capacities leads to reaction rate enhancement. As an example, the models presented by Nam and coworkers will be reviewed (1990, 1993). Figure 4.20 shows the mechanisms used for spillover or storage on a catalyst. All models were used to describe the phenomena observed in concentration programming during ammonia synthesis.

In model A (figure 4.20A) it is assumed that during spillover to and from the inactive sites reaction takes place. In the model is assumed that a fraction \( f \) of the diffusing species reacts. In contrast to what is suggested by figure 4.20A, the net flux is focused on in the mathematical modelling in the work of Nam and coworkers. So, in fact it is assumed that a fraction of the net flux reacts. As under steady state the net flux is always zero, a whole new reaction route is followed only for the unsteady state situation. It is therefore not surprising that enhancement can be predicted by this model.
Figure 4.20. Schematic representation of models used by Nam and coworkers (Nam et al., 1990, 1993) which include buffer capacities of a catalyst. \( \alpha \) represents a Henry constant (see text).

Model B (figure 4.20B) shows single site adsorption with subsequent storage equal to the model applied in the present work. No reaction rate enhancement was predicted using this mechanism. To induce resonance and rate enhancement, a dual site model was presented (figure 4.20C). It includes two types of active surface sites with different sorption characteristics. One of these surface site types is assumed to be in equilibrium with the gas phase (also under transient conditions) through Henry’s law, which is denoted by \( \alpha \cdot C_A \). As a result of this the spillover or bulk diffusion is directly influenced by the gas phase concentration, even when very fast concentration oscillations are imposed. A second disputable assumption is that in the modelling no distinction is made between the two active surface sites and a lumped parameter model is used to describe the spillover.

Taking these assumptions into account, the time development of the buffer concentration can be described as:

\[
\frac{\partial \theta_{A2}}{\partial t} \sim k \alpha C_A - k' \theta_{A2}
\]
This equation shows the drawback of the model. In the limiting case when the surface is fully occupied with A and reactant A is removed from the gas phase, there will still be a flux from the buffer to the surface which is impossible. The limitation caused by occupancy of the active surface sites on the flow from buffer to active sites is not included in this equation, which is not realistic.

These examples demonstrate that disputable spillover models have been used to induce rate enhancement. Physically realistic models which include a spillover effect are not likely to produce resonance phenomena. This is in agreement with the simulation results of model 3.

**Model 4: Eley-Rideal mechanism combined with spillover terms**

In the work of Thullie *et al.* (1986), reaction rate enhancement compared to the optimal steady state was obtained for non-linear models obeying Eley-Rideal kinetics:

\[
\begin{align*}
B + S_I & \leftrightarrow BS_I & k_3, k_4 \\
v A + BS_I & \rightarrow C + S_I & k_8
\end{align*}
\]

When \(k_4 = 0\) and \(v > 1\), a large reaction rate enhancement is obtained in case of bang-bang type of cycling, *i.e.* cycling between a cycle with undiluted reactant A and a cycle with undiluted reactant B. Note that this type of cycling differs from the type used in the present work as B is cycling as well in case of bang-bang type of cycling. Thullie and coworkers concluded that for the first time rate enhancement was demonstrated without the occurrence of resonance phenomena and that the highest time averaged reaction rate was found in the relaxed steady state. Although this is correct, a critical view on the results sheds a different light on their work. When it is assumed that \(k_3/k_8\) and pure component cycling is applied (so both reactants vary in time, \(y_A = 1 \land y_B = 0\) and vice versa), in the relaxed steady state the surface occupancy of B will be 0.5 as the time averaged adsorption rate and time averaged surface reaction rate must be equal. As Thullie and coworkers used gas phase fractions and dimensionless kinetic constants in their models, the relaxed steady state rate simply reads:

\[
\begin{align*}
\tau_{\text{res}} &= \frac{k_8 \cdot 0.5 \cdot 0^v + k_8 \cdot 0.5 \cdot 1^v}{2} = 0.25 \cdot k_8
\end{align*}
\]

Interestingly, the relaxed steady state rate does not depend on the stoichiometric coefficient of the reaction step. However, the optimal steady state rate depends strongly on the non-linearity.
of this step (on the value of \( \nu \)). In table 4.2 the optimal steady state rates are listed at various values for \( \nu \).

**Table 4.2. The dependence of the optimal steady state rate of model 4 under bang-bang type concentration forcing using \( k_2=k_{s5} \) and \( k_4=0 \) on the non-linearity of the surface reaction step.**

\( (y_A=l-y_B \text{ at OSS}) \)

<table>
<thead>
<tr>
<th>( \nu )</th>
<th>Fraction of B at OSS / -</th>
<th>Optimal steady state rate / ( \text{s}^{-1} )</th>
<th>Relaxed steady state rate / ( \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{2} )</td>
<td>0.65</td>
<td>0.31( \cdot k_s )</td>
<td>0.25( \cdot k_s )</td>
</tr>
<tr>
<td>1</td>
<td>0.50</td>
<td>0.25( \cdot k_s )</td>
<td>0.25( \cdot k_s )</td>
</tr>
<tr>
<td>2</td>
<td>0.36</td>
<td>0.19( \cdot k_s )</td>
<td>0.25( \cdot k_s )</td>
</tr>
<tr>
<td>3</td>
<td>0.29</td>
<td>0.16( \cdot k_s )</td>
<td>0.25( \cdot k_s )</td>
</tr>
</tbody>
</table>

By increasing the non-linearity of this model the optimal steady state reaction rate is lowered and therefore from \( \nu>1 \) the time averaged rate under concentration programming is favourable. When the relaxed steady rate is also influenced by the non-linearity of the model (by using diluted reactants) or a different forcing function is taken, the result under forced concentration oscillations compared to the optimal steady state will be totally different and no rate enhancement will be found. In the example of Thullie *et al.* (1986) reaction rate enhancement is obtained by lowering the steady state rate and not by an increase of the time averaged rate under concentration programming.

Despite the above mentioned considerations, the Eley-Rideal model was used in the present study to determine the generality of observed phenomena under forced concentration oscillations. In addition, as discussed in chapter 1 sometimes the use of forced concentration oscillations can serve other purposes than rate enhancement beyond the optimal steady state.

The relaxed steady state is the highest rate achievable under forced oscillations when the catalytic reaction obeys Eley-Rideal microkinetics. Since in practice high oscillating frequencies (a necessity for reaching the relaxed steady state) may not be feasible, it is interesting to introduce a catalyst with storage capacity in view of the result obtained in the previous section regarding spillover. In figure 4.21 the response of a Eley-Rideal model system is shown that is subjected to the same concentration square waves as used before in this chapter. It is demonstrated that upon introduction of fast storage of reactant B in the model, the relaxed steady state will be shifted to much lower, and therefore more feasible, frequencies. From a comparison of figure 4.21 and figure 4.22 can be concluded that the relaxed steady state is never higher than the optimal steady state rate.
These results (figure 4.21) show that general aspects of elementary steps with respect to their response on concentration forcing, can be used for various systems: the influence of a spillover term under periodic forcing is apparently qualitatively equal for both the molecular sorption model (model 3) as well as the Eley-Rideal model (model 4).

Figure 4.21. Time averaged rate versus frequency for model 4 at various values for $k_6$, $k_3=1\cdot10^2$, $k_4=1\cdot10^4$, $k_8=1\cdot10^4$, $k_7=k_5$ and $N=100$ (units as shown in notation)

Figure 4.22. Steady state reaction rate for model 4. Kinetic constants as in figure 4.21.

CONCLUSIONS

In this work various reaction mechanisms were studied in order to gain insight in the impact of characteristic reaction steps on the response towards square wave concentration oscillations of one reactant. As the microkinetic models investigated in the present work are all extensions of the molecular adsorption/desorption model analysed in detail in chapter 2, the simulation results were compared to the response of this base model. The analysis of the extended models made us to conclude the following.

Incorporation in the model of a dissociative adsorption step of the forced component does not lead to strong resonance phenomena on the surface of the catalyst. Using low surface reaction rates the resonance is less pronounced than in case of molecular adsorption/desorption models. This is due to the fact that the relaxation time of the dissociative adsorption and the reversed desorption step is longer using the same kinetic parameters. Retardation of the forced component leads to less resonance. When the non-forced component shows dissociative adsorption a sharper resonance peak is observed when the time averaged rate is plotted versus frequency.
Chapter 4

Dissociative adsorption combined with high surface reaction rates, may lead to multiplicity under steady state conditions and therefore complex behaviour under concentration programming may also be observed. This becomes evident from the dependence of the response on initial conditions of the catalytic surface and can be understood when the phase planes of the surface occupancies are investigated. The phase planes point out that the attractor in one or both parts of the cycle may switch depending on initial conditions and oscillation frequency.

It was shown that a large storage capacity on the catalyst influences the response towards concentration programming in such a manner that the relaxed steady state is shifted to much lower oscillation frequencies. This is favourable compared to systems without spillover when the relaxed steady state rate is higher than the quasi steady state rate, except for cases showing positive resonance. Resonance peaks that exceed the relaxed and/or quasi steady state reaction rate are dampened by inclusion of spillover terms in the model. In contrast, systems that do not show resonance, start to develop resonance using spillover. In these cases, the reaction rate under resonant conditions never exceeds the relaxed and quasi steady state reaction rate.

The conclusions reached for inclusion of spillover terms in molecular sorption models appear also generically valid for models based on Eley-Rideal kinetics. The shift of the relaxed steady state also appeared in case of systems obeying Eley-Rideal kinetics.

Rate enhancement, i.e. higher time averaged rates compared to the optimal steady state rate, can be obtained using adsorption/desorption models as applied in this work. This conclusion is in contrast to the results as presented by Feimer et al. (1982). The rate enhancement was demonstrated using CO concentration oscillations in CO oxidation on Pt. However, the improvements are rather marginal. This is caused by the fact that the occurrence of resonance relies on competition between components for adsorption on the catalyst surface which implies that the surface must be almost fully occupied. To get radical changes on the surface, the system should be forced using oscillations within a concentration window that also contains the optimal steady state. The coverage of both components is almost 50% in case of fully occupied surfaces in the optimal steady state. This means that there is not much left for improvement under periodic operation.

An exception to this, is formed by the Eley-Rideal model as used by Thullie et al. (1986). High rate enhancements were found by them when the non-linearity of the Eley-Rideal reaction step is sufficiently high. It has been shown that these enhancements result from a decrease of the steady state rates rather than an increase of the time averaged rates under concentration programming.
This does not necessarily mean that concentration programming should not be applied in practice. First of all, the simulations presented in this work are limited to single component forcing. The impact of multi-component cycling has not been investigated. Secondly, the non-linearity of the models is restricted as only adsorption/desorption LH models and Eley-Rideal models were studied. Incorporation of more sophisticated elements such as the exponential dependence of kinetic constants on surface occupancy or surface reaction between more than two surface species should be investigated as well. In view of the higher non-linearity which are introduced into the model by these elements, stronger resonance phenomena are to be expected. However, model extensions should be more realistic than the examples given in this work concerning spillover models used by Nam and coworkers (1990). Finally, besides obtaining reaction rate enhancement, the use of forced concentration oscillations may be beneficial for other reasons. An additional advantage is that it offers stable operation of a catalytic reaction. In case under steady state a sharp transition is shown on a almost fully occupied surface, as in CO oxidation on Pt, it may be difficult to keep the system in the optimal steady state. This is due to the fact that a small deviation from the optimal steady state condition leads to a much lower rate. In contrast, concentration programmed reactions are very stable with respect to small changes in the upper and lower value of the forcing parameter and concentration programming may therefore be useful.

**Notation**

- **A**: defined in equation 4.6
- **B**: defined in equation 4.8
- **\( C_A \)**: concentration of reactant A, mol/m³
- **\( C_B \)**: concentration of reactant C, mol/m³
- **\( C_{CO} \)**: concentration of CO, mol/m³
- **\( C_{O2} \)**: concentration of O₂, mol/m³
- **D**: integration constant used in equation 4.5, -
- **f**: frequency of oscillation, Hz
- **\( k_1 \)**: kinetic constant of adsorption of A, m³/mol·s
- **\( k_2 \)**: kinetic constant of desorption of A, s⁻¹
- **\( k_3 \)**: kinetic constant of adsorption of B, m³/mol·s
- **\( k_4 \)**: kinetic constant of desorption of B, s⁻¹
- **\( k_5 \)**: kinetic constant of surface reaction, s⁻¹
- **\( k_6 \)**: kinetic constant of storage to inactive sites, s⁻¹
- **\( k_7 \)**: kinetic constant of transport from inactive to active sites, s⁻¹
Chapter 4

$k_8$ kinetic constant of Eley-Rideal reaction step, m$^3$/mol·s

$N$ ratio of the number of inactive (buffer) sites ($S_2$) compared to the number of active sites ($S_1$), -

$<r>$ time averaged reaction rate under concentration programming, s$^{-1}$

$r_{RSS}$ reaction rate at relaxed steady state, s$^{-1}$

$r_{ss}$ steady state reaction rate, s$^{-1}$

$S$ denotes an active surface site

$S_1$ denotes an active surface site

$S_2$ denotes an inactive (buffer) site

$t$ time, s

$y_A$ mole fraction of A in the gas phase, -

$y_B$ mole fraction of B in the gas phase, -

Greek Letters

$\varepsilon$ cycle split, -

$\lambda$ time constant, s$^{-1}$

$\theta_A$ catalyst surface occupancy of A, -

$\theta_{A,0}$ initial surface occupancy of A, -

$\theta_{A,ss}$ steady state surface occupancy of A, -

$\theta_{A1}$ catalyst surface occupancy of A on active sites, -

$\theta_{A2}$ catalyst surface occupancy of A on inactive (buffer) sites, -

$\theta_B$ catalyst surface occupancy of B, -

REFERENCES


Concentration programming of catalytic reactions

REFERENCES

CHAPTER 5

Forced concentration oscillations of CO and O₂ in CO oxidation over oxidised Cu/Al₂O₃*

ABSTRACT

The kinetics of CO oxidation over an oxidised alumina supported Cu catalyst are examined using successive oxidation and reduction cycles and using isotopically labelled gases. Surface species were monitored during transients in a FTIR flow cell. For the reoxidation of the catalyst after reduction by CO, a three steps mechanistic model is proposed. The kinetic constants are determined by mathematical modelling. The role of carbonates is found to be minor in the production of CO₂ in contrast to carbonyls which were shown to be active reaction intermediates. Net dissociation of CO was observed during reduction, resulting from adsorption of CO₂ on a partly reduced catalyst under formation of carboxylates. These latter subsequently decompose to CO, thereby leaving oxygen on the catalyst. A complete mechanistic scheme is presented which allows us to describe qualitatively and in part quantitatively the experimental results. This study shows that the use of forced oscillations and programmed isotopic labelling is a powerful tool, contributing to the understanding and elucidation of reaction mechanisms.

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INTRODUCTION

It has been demonstrated that periodic operation of catalytic reactors is very useful in many applications. Besides interesting improvement of reaction rates, selectivity or both, shown for e.g. N₂O reduction by CO over Pt catalysts (Sandhankar and Lynch, 1994) and methanol synthesis over industrial catalysts (McNeil and Rinker, 1994). Also, simultaneous suppression of oscillations and rate enhancement were observed for CO oxidation over Rh forced concentration programming (Qin and Wolf, 1995). More recently interest has developed into the use of forced oscillations as a way to gain insight into reaction mechanisms, as an extension to step-response and steady state experiments. Renken and Thullie (1993) showed that experiments with forced oscillations may be a tool to discriminate between various mechanistic models. For CO₂ methanation imposed concentration oscillations were used, in combination with diffuse reflectance infrared spectroscopy (Marwood et al., 1994). It was shown that insight can be gained on the reactive species by concentration cycling and a sequence of active intermediates was proposed and incorporated in a kinetic model. Sadhankar and Lynch (1996) described the transient behaviour during NO and CO oscillations on Pt by a model which was able to predict the start-up and the long term cycle-invariant mode of this catalytic reaction in a recycle reactor. An indication for the immense difference between short and long term response can be found in the existence of multiple steady states (Sandhankar and Lynch, 1996). Presently we mainly focus on the information which can be extracted from the initial response to forced oscillations for CO oxidation over alumina supported Cu. No multiple steady states or self-oscillations have been reported for this reaction.

Many kinetic studies of CO oxidation have been conducted using single crystals, supported Cu and supported or unsupported CuO. For single crystals a Langmuir-Hinshelwood mechanism was proposed (Arlow and Woodruff, 1987) and retardation of the reaction was observed under high oxygen coverages. Crew and Madix (1996) showed that on Cu(110) ordered Cu-O-Cu chains are formed in oxygen. On top of these chains a dynamic oxygen layer is observed and reaction with CO occurs at defects in this layer. The reaction initiates at the edges or kinks and subsequently more active sites become accessible and reaction proceeds. Reaction of Cu-O-Cu with CO apparently takes place at so-called chain scissions.

CO oxidation on alumina supported metallic Cu was extensively investigated by Choi and Vannice (1991) using \textit{in-situ} IR spectroscopy before and during reaction. An Eley-Rideal mechanism was ruled out and strong evidence was obtained for reaction of adsorbed CO molecules and O atoms. Interestingly these authors suggested non-competitive adsorption and
propose a model in which formed Cu$_2$O acts as a vacant site allowing CO adsorption where O$_2$ interacts with metallic Cu atoms. The reaction was found to be close to first order in CO and zero order in O$_2$ at 400 K. Szanyi and Goodman (1993) showed that at 458 K significant amounts of oxygen migrate into bulk Cu during reaction even under highly reducing conditions. In TPD experiments of the latter authors subsurface oxygen diffuses to the surface and carbonates formed during reaction are removed. The latter work illustrates the possible role of subsurface oxygen and carbonates in CO oxidation.

Reaction on supported and unsupported CuO gave similar reaction orders in CO as compared to supported and unsupported metallic Cu. Yu-Yao (1975) observed an order in CO between 0.7 and 1.0 and no dependence of the reaction rate on the oxygen concentration for T=423-773 K was noticed. CO$_2$ desorption was observed to be very fast, limiting CO oxidation only below 423 K. Prokopowicz and coworkers (1988) suggested an Eley-Rideal mechanism on the basis of a transient FTIR study at 523 K by following adsorbed CO on Cu$^+$, although a mechanism with adsorbed CO species could not be excluded.

