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MODELLING THE TRANSIENT KINETICS OF HETEROGENEOUS CATALYSTS. CO-OXIDATION OVER SUPPORTED Cr AND Cu

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Abstract—This article illustrates the capabilities of the step response method in the determination of the mechanism and kinetics of a heterogeneously catalyzed reaction. The step response method was applied to investigate the CO oxidation over alumina-supported chromium and copper. Detailed mechanisms of this reaction were determined by measuring the isothermal reduction and oxidation of the catalysts via switching the gas-phase composition from inert (He) to either reducing (CO) or oxidizing (O₂) conditions. Modelling the obtained response curves has given information on the reaction rate constants of the elementary steps in the CO oxidation over the Cr and Cu catalyst. Here, only a minimum number of reaction steps and parameters have been used, but they are still physically acceptable. The reduction of the Cr catalyst was found to proceed via reaction of adsorbed CO. The activation energy of this process is 95 kJ mol⁻¹. The dispersion of the Cr catalyst is 20%, whereas only half the metal atoms at the catalyst surface participate in the oxidation and reduction. The latter metal atoms are coordinated to about four removable oxygen atoms. Reduction of the Cu catalyst takes place in three steps: first oxygen on the surface is removed via reaction of CO from the gas phase. Next the oxygen in the surface is removed via reaction of adsorbed CO, and finally the oxygen from the bulk of the catalyst that has diffused to the surface is removed. The activation energy of all three processes has been determined. The dispersion of the Cu catalyst was found to be about 22%.

INTRODUCTION

In heterogeneous catalysis much effort is put into establishing the reaction mechanism and reaction kinetics. This information is very important not only from a fundamental but also from a practical point of view, as knowledge on the catalytic reaction is essential for finding effective catalysts and optimal application conditions. Mostly, steady-state kinetic experiments are used for testing the catalyst performance, whereas spectroscopic techniques are used for observation of the surface and identification of adsorbed species. Unfortunately the steady-state kinetic studies provide only limited mechanistic information and essentially no information on the dynamic behavior of the catalyst. Furthermore, steady-state studies often do not give the parameter values of the individual elementary steps, since the determined reaction rate constants represent lumped parameters. Finally, the spectroscopic studies often do not provide much information on the catalyst under practical reaction conditions and do not indicate which intermediates are important during reaction. However, transient techniques are

complementary to the steady-state reactor experiments and the spectroscopic studies, so leading to a complete picture of the reaction system.

In transient techniques a perturbation is introduced to a system by changing one or more of the state variables pressure, temperature or concentration, either in the form of a step, pulse or wave. Subsequently, the response of the system to this perturbation is measured and analyzed. The transient response method using concentration changes is especially useful for studying heterogeneously catalyzed reactions. The simplest way of changing the concentration is in the form of a step. The basis of this so-called step response technique as applied to heterogeneous catalysis was originally laid down by Tamaru (1964) and reviewed by Kobayashi and Kobayashi (1974), Bennett (1976) and Biloen (1983) and more recently by Mirodatos (1991) and Tamaru (1991). The present study aims to illustrate the capability of the step response method in the determination of the reaction mechanism and reaction kinetics of the CO oxidation over an alumina-supported Cr and Cu catalyst.

Previous research has shown that a Cu–Cr catalyst has a relatively high activity for the conversion of CO and NO (Kapteijn *et al.*, 1993). Accordingly, this catalyst might be an alternative

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for the commercially used exhaust gas catalysts, which are based on the scarce and expensive noble metals Pt and Rh. Knowledge of the mechanism and kinetics of the occurring reactions is essential to predict the performance of the Cu–Cr catalyst under realistic reaction conditions. As the exhaust gas composition typically changes between oxidizing and reducing, especially information on the behavior of the catalysts under dynamic conditions is necessary. First, the Cr and Cu catalyst were investigated separately and the results are used to illustrate the capabilities of the step response technique.