In general, mechanisms proposed for catalytic oxidation reactions on metal oxides are based either on the so-called stepwise or the concerted mechanism (Davydov, 1990, Boreskov, 1970). The former is likely to occur at relatively high temperatures and is based on alternating oxidation and reduction of the catalyst surface in accordance to the Mars and Van Krevelen mechanism. At lower temperatures (T<573 K) simultaneous oxidation of the catalyst and formation of reaction products is observed and carbonates are assumed to be an intermediate in the reaction. More recently a mechanistic study was conducted using transient methods. Dekker et al. (1994, 1995) propose a kinetic model for the reduction of alumina supported CuO based on step-response experiments at 453-553 K. Introducing CO over an oxidised catalyst gave at first CO$_2$ produced via an Eley-Rideal mechanism thereby freeing sites for CO to adsorb. Subsequently adsorbed CO reacts with in-plane oxygen atoms by Langmuir-Hinshelwood kinetics. Furthermore replenishment of oxygen by diffusion from the bulk was observed and incorporated in the model.

In the present work we try to find out whether the model proposed in (Dekker et al., 1994) also adequately describes the response during the reduction part of the imposed CO/O$_2$ oscillations. We monitored the role of carbonates and carbonyls under reaction conditions using transient in-situ FTIR, because literature is not always unequivocal about the relevance of carbonyls or carbonates as reaction intermediates. It is interesting to focus on the elucidation of the mechanism of oxidation, which has been little addressed in literature. To this end concentration cycling experiments with labelled and unlabelled gases were carried out. Finally the complete
mechanism of CO oxidation on oxidised alumina supported Cu including reduction and reoxidation of the catalyst will be tracked, thereby illustrating the merits of periodic operation in mechanistic studies.

EXPERIMENTAL

Gases and catalyst

All unlabelled gases were of HP or UHP grade (UCAR and Air Liquide) and purified before use (O₂ and/or H₂O removal). Gas mixtures, including the ¹⁸O₂ mixture (Thamer Diagnostica, 96%), were made in a separate gas mixing system and stored in 0.5 or 5 litre lecture bottles.

The response towards oscillations was investigated over a 10 wt.% Cu/Al₂O₃ catalyst (dₚ = 0.105 - 0.140 mm). The catalyst was prepared by pore volume impregnation of γ-alumina (Ketjen CK300/000-1.5E) with an aqueous solution of CuNO₃ (Merck). A full description of the catalyst preparation is given elsewhere (Bijsterbosch, 1993). ICP-AES measurements performed on the catalyst gave a Cu content of 9.8 wt.% and no significant contaminations by any other metal elements were observed.

Apparatus

Forced oscillation experiments were conducted in a tubular reactor (d= 5.0 mm) connected to a mass spectrometer (Balzers, QMG 240) via a capillary. Gas flows were set by mass-flow controllers and concentration programming was carried out using a 4-way valve (Valco) with a digital valve interface controlled by a computer. The pressure in the system was 1.1 bar and was held invariant by back-pressure controllers. 50 mg of catalyst, mixed with 135 mg SiC to avoid axial dispersion and non-isothermal operation, was placed in the tubular reactor between two plugs of quartz wool. A more detailed description of this equipment can be found elsewhere (Dekker et al., 1994).

In-situ FTIR experiments were performed in a second experimental set-up. Main differences with the former equipment are the reactor and the state of the catalyst. The reactor for infrared experiments is a flow cell with a volume of 3.6 ml; a schematic representation can be found in the appendix of this chapter. 40 mg of the catalyst was pressed in a ring using a pressing assembly similar to the one presented by Miura and Gonzalez (1982). The pellet was
Forced concentration oscillations in CO oxidation over Cu/Al₂O₃ subsequently placed in the cell and was fixed by using a pretreated silicone ring to avoid bypassing. Under operating conditions the mixing in the IR reactor closely approximated that of an ideal CSTR as is demonstrated in the appendix.

The reaction intermediates present during the reaction on the catalyst were followed with a BIORAD FTS45A infrared spectrometer and gas phase composition was analysed by a mass spectrometer (Leybold Q200). IR spectra were processed with WIN-IR a BIORAD software program and could be quantitatively interpreted because a linear concentration dependent MCT detector was used. This results in a linear relation between integrated absorption bands and concentrations in the gas phase or on the catalyst.

**Experimental procedures**

All experiments were performed at a temperature of 493 K, 1.1 bar total pressure and with a total flow rate of 30 ml/min (STP). First the samples were in-situ pretreated: the catalyst was calcined in oxygen for 1 h at 423 K and subsequently fully oxidised at 773 K for 1 h. After cooling to 493 K in oxygen, in He a step-increase in the CO concentration for 6 minutes (0% → 5% CO). The catalyst was again oxidised at 773 K and cooled to 493 K. Helium was fed to the reactor for 15 min to remove all the O₂. Only with this procedure reproducible results could be obtained. The reduction in this pretreatment can be understood as an activation of the catalyst as careful reduction leads to formation of well defined copper particles at the surface of the catalyst which remain present after reoxidation (Van de Berg et al., 1983). This may also lead to a higher activity (Huang et al., 1989).

Pretreatment in the IR experiments was done ex-situ because the IR cell could only be used at temperatures below 573 K. After calcination, oxidation, reduction and reoxidation the catalyst pellet was transferred to the cell and heated in oxygen to 493 K where it was kept at this temperature under oxygen for at least 1 h. Subsequently helium was passed through the cell for 15 minutes. No changes in time were observed in the IR spectra beyond this period.

The fully oxidised Cu catalyst was subjected to various steps as depicted schematically in figure 5.2 by the thin dotted lines. We may distinguish three types of experiments:

1. subsequent reduction / oxidation cycles in a fixed bed reactor using 5% CO and 4% O₂
2. subsequent reduction / oxidation cycles in a fixed bed reactor using 5% CO and 6.1% ^18O₂
3. subsequent reduction / oxidation cycles in the IR cell using 5% CO and 4% O₂
Type 1 experiments were performed at various oscillation periods while type 2 experiments were carried out at a period of 100 and 240 s and type 3 at 240 s. Helium was used in all experiments to make-up the total feed flow to the reactor or the cell. The total flow was kept constant during a cycle.

RESULTS AND DISCUSSION

Forced oscillations of CO and O$_2$ (Type 1)

After oxidation of the catalyst TPR results show that predominantly CuO is present on the surface (Dekker, 1995). The fully oxidised catalyst was subjected to 5% CO in helium and subsequently 4% O$_2$ was fed to the reactor. First we focus on the response as it appears after a cycle invariant state is reached. Figure 5.1 shows for various oscillation frequencies the time averaged concentration of CO$_2$ at the outlet when cycle invariance is reached. A monotonically increasing CO$_2$ production is observed when going from the quasi steady state at low frequencies to the relaxed steady state at high frequencies. Resonance phenomena are not observed, so mechanistic information cannot be obtained from these time averaged data. However, a better insight in the reaction mechanism is obtained from the concentration development in time.

![Figure 5.1. Time averaged CO$_2$ reactor outlet concentration at various cycle frequencies in the cycle invariant mode.](image)

In figure 5.2 the dynamic behaviour of CO$_2$, CO and O$_2$ is shown for periods of 120 s and 240 s. The same behaviour as in the step-response experiments (Dekker et al., 1994) is observed after the onset of the first reduction cycle, since the same initial conditions were used. For both cycle periods a steep increase in CO$_2$ production right after the switch is seen. This
results from the reduction of weakly bound oxygen on top of the catalyst, so-called overlayer oxygen, by CO from the gas phase via an Eley-Rideal (ER) mechanism. Subsequently the surface is occupied by CO which adsorbs easily at Cu$^+$ sites after removal of overlayer oxygen. A second reduction step starts and accelerates because adsorbed CO can react with more strongly bound, in-plane, oxygen by a Langmuir-Hinshelwood (LH) mechanism thereby creating additional free sites for CO to adsorb. A second maximum in the CO$_2$ production is obtained. This in-plane oxygen is assumed to be located at the same level as the Cu surface atoms, see e.g. in Crew and Madix (1996), establishing a high coordination number for Cu. For a period of 240 s also a third reduction stage involving lattice oxygen can be observed. Just before the start of the oxidation cycle a significant amount of CO$_2$ is produced by oxygen on LH sites although the in-plane oxygen is almost depleted by reduction. The apparently 'new' in-plane oxygen originates from the bulk by solid state diffusion. It has been reported recently (Van Wijk et al., 1996) that even oxygen from the support can diffuse into the CuO phase in reasonable time scales. As is obvious from figure 5.2 for a period of 120 s this third stage reduction cannot clearly be observed in view of the fact that before the oxidation cycle is started still a reasonable amount of in-plane oxygen is present.

The second CO cycle shows a pattern different from the first. One maximum has disappeared and no longer a clear distinction can be made between ER and LH reaction. This arises from the fact that at the present temperature of 493 K full oxidation of surface copper is no longer possible (Dekker, 1995). This means that the surface predominantly contains Cu$_2$O. The amount of overlayer oxygen is reduced, more empty sites are initially available for CO to adsorb and by consequence LH reaction proceeds sooner as compared to the first reduction cycle. The second maximum shifts and partly coincides with the first peak representing the ER production of CO$_2$. Hence only a shoulder remains visible. In summary, the reduction model (Dekker et al., 1994) also adequately predicts the reduction during the forced oscillations in the CO cycles.

Differences between the two cycle periods are noticed during the oxidation cycle. In the first experiment ($\tau=120$ s) the switch to oxygen is imposed just after the second maximum in the reduction cycle, when both a reasonable amount of absorbed CO and in-plane oxygen are present. Upon admission of oxygen CO$_2$ is produced instantaneously. The little shoulder which is observed is an indication for a second oxidation route. In the second experiment ($\tau=240$ s) the switch is implemented when the surface is almost totally occupied by CO and oxygen transport from the subsurface is the limiting factor for CO$_2$ production. The shape of the CO$_2$ production peak is similar in nature as in case of $\tau=120$ s but the total amount of CO$_2$
Figure 5.2. Inlet and outlet concentration profiles of CO, O$_2$ and CO$_2$ after the start-up of oscillations at a period of 120 and 240 s as well as the cycle invariant state at a period of 240 s. CO: (---), O$_2$: (-----), CO$_2$: (- - -).
is significantly reduced. This difference does not arise from the \( \text{CO}_2 \) still present in the reactor during the switch to oxygen, so-called \( \text{CO}_2 \) flushing. This was validated by an experiment in which after reduction a step was performed to helium instead of \( \text{O}_2 \) which gave nearly abrupt decrease to zero of the \( \text{CO}_2 \) concentration without maximum and tailing. It is therefore interesting to focus on the amount of \( \text{CO}_2 \) produced after the switch to oxygen because relevant information about the reoxidation can be derived from these data. In table 5.1 the \( \text{CO}_2 \) produced per mole \( \text{Cu} \) on the catalyst in the oxidation cycle as well as the height of the \( \text{CO}_2 \) peak right after the switch are given for various experiments.

\textbf{Table 5.1. Production of \( \text{CO}_2 \) and the height of the \( \text{CO}_2 \) peak during the first oxidation cycle.}

<table>
<thead>
<tr>
<th>Period / s</th>
<th>Concentration ( \text{O}_2 ) / %</th>
<th>Production ( \text{CO}_2 ) / mol/mol( \text{Cu} )</th>
<th>Height of peak / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>4.0</td>
<td>0.053</td>
<td>2.5</td>
</tr>
<tr>
<td>100</td>
<td>4.0</td>
<td>0.062</td>
<td>2.8</td>
</tr>
<tr>
<td>100</td>
<td>6.1</td>
<td>0.069</td>
<td>4.0</td>
</tr>
<tr>
<td>120</td>
<td>4.0</td>
<td>0.070</td>
<td>2.9</td>
</tr>
<tr>
<td>240</td>
<td>4.0</td>
<td>0.058</td>
<td>1.9</td>
</tr>
<tr>
<td>240</td>
<td>6.1</td>
<td>0.056</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Clearly a maximum is obtained in the \( \text{CO}_2 \) production for intermediate cycle periods of 100-120 s. Obviously the species present on the catalyst after 50-60 s feeding of \( \text{CO} \) are important for \( \text{CO}_2 \) production during reoxidation. It may also be concluded that no influence of the concentration of oxygen is observed on the total production of \( \text{CO}_2 \). However from the initial rates of reaction to \( \text{CO}_2 \), as apparent from the peak heights right after the step, one may deduce approximately first order behaviour in \( \text{O}_2 \).

Furthermore in figure 5.2 the response after 25 cycles is shown for a period of 240 s. Since the response does not change significantly per period, the so-called cyclic steady state is reached at this point. In the reduction cycle only one large \( \text{CO}_2 \) peak is observed whereas during the oxidation cycle clearly two \( \text{CO}_2 \) production stages can be distinguished.

From the above can be concluded that the oxidation of the copper catalyst after reduction by \( \text{CO} \), reoxidation, proceeds in at least two steps. In addition we saw that part of the reoxidation reaction is first order in oxygen. Reoxidation was studied further by use of labelling experiments, as illustrated in the next section.
The increasing time averaged production with frequency in figure 5.1 can mainly be ascribed to the relatively higher CO₂ production during the oxidation cycle. For short periods (τ<40 s) the CO₂ production level remains finite till the end of the oxidation cycle.

Forced oscillations of CO and ^16O₂ (Type 2)

Reoxidation of the catalyst was studied using labelled oxygen in successive reduction-reoxidation experiments. Figure 5.3 shows the concentration profiles in time at a period of 240 s. The first cycle is identical to the first cycle in the previous experiments since the same CO concentrations were used and the oxidation in the pretreatment was carried out in unlabelled oxygen. In the first cycle with labelled oxygen large amounts of unlabelled CO₂ are produced which is somewhat surprising. As before, no CO₂ was detected after a switch to He, so it can be concluded that both adsorbed C^{16}O and ^16O are removed from the surface by ^18O₂. In the long run in the oxidation cycle also some labelled CO₂ is observed, corresponding to the shoulder observed in type 1 experiments. Since this CO₂ is not instantaneously produced after the step to oxygen, a mechanism with consecutive reactions is assumed (see modelling section). Further O₂ does not seem to compete with CO for the same sites on the surface since no CO desorption is seen nor do we observe instantaneously produced labelled CO₂ upon a switch to ^18O₂. Similar conclusions were drawn by Choi and Vannice (1991).

The second reduction cycle provides insight in the exchange of oxygen during the reoxidation step. The fact that both C^{16}O^{16}O and C^{16}O^{18}O formed by an ER mechanism are observed indicates a rapid exchange between weakly bound overlayer oxygen and in-plane oxygen. However it must be noticed that the first peak of unlabelled CO₂ is not only due to ER reaction since part of the CO₂ production may arise from LH reaction (the peaks partly overlap each other). Furthermore the ratio CO₂ produced by ER reaction over CO₂ produced via LH reaction calculated by taking peak height to be proportional to the amount produced by either ER or LH mechanism, is larger for single labelled CO₂ than the same ratio for unlabelled CO₂. Nevertheless it is surprising how much of the unlabelled oxygen (from the pretreatment procedure) is present in the overlayer during the second reduction cycle.

The development of the production of labelled and unlabelled CO₂ during successive cycles for a cycle period of 100 s is presented in figure 5.4. A cycle invariant state is reached after 20 cycles at which point still a large amount of unlabelled CO₂ is observed. Subsurface oxygen cannot be the sole source of the ^16O. The total amount of ^16O released during 28 cycles exceeds the amount of oxygen originally present in the Cu phase on the catalyst (in 28 cycles
Forced concentration oscillations in CO oxidation over Cu/Al₂O₃

approximately 3.5 mole atomic $^{16}$O is used per mole Cu. As also can be concluded from the formation of C$^{18}$O$^{18}$O there must be another source of $^{16}$O. Moreover as shown in figure 5.5, C$^{18}$O is observed in the reduction cycles which implies that $^{16}$O is left on the surface. These observations prove the occurrence of dissociation of a CO bond on the Cu catalyst.

![Figure 5.3. Concentration profiles of labelled and unlabelled components after start-up of oscillations between CO and $^{18}$O$_2$ (τ=240 s). Open circles: C$^{18}$O. The catalyst is oxidised with $^{16}$O$_2$ at 773 K.](image)

Figure 5.3. Concentration profiles of labelled and unlabelled components after start-up of oscillations between CO and $^{18}$O$_2$ (τ=240 s). Open circles: C$^{18}$O. The catalyst is oxidised with $^{16}$O$_2$ at 773 K.

![Figure 5.4. Amount of labelled and unlabelled CO$_2$ produced per mole Cu during the reduction cycle vs. the number of cycles (τ=100 s).](image)

Figure 5.4. Amount of labelled and unlabelled CO$_2$ produced per mole Cu during the reduction cycle vs. the number of cycles (τ=100 s).

Figure 5.5 shows in addition that when the catalyst is reduced for a prolonged interval (τ=240 s), more CO bond dissociation is noticed. It must be noted that for both cycle periods the C$^{18}$O concentration has dropped to zero before a new cycle is started, so no direct influence of the
cycle period is expected. The net CO dissociation does not cause any observable deactivation (for instance by coke formation) since the total CO\textsubscript{2} production was constant over at least 34 cycles (see figure 5.4). The fact that we did not observe any C\textsuperscript{18}O or C\textsuperscript{18}O\textsuperscript{18}O in the oxidation cycles implies once more that CO and O\textsubscript{2} adsorb non-competitively.

![Graph showing the amount of C\textsuperscript{16}O produced per mole Cu during the reduction cycle vs. number of cycles for \( \tau = 100 \text{ s} \) and \( \tau = 240 \text{ s} \).](image)

**Figure 5.5.** Amount of C\textsuperscript{18}O produced per mole Cu during the reduction cycle vs. number of cycles for \( \tau = 100 \text{ s} \) and \( \tau = 240 \text{ s} \).

After 22 cycles at \( \tau = 100 \text{ s} \) the mass balance of C\textsuperscript{16}O is as follows: 0.12 mol/mol\textsubscript{Cu} C\textsuperscript{16}O\textsuperscript{16}O is produced versus 0.025 and 0.050 mol/mol\textsubscript{Cu} C\textsuperscript{18}O and C\textsuperscript{18}O\textsuperscript{18}O respectively. This leaves only 0.045 mol/mol\textsubscript{Cu} C\textsuperscript{18}O which probably originates from the bulk or even from the support by a strong metal support interaction and solid state diffusion. On the longer run this C\textsuperscript{16}O source will slowly be depleted.

Interestingly, the observed effective CO dissociation has never been observed for a Cu catalyst under the present conditions. A mechanistic explanation for this is found in methanol synthesis literature. Frost (1988) and Millar et al. (1993) noted that CO\textsubscript{2} is able to adsorb on a CuO or ZnO particle which contains defects by reduction. A metal-metal oxide combination forms a carboxylate species with CO\textsubscript{2} which may subsequently decompose, thereby leaving oxygen on the surface. This mechanism would lead to a C\textsuperscript{18}O production dependent on the concentration of C\textsuperscript{18}O\textsuperscript{18}O and C\textsuperscript{18}O\textsuperscript{16}O and the amount of defect, partly reduced sites. As the concentration of C\textsuperscript{18}O\textsuperscript{18}O and C\textsuperscript{18}O\textsuperscript{16}O is high at the start of the second reduction cycle (see figure 5.3) and the amount of defect sites is probably high at the end of this cycle, the C\textsuperscript{18}O concentration profile in time must contain an optimum approximately in the middle of the cycle, which is indeed the case (see figure 5.3; open circles). Furthermore a higher C\textsuperscript{18}O production at longer reduction periods (figure 5.5; \( \tau = 240 \text{ s} \) vs. \( \tau = 100 \text{ s} \)) can be explained as well by the fact that there will be more defect or reduced sites after longer reduction times.
Switching back to unlabelled oxygen (figure 5.4) results in a considerable amount of labelled CO₂ produced after one period, demonstrating that the catalyst acts as an oxygen buffer. Even at temperatures far below the pretreatment temperature of 773 K Cu can be oxidised in the oxidation cycle since we found labelled CO₂ for many periods after the switch to ¹⁶O₂.

In summary CO₂ production in the oxidation cycle proceeds in two stages. Instantaneous production of CO₂ in the oxidation cycle results from reaction of CO and O already adsorbed on the surface. In the second stage CO coordinated to Cu sites without an in-plane oxygen “neighbour”, reacts. To this end first oxygen has to adsorb on a vacant site nearest to this Cu site before reaction to CO₂ occurs. A representation of the mechanism is presented in the modelling section. Furthermore labelling experiments let us to conclude that dissociation of CO effectively takes place, leaving oxygen on the surface of the catalyst during reduction. Adsorption of CO₂ on a partly reduced catalyst under formation of a carboxylate species and decomposition of this complex can be an explanation for the observed. In the next section we will focus on the structure of the active species and find support for the proposed mechanism using transient FTIR experiments.

**Transient FTIR (Type 3)**

In figure 5.6 the CO₂ concentration profile in the cycle invariant state is given as well as the areas of the IR peaks of the possible reaction intermediates: carbonyl (2000-2200 cm⁻¹) and carbonate-like (1200-1700 cm⁻¹) species. Whereas separate reduction by ER and LH mechanism were observed in type I experiments, we never saw two CO₂ production peak maxima in the IR experiments. Simulations show that this may be attributed due to the different reactor hydrodynamics of a fixed bed on the one hand and the FTIR cell on the other. The FTIR flow cell behaves approximately as a CSTR. In addition the catalyst may be changed by the preparation of the pellet.

A small, scarcely visible amount of instantaneous formed CO₂ (figure 5.6, t=0), is probably produced by ER mechanism. The CO₂ concentration passes through a maximum and slowly descends to a value similar as in type 1 experiments. Probably diffusion of oxygen from the subsurface determines the production of CO₂ at this point. The carbonyl band intensity increases with a delay compared to the CO₂ peak. Within the reduction cycle the carbonyl band does not reach its maximum intensity. Whereas CO adsorption on Cu is known to be very fast, the carbonyl band intensity increases only gradually. This suggests that CO-Cu⁺ is an active reaction intermediate. Moreover the maximum in CO₂ production coincides with an
inflection point in the carbonyl profile. The reduction mechanism as proposed by Dekker et al. (1994) properly describes the response in the sense that reduction proceeds in three steps.

![Figure 5.6. Concentration of CO₂ and IR absorbance intensities of carbonyl and carbonate groups in the cycle invariant state. Response on a switch to helium instead of oxygen is shown for the carbonyl group.](image)

The total carbonate absorbance (1200-1700 cm⁻¹) must be interpreted with care since the extinction coefficient of various types of carbonates differs significantly. More information is obtained by investigation of the IR spectra at various time scales discussed hereafter. The intensity of the carbonate band is correlated to the CO₂ concentration because presence of CO₂ always results in absorbance in the carbonate region (Bijsterbosch, 1993). However after the switch to oxygen the carbonates no longer follow the CO₂ response as delayed formation of these species is observed. The rather sharp maximum in CO₂ production, similar with observations in type 1 experiments, coincides with rapidly decrease of carbonyl species. In order to verify that the steep decrease of carbonyl is not attributed to desorption of CO, in one experiment a step from 5% CO to helium was implemented (see the separate line in figure 5.6). In helium the decline of carbonyls is much slower, strongly suggesting that carbonyl and not the carbonate groups are the source of CO₂ in the oxidation cycle.

During reoxidation the absorbance due to carbonates remains more or less stable at a high level even in the absence of CO₂ and carbonyls. During successive reduction/oxidation cycles a steady increase in the carbonate occupancy is observed. Since the catalyst activity is not reduced after dozens of cycles (as mentioned before), the absolute amount of carbonates is likely to be small compared to the amount of Cu atoms present at the outer surface of the catalyst.
Additional information about the mechanism and (reactive) surface species is obtained from figure 5.7, showing individual spectra at various time intervals during the reduction cycle. For all spectra the same background, the oxygen pretreated Cu catalyst, is taken. The CO$_2$ observed around 2350 cm$^{-1}$ is gaseous CO$_2$. Carbonyl species are observed at 2121 cm$^{-1}$ upon introduction of CO in the cell. A shoulder at higher wavenumbers, 2136 cm$^{-1}$, is developing while reaction proceeds. Both bands are due to carbonyl groups. The low frequency band is often attributed to CO on Cu$_2$O (Busca, 1987). The high frequency band cannot be assigned with certainty, though it has been reported that various oxidised Cu crystal faces give peaks at wavenumbers of 2115-2137 cm$^{-1}$ (Choi and Vannice, 1991). Although the high frequency band increases during the CO cycle, the maximum of the carbonyl peak shifts from 2121 to 2116 cm$^{-1}$ due to a net reduction of the surface of the catalyst. No CO on Cu$^0$ is observed as in that case we would expect a shoulder on the low frequency side of the 2121 cm$^{-1}$ band, the region where CO-Cu$^0$ is expected (Busca, 1987). However we should take into account that the extinction coefficient for Cu$^0$-CO complexes is relatively low and absorption bands are probably hardly observed (Shepot'ko et al., 1994).

The various carbonate species are observed at 1200-1700 cm$^{-1}$. Table 5.2 gives an overview of assignments of carbonate complexes in a reducing but also in an oxidising environment (Dovydov, 1990, Bijsterbosch, 1993). The remaining intensity bands could not precisely be assigned to a carbonate complex. Monodentate and bidentate carbonate species have vanished after some time during the reduction while in oxygen when CO$_2$ already has disappeared still reasonable amounts are observed (not shown here). The bidentate carbonate band intensity
even increases; both monodentate and bidentate carbonate are relatively stable in an oxidising environment. Non coordinated carbonates are following the CO₂ response closely and are also observed when CO₂ alone is introduced in the cell with the Cu catalyst. However as mentioned before it is not very likely that the impact of the carbonates is significant and these groups are assumed to be spectators.

In view of the dissociation mechanism as proposed before, it is relevant to focus on the regions of absorption of the carboxylate group. During reduction of the catalyst an increase of the bands of the symmetrical as well as the anti-symmetrical stretching vibration is observed. This observation and the shift of the carbonyl band towards lower wavenumbers due to a partial reduction of the catalyst, are both in agreement with the suggested mechanism. Therefore the effective dissociation of the CO bond is likely to occur via the carboxylate intermediate.

**Table 5.2. Assignment of IR bands in the 1200-1700 cm⁻¹ region during CO oxidation on the Cu catalyst.**

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Species</th>
<th>Development in CO</th>
<th>Development in O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1640</td>
<td>Bidentate carbonate</td>
<td>Decrease</td>
<td>Increase</td>
</tr>
<tr>
<td>1585</td>
<td>Carboxylate (anti-symm.)</td>
<td>Minor increase</td>
<td>Decrease</td>
</tr>
<tr>
<td>1527</td>
<td>Monodentate carbonate</td>
<td>Present at high CO₂</td>
<td>Always present</td>
</tr>
<tr>
<td>1420</td>
<td>“Free” carbonate*</td>
<td>Following CO₂</td>
<td>Following CO₂</td>
</tr>
<tr>
<td>1392</td>
<td>Carboxylate (symm.)</td>
<td>Increase</td>
<td>Slight decrease</td>
</tr>
</tbody>
</table>

*Non-coordinated

A remarkable negative absorption band at 1600 cm⁻¹ compared to the oxidised catalyst could not be assigned to a surface species. This negative band is apparently related to the removal of oxygen from the surface, as it disappears in the oxygen cycle. It might be attributed to surface restructuring under reducing conditions, as for instance reported in Crew and Madix (1996). Metal-oxygen fundamental vibrations are only found below 1200 cm⁻¹ (Davydov, 1990) and molecular oxygen (1500-1700 cm⁻¹) is not observed at high temperatures so these bands cannot be responsible for this observation.
Modelling of the reoxidation reaction

To verify the proposed mechanism for oxidation of the partly reduced catalyst, gas phase composition measured at the outlet of the reactor was fitted on several rate equations. Responses in the first oxygen cycle of experiments with periods of 60, 120 and 240 s were used. The objective function that was minimised by non-linear regression using a Simplex search routine for parameter estimation, was:

\[
\Phi = \sum_{i=1}^{n} (y_{CO_2,i}^{obs} - y_{CO_2,i}^{calc})^2 + \sum_{i=1}^{n} (y_{O_2,i}^{obs} - y_{O_2,i}^{calc})^2
\]  

5.1

Modelling equations were solved by numerical integration (Runge-Kutta-Fehlberg algorithm) of partial differential equations using the Numerical Methods of Lines (Schiesser, 1991). Axial dispersion is neglected since no differences in the outlet concentration profiles in time were measured between tracer experiments in an empty reactor and one filled with the Cu catalyst. In addition calculations showed that the axial dispersion coefficient is at maximum \(10^{-1}\) m\(^2\)/s for the components of interest and no significant differences were obtained in simulations with and without axial dispersion using this value of the dispersion coefficient. The partial differential equations used are thus of the following general form:

\[
\frac{\partial c_j}{\partial t} = -v \frac{\partial c_j}{\partial z} + r_j \frac{1 - \epsilon_b}{\epsilon_b} \quad (j \text{ denotes } CO_2 \text{ or } O_2) \]  

5.2

\[
\frac{\partial c_{k*}}{\partial t} = r_k. \quad (k* \text{ denotes surface complexes})
\]  

5.3

where \(v=0.11\) m/s, \(\epsilon_b=0.4\) and the catalyst bed height was 0.010 m.

The mechanistic model for the reoxidation as derived especially from type 1 and type 2 experiments, is depicted below. To illustrate the results as they were obtained in labelling experiments, the mechanism is written down as if it were a type 2 experiment: the oxygen used is isotopically labelled.
First oxidation takes place of sites on which both CO and O are adsorbed and CO\textsubscript{2} is produced (1). Oxidation of sites on which only CO is present (2) leads to a new site which can react via step (1). In the labelling experiment this leads to the formation of a single labelled CO\textsubscript{2}. Finally a third step is introduced (3) to account for the fact that the amount of oxygen consumed in the oxidation cycle exceeds by far the amount of CO\textsubscript{2} produced. It is therefore obvious that besides sites containing CO other sites were oxidised as well without producing CO\textsubscript{2}. The second reaction is assumed to be faster than reaction (3) because the product of the latter reaction cannot contribute to the oxidation in the second reaction step. More detailed presentation of the surface complexes is given in the conclusion section (figure 5.9). The parameters to be determined are the initial fractions of COO*, CO* and * and the values for k\textsubscript{1}-k\textsubscript{3}. The initial CO\textsubscript{2} concentration was assumed to be constant over the catalyst bed.

Attempts were made to fit all 6 parameters which did not result in accurate values for k\textsubscript{1} and k\textsubscript{2}. Therefore reaction 1 and 2 were combined:

\[
2 \text{COO}^* + \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{O}^* \quad (1a)
\]

\[
2 * + \text{O}_2 \rightarrow 2 \text{O}^* \quad (3)
\]

In principle this would lead to erroneous results since CO* (2) is now also oxidised in one step and therefore half the amount of oxygen is needed for the oxidation of these species. However, the amount of oxygen consumed by this reaction is minor compared to the other steps as can be concluded from figure 5.3. The quantity of labelled CO\textsubscript{2} after the oxygen step is relatively small compared to the quantity of unlabelled CO\textsubscript{2}. So, not all kinetic constants could be estimated separately (k\textsubscript{1a} is a lumped parameter). Nevertheless, valuable results are obtained concerning the validity of this model, especially by focusing on the initial amounts of the surface species.
In the manner sketched, accurate values for all constants and initial values of the surface species were obtained. In figure 5.8 the experimental concentrations as well as the calculated concentrations of CO$_2$ and O$_2$ are given for the three periods. Note that the experimental values for $t=120$ and 240 s are the same as presented in figure 5.2; see the first 30 seconds of the first oxidation cycles. It may be concluded that the calculated CO$_2$ profiles approximate the observed ones closely. Although the measured O$_2$ development in time is not as well described as the CO$_2$ profile, the general trend is well predicted. Table 5.3 gives the estimated values of the parameters and their 95% error intervals. $k_{1a}$ was fixed at the value found for $t=240$ s. No accurate value could be determined for small periods since the CO$_2$ concentration initially followed the input oxygen concentration for which a polynomial function was taken, to account the non-ideal step function.

The kinetic constants for the reoxidation resulting in CO$_2$ production (1 and 2) were approximately twice as high as the constants of the oxidation of empty sites (3). Nice agreement is observed between the initial amounts of sites with adsorbed CO, [CO$_2^*$]+[CO$^*$], and the amount of CO$_2$ produced according to table 5.1. The estimated initial values can also be well explained by the knowledge we have about the mechanism. At a period of 60 s the switch to O$_2$ is made when only few sites are totally reduced so the amount of empty reduced sites is lowest of the three periods. Also a comparatively small amount of sites with adsorbed CO are present; the production by the LH reaction has not yet reached its maximum at the step to the oxygen cycle (see figure 5.2, t=30 s) and there are only a few sites on which CO can adsorb. In the 120 s experiment the switch was performed just after the maximum in LH
reaction. Therefore many sites with adsorbed CO and adsorbed oxygen in the neighbourhood are present. Reduction has not proceeded to the extent as for \( \tau = 240 \) s, so the amount of reduced sites, \([^*]\), is in-between the values at \( \tau = 60 \) and \( \tau = 240 \) s. Finally we see comparatively more reduced sites at \( \tau = 240 \) s which is obvious since the reduction cycle is longer. Less sites with adsorbed CO are present than for \( \tau = 120 \) s since more CO has been converted by LH reaction and almost all the oxygen has reacted. Hence, the introduced oxygen reacts first with sites on which only CO is present (2) whereupon in a second step CO\(_2\) is produced (1). By that time part of the CO will have been desorbed and less CO\(_2\) will be observed, as indeed is the case.

<table>
<thead>
<tr>
<th>Cycle period / s</th>
<th>( k_{1b} ) / m(^3) mol(^{-1}) s(^{-1})</th>
<th>( k_3 ) / m(^3) mol(^{-1}) s(^{-1})</th>
<th>Initial ([\text{CO}<em>2^<em>]+[\text{CO}^</em>]) mol/mol(</em>{\text{Cu}})</th>
<th>Initial ([^*]) mol/mol(_{\text{Cu}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.65*</td>
<td>0.48±0.034</td>
<td>0.052±0.0023</td>
<td>0.13±0.021</td>
</tr>
<tr>
<td>120</td>
<td>0.65*</td>
<td>0.31±0.067</td>
<td>0.070±0.0083</td>
<td>0.21±0.030</td>
</tr>
<tr>
<td>240</td>
<td>0.65±0.016</td>
<td>0.35±0.029</td>
<td>0.058±0.010</td>
<td>0.27±0.053</td>
</tr>
</tbody>
</table>

\(^b\)Parameter fixed at this value

Table 5.3. Estimated parameters for the reoxidation and their 95% confidence interval at various periods.

**CONCLUSIONS**

Vital information on the oxidation of CO over Cu-on-alumina could in an elegant manner be obtained by separately investigating the reduction / oxidation processes in successive reaction cycles. In agreement with earlier work the reduction of the fully oxidised catalyst was shown to proceed first by removal of overlayer oxygen via an ER mechanism (figure 5.9, a) and subsequently by removal of in-plane oxygen via a LH mechanism (b). Concurrent to the latter, in-plane oxygen is slowly replenished by subsurface oxygen diffusion (c), or the catalyst can be further reduced (d). An intriguing phenomenon is the fact that during an extended period of subsequent reduction (with C\(^{16}\)O) and reoxidation (with \(^{18}\)O\(_2\)), the oxidation process is accompanied by the release of substantial amounts of C\(^{16}\)O\(^{18}\)O. The origin of the second \(^{16}\)O can only be explained by an effective dissociation of CO, as is confirmed also by the observed C\(^{18}\)O\(^{18}\)O and C\(^{18}\)O production. This is the more true for a severely reduced catalyst, containing relatively many defect sites. A mechanism in which CO\(_2\) adsorbs on these sites under formation of carboxylates and subsequently decomposes towards CO and an oxidised species, is proposed (e).
Forced concentration oscillations in CO oxidation over Cu/Al₂O₃

For the reoxidation a mechanism is suggested consisting of three steps that allow to describe the response in the oxidation cycle in a satisfactory manner. The first step (f) is formed by oxidation of sites with adsorbed CO and O₂, and results in instantaneous production of CO₂. The second step (g) consists of oxidation of a site with adsorbed CO without the presence of...
in-plane oxygen. Subsequently these oxidised species give CO$_2$ via (f). Finally also sites are oxidised without production of CO$_2$ (h). Exchange of in-plane oxygen with bulk oxides and with oxygen in the overlayer is shown for the reoxidised species (i). Note that in the present study only a mechanism is given for the reoxidation during the first reduction/oxidation cycles. As demonstrated in the labelling experiments, after a few cycles a mechanism needs to be assumed in which decomposition of carboxylate species, originating from CO$_2$ adsorption, is included.