EXPERIMENTAL

Gases and catalyst

All gases were of HP or UHP grade (UCAR) and were purified (O_2 and/or H_2O removal) before use. The gas mixtures were prepared in a separate gas mixing system and stored in lecture bottles.

The CO oxidation was investigated over a 10 wt% CuO/Al_2O_3 ($d_p = 0.105$ – 0.140 mm) and a 10 wt% Cr_2O_3/Al_2O_3 ($d_p = 0.15$ – 0.25 mm) catalyst. In the experiments 50 mg of the Cu and the Cr catalyst was used. A complete description of the catalyst preparation is given elsewhere (Bijsterbosch *et al.*, 1992).

Apparatus

The apparatus in which the step response experiments were performed basically consisted of a gas feed section, a reactor section and a gas analysis section. Feed gas switching was carried out using a pneumatically operated four-way valve. In order to minimize pressure disturbances, the pressure in the flow lines was continuously monitored with a differential transducer and equalized/controlled by back-pressure controllers. The catalyst was placed in a quartz reactor retained in a temperature-controlled oven. Isothermal operation was assured by the presence of an aluminum cylinder around the reactor. For the same reason the catalysts were diluted with SiC (volume ratio catalyst:SiC = 1:1.1, $d_p = 0.2$ – 0.5 mm). A small part of the product gas was separated via a capillary for analysis in the quadrupole mass spectrometer (Balzers, QMG 240). Signal analysis, mass selection, sample rate, data collection and data storage were controlled by a personal computer equipped with a Balzers software program. The raw data were corrected for background levels, fragmentation contributions (CO_2 to CO) and mass spectrometer sensitivity for the different molecules. Finally, the corrected data were represented as the molar fraction in the product gas mixture. A detailed description of the step response equipment can be found elsewhere (Dekker *et al.*, 1993, 1994).

Procedures

All experiments were performed at atmospheric pressure with a flow rate of 30 ml min^{-1} (STP).

First, the samples were subjected to an *in situ* pretreatment in which the temperature was raised to 773 K (5 K min^{-1}) in an oxygen flow. The catalysts were kept at 773 K for 1 h and subsequently cooled to reaction temperature under the oxygen flow. This pretreatment resulted in the so-called fully oxidized catalysts. Next, the fully oxidized catalysts were subjected to the steps given in Fig. 1 at reaction temperature. Here, the inert gas (He) and the reducing and oxidizing mixture were passed over the catalysts for 240 s. The fully oxidized Cr catalyst was subjected to the step sequence in the temperature range 533–613 K. The fully oxidized Cu catalyst is much more easily reduced than the Cr catalyst, and therefore the Cu catalyst was subjected to the step sequence at lower temperatures, 413–553 K. The experiments were found to be reproducible.

For a correct interpretation, the response curves were compared with a gas-phase step change performed over SiC and Al_2O_3 at the same experimental conditions. These step changes have shown that no CO and O_2 and hardly any CO_2 desorbs from SiC/ Al_2O_3 . The amount of CO_2 formed in a step was calculated by measuring the area under the CO_2 production curve and converting it to moles. The total amount of $CO + CO_2$ (ΣCO_x) adsorbing at the catalyst in either step (i) or (iii) was calculated by subtracting the amount of CO and CO_2 measured in the outlet from the amount of CO fed. The amount of O_2 adsorbing at the catalyst in steps (ii) and (iv) was calculated in a similar way. The error in the determination of the amounts adsorbed or desorbed is estimated to be about 15% at most.

MATHEMATICAL MODELLING

The reaction rate constants of the elementary steps in the CO oxidation over the Cr and Cu catalyst were determined by fitting the gas-phase composition measured at the exit of the reactor on several rate equations by nonlinear regression. For the Cr catalyst the objective function that was minimized was the sum of squares of the residual CO and CO_2 gas-phase fraction, that is the difference between the observed and calculated value:

$$OF_{Cr} = \sum_{i=1}^n (y_{CO_2}^{obs} - y_{CO_2}^{cal})^2 + \sum_{i=1}^n (y_{CO}^{obs} - y_{CO}^{cal})^2 \quad (1)$$

Since the CO and CO_2 responses were complementary for the Cu catalyst, in this case the objective function to be minimized contained only the sum of squares of the residual CO_2 fraction:

$$OF_{Cu} = \sum_{i=1}^n (y_{CO_2}^{obs} - y_{CO_2}^{cal})^2 \quad (2)$$

The minimization was achieved by optimization of the rate parameters according to Simplex and Levenberg–Marquardt methods.