It was demonstrated that the formation of CO$_2$ during the reoxidation cycle is accompanied by a rapid decrease in copper carbonyl, not attributable to desorption. Hence, formation of CO$_2$ is likely to proceed over these carbonyl species rather than through other intermediates such as carbonates. This is in accordance with the mechanism presented above. It is shown that carbonates probably are spectators without any contribution to the reactions of our interest.

The presented study is an example of the use of forced oscillations in heterogeneous catalysis. Mechanistic insights could be gained from experiments with transients at different time scales, accomplished by imposing oscillations at various periods.

**NOTATION**

- $c_i$: concentration of component $i$, mol/m$^3$
- $d_i$: inside diameter of the reactor, m
- $F$: gas flow rate at STP, ml/min
- $k_j$: reaction rate constant of reaction step $j$, see text
- $t$: time, s
- $t_{cell}$: residence time in the IR cell, s
- $v$: gas velocity in the reactor, m/s
- $y_{CO}$: fraction of CO in the gas phase, -
- $y_{i,obs}^j$: observed fraction of component $i$ at the reactor exit, -
- $y_{i,calc}^j$: calculated fraction of component $i$ at the reactor exit, -
- $z$: axial distance along the catalyst bed, m

**Greek letters**

- $\varepsilon_b$: void fraction of the catalyst bed, -
- $\tau$: cycle period, s
- $\Phi$: objective function to be minimised, -
REFERENCES


**APPENDIX**

In the work described in this chapter and in chapter 6, two transmission IR flow cells were used which were developed at the Department of Chemical Engineering of the University of Amsterdam. These cells allowed us to conduct experiments at temperatures up to 623 K and pressures lower than 5 bar (tested in H₂). By their low volumes, the IR flow cells are suited for performing transient experiments in which concentration steps are imposed.

The main difficulties in the development of the IR flow cells were due to requirements such as the low volume and the possibility of operating under relatively high pressures and high...
temperatures. Furthermore, the cells should be easily modelled using a simple reactor design. Therefore the catalyst pellet was to be fixed in the middle of the cell without having by-passing of gas. The problems related to these requirements are among others leaking of the cell and breaking of windows due to expansion. The design that overcame these problems is shown in figure 5.10.

The cell consist of two parts (housings) which can be unscrewed to insert the catalyst pellet. A copper ring is used to connect the two parts. A pellet, made of 40 mg pure catalyst, is prepared under high pressure in a pressing assembly. During this process the catalyst pellet is pressed into a groove of a ring which acts as sample holder. This ring is subsequently placed in the cell and fixed with a ring made of silicone (silicone: Versachem 999) to avoid by-passing and breaking of the catalyst pellet when the cell is closed. Prior to use, the silicone ring is heated in air at 300°C for 2 h. In this way the influence on experiments of contaminations present in the silicone is absent.

The IR flow cell is placed into a specially equipped oven (see figure 5.11) which is heated by four heating rods. This set-up allows isothermal operation which was verified by replacing one of the CaF$_2$ windows by a stainless steel “window” with an adjustable thermocouple. By moving the thermocouple back and forward the temperature in the cell was measured at 220°C. Variation remained within a few degrees from 220°C. The complete system, cell plus
oven, can be adjusted in horizontal and vertical position in order to use the transmitted IR beam optimally.

Figure 5.11. Schematic representation of the IR flow cell positioned in the oven.

Two IR flow cells were developed which were similar in essence and have equal diameters (28 mm). The cells differ in internal volume (and length). The first cell, used in this chapter, has an effective volume of 3.6 ml whereas the second cell, used in the work presented in chapter 6, has a volume of 2.5 ml. The hydrodynamics of both cells can be well approximated by a CSTR model when gas flows are applied between 30 and 100 ml/min. In figure 5.12 the responses of the flow cells after a step to 5% CO in helium are shown. The data were collected by means of integration of the IR absorption peaks following by a normalisation. The residence time of the IR cells was estimated using the following equation, derived from the design equation of a CSTR:

\[
y_{\text{CO}}(t) = y_{\text{CO}}^{0} \left(1 - \exp \left(-\frac{t}{t_{\text{cell}}} \right)\right)
\]

in which \(y_{\text{CO}}^{0}\) denotes the fraction CO in the gas and \(t_{\text{cell}}\) the residence time in the IR cell. As can be concluded from figure 5.12 the CSTR reactor model describes the response very well for both IR flow cells. On basis of the estimated residence time and the applied gas flow rates, the volume of the cells could be calculated. For the two cells respectively averaged volumes of 3.8 and 2.6 ml were found. Based on dimensions, their volumes value the above mentioned 3.6 and 2.5 ml, which are in close agreement with the fitted volumes. Therefore equation 5.4 was used whenever a catalytic reaction in the IR flow cell was modelled.
Figure 5.12. Response of the two cells towards a step of 5% CO in helium at 220°C measured by IR. 1) $V_{cell}=3.6$ ml and $F=30$ ml/min (STP). 2) $V_{cell}=3.6$ ml and $F=60$ ml/min. 3) $V_{cell}=2.5$ ml and $F=30$ ml/min. The lines show the results of fitting the data using equation 5.4.

ACKNOWLEDGEMENTS

Theo Nass, Co Zoutberg, Bart van der Linden and Danny Brands are gratefully acknowledged for their contribution to the design and construction of the Transient FTIR cell.
Figure 14. Schematic representation of the IR flow cell positioned in the oven.

The cathode of the cell is marked in 103. The IR beam will pass through the cell, which is contained in the oven. The IR beam will then pass through the detector.

The cell is used to determine the concentration of a substance in solution. The cell has an effective volume of 0.6 ml, whereas the second cell used in the work presented in chapter 6 was a mere 0.5 ml. The hydrodynamics of both cells are different, as the first cell is a CSTR model when gas flows are applied between 0.5 and 10.6 m/s. In figure 3.12 the concentration of sample is plotted as a function of the absorbance. The absorbance peaks following by a normalization of the absorbance as a result of the IR absorption peaks following by a normalization.

The absorbance from the IR cell was calculated using the following equation, derived from the Beer-Lambert law:

\[ A = \varepsilon c l \]

where:
- \( A \) is the absorbance
- \( \varepsilon \) is the molar absorptivity
- \( c \) is the concentration of the solution
- \( l \) is the path length

This equation can be used to determine the concentration of a substance in solution, given the absorbance, molar absorptivity, and path length.

The absorbance was calculated using the following values:
- Path length: 3.6 mm
- Molar absorptivity: 5.6
- Concentration: 0.5

The absorbance was then calculated using the above equation.

In conclusion, the IR cell was used to determine the concentration of a substance in solution, using the Beer-Lambert law. The absorbance was calculated using the above equation, and the results were normalized for further analysis.
CHAPTER 6

CO oxidation over Pt/Al$_2$O$_3$: self-oscillations and forced oscillations*

**ABSTRACT**

Single crystal Pt is well known to demonstrate oscillatory and complex dynamic behaviour, for instance during the catalytic oxidation of CO. This type of behaviour is also observed for presently investigated supported Pt catalysts. In the present case self-oscillations have been examined during CO oxidation on EUROPT-3, using *in-situ* FTIR, applied to both steady state experiments and during step response, transient isotopic labelling and concentration programming experiments. The goal of the present investigation was to establish the feedback mechanism that is essential in explaining complex dynamic behaviour and to apply periodic operation to suppress the self-oscillations. For low CO/O$_2$ ratios the reaction demonstrates so-called regime I kinetic behaviour with reaction orders in CO and O$_2$ being respectively one and zero. Platinum is slowly oxidised, thereby blocking sites for adsorption and subsequent reaction. At a critical point, corresponding to a degree of oxidation of the Pt of approximately 61%, regime II type behaviour is observed: the system exhibits multiplicity and self-oscillations. With progressing oxidation of Pt both the period and the amplitude of the oscillations increase. Although the existence of oxidised Pt seems to be correlated to the emergence of self-oscillations, quantitative analysis of the oxidation and reduction kinetics of Pt reveals that the dynamics of these reaction steps are at least two orders of magnitude too slow to act as feedback mechanism. A qualitative comparison of other known feedback mechanisms indicates that a phase transition mechanism can describe the observed self-oscillations. It is shown that forced concentration oscillations suppress the self-oscillations. Periodic reduction of the catalyst in CO is effective in keeping the amount of oxidised Pt low, and thereby prevents the system from entering regime II.

* Accepted for publication in Chemical Engineering Science.
INTRODUCTION

Self-oscillations during oxidation of CO on platinum have been the subject of many studies. An extended review was presented by Razon and Schmitz (1986). Further publications on the subject have been presented by Schüth et al. (1993), Slin'ko and Jaeger (1994) and Imbihl and Ertl (1995). Though the mechanism underlying self-oscillations is subject to debate, agreement exists that CO oxidation follows a Langmuir-Hinshelwood (LH) type reaction path, involving irreversible dissociative adsorption of O\textsubscript{2} and reversible adsorption of CO (Engel and Ertl, 1979). The controversy regarding the mechanism focuses on the so-called feedback mechanism, imperative in order to demonstrate oscillatory behaviour. Clearly, a simple LH model in itself is not of a sufficient high order of non-linearity to show complex dynamic behaviour. For such a model the Poincaré Benixon criterion is satisfied at all times and by consequence the LH model can not demonstrate oscillations (see for instance Ivanov et al., 1980). An additional, relatively slow, non-linear feedback is required in conjunction with the LH model. The nature of this feedback mechanism forms a subject of the present study.

One of the most simple feedback mechanisms is introduced when the assumption that the gas phase concentrations are invariant is relaxed and a reactor model is taken into account. In case of depletion of the gas phase, the periods of the oscillations will be of the order of the reactor residence time. Strong non-linearity can also arise from the inclusion of temperature dependent kinetic constants. In this way oscillations are easily constructed by the exponential term in these constants.

In the present study a low loaded catalyst was used in combination with low concentrations of CO. Temperature effects were therefore absent. In addition, periods of oscillations found in the experiments were sometimes shorter and often much longer than the reactor residence time. Therefore the variability of gas phase concentrations is not the (primary) feedback mechanism.

For the catalytic system at hand, the following (other) phenomena have also been proposed as being the feedback mechanism:

1. slow oxidation and reduction of platinum particles (redox model)
2. variation of sticking coefficients by sorbate induced surface restructuring of the Pt (phase transition)
3. deactivation of the surface with carbon atoms and re-activation by reaction with oxygen
4. coverage dependent activation energies of CO desorption and surface reaction (sorbate-sorbate interaction)

**Redox model**

In the redox model, it is assumed that part of the active surface covered by chemisorbed oxygen is transformed into an inactive state, as an oxide of platinum is formed (Sales et al., 1982). A slow reduction of the oxide by CO re-establishes the active state. Both processes are comparatively slow in case of CO oxidation. Investigation of the reduction rates led Turner and Maple (1984) to conclude that the oxidation/reduction mechanism is valid since the time scales of reduction and self-oscillations are similar. Further experimental evidence in support of this mechanism was provided in *in-situ* X-ray diffraction experiments (Hartmann et al., 1994). These authors showed that Pt undergoes a periodic oxidation and reduction in the oscillatory regime.

**Surface restructuring**

For single crystal Pt surfaces, the origin of oscillations under low pressure conditions was unambiguously identified as arising from structural changes. Lynch et al. (1986) postulate the same mechanism for supported metal catalysts. Their model requires that at least a part of the Pt sites are subject to structural changes. The best understood and most thoroughly investigated is the Pt(100) hex ↔ lxl mechanism, first proposed by Ertl et al. (1982). Initially the Pt(100) is clean and exhibits a hexagonal configuration on which CO may adsorb and oxygen adsorption is almost negligible. As of a critical CO coverage, a transformation to the lxl phase takes place. Oxygen is able to adsorb on this surface and reaction between CO and O is initiated. As a result, the CO coverage decreases and a second critical coverage is reached at which the surface reverts back to the hexagonal phase. The cycle begins anew. The difference in sticking coefficients for O₂ on the two structures is essential and was also demonstrated for Pt(100)/Pt(210) (Slin’ko and Jaeger, 1994).

**Catalyst deactivation**

Burrows et al. (1985) and Collins et al. (1987) developed a model encompassing the formation of carbon. Formation of a blocking carbon layer and its subsequent removal are postulated to explain the oscillations. In principle this leads to the same formalism as for the oxidation/reduction model: the variation in the number of active sites is the underlying driving force responsible for the oscillations.
Sorbate - sorbate interaction

Finally, another feature that may induce instabilities is the incorporation into the LH model of a linear dependence of both the activation energy of the CO desorption and the surface reaction on the surface coverage of CO. Frank (1997) used this feedback mechanism, which can be rationalised by assuming repulsive interactions between adsorbed molecules, to explain the observed self-oscillations on platinum during NO reduction by CO. Desorption of CO is assumed to be facilitated whereas reaction of CO$_{ads}$ and O$_{ads}$ becomes increasingly difficult at high CO coverages.

In practice, self-oscillatory and chaotic behaviour in a catalytic system (reactor) are undesired. Periodic operation can be used to modify the kinetic behaviour of a catalytic system in such a way that self-oscillations disappear. It may be used in case (chaotic) self-sustained oscillations are undesired and these dynamic responses can not be reduced to an acceptable level by a proportional integral (PI) or non-linear feedback control. Vibrational control, i.e. the manipulation of reactor input variables, may be successfully applied to stabilise catalytic reactors. A sinusoidal vibration on the CO and O$_2$ flow rate reduces the amplitude of CO$_2$ concentration oscillations on Rh/SiO$_2$ to one-tenth of the constant flow rate case (Qin and Wolf, 1995). Temperature self-oscillations in a CSTR in which an exothermic reaction takes place, can also be suppressed by input flow oscillations as shown by Cinar et al. (1987). These authors used the second order exothermic reaction between Na$_2$S$_2$O$_3$ and H$_2$O$_2$ as an example to show that periodic oscillations in the input flow rates can assure an asymptotically stable periodic operation in the vicinity of an unstable equilibrium point. Lehman et al. (1995) demonstrated that insertion of large amplitude oscillations in a CSTR with a delayed recycle stream, inducing a feedback mechanism, makes it possible to operate under previously unstable states at relatively high conversions. The present work differs from the work discussed so far, as no zero averaged vibration, i.e. a symmetric oscillation around an average value, is applied. It is aimed in this work to apply forced concentration oscillations to suppress the observed self-oscillations on the supported Pt catalyst used in this study.

In order to fully understand the response on imposed concentration oscillations the mechanism underlying self-oscillations must be elucidated. An univocal mechanism for self-oscillations on supported platinum and a quantitative analysis of both the non-forced and the forced catalytic system, are still lacking. Therefore the objective for the present study is twofold:

- elucidation of the feedback mechanism during self-oscillations on the supported Pt catalyst
- application of forced concentration oscillations to suppress self-oscillations
SIMULATION MODELS

In case of a microkinetic model and a model that includes a CSTR or a differentially operated PFR, the dynamics of a system can be expressed as a set of coupled first order differential equations. An analysis of the Jacobian matrix by calculation of the determinant and the trace, provides information on the stability of a system. Local stability is assured when both the sign of the determinant is positive and the sign of the trace is negative. When for the CO oxidation reaction both microkinetics and the gas phase mass balance (reactor model) is incorporated in the model the dimension of the dynamic system is at least 5. Finding parameters for which the system exhibits oscillations in a two dimensional system is usually not easy. The analysis of a multi-dimensional system (≥5) is even more complicated in the sense that oscillation regions cannot readily be identified.

Another approach for the analysis of such a system is demonstrated in Jansen and Nieminen (1997). It provides a better insight in the mechanism underlying oscillations, especially in case of catalytic reactions. The system of differential equations is divided in two parts. First the equations of the kinetic model in fast variables, i.e. variables showing fast dynamic behaviour, are investigated and the region of parameters where multiple steady states appear can be located. Then the model is completed by addition of slow feedback steps and parameters can be found for which a unique, unstable steady state, surrounded by a limit cycle arises. This approach is illustrated in the following example.

Presume the reaction mechanism for CO oxidation can be represented by

\[
\begin{align*}
\text{CO} + \ast & \leftrightarrow \text{CO}^* \quad \text{adsorption/desorption of CO} \\
\text{O}_2 + 2 \ast & \rightarrow 2 \text{O}^* \quad \text{dissociative adsorption O}_2 \\
\text{CO}^* + \text{O}^* & \rightarrow \text{CO}_2 \quad \text{surface reaction}
\end{align*}
\]

For this microkinetic model the following ordinary differential equations apply in case of a CSTR:

\[
\begin{align*}
\tau \frac{d}{dt} P_{\text{CO}} &= (P_{\text{CO,in}} - P_{\text{CO}}) + \left(-k_{\text{ads,CO}} P_{\text{CO}} \theta_f + k_{\text{des,CO}} \theta_{\text{CO}}\right) \frac{RT N_{\text{sites}}}{Q} \\
\tau \frac{d}{dt} P_{\text{O}_2} &= (P_{\text{O}_2,in} - P_{\text{O}_2}) + \left(-k_{\text{ads,O}_2} P_{\text{O}_2} \theta_f^2\right) \frac{RT N_{\text{sites}}}{Q}
\end{align*}
\]
\[ \frac{d}{dt} P_{CO} = \left( P_{CO, in} - P_{CO} \right) + \left( k_{reaction} \theta_{CO} \theta_{O} \right) \frac{RT N_{sites}}{Q} \]  

6.3

\[ \frac{d}{dt} \theta_{CO} = k_{ads,CO} P_{CO} \theta_f - k_{des,CO} \theta_{CO} - k_{reaction} \theta_{CO} \theta_{O} \]  

6.4

\[ \frac{d}{dt} \theta_{O} = 2 k_{ads,O} P_{O_2} \theta_f^2 - k_{reaction} \theta_{CO} \theta_{O} \]  

6.5

where \( \theta_{CO} \) and \( \theta_{O} \) are surface coverages of CO and atomic oxygen, and \( \theta_f \) is the fraction of vacant sites on the surface. \( Q \) stands for the volumetric flow rate. Here, the oxidation/reduction mechanism is used as feedback mechanism and, for sake of clarity, is represented by the following relatively simple expression:

\[ \frac{d}{dt} \theta_{ox} = k_{ox} P_{O_2} \theta_f - k_{red} P_{CO} \theta_{ox} \]  

6.6

in which \( \theta_{ox} \) denotes the fraction of oxidised platinum. The balance equation is given by

\[ \theta_f = 1 - \theta_{CO} - \theta_{O} - \theta_{ox} \]  

6.7

Steady state solutions of equation 6.1-6.5, the model in fast variables, were calculated using the conditions (partial pressures etc.) and the properties of the experimental equipment as described in the next section. Kinetic constants were taken from literature (Campman, 1996 and Kaul et al., 1987). In figure 6.1 and figure 6.2 the fraction of vacant sites is plotted versus the fraction of sites that is oxidised. An interval (regime II) can be observed where there is bistability: 0.7<\( \theta_{ox} \)<0.8. At low \( \theta_{ox} \) the active sites are primarily covered with atomic oxygen and the reaction rate is relatively high (regime I). The CO inhibition regime is obtained for highly oxidised platinum. In this so-called regime III adsorbed CO inhibits the adsorption of \( O_2 \) which results in a low \( CO_2 \) production rate. In principle this system does not exhibit oscillations and only hysteresis is observed. Introduction of the steady states of the feedback equation, representing a kinetic model in slow variables, renders occurrence of oscillations possible. The steady state condition of the feedback step is derived from equation 6.6:

\[ \theta_f = \frac{k_{red} P_{CO}}{k_{ox} P_{O_2}} \theta_{ox} \]  

6.8
Since the rate constants $k_{\text{red}}$ and $k_{\text{ox}}$ are small as compared to the other constants (see equation 6.1-6.5), the consumption of CO and O$_2$ due to the feedback reactions is negligible. In case of relatively high values for the ratio $k_{\text{red}}/k_{\text{ox}}$, for instance as in figure 6.1 with $k_{\text{red}}/k_{\text{ox}}=1.0$, there is a point of intersection of equation 6.8 and the upper branch of $\theta_f$ for low values of $\theta_{\text{ox}}$. A stable steady state is obtained denoted by the marker. For low values of $k_{\text{red}}/k_{\text{ox}}$ a stable state on the lower branch of $\theta_f$ is obtained at high $\theta_{\text{ox}}$. Intermediate values, for instance $k_{\text{red}}/k_{\text{ox}}=0.05$, give rise to self-oscillations since in these cases there are no points of intersection (figure 6.2). For a single value of $k_{\text{red}}/k_{\text{ox}}$ two feedback branches are obtained since besides on $\theta_{\text{ox}}$ and $k_{\text{red}}/k_{\text{ox}}$, $\theta_f$ depends on the partial pressures of CO and O$_2$ (equation...
which vary with the steady state. As a discontinuity exists in the steady state branches, there is also one in the feedback curves. When the system is on the steady state branch denoted with s.s.1, the feedback branch f.b.1 will drive it from the upper to the lower level. Subsequently, the system located on s.s.2 will be attracted by f.b.2. In this way the trajectory as indicated in figure 6.2 is followed.

The resulting oscillations are shown in figure 6.3. The absolute values for $k_{\text{red}}$ and $k_{\text{ox}}$ determine the oscillation period and amplitude (figure 6.3a, 6.3b). For high values of both parameters the feedback step acts as primary mechanism and the other steps in the scheme, the basic LH mechanism represented by equation 6.1-6.5, will conform to this step. The initial self-oscillations are quickly dampened as is observed in figure 6.3c.

![Figure 6.3. Computational results of the start-up of CO oxidation on platinum. Initial conditions: $\theta_{\text{CO}}=\theta_{\text{O}}=0$. $k_{\text{red}}=0.05 \cdot k_{\text{m}}$. Other kinetic constants as given in figure 6.1.](image)

The above illustrates the way of analysis used in this chapter and shows additionally that the feedback mechanism must fulfil strict conditions to serve as driving force for self-oscillations. However, this method is not always applicable. In case the coverage dependent activation energy is used as feedback mechanism, the approach using eigenvalues of the Jacobian matrix must be applied, as no distinction can be made between a slow and fast process.

**EXPERIMENTAL**

**Gases and catalyst**

All gases used were of HP or UHP grade (UCAR and Air Liquide). Gas mixtures, including the $^{18}$O$_2$ and $^{13}$CO mixtures (Thamer Diagnostica, 96% and 99% respectively), were made in a separate gas mixing system and stored in 0.5 or 5 litre lecture bottles.
The catalyst used in this work was a 0.3 wt.% Pt/Al$_2$O$_3$ catalyst (EUROPT-3, coded CK303, d$_p$ = 0.125 - 0.177 mm), kindly supplied by AKZO-Nobel. The mean particle size of the Pt clusters is about 1 nm (Bond and Cunningham, 1997). ICP-AES measurements performed on the catalyst gave a Pt content of 0.28 wt.% and no significant contaminations by any other metal elements were observed (Fe: 0.015 wt.%). In Bond (1993) other chemical and physical characteristics are presented. Notable is the relatively high Cl-content (1.0 wt.%). It was asserted that heat transfer effects are absent and that the system could be regarded as being isothermal.

**Apparatus and pretreatment**

*In situ* FTIR experiments were performed in the experimental set-up described in van Neer *et al.* (1997). 40 mg of catalyst was pressed in a ring using a pressing assembly. The pellet was subsequently placed in a pretreatment cell (without windows) and pretreated as recommended by Bond (1993):

- heat in air (30 ml/min STP) at 10 K min$^{-1}$ to 673 K; remain there for 2 h and cool in air to ambient temperature
- flush with He
- heat in H$_2$ (30 ml/min STP) at 5 K min$^{-1}$ to 673 K; remain there for 2 h and cool in H$_2$ to ambient temperature

After pretreatment the pellet was placed in the IR reactor cell and fixed near the inlet thereby using a pretreated silicone ring to avoid bypassing. The IR cell is similar to the one used in chapter 5, however its volume is smaller (V=2.5 ml). Another reduction was performed at 573 K for 1 h before the (IR) experiments were carried out. Below a catalyst pretreated according to the complete procedure is denoted as a "fresh" catalyst. More characteristics of the IR cell are presented in the appendix of chapter 5.

Prior to the experiments performed in the IR reactor cell, experiments in a tubular reactor were conducted to explore the various kinetic regimes in CO oxidation on Pt. The same amount of catalyst (40 mg) was loaded in a tubular reactor (see van Neer *et al.*, 1997). The applied gas flow rate and temperature were equal to those used in the IR reactor cell.
Experimental procedures

All experiments were performed at a pressure of 1.1 bar, a temperature of 493 K and with a total flow rate of 30 ml/min (STP). After pretreatment IR background spectra of the catalyst were taken at reaction temperature under helium flow (scan rate: 20 or 40 kHz; resolution: 2 cm⁻¹; aperture: open). Next, the gas phase composition was changed by a step to a CO/O₂/He mixture. Several gas phase CO molar fractions were used and the molar oxygen fraction was 5%, unless noted otherwise. FTIR and mass spectrometer analysis could be applied simultaneously after the imposed concentration steps. Qualitative and quantitative interpretation of the obtained spectra was done in comparison to a variety of background spectra as indicated in the text.

Thermogravimetric experiments were performed to estimate the CO and oxygen uptake of the catalyst. About 400 mg of catalyst precursor was mounted in a porous basket in a Setaram TG85 thermobalance. The sample was calcined in an air flow of 120 ml/min and heated to 673 K at a rate of 10 K/min and maintained at this temperature for 2 hours. Subsequently, the sample was cooled down to room temperature under an air flow and flushed with argon. After calcination the sample was reduced in pure hydrogen for 2 hours at 673 K. A flow of 120 ml/min and a heating rate of 5 K/min were used. The sample was cooled down under hydrogen and temperature was raised to 493 K under an argon flow. At t=0 a step was performed to air (120 ml/min) and the weight increase was monitored until a plateau had been reached. The same procedure was followed in case of the CO adsorption measurements. Instead of air a 2% CO in helium mixture was used. Finally, alumina (CK300) was measured for reference.

RESULTS AND DISCUSSION

Kinetic regimes

From the exploratory experiments conducted in the tubular reactor equipment the various kinetic regimes were identified. The CO₂ production vs. CO inlet concentration is shown in figure 6.4. In this experiment, CO concentrations were varied and subsequently each state was analysed for a few minutes (at least 5 min). Stable steady states are represented as filled circles and open circles represent the maximum or minimum values of CO₂ during self-oscillations. The dotted lines denote the amplitudes of the oscillations. For $P_{CO}<115$ Pa the system exhibits regime I kinetic behaviour: high conversions and an apparent positive order in CO are observed. For $P_{CO}>290$ Pa a negative order in CO and low reaction rates are obtained:
the system is located in the CO inhibition regime (regime III). At intermediate partial pressures of CO self-oscillations are observed (regime II). The amplitude of these oscillations increases with $P_{CO}$. For $P_{CO}=290$ Pa the amplitude collapses to zero in a discontinuous transition. The period of the oscillations shows a minimum which is located in the middle of regime II.

![Graph showing CO$_2$ partial pressure at the outlet of the tubular reactor vs. the inlet pressure of CO. Stable steady states are represented as filled circles and open circles represent the maximum or minimum values of CO$_2$ during self-oscillations. The dotted lines denote the amplitudes of the oscillations. Squares denote the period of the self-oscillations. $P_{O_2}=5500$ Pa; $T=493$ K; $Q=30$ ml/min.]

The results obtained above are in agreement with the generally known behaviour of CO oxidation on platinum (see for instance Böcker and Wicke, 1985). On basis of these results, several gas compositions were tested in the IR system. Experiments were performed in the intermediate regime (regime II) in order to elucidate the mechanism underlying oscillations.

**Occurrence of self-oscillations**

In the IR equipment, first the response of a fresh catalyst after a step change from helium to a 0.26%CO/5%O$_2$ reaction mixture ($P_{CO}=286$ Pa and $P_{O_2}=5500$ Pa) was investigated. Figure 6.5 gives the responses of CO, O$_2$ and CO$_2$ obtained by mass spectrometry. CO first reaches a maximum and then slowly decreases to zero. This can be understood by the fact that CO adsorbs fast as compared to O$_2$. Hence, initially CO adsorbs preferentially at the catalyst without occupying all sites and no reaction occurs. Subsequently oxygen adsorbs and reaction starts. Thus empty sites are created which are replenished by CO and O$_2$. Nearly all CO is removed from the gas phase. Under the present conditions at longer time scales approximately 100% conversion of CO is obtained (figure 6.5). Interestingly, although from the chosen gas
composition it was expected that self-oscillations would occur (see figure 6.4), no self-oscillations are obtained in this equipment.

![Figure 6.5. Response curves after a step change from helium to 0.26%CO/5%O₂ over fresh EUROPT-3 at 493 K.](image)

When the same experiment is performed after ageing the catalyst under regime III conditions (i.e. the catalyst is exposed to 1-3% CO and 1-5% O₂ mixtures at 493 K for at least 5 h), a different response is obtained (figure 6.6). The maximum in the CO response is higher and prolonged, indicating a lower activity of the catalyst. Furthermore, after approximately 100 s harmonic self-oscillations are obtained with a difference between maxima and minima of 100 Pa (based on CO or CO₂) and a period of 11 s. Note that the period is approximately twice the residence time of the cell (τ~5 s), so the oscillations are at least in part of the kinetic type. The outlet partial pressure of CO₂ initially has an average value of 180 Pa, 37% lower compared to the fresh catalyst, and follows a slightly declining trajectory in time.

![Figure 6.6. Response curves after a step change from helium to 0.26%CO/5%O₂ over aged EUROPT-3 at 493 K.](image)
In order to restore the original activity of the catalyst, a reduction cycle of 2 hours was applied. A flow of 30 ml/min of pure hydrogen was fed to the cell at 573 K. The response after the same step change from helium to the reaction mixture at 493 K, is shown in figure 6.7a. The CO$_2$ production rate is increased by the reduction, but the activity level of the fresh catalyst is not regained. The self-oscillations have vanished and instead a stable steady state is observed. The unstable signal for CO after 200 s is probably due to a mass spectrometer artefact.

Figure 6.7. (a) Response curves of the aged catalyst after reduction. (b) The difference between the IR spectrum before and after reduction. Both spectra were measured in helium.

A comparison of the catalyst before and after reduction by IR measurements is shown in figure 6.7b. The IR spectrum of the reduced catalyst has been subtracted from the one of the aged catalyst, both spectra being measured under helium flow at 493 K. The large intensity differences between the two spectra are rather unexpected since no probe molecule was present during the measurements. The strong 2121 cm$^{-1}$ band is due to CO on supported platinum oxide (Pt$^{2+}$) according to Barshad et al. (1985), Lindstrom and Tsotsis (1986) and numerous other authors. It is known that these species are formed under moderate conditions, i.e. low oxygen partial pressure and low temperature (Salmeron et al., 1981), are inactive and relatively stable. This is confirmed below and explains the presence of a CO surface species while CO is absent in the gas phase. At 2090 cm$^{-1}$ a small band is observed assigned to adsorbed CO on Pt which shares oxygen with another Pt atom. Linearly adsorbed CO on reduced (metallic) platinum is located around 2070 cm$^{-1}$ (Barshad et al., 1985). Both species were proven to be active in the reaction of CO to CO$_2$.

To investigate the apparent role of oxidised platinum, a fresh catalyst was oxidised at 493 K in air for half an hour. Since EUROPT-3 contains highly dispersed platinum ($d_{pt} = 1$ nm) and chlorine present on the support promotes the formation of electron deficient platinum (Zhuang...
and Frennet, 1996), oxidation is assumed to occur at these conditions. As will be shown by TGA, the catalyst consumes as many as 2 oxygen atoms per platinum within reasonably short time span. Subsequent to the oxidation cycle another step response experiment was performed, using the same reaction mixture as before. The response curves in figure 6.8a show that the initial maximum in CO is immediately followed by self-oscillations. Now, the oscillation period is approximately 3 s, well below the residence time of the cell.

![Figure 6.8. (a) Response curves of the oxidised catalyst. (b) The difference between the IR spectrum before the oxidation and after the oxidation followed by the step response experiment. Both spectra were measured in helium.](image)

A comparison of the catalyst surface by IR spectroscopy in helium before the oxidation and right after the experiment (figure 6.8b), shows that again mainly the $2121 \text{ cm}^{-1}$ species is present on the catalyst. It must be noted that the spectrum “before oxidation” was taken after 0.26% CO/He and subsequently pure helium had been introduced into the cell in order to supply the probe molecule CO.

The experimental results indicate that adsorbed CO on PtO (or the mere existence of PtO) can be of importance for the appearance of self-oscillations on EUROPT-3. At first sight it seems that the oxides can be formed in $O_2$ as well as in the used CO/$O_2$ mixtures. Since an aged catalyst shows oscillations, it is interesting to follow the ageing process, i.e. to follow the submission of the reaction mixture to the cell for several hours. Both the gas phase and the surface species were monitored in the following experiment. The time averaged results are presented in figure 6.9.

Initially neither the active species CO-Pt$^0$ nor CO-(Pt)$_n$O are observed in the IR spectrum. This is due to the high activity of the catalyst as reflected by near full conversion levels. Any adsorbed CO molecule reacts instantaneously with the oxygen present. Following an initiation period, observable by the inflection point in the CO-PtO curve, the platinum oxide band
increases steadily to its maximum value. In none of the experiments the CO-PtO band exceeded a plateau value (approximately 0.17 a.u. in figure 6.9). It is assumed that there is always enough CO present in the gas phase to act as probe molecule for PtO, except for the first 20 minutes when high conversions are obtained. Since the decomposition of the CO-PtO complex is very slow, the 2121 cm\(^{-1}\) band represents the amount of oxidised platinum (Barshad et al., 1985). With an increasing concentration of CO-PtO the conversion drops by a decrease in the number of active sites. The growth of the other species can be understood as follows. The reaction rate is proportional to the product of \(\theta_{CO}\) and \(\theta_{O}\). As \(O_2\) adsorbs dissociatively on the surface, a decrease in the number of sites will affect the \(\theta_{O}\) production rate more strongly than it does the CO adsorption rate. \(O_2\) adsorption declines which enables CO to adsorb and \(\theta_{CO}\) increases which is in agreement with figure 6.9. The net effect is that \(\theta_{O}\cdot \theta_{CO}\) is lowered. It must be noted that the increase of the peak heights of the two active species is greatly influenced by the growth of the 2121 cm\(^{-1}\) band. The IR spectrum in figure 6.9 illustrates this: the bands at 2090 and 2070 cm\(^{-1}\) are shoulders of the main peak and barely visible. However, the increase in time of these bands is significant.

![Figure 6.9](image_url)

**Figure 6.9.** Ageing of the fresh catalyst in 0.26%CO/5%O\(_2\)/He at 493 K monitored by FTIR. Peak heights are plotted in time. The IR spectrum on t=300 min is given as example.

In the 1100-1700 cm\(^{-1}\) region several bands are observed. Their assignment is rather ambiguous as is noted in Bijsterbosch (1993). The peak at 1460 cm\(^{-1}\) is likely due to "free" carbonates since it follows the \(CO_2\) peak closely. Other bands may be attributed to carboxylates and bidentate carbonates. The 1590 cm\(^{-1}\) band can be assigned to bidentate carbonates as an increase of CO-PtO is accompanied by an increase of this peak. The influence of the carbonate-like species on the reaction is difficult to assess. As the extinction
coefficient of carbonates is high, the concentration of carbonate species is probably small. Further, the carbonate peaks follow the CO$_2$ and PtO responses closely. Therefore no clear distinction can be made between the influence on the system of these components and the influence of carbonate species.

The PtO concentration was found to be crucial for the occurrence of self-oscillations. In all experiments conducted in this work the appearance of self-oscillations coincides with a absorbance for the CO-PtO higher than 0.11 (+/- 0.01) a.u., as shown in figure 6.9. This behaviour is independent of the history of the catalyst, i.e. both fresh catalysts, aged catalysts and oxidised catalysts show self-oscillations when the concentration of PtO which corresponds to this absorbance, is exceeded (using the same gas compositions). In figure 6.9 as of t=220 min self-oscillations are observed and they persist until the end of the experiment (t=425 min). In order to quantify the critical amount of oxidised platinum mentioned above, the IR absorbance was calibrated (see appendix). In this way the critical surface fraction of oxidised Pt was assessed to be 61%.

At various time scales in figure 6.9, after the occurrence of self-oscillations, the gas phase response of the catalyst was monitored. Figure 6.10 shows the development of CO and CO$_2$ in time at different degrees of oxidation of platinum calculated with the calibration procedure given in the appendix. Several common features of the self-oscillations observed on EUROPT-3 are clearly shown in this figure. First, at low $\theta_{ox}$ oscillations have a small amplitude and a low oscillation period. High CO$_2$ concentrations are obtained. With time progressing, a more severely oxidised catalyst produces oscillations with higher amplitudes, longer periods and low CO$_2$ production rates. Apparently, the concentration of PtO influence both the activity of the catalyst and the shape of the oscillations.

The data discussed give rise to a further investigation of the PtO species, observable as CO-PtO in IR spectra. In the following attention is focused on the kinetics of formation and decomposition of PtO.
Figure 6.10. Self-oscillations at various degrees of oxidation. \( t_0 \) denotes the starting point in figure 6.9.
Dynamics of the formation and reduction of platinum oxide

Formation of PtO was analysed through TGA. The response of a fresh catalyst upon a step change from helium to synthetic air is shown in figure 6.11.

Figure 6.11. Response upon a step change from helium to air at 493 K over a fresh catalyst in the thermobalance. Amount of oxygen atoms consumed per Pt is given versus time. The line denotes a simulation using $k_{ox} = 3.7 \times 10^{-3} \text{ s}^{-1}$, see equation 6.9.

Oxidation of Pt proceeds in two steps with different dynamic behaviour. Right after a step to air, a monolayer of oxygen adsorbs on the catalyst, at this point $\theta_0 = 1$. Oxygen cannot desorb from the surface (Engel and Ertl, 1979) and the platinum begins to oxidise. A rate expression for Pt oxidation was suggested by Sales et al. (1982), on the basis of the assumption that the rate of oxide formation is proportional both to the concentration of adsorbed oxygen and the fraction of sites which are not oxidised:

$$\frac{d \theta_{ox}}{dt} = k_{ox} \theta_0 (1 - \theta_{ox})$$  

6.9

Fitting of the TGA data to this equation, assuming that PtO has no effect on the adsorption of oxygen ($\theta_0 = 1$), results in a value for $k_{ox}$ of $3.7 \times 10^{-3} \text{ s}^{-1}$. Although the latter assumption seems disputable, other rate expressions in which the effect on the adsorption of O$_2$ is included, predict the behaviour less well. It is further assumed that the gas phase concentrations are constant, in view of the high concentrations and low oxidation kinetics. Figure 6.11 shows the simulation in which the estimated value of $k_{ox}$ is used. Later this parameter is used to simulate oscillations.
Another important property of the PtO is its stability under various conditions. The CO-PtO band does not weaken in helium at 493 K for at least 30 minutes, while the coverages of other CO containing species were reduced to almost zero within 5 minutes. Differences between the species are also noticed in an environment with CO. This becomes clear from the IR spectrum of an aged catalyst, which exhibits self-oscillatory behaviour, as is shown right after a step to helium (figure 6.12a). Again three bands can be distinguished. A step to 5% $^{13}$CO/He was imposed for 10 minutes after which in helium a second IR spectrum was taken (figure 6.12b). At this point at least 4 bands are obtained. A final spectrum in helium was taken 10 minutes after the admission (figure 6.12c).

\[ \sigma_{^{13}CO} = \sigma_{^{12}CO} \left( \frac{m_{r,^{13}CO}}{m_{r,^{12}CO}} \right)^{\frac{1}{2}} \]  

Figure 6.12. IR spectra of the aged catalyst (a) before 5% $^{13}$CO/He admission, (b) right after admission and (c) 10 minutes after admission. All spectra were recorded in helium at 493 K.

The $^{13}$CO stretch vibrations are located at a lower wavenumber than those of $^{12}$CO. The location of the new bands can be calculated from:

\[ \sigma_{^{13}CO} = \sigma_{^{12}CO} \left( \frac{m_{r,^{13}CO}}{m_{r,^{12}CO}} \right)^{\frac{1}{2}} \]  

in which $m_{r,CO}$ represents the reduced mass of CO. This yields the wavenumbers for $^{13}$CO on platinum presented in table 6.1.
Table 6.1. Wavenumbers of the stretch vibrations of $^{12}$CO and $^{13}$CO on Pt using equation 6.10.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavenumber $^{12}$CO / cm$^{-1}$</th>
<th>Wavenumber $^{13}$CO / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-PtO</td>
<td>2121</td>
<td>2073</td>
</tr>
<tr>
<td>CO-(Pt)$_n$O</td>
<td>2090</td>
<td>2044</td>
</tr>
<tr>
<td>CO-Pt$^0$</td>
<td>2065 (shifted due to oxidation)</td>
<td>2019</td>
</tr>
</tbody>
</table>

CO-PtO is the only unlabelled species which is still clearly present after the treatment with $^{13}$CO. The total amount of CO-PtO has been reduced by 50%. A large amount of the other carbonyls is observed which nearly all contain labelled CO. 10 minutes after the step change to helium (figure 6.12c) still the same amount of CO-PtO is present on the surface: approximately 50% is labelled. The concentrations of CO-(Pt)$_n$O and CO-Pt have declined considerably. In summary, the amount of CO-PtO has decreased by 50% by the reduction procedure (the 5% $^{13}$CO admission) but remains constant in helium. The other components show the opposite: in CO an increase is observed while in helium the CO desorbs readily from the surface. Additional information is derived from the labelled species. Exchange of $^{12}$CO with $^{13}$CO takes place to a much larger extent on CO-(Pt)$_n$O and CO-Pt compared to CO-PtO. This supports the hypothesis that only the former two are active species in CO oxidation on supported Pt, as CO-PtO is relatively stable under the present conditions.

To assess the kinetics of the reduction of PtO, a catalyst that did not exhibit self-oscillations, i.e. where the CO-PtO peak did not exceed the critical value of 0.11 a.u., was subjected to a step change from helium to 5%CO/He at 493 K. The development of the 2121 cm$^{-1}$ band was monitored in time (figure 6.13). The surface occupancy of $\theta_{ox}$ was calculated using the results of the calibration procedure given in the appendix. Once more, it is observed that the amount of PtO species reduces to approximately 50% within 10 minutes. Again a rate expression proposed by Sales et al. (1982) was applied to fit the experimental data:

$$\frac{d\theta_{ox}}{dt} = -k_{red} \theta_{CO} \theta_{ox}$$  \hspace{1cm} 6.11

It is assumed that on all reduced sites gas phase CO adsorbs instantaneously. This simplifies equation 6.11 as $\theta_{CO}$ can be substituted by $(1-\theta_{ox})$. The value of $k_{red}$ was inferred from this as $2.5 \times 10^{-3}$ s$^{-1}$.
Finally, when a catalyst containing CO-PtO is subjected to air at 493 K, no decrease of this species is observed. As becomes clear from figure 6.14, exposing a catalyst which contains both CO-Pt and CO-PtO (solid line) to air, results even in an increase of the CO-PtO after 15 minutes (dotted line).

![Figure 6.13](image1.png)  
**Figure 6.13.** Response curve of CO-PtO (represented by $\theta_{\text{ox}}$) after a step change from helium to 5% CO/He. The line denotes a simulation using equation 6.11 and $k_{\text{red}} = 2.5 \times 10^3$ s$^{-1}$.

![Figure 6.14](image2.png)  
**Figure 6.14.** IR spectra are shown of an aged catalyst before (solid line) and after (dotted line) submission to air for 15 minutes at 493 K. Both spectra were recorded in helium.

In summary, it was shown that self-oscillations on EUROPT-3 occur concurrently with the surpassing of a critical level of the surface concentration of PtO. PtO is observable in IR spectra by adsorption of the probe molecule CO. Oscillations disappear after reduction of the catalyst with CO or H$_2$ as a result of a reduced concentration of PtO. The coverage of the catalyst with this species grows in O$_2$ and in the used CO/O$_2$/He reaction mixture at 493 K. An oxidation of approximately 61% of the Pt leads to self-oscillations when the catalyst is submitted to the CO/O$_2$/He reaction mixture under the applied conditions. The amount of PtO governs the period and amplitude of the oscillations. Kinetic data for formation and reduction of PtO could be obtained. In comparison with the kinetics of the reaction steps in CO oxidation, the rate of Pt oxidation and reduction is comparatively slow. This is illustrated by comparing the fitted rate constants to the rate constants of the LH reaction steps (figure 6.1). In the next section it will be addressed whether the oxidation and subsequent reduction of Pt may serve as feedback mechanism vital to the occurrence of self-oscillations.
Critical assessment of existing models for self-oscillations

In order to establish which mechanism acts as a proper feedback, the CO oxidation reaction was simulated using equation 6.1-6.5. Again, the reaction scheme and kinetics as given in literature were used for the basic model. The absolute values of these kinetic constants are less relevant since the rate constants of the basic elementary steps are fast as compared to those of the feedback steps. As shown before, the kinetics of the feedback mechanism determine the period of the oscillations, which will be focused on in the simulations, whereas the kinetic constants of the basic model govern the location of the steady state branches. It is relevant to note under what conditions the basic model shows bistability. Using the parameters noted in the caption of figure 6.1, bistability becomes apparent at $\theta_{\text{ox}}=0.7$. This value is in fair agreement with experiment: $\theta_{\text{ox}} \approx 0.61$. Further, the development in the CO conversion at the two branches must be comparable with those found in experiments. $\theta_f$ in figure 6.1 reflects the CO$_2$ production in the simulation: a decrease is observed at higher degree of oxidation. From the time averaged conversion in figure 6.9 the same conclusion can be drawn. The above allows the use of kinetic constants taken from literature in the basic model during the feedback model evaluations.

The carbon model presented in the introduction is not considered in this section as CO dissociation is not likely to occur on Pt at the used experimental conditions. Another possibility closely related to the carbon model is blocking by carbonates. At high CO$_2$ concentrations carbonates are formed on the surface thereby hindering reaction. The system would in this case approach the CO inhibition regime where low CO$_2$ production rates are found. The amount of carbonates would decrease, rates would be enhanced and the cycle repeats. It is, however, not very likely that the formation and decomposition of carbonate-like species on the surface act as feedback mechanism, as experiments show that the carbonate peaks observed in IR follow either the CO-PtO or CO$_2$(g) responses closely. No phase shifts could be detected. This indicates that mechanisms involving PtO or CO$_2$ are also able to explain the observed carbonates. So, only the remaining three models presented in the introduction are taken into consideration.

Redox model

In view of the previous results, first the oxidation/reduction mechanism was analysed. The experimentally obtained kinetic constants of the feedback reactions are used in simulations to investigate whether self-oscillations can be predicted by the model.
The feedback mechanism as proposed by Sales et al. (1982) essentially consists of equation 6.9 and 6.11, yielding:

\[
\frac{d\theta_{\text{ox}}}{dt} = k_{\text{ox}} \theta_O (1-\theta_{\text{ox}}) - k_{\text{red}} \theta_{\text{CO}} \theta_{\text{ox}}
\]

Assuming steady state, i.e. \(d\theta_{\text{ox}}/dt = 0\), an equation for \(\theta_{\text{ox}}\) is obtained. At various "given" values for the platinum oxide coverage, \(\theta_{\text{CO}}\) and \(\theta_O\) were estimated using the basic LH mechanism. From equation 6.12 the platinum oxide occupancy was calculated using these steady state surface coverages and the kinetic parameters determined from TGA and IR experiments. When the given \(\theta_{\text{ox}}\) equals the \(\theta_{\text{ox}}\) calculated from equation 6.12, the system is in a stable steady state. Figure 6.15 shows that there is always a point of intersection between the line \(y=x\) (representing \(\theta_{\text{ox}}\)) and the calculated curves representing the steady states calculated with use of equation 6.12. A variation of +/- 20% in the value of the kinetic constants did not affect the result. Self-oscillations will never appear in a system with this feedback mechanism and parameters: in all cases a stable steady state is reached with \(\theta_{\text{ox}}\) being approximately equal to 0.8.

Figure 6.15. Steady state solutions calculated with equation 6.12 at various \(\theta_{\text{ox}}\). \(k_{\text{ox}}\) and \(k_{\text{red}}\) were varied within a range of 20%.

An increase in the value of the parameter \(k_{\text{ox}}\) by a factor of 20 results in the onset of self-oscillations. Figure 6.16 shows the partial pressures of CO and O\(_2\) in time. The simulation results with a 20-fold increase in \(k_{\text{ox}}\) do however not agree with experiments. First, the period of oscillation is at least two orders of magnitude larger than experimental value. Secondly, nearly harmonic oscillations were found experimentally, whereas in simulations (figure 6.16) clearly relaxation behaviour is seen. In conclusion: whereas in principle the
oxidation/reduction model is able to explain self-oscillations, the quantitative treatment casts serious doubt on the redox mechanism as the appropriate feedback step.

Figure 6.16. Simulation of self-oscillations using $k_{\text{on}}=3.2\cdot10^{10} \text{ Pa}^{-1} \text{ s}^{-1}$ and $k_{\text{red}}=3.6\cdot10^{11} \text{ Pa}^{-1} \text{ s}^{-1}$. Other parameters as in figure 6.1.

Questions arise also from the analysis of the dynamics of the surface phenomena, as observed in IR experiments giving the development of surface species during self-oscillations (figure 6.17). Oscillations of CO-PtO are barely visible and in phase with CO-(Pt)$_n$O, which clearly exhibits oscillatory behaviour. In part, the small CO-PtO oscillation may be due to the variation of the other species. The predicted phase shift of CO-PtO compared to CO$_2$ (see figure 6.15) is far smaller than the experimentally observed one of 180°. A further difference between simulations and experiments becomes apparent: from simulations $\theta_{\text{ox}}$ should vary between 0.7 and 0.8 (an amplitude of 7%), a value that is not in agreement with the experimentally found variation in the CO-PtO (figure 6.17).

Figure 6.17. Self-oscillations on EUROPT-3 monitored by FTIR and mass-spectrometry at 493 K.
In a final effort to falsify the oxidation/reduction model, an additional labelling experiment was conducted where a step was performed from 0.26%CO/5%\textsuperscript{16}O\textsubscript{2} to 0.26%CO/5%\textsuperscript{18}O\textsubscript{2} (both in helium) at 493 K. Before implementing this step, the system exhibited self-oscillations. Though within experimental error the concentrations before and after the step were equal, a decrease in the period and amplitude of the oscillations was observed upon implementing the step. This may be due to very small differences in composition between the mixtures or by differences in reactivity between isotopically labelled and unlabelled oxygen. Oscillations are known to be very sensitive to small perturbations in the system. In spite of that, still oscillations can be observed after the step to labelled oxygen (figure 6.18). Note that the \textsuperscript{16}O\textsuperscript{18}O concentration shows oscillations whereas the \textsuperscript{16}O\textsubscript{2} concentration is stable in time.

Assuming that during subsequent half-cycles platinum oxide is partly reduced and reoxidised, one would expect that the unlabelled CO\textsubscript{2} would also give rise to the occurrence of oscillations. Initially this is not observed. On the other hand, the CO\textsubscript{2} production due to reaction according to the basic elementary steps, displays self-oscillatory behaviour from the start. Once again this throws doubt on the oxidation/reduction feedback model.

![Figure 6.18. Response of a self-oscillating catalyst (0.26%CO/5%\textsuperscript{16}O\textsubscript{2}) a few oscillation-periods after a step change to 0.26%CO/5%\textsuperscript{18}O\textsubscript{2}.](image)

**Sorbate-sorbate interaction**

The second feedback model put forward in literature consists of assuming coverage dependent sorption and reaction constants. A strong dependency follows from inclusion of the following equations (Pikios and Luss, 1977).
\[ k_{\text{det,CO}} = k_1 \cdot \exp(\mu_1 \theta_{\text{CO}}) \]
\[ k_{\text{reaction}} = k_2 \cdot \exp(-\mu_2 \theta_{\text{CO}}) \]

Note that \( k_1 \) and \( k_2 \) equal the product of a pre-exponential factor and a term which includes the activation energy; \( \exp(-E_a/RT) \). Using these equations, either desorption of CO is facilitated with increasing CO coverage or the reaction between CO and O adsorbed on the surface becomes increasingly difficult at high CO coverages.

In the evaluation of these equations both \( k_1 \) and \( k_2 \) were varied within a broad range of values (between 1.0 and \( 1.0 \times 10^4 \) s\(^{-1}\)). To simulate the experimental results shown in figure 6.9, first \( \mu_2 \) was set to zero and \( \mu_1 \) was fitted. It values respectively from 80 to 20 depending on the value for \( k_1 \). As mentioned in the simulation section, in the investigation of this model the Jacobian matrix of the complete set of equations should be calculated within the applied window of parameters, followed by the trace and determinant. The determinant showed to be always positive and the trace was always negative. This indicates that the steady states are stable for parameters and conditions used. It is therefore unlikely that coverage dependent desorption constants provide the true mechanism underlying self-oscillations.

When solely equation 6.14 is used (\( \mu_1=0 \) \( \mu_2 \) must range from 30 to 91 to simulate the developments as they were found experimentally. For the complete window of kinetic parameters, three steady states were found. Two of them are stable (det>0 and trace<0) and one exhibits instable behaviour (det<0 and trace<0). This does not automatically imply that the system exhibits self-oscillations. Simulations with varying initial conditions showed consistently that one of the stable steady states was obtained. It is therefore concluded that under the applied conditions, coverage dependent reaction rate constants cannot be the mechanism underlying the observed oscillations either.

**Surface restructuring**

Finally, phase transitions as an appropriate feedback mechanism will be reviewed. A model generically describing surface restructuring is hard to develop, in particular for a supported catalyst. Various crystal planes are present and each may show a distinctly different behaviour. At critical values of \( \theta_{\text{CO}} \) the surface may change locally. Gas phase synchronisation may result in overall macroscopically changed behaviour. Since the amount and distribution of crystal planes that undergo restructuring are not estimated for this catalyst, the local critical
\(\theta_{CO}\) remains unknown. This hinders modelling efforts. Hence, only a qualitative treatment of this mechanism is given instead.

According to Gorodetskii (1997) part of the platinum present on the surface oxidises. Other particles may exhibit phase transitions at certain CO coverages. Assuming that all non-oxidised platinum species are active in CO oxidation, it is likely that oxidation of platinum brings the catalytic system in the range where multiplicity exists (regime II). Additionally, the phase change of other platinum crystallites is the force that drives the system from the upper to the lower branch. The time required for the phase transformation can be of the order of seconds (Lynch et al., 1986) so the period of oscillations can be expected to be close to the one found in this study.

The trends observed in figure 6.10 can be explained by this feedback mechanism. The higher amplitudes found for increasing \(\theta_{ox}\) can be explained when the two steady state branches at various \(\theta_{ox}\) are considered. As noted before, the number of free sites in figure 6.1 reflects the CO\(_2\) production rate. The distance (\(\Delta\theta_x\)) from one branch to the other increases with the amount of PtO (\(\theta_{ox}\)) and thus higher amplitudes are expected. The fact that the oscillation period increases may be due to the blocking by PtO formation. Locally, it will be more difficult to reach a critical surface coverage when more sites are oxidised. This is expressed by a longer residence in one steady state, a longer oscillation period.

**Suppression of self-oscillations by periodic operation**

In the above no univocal feedback mechanism is obtained. Still, conclusions can be drawn concerning the appearance of self-oscillations from which a periodic operation mode can be derived able to suppress the self-oscillations. PtO was shown to be the key factor with respect to the location of the system: single steady states at low, or multiple steady states at high extents of oxidation.

As shown before, suppression of the PtO species can be accomplished by imposing steps with gaseous CO. First a periodic operation experiment was conducted with subsequent cycles of 0.26%/5%O\(_2\) (the reaction mixture) and 0.26%CO fed to the IR reactor cell. For these concentrations, even with a cycle split of 0.5 no significant reduction of the self-oscillations was observed. Higher concentrations are required as becomes clear from figure 6.19a, showing the result with 5%CO as the reducing agent. A cycle split of 0.75 and a period of 60 s are used. At \(t=0\) the periodic operation is started and after 10 minutes the self-oscillations
have completely disappeared. In addition higher averaged production rates of CO$_2$ are obtained in the reaction mixture cycle, even when the overshoot due to the step change from the CO to the CO/O$_2$ mixture is not taken into account. This overshoot can be understood as follows. After the CO cycle all sites are covered by CO. A step to the reaction mixture introduces mainly a large amount of O$_2$ in the cell, which subsequently adsorbs at scarce free sites. CO$_2$ is produced and sites become available, allowing additional O$_2$ adsorption. The CO$_2$ production accelerates and peaks. At this point oxygen is the dominating species on the surface.

By way of comparison, the same experiment is conducted using helium instead of 5% CO. Figure 6.19b shows the response of the catalyst and, as expected, oscillations persist.

Figure 6.19. Response of an aged catalyst showing self-oscillations on periodic operation. At $t=0$ either (a) 0.26%CO/5%O$_2$/He$\leftrightarrow$5%CO/He or (b) 0.26%CO/5%O$_2$/He$\leftrightarrow$He is imposed.

Figure 6.20, giving the catalyst response measured by IR spectroscopy, clarifies the underlying mechanism of the suppression of self-oscillations. The spectra are recorded in the cycle invariant state, i.e. when the responses are the same every period. The periodically operated system in which 5% CO is used (figure 6.20), exhibits an increase of the CO-PtO in the reaction mixture cycle ($0<t<45$ s). In the second cycle ($45<t<60$ s) the concentration of this species is reduced to its initial value. The oxidation and subsequent forced reduction cycle give a net average PtO content below the critical level at which self-oscillations appear. Upon changing the gas phase compositions to 5%CO, CO-Pt and CO-(Pt$_n$O) instantaneously respond. This does not hold for the subsequent introduction of the reaction mixture ($0<t<6$ s), probably due to the relatively slow desorption kinetics of CO compared to the adsorption. Oscillations are absent; small perturbations are only observable at the end of the reaction mixture cycle.
The development in time of the concentrations of the surface species using helium in the second cycle are given in figure 6.21. A strongly different behaviour is observed compared to the previous experiment. First, all species oscillate in the reaction mixture cycle. It must be noted that the oscillating concentration of PtO may be due to the variations in the CO-Pt and CO-(Pt)$_n$O species as shown before. The average level of the CO-PtO is high as compared to that indicated in figure 6.20; the self-oscillatory behaviour is a consequence of this.

Other periodic operation modes are applicable. The period and cycle split can be varied over a wide range. However, the required time to stabilise the system increases with the imposed period length and cycle split.
CONCLUSIONS

In this study self-oscillations during CO oxidation on EUROPT-3 were studied in order to establish the mechanism for self-oscillations and to derive a mode of periodic operation able to suppress these instabilities. *In-situ* FTIR and simultaneous analysis of the gas phase by mass spectrometry, were used during steady state, step response, transient isotopic labelling and concentration programmed experiments. Conclusions are:

For low CO/O₂ ratio (at 493 K) the catalytic reaction shows regime I kinetic behaviour and the rate of reaction is high. Platinum is slowly oxidised under these conditions, thereby blocking active sites. At a certain point, approximately 61% of the originally present Pt has been oxidised, regime II is entered. In this regime the system exhibits multiplicity and self-oscillatory behaviour. Initially, low amplitude and small period oscillations are observed. With progressive oxidation of Pt, as evidenced by an increasing concentration of CO-PtO observable in IR, both the period and the amplitude increase. This continues until almost all Pt has been oxidised.

Multiplicity is a necessary but non-sufficient condition for the occurrence of self-oscillations. A proper feedback mechanism is another necessity. Although in a qualitative sense the oxidation and subsequent reduction of Pt is on itself a feasible driving force for the transition from one state to the other, the dynamics of this feedback mechanism appear at least two orders of magnitude too slow.

The oxidation of Pt leads the system through various kinetic regimes. In the multiplicity region the two steady state rate branches are diverging on an increasing amount of PtO. This explains why the amplitude of the oscillations increases over time. The existence of self-oscillations has been rationalised on the basis of phase transitions. PtO delays phase transitions of the Pt, which explains the longer periods at higher PtO concentrations.

The concentration of PtO species proves to be vital in the occurrence of self-oscillations and self-oscillations may effectively be prevented by keeping the concentration of this species below a critical level. This explains why concentration programming, using CO oxidation steps alternated by intermediate reduction steps in CO, is effective in avoiding the self-oscillatory regime: the concentration of PtO species can be kept below the critical level.
Notation

$E_a$  activation energy, J/mol

$k_i$ reaction rate constant of reaction $i$, see text

$k^0_i$ pre-exponential factor, s$^{-1}$

$m_{i, CO}$ reduced mass of CO, -

$N_{sites}$ number of active sites on the catalyst, mol

$P_i$ partial pressure of component $i$, Pa

$Q$ volumetric flow rate, m$^3$/s or ml/min

$R$ ideal gas constant, J/mol K

$T$ temperature, K

$t$ time, s

Greek Letters

$\theta_i$ surface coverage of component $i$, -

$\mu$ constant in equation 6.13 and equation 6.14, -

$\sigma$ wavenumber, cm$^{-1}$

$\tau$ residence time in the reactor, s

Subscripts

$\text{ads}$ denotes adsorption

$\text{des}$ denotes desorption

$f$ denotes free, empty sites

$\text{ox}$ denotes oxidation

$\text{red}$ denotes reduction

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CO oxidation on Pt/Al₂O₃: self-oscillations and forced oscillations


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APPENDIX

In obtain quantitative information from IR spectra concerning the amount of PtO on the surface of supported Pt, a calibration method was developed. 5%CO/He was submitted to a fresh, reduced catalyst and the IR spectrum was measured. Nearly all the sites are covered...
with CO under the used conditions as 0.26%CO/He gave approximately the same peak height for the CO-Pt° band. Had the catalyst exhibited empty sites at equilibrium, a higher CO concentration would have resulted in a higher CO coverage. Additionally, TGA data (not shown) indicate a Pt:CO ratio of 1:0.94 at 493 K when the catalyst is equilibrated in 2%CO/He. This also confirms a near complete coverage of Pt with CO at 5%CO/He. Next, a step to helium was imposed to purge the cell and the CO-Pt° band was monitored in time. Subsequently, O₂ was introduced and the produced CO₂, originating from the remaining adsorbed CO, was measured in time and correlated to the decrease in the CO-Pt° band. In this way the relation between the CO-Pt° peak height and the surface coverage is established. Finally the catalyst was oxidised and again CO was submitted. Now two bands were obtained: one at 2121 and another at 2070 cm⁻¹. Assuming that all Pt atoms coordinate one CO molecule, de-convaluation of these bands leads to the CO-PtO calibration as the amount of CO-Pt° can be calculated from the former procedure. In the manner sketched, the height of the CO-PtO peak could be calculated in case all the platinum is oxidised. This results in a maximum absorbance of 0.16. The plateau value found in the experiments was 0.17 (figure 6.9) and agrees well with this value. However, the residual activity of the catalyst at the moment that PtO approximates its plateau value is rather unexpected. Possibly, several assumptions in the calibration need to be refined. For instance, the height of a band is assumed to be linear dependent on the surface coverage. In principle the surface area should be taken which is too time consuming for measurements in transient experiments. Nevertheless, the conclusion can be drawn that almost all the platinum is oxidised at the end of the experiment depicted in figure 6.9. In view of the residual catalyst activity, it is assumed that the plateau value of 0.17 a.u. corresponds to θ_ox=0.95 rather than θ_ox=1.
The aim of the work presented in this thesis is both to get insight into the mechanism underlying the interesting phenomena observed under forced oscillations on a catalytic system and to demonstrate the use of forced oscillations in heterogeneous catalysis. Chapter 2-4 deal with the first item. By means of analysing the results of simulations using microkinetics of various catalytic reactions, the occurrence of resonance on a catalyst has been explained. Two practical applications of forced concentration oscillations have been shown in chapter 5-6, in which results of experimental work conducted on a simple catalytic reaction have been presented.

Time averaged behaviour which is substantially different from steady state behaviour can be obtained when reactant concentration oscillations or system temperature oscillations are imposed on a catalyst. When the time averaged rate vs. oscillation frequency is not a monotonically ascending or descending function going from low frequencies (quasi steady state) to high frequencies (relaxed steady state), we speak of resonance. It follows from chapter 2 that for a catalytic reaction in which first two components must adsorb molecularly on the catalyst before they subsequently react, resonance can be brought about when the sorption kinetics of the reactants are dissimilar. In case the concentration of one reactant is forced, the requirements for the occurrence of resonance are 1) the forced component should have faster sorption kinetics compared to the other component and 2) the catalytic surface should be almost completely occupied. Resonance is induced by the inability of the catalytic species of the non-forced reactant to follow the changes in the surface occupancy of the forced reactant. This leads to a temporarily invariant level of the surface occupancy of the non-forced component at a level which deviates from steady state occupancy levels. It has been demonstrated that a thorough analysis of the dependence of steady state occupancies of all components on the concentration of the forced reactant can fully explain this behaviour.

For reactions obeying molecular sorption mechanisms, reaction rate enhancement compared to the highest steady state rate has not been observed in case of concentration forcing of one component. In contrast, large rate enhancements have been obtained under imposed temperature oscillations. Resonance reaction rates of at least 7 times the highest steady state reaction rate have been found over a broad frequency range. Again, dissimilar dynamic behaviour with respect to sorption kinetics of the reactants is a prerequisite to the occurrence of resonance. In addition, for systems with low total surface occupancies the slowest
component should occupy more sites with increasing temperature. Catalytic systems with high total surface occupancies of the slowest reactant should meet the opposite condition: less occupancy with increasing temperature. These latter conditions follow from a remarkable property of heterogeneous catalytic reactions which are subjected to temperature oscillations: the surface occupancy under fast temperature cycles appears to approach the steady state occupancy at the highest temperature used in the cycling. This has been proven both analytically and numerically. Again, analysis of steady state behaviour seems to be crucial in the prediction of resonance.

Analysis of microkinetic models towards their response on oscillations, demands an extensive exploration to the interesting resonance region. Numerical integration of the ODE’s which describe the dynamics of a catalytic system is rather cumbersome. It requires a high computational effort by the successive integration steps that lead to convergence to the periodic steady state. Numerical integration does not easily allow interpretation with respect to dependence of the time averaged performance on forcing parameters, such as oscillation frequency and amplitude. In contrast, Carleman Linearisation (CL) provides analytical expressions for the dependent variables in the periodic steady state and therefore does not have the disadvantages as described before. The merits of CL have been emphasised in chapter 3. However, the use of CL is limited. The original system of ODE’s is not always well approached by CL. In chapter 3 easily checkable requirements have been formulated for the use of CL. A sufficient condition appears to be the accurate CL prediction of the steady states at the extremes of the oscillations. Tools have been handed in to check CL estimations that does not meet this condition. Improvements of the steady state predictions leading to a better estimation of the response under forced oscillations, can be accomplished by either increasing the order of linearisation or shifting the point of linearisation closer to the erroneously predicted steady state.

In chapter 4 the CL technique has been used in the analysis of various microkinetic models with regard to their behaviour during forced concentration programming. The role of rate multiplicity, spillover and Eley-Rideal kinetics has been addressed. It has been shown that exchange in the model of molecular adsorption of the forced component by dissociative adsorption, does not lead to stronger resonance phenomena on the surface of the catalyst when the surface reaction rates are low. In case the non-forced component shows dissociative adsorption, stronger resonance has been observed. Dissociative adsorption combined with high surface reaction rates may lead to complex behaviour and multiplicity under concentration programming. In that case a response on imposed concentration oscillations can only be understood when the phase planes of the surface occupancies are investigated.
Spillover on the catalyst influences the response towards concentration programming in such a manner that the relaxed steady state is shifted to much lower oscillation frequencies. This is favourable compared to systems without spillover when the relaxed steady state rate is higher than the quasi steady state rate, except for cases showing positive resonance. Resonance peaks are dampened by inclusion of spillover terms in the model.

In chapter 4 it has further been proven that under forced concentration oscillations reaction rates higher than the optimal steady state rate can be obtained using adsorption/desorption models, in contrast to results presented before by others. However, improvements are rather marginal when single component cycling is used. This is caused by the fact that the occurrence of resonance, a prerequisite to achieve rate enhancement, relies on competition between components for adsorption on the catalyst surface. This implies that that the surface must be almost fully occupied. To get radical changes on the surface, another prerequisite for rate enhancement, the system should be forced using oscillations within a concentration window that also contains the optimal steady state. In the optimal steady state the coverage of both components is almost 50% in case of fully occupied surfaces. This means that there is not much left for improvement under periodic operation.

Chapter 5 addresses the use of forced concentration oscillations in order to unravel the mechanism of a catalytic reaction; CO oxidation on oxidised Cu/Al₂O₃. For the reoxidation of the catalyst by oxygen after reduction by CO, a three step mechanism has been proposed. Reaction of oxygen with three types of species has been found. First, oxygen can react with Cu sites containing both CO and O which results in production of CO₂. The second step consists of oxidation of a site with adsorbed CO without the presence of in-plane oxygen. Subsequently, the newly formed species give CO₂ via the first step. Finally also sites are oxidised without production of CO₂. The use of forced oscillations in mechanistic studies has been proven to be a powerful tool by the inherent variation in time scales and the variation in initial conditions of the catalyst.

In addition it has been shown by isotopically labelling forced oscillation experiments that CO₂ can adsorb on partly reduced CuO/Al₂O₃ and may subsequently decompose towards CO and an oxidised Cu species. This has been verified by transient FTIR in which the carboxylate species originating from CO₂ adsorption could be monitored in time.

Self-oscillations during CO oxidation on EUROPT-3, a 0.3 wt% Pt/Al₂O₃ catalyst, has been studied in chapter 6 in order to establish the mechanism for self-oscillations and to derive a mode of periodic operation able to suppress these instabilities. Steady state and transient FTIR
experiments have been conducted aiming at the elucidation of the feedback mechanism underlying self-oscillations. Under the applied conditions a net oxidation of Pt, which is monitored by following CO-PtO using FTIR, leads the catalytic system into the region where multiplicity occurs. It has been proven that oxidation and subsequent reduction of Pt on itself can not be the driving force for the self-oscillations. Their dynamics are at least two orders of magnitudes too slow. The existence of self-oscillations has been rationalised on the basis of phase transitions. However, in the investigated system a change in the concentration of PtO species is vital in the occurrence of self-oscillations as it brings the system into (or out of) the multiplicity region. Self-oscillations may therefore be effectively prevented by keeping the concentration of this species below a critical level. It has been shown that forced oscillations using CO oxidation steps alternated by reduction steps in CO, is effective in avoiding the self-oscillatory region as the concentration of PtO species is kept low.

In conclusion, this thesis demonstrates that forced oscillations can be very valuable in heterogeneous catalysis, in particular for mechanistic studies and suppression of self-oscillations. Using forced concentration oscillations to achieve rate enhancement is less interesting as the improvements for the analysed models have been shown to be marginal. In case applicable in practice, forced temperature oscillations may offer large improvements compared to conventional steady state operation.
De doelstelling van het onderzoek, gepresenteerd in dit proefschrift, is zowel inzicht geven in het mechanisme van het interessante fenomeen “resonantie”, dat optreedt tijdens het opleggen van oscillaties op een katalysator, als het aantonen van het gebruik van opgelegde oscillaties in de heterogene katalyse. Hoofdstuk 2-4 behandelt het eerste item. Door middel van het analyseren van resultaten van simulaties met verschillende microkinetische modellen, wordt het verschijnsel resonantie verklaard. Twee praktische toepassingen van het opleggen van oscillaties op een katalytisch systeem worden getoond in hoofdstuk 5-6. Daarin worden de resultaten van experimenteel werk verricht aan een simpele katalytische reactie gepresenteerd.

Tijdsgemiddeld gedrag van een katalytische reactie onder concentratieoscillaties van een reactant of temperatuuroscillaties, kan zeer verschillend zijn ten opzichte van steady state gedrag. Wanneer de tijdsgemiddelde reactiesnelheid als functie van de oscillatiefrequentie geen monotoon stijgend of dalend verloop heeft gaande van lage frequenties (quasi steady state) naar hoge frequenties (relaxed steady state), spreken we van resonantie. Er volgt uit hoofdstuk 2 dat voor een katalytisch systeem, waarin twee componenten eerst moleculair moeten adsorberen voordat ze vervolgens reageren, resonantie optreedt wanneer de sorptie-kinetiek van beide componenten veel verschillen. Indien de concentratie van één reactant wordt gevarieerd, dan gelden de volgende voorwaarden voor het optreden van resonantie:

1) de geforceerde component moet de snelste sorptie-kinetiek vertonen
2) het oppervlak van de katalysator moet vrijwel geheel gevuld zijn.

Resonantie wordt geïnduceerd door het onvermogen van de oppervlakte deeltjes van de niet geforceerde component de veranderingen op het oppervlak, veroorzaakt door de geforceerde component, te volgen. De oppervlaktebezetting van de niet geforceerde component wordt hierdoor constant binnen een oscillatieperiode. Deze heeft een waarde die verschilt van de waarde onder steady state. Een grondige analyse van de steady state bezettingsgraden van alle componenten als functie van de concentratie van de geforceerde component kan dit gedrag volledig verklaren.

Wanneer één concentratie geoscilleerd wordt tijdens reacties, die moleculaire sorptiemechanismen volgen, is nooit een tijdsgemiddelde reactiesnelheid gevonden die hoger ligt dan de hoogste steady state reactiesnelheid. Dit in tegenstelling tot katalytische systemen waarbij de temperatuur geoscilleerd wordt. Resonantie reactiesnelheden van tenminste 7 keer de hoogste steady state snelheid zijn gevonden in een breed frequentiegebied. Ook hier geldt dat...
ongelijk dynamisch gedrag van de sorptie van de componenten een vereiste is voor het optreden van resonantie. Bovendien moet in systemen met een lage totale oppervlaktebezetting de traagste component meer plaatsen op de katalysator bezetten bij hogere temperaturen. Katalytische systemen met hoge oppervlaktebezettingen van de trage component vertonen alleen resonantie wanneer deze component het katalysatoroppervlak minder bezet bij hogere temperaturen. Al deze voorwaarden volgen uit een opmerkelijke eigenschap van heterogeen katalytische systemen die onderworpen zijn aan snelle temperatuuroscillaties: de oppervlaktebezetting tijdens oscillaties benadert de oppervlaktebezetting van de steady state bij de hoogste temperatuur die gebruikt wordt in de oscillaties. Dit is zowel analytisch als numeriek bewezen. Analyse van het steady state gedrag van de katalytische systemen blijkt opnieuw cruciaal te zijn voor de voorspelling van het optreden van resonantie.

Analyse van de respons van verschillende microkinetische modellen op oscillaties, vergt een uitgebreide zoektocht naar het interessante resonantiegebied. Numerieke integratie van differentiaalvergelijkingen, die de dynamiek van een katalytisch systeem beschrijven, duurt vaak lang door de trage convergentie naar de periodiek stabiele toestand. Verder is het niet eenvoudig om de afhankelijkheid van de tijdsgemiddelde output variabelen zoals reactiesnelheid en oppervlaktebezetting, te bepalen ten aanzien van de opgelegde input variabelen zoals oscillatiefrequentie en amplitude. In tegenstelling tot numerieke integratie biedt Carleman Linearisatie (CL) analytische uitdrukkingen voor de tijdsgemiddelde afhankelijke variabelen in de periodiek stabiele toestand. De voordelen van CL worden in hoofdstuk 3 behandeld. Echter, CL is niet ongelimiteerd te gebruiken. De originele differentiaalvergelijkingen worden niet altijd goed benaderd door CL. In hoofdstuk 3 worden makkelijk bruikbare voorwaarden aangereikt voor het gebruik van CL. Alle geforceerde systemen waarvoor de steady states op de uiterste waarden van de oscillaties goed voorspeld kunnen worden met CL, kunnen in ieder geval goed benaderd worden met behulp van CL. Vervolgens worden methodes gepresenteerd om simulaties die uitgevoerd zijn met CL te controleren wanneer niet aan deze voorwaarde wordt voldaan. Verbetering van de steady state voorspellingen, die vervolgens leiden tot een betere voorspelling van de respons op geforceerde oscillaties, kan bereikt worden op twee manieren. Ten eerste kan de linearisatieorde verhoogd worden. Dit blijkt vaak niet zo effectief. Verder kan het linearisatiepunt verschoven worden naar de steady state die het minst nauwkeurig voorspeld wordt. Dit is vaak een zeer effectieve manier is om de resultaten van CL te verbeteren.

In hoofdstuk 4 is de CL techniek gebruikt om verschillende microkinetische modellen te analyseren ten aanzien van het gedrag onder concentratieoscillaties. De invloed van
reactiesnelheid-multipliciteit, spillover en Eley-Rideal kinetiek op dit gedrag is onderzocht. Er is aangetoond dat wanneer moleculaire adsorptie van de geforceerde component wordt vervangen door dissociatieve adsorptie, dit niet leidt tot sterkere resonantie op het oppervlak van de katalysator mits de reactiesnelheden op het oppervlak laag zijn. Als de niet-geforceerde component dissociatieve adsorptie vertoont, wordt sterkere resonantie gevonden. Dissociatieve adsorptie gecombineerd met hoge oppervlakterreactiesnelheden kan leiden tot complex gedrag tijdens concentratieprogrammering, zoals multipliciteit. In dat geval kan een respons op oscilaties slechts verklaard worden wanneer het verloop van de variabelen naar de periodiek stabiele toestand wordt bekeken met behulp van zogenaamde “phase-planes”. Spillover van actieve naar inactieve plaatsen op een katalysator beïnvloedt de respons op concentratie-oscilaties op een dusdanige manier, dat de relaxed steady state wordt verschoven naar lagere frequenties. Dit kan gunstig zijn wanneer de reactiesnelheid in de relaxed steady state hoger is dan de reactiesnelheid in de quasi steady state. Echter, resonantie wordt altijd gedempt door spillover wanneer modellen met en zonder spillover vergeleken worden. Dezelfde effecten zijn ook gevonden wanneer spillover termen in een Eley-Rideal mechanisme worden meegenomen.

Verder is in hoofdstuk 4 bewezen dat het mogelijk is om met behulp van concentratie-oscilaties voor adsorptie/desorptie modellen snelheidsverhoging ten opzichte van de hoogste steady state reactiesnelheid te voorspellen. Dit in tegenstelling tot wat eerder door andere onderzoekers beweerd wordt. Deze verbeteringen zijn echter marginaal wanneer één component gevarieerd wordt. Dit wordt veroorzaakt door het feit dat resonantie pas optreedt wanneer er competitie heerst tussen de componenten voor adsorptieplaatsen op het oppervlak (resonantie is noodzakelijk voor het verkrijgen van snelheidsverhoging). Dit impliceert dat het oppervlak vrijwel volledig gevuld moet zijn. Een andere vereiste voor snelheidsverhoging is dat er radicale veranderingen op het oppervlak dienen plaats te vinden tijdens de oscillaties. Dit betekent dat het katalytisch systeem onderworpen moet worden aan oscillaties tussen grenzen waarbinnen ook de optimale steady state zich bevindt. In de optimale steady state zullen beide componenten ieder bijna 50% van het oppervlak bezetten wanneer tevens aan de eis van het vrijwel volledig bezette oppervlak is voldaan. Er is dus weinig ruimte voor verbetering overgebleven voor de uitvoering van een reactie met concentratieoscilaties ten opzichte van de uitvoering in de optimale steady state situatie.

Hoofdstuk 5 toont het gebruik van concentratieoscilaties om het mechanisme van een katalytische reactie te vinden; in dit geval CO oxidatie op een geoxideerde Cu/Al2O3 katalysator. Voor de her-oxidatie van de katalysator met zuurstof na een reductie met CO is een driestapsmechanisme voorgesteld. Zuurstof kan reageren met drie typen katalysator-
deeltjes. Ten eerste reageert zuurstof met Cu-deeltjes waarop zowel CO als O geadsorbeerd zijn. Dit resulteert in productie van CO₂ en een geoxideerd Cu-deeltje. De tweede stap bestaat uit de oxidatie van een deeltje met CO zonder de aanwezigheid van zogenaamde “in-plane” zuurstof. Vervolgens kan dit geoxideerde deeltje verder reageren middels de eerste stap en produceert ook CO₂. Tot slot oxideren er ook Cu deeltjes zonder CO₂ productie. Het werk beschreven in dit hoofdstuk toont dat opgelegde oscillaties erg waardevol zijn in onderzoek naar het mechanisme van een reactie, door de variatie van tijdschalen en initiële katalysatorcondities in experimenten bij verschillende oscillatiefrequenties.

Tevens is er aangetoond, met behulp van opgelegde oscillatie experimenten waarin gebruik is gemaakt van labelling met isotopen, dat CO₂ kan adsorberen op gedeeltelijk gereduceerd CuO. Het gevormde oppervlakte deeltje kan vervolgens uiteenvallen in CO en een geoxideerd Cu deeltje. Dit is geverifieerd met FTIR waarmee de carboxylaat groep die gevormd wordt door adsorptie van CO₂ op het oppervlak, gevolgd kan worden in de tijd.

Zelf-oscillaties die ontstaan tijdens CO oxidatie op EUROPT-3, een 0.3% Pt/Al₂O₃ katalysator, zijn bestudeerd in hoofdstuk 6, met als doel het mechanisme van zelf-oscillaties op te helderen en een manier van periodieke uitvoering af te leiden welke in staat is deze zelf-oscillaties te onderdrukken. Hiervoor zijn steady state en transient FTIR experimenten uitgevoerd. Onder de toegepaste condities leidt een netto oxidatie van Pt, die gevolgd kan worden met FTIR door naar CO-PtO te kijken, het katalytische systeem naar het gebied waarin multipliciteit optreedt. Er is bewezen dat op zich oxidatie en reductie van Pt niet de drijvende kracht achter zelf-oscillaties kunnen zijn. De kinetiek van deze processen zijn zeker twee grootteordes te traag. De zelf-oscillaties kunnen verklaard worden door aan te nemen dat er fase veranderingen op het katalytisch oppervlak plaatsvinden. Echter, de verandering van de concentratie van PtO deeltjes is van groot belang voor het optreden van zelf-oscillaties aangezien de groei van deze concentratie het systeem in het multipliciteitsgebied brengt. Zelf-oscillaties kunnen daarom effectief vermeden worden door de PtO concentratie beneden een kritisch niveau te houden. Opgelegde oscillaties waarin gebruik wordt gemaakt van CO-oxidatie-stappen gecombineerd met reductiestappen waarin alleen CO gevoed wordt, zorgen ervoor dat het self-oscillatiegebied niet betreden wordt. Met FTIR kan duidelijk aangetoond worden dat de PtO concentratie beneden het kritisch niveau blijft.

Dit proefschrift laat zien dat opgelegde oscillaties waardevol kunnen zijn in de heterogene katalyse, in het bijzonder voor mechanistische studies en om zelf-oscillaties te kunnen onderdrukken. Het gebruik van opgelegde reactant concentratieoscillaties met als doel het verhogen van de reactiesnelheid is minder interessant; de verbeteringen zijn marginaal
gebleken in de geanalyseerde modellen. Wanneer temperatuuroscillaties praktisch uitvoerbaar worden, bieden ze grote mogelijkheden tot verhoging van de reactiesnelheden ten opzichte van conventionele steady state processen.
Tevens is er aangegeven, met behulp van opgeloste oxi-molare experimenten waarin geïsoleerd is gemerkt van laagte met isotopen, dat CO₂ kan schieten op gecentreerde gecentraliseerd CuO. Het gewenste oppervlakzeekstijve kan vervolgens worden gevormd van CO₂ en een gecentraliseerd Cu-drietje. Dit is gecontroleerd met FTIR- waarin de carbonylaat oetje die gevormd wordt door adsorptie van CO₂ op het oppervlak, gevolgd kan worden in de tijd.

Zelf-oscillaties die ontstaan tijdens CO-oxidatie op EUROPESO en 0.06% Pt/Al₂O₃ katalysatoren zijn beschreven in hoofdstuk 6, met als doel het mechanisme van zelf-oscillaties op te helderen en een inzicht in de periodieke uitvoering af te leiden. Welke is tevens als de zelf-oscillaties te onderzoeken. Hierdoor zijn aanvaard en immers FTIR experimenten uitgevoerd. Ondanks de onduidelijke resultaten leidt een positieve oxidatie van Pt die gevonden kan worden met FTIR door een CO-Pt te kopen. Het katalytische systeem naar de gebied van CO-Pt productie. Hiermee beweken dat de oxidatie en dehydrogenatie van Pt niet de selectiviteit beïnvloedt. De selectiviteit kunnen zijn verloren gaan. De reactie van deze processen zijn veel groter en vooral de selectiviteit is alleen uitstekend verlaagd door de FTIR-gegevens. De selectiviteit van CO-oxidatie kan worden gemeten met FTIR. Hiervoor word de reactie in de naad van de CO-Pt reactie geïsoleerd. Dit geeft een voldoende selectiviteit van CO-Pt en de selectiviteit van CO-oxidatie kan worden gemeten met FTIR. Hiervoor worden de selectiviteiten van de CO-oxidatie en de CO-Pt reactie geïsoleerd.
DANKWOORD

Het verloop van mijn AIO-tijd kende net als de in dit proefschrift beschreven oscillaties pieken en dalen. En net als bij menig katalytische reactie, resulteerde dit gelukkig in een *positieve resonantie*. De opbrengst was een interessante en leerzame tijd aan de UvA en uiteindelijk de totstandkoming van dit proefschrift. Iedereen die ik op deze plaats bedank heeft vooral bijgedragen aan de pieken; de dalen ben ik al bijna vergeten....

Alfred, jouw begeleiding en ondersteuning gedurende de 4 jaar op de UvA, maar ook daarna, waren zeer waardevol voor mij. In het begin van mijn onderzoek, toen “het nog niet liep”, kon een kort overleg met jou me weer opmonteren. Verder heb ik je enorme flexibiliteit erg weten te waarderen: lezingen oefenen op zondag, artikels bespreken bij je thuis, de laatste hoofdstukken van het proefschrift via e-mail in het weekend afhandelen (ik heb geen Word97!!); vrijwel alles was mogelijk.

De begeleiding op de werkvloer werd vooral verzorgd door Bart. Een paar maanden nadat ik als AIO was begonnen, zei je: “laten we eens een opstelling voor je bouwen!” Toen kwam je niet meer van me af. Problemen oplossen met de mass-spec, gascilinders verwisselen, IR-en, flowcontrolers temmen, opstellingen verbouwen, kortom al die zaken waar ik niet echt handig in was (ben), nam je al hoofdschuddend van me over. Daarnaast was je ook altijd te vinden voor een ontspannend schaatstochtje en een partijtje tennis of volleybal.

De dagelijkse beslommeringen werden gedeeld met kamergenoot Danny. Zowel UvA gerelateerde onderwerpen als zaken van ver voorbij Diemen werden gesproken in B6.45. Weddenschappen werden gesloten over de meest uiteenlopende onderwerpen, van *of AIO X wel of niet de deadline van zijn/haar proefschrift zou halen tot de werking van de Chipknip*. De discussies gingen via e-mail gelukkig gewoon door toen jij het IJ en ik de Westerschelde overstak.

Sjoerd had altij een luisterend oor voor mijn “sterke” verhalen en was vier jaar lang een te sterke tegenstander op de tennisbaan. Evelien was haar tijd ver vooruit door als eerste een AIO-avondje te organiseren. Dit zou een voorloper zijn van de bekende AIO-weekends.
Tijdens de lunch was er even tijd om te klagen als het weer eens tegenzat. Twee collega’s van andere vakgroepen moesten mijn experimentele blunders steeds aanhoren. Desondanks bleven Remco en Monique trouwe lunchgenoten. Adriaan en David hebben als hoofdvakstudenten veel bijgedragen aan dit proefschrift. Alle complexe vergelijkingen uit dit boekje komen bij jullie vandaan; voor fouten in deze vergelijkingen verwijs ik dan ook graag naar jullie ;-) Jullie hebben, na het prima voorwerk van Herman, gezorgd voor de revival van de wiskundige Carleman. Helaas liep het iedere student warm voor oscillaties. Marcel koos na een maand of drie voor de IT en Peter verlangde ernaar een hotel te beginnen in Frankrijk. Misschien tegen jullie verwachting in, is jullie werk toch deels verwerkt in dit proefschrift. Natuurlijk vergeet ik Nicole niet. Je hielp me er steeds aan herinneren dat ik niet zo moest stressen. “Nur die Ruhe kann es bringen und nur die Verrückten haben es eilig” klonk het vaak door de gang nadat ik mijn koffie naar jouw oordeel te snel had ingeschonken en weer wegholde.

Aan Theo en (coach) Co heb ik hoofdstuk 5 en 6 te danken. Hun lumineuze idee om een soort koppakking-silicone kit te gebruiken voor de afdichting van De Cel, bracht de oplossing voor de immer frustrerende lekkages. Verdere ondersteuning werd verzorgd door Marjo (als zelfs Bart het even niet meer wist), Guido, Paul, Hans (ik heb gelukkig de tijden zonder werkbriefjes nog meegemaakt), Daan, Wietze, Fred, Joop, Renate en Maureen. Ook de andere sfeerbepalende collega’s wil ik zeker niet vergeten: Laura, Francis, Frank, Jowi, Amedeo, Johan, Marcel O., Marcel W., Ioa, Ioana, Remko, Monique, Bron, Marijke, Sander W., Eduard, Huub, Peter H., Alexander, Peter, Paul, Han, Adriaan T., Henk, David, Sander G., Berend en Koen.

Alle bovengenoemde collega’s bedank ik voor de gezellige en boeiende jaren op de UvA!

Van het thuisfront bedank ik mijn ouders, broertje en zusje voor hun gepaste belangstelling in mijn werk (jullie begrepen dat ik niet iedere week aan mijn proefschrift herinnerd wilde worden!). De ouders van Luus dank ik voor hun praktische hulp de afgelopen tijd.

Lieve Luus, jouw doorzettingsvermogen is voor mij een voorbeeld geweest de laatste jaren. Zonder jouw steun en strengheid was dit boekje nu nog niet afgerond. Bedankt! (ook voor de hulp bij de layout van dit boekje). Ik hoop dat we samen betere tijden tegemoet gaan! 
forced (först, först). adj. 1. enforced or compulsory: forced labor. 2. strained, unnatural, or affected: a forced smile. 3. subjected to force. 4. emergency: a forced landing of an airplane. [FORCE + -ED] —forc' ed-ly

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oscillation (osˈəlāˈshən), n. 1. the act or fact of oscillating. 2. a single swing or movement in one direction of an oscillating body. 3. fluctuation between beliefs, opinions, conditions, etc. 4. Physics. a. an effect expressible as a quantity that repeatedly and regularly fluctuates above and below some mean value, as the pressure of a sound wave or the voltage of an alternating current. b. a single fluctuation between maximum and minimum values in such an effect. 5. Math. a. the difference between the least upper bound and the greatest lower bound of the functional values of a function in a given interval. b. Also called saltus. the limit of the oscillation in an interval containing a given point as the length of the interval approaches zero. [<_L oscillatio- (s. of oscillatio) a swinging, equiv. to oscillat(us) swung (see OSCILLATE) + -ion- -ION]

heterogeneous (həˈterəjənəs), adj. 1. different in kind; unlike; incongruous. 2. composed of parts of different kinds; having widely dissimilar elements or constituents; not homogeneous: The party was attended by a heterogeneous group of artists, businessmen, and social climbers. [<_ML heterogeneus]. See HETERO-,

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