Fig. 1. Steps (i)–(iv) performed over the fully oxidized Cr and Cu catalyst.

The fractions CO and CO₂ at the exit of the reactor were calculated via numerical integration of the set of coupled partial differential equations describing the gas-phase composition and surface coverage as a function of time and place in the catalyst bed. The basic conservation equations of the gaseous and surface species in the catalyst bed (i.e. from $z = 0$ to $z = L$) are

$$\frac{\partial c_j}{\partial t} = -v \frac{\partial c_j}{\partial z} + r_j \frac{1 - \epsilon_b}{\epsilon_b} \quad (3)$$

$$\frac{\partial c_{k\Box}}{\partial t} = r_{k\Box} \quad (4)$$

where $L = 0.01$ m, $v = 0.064$ m s⁻¹, $\epsilon_b = 0.4$.

The concentration of a component j in the gas phase c_j is converted to the molar fraction in the gas phase x_j via the ideal gas law. The concentration of a component k adsorbed on the catalyst $c_{k\Box}$ is converted to the fractional coverage $\theta_{k\Box}$ via the total concentration of active sites. The computer software package PDECOL (Madsen and Sincovec, 1979) was used to solve the resulting set of coupled nonlinear partial differential equations.

The axial dispersion over the catalyst bed was excluded from the model, since the CO response after a step change from He to 5% CO/He over an empty reactor was identical to that over a reactor filled with Al₂O₃. However, this so-called blank run did not give an ideal CO step response. Therefore the axial dispersion over the tubing between the switching valve and the catalyst bed has to be taken

into account. This was accomplished by using a polynomial function in time describing the blank run, $f(t)$, as the input function.

Since the values of the catalyst bed length L and the flow rate v are not known with full certainty, the influence of a change in the value of L and v on the calculated parameter values in the kinetic model was also investigated. It was found that a change in L or v only had a minor influence on the parameter values.

RESULTS AND DISCUSSION

Cr/Al₂O₃

Reduction and oxidation of fully oxidized Cr/Al₂O₃

Figure 2 gives the CO, CO₂ and ΣCO_x (CO + CO₂) responses after a step change from He to 5% CO/He over the fully oxidized chromium catalyst at 533 K and 573 K (step i). The figure shows that the reduction proceeds in one step in which the amount of CO₂ produced increases, reaches a maximum, and subsequently slowly decreases in time. The CO response displays the opposite behaviour. The ΣCO_x response indicates that CO is retained at the catalyst. The CO retention does not start instantaneously but only when the reduction of the catalyst has been progressed to some extent. The shape of the response curves can be explained by reaction of adsorbed CO to CO₂. Since initially only a small amount of sites are available for CO adsorption, only a small amount of CO₂ can be formed. More sites for CO adsorption are generated when CO reacts to CO₂, resulting in an

Fig. 2. Response curves of CO_2 , CO and ΣCO_x after a step change from He to 5% CO/He over fully oxidized $\text{Cr}/\text{Al}_2\text{O}_3$, step (i), at 533 K and 573 K.

Table 1. The amount of CO_2 produced, CO retained and O consumed in steps (i)–(iv) over $\text{Cr}/\text{Al}_2\text{O}_3$ at several temperatures, expressed in mol per mol Cr in the catalyst

T_r (K)	Step (i)		Steps (ii) and (iv)		Step (iii)	
	CO_2 prod.	CO ret.	O cons.	CO_2 prod.	CO_2 prod.	CO ret.
533	0.30	0.16	0.25	0.06	0.27	0.06
553	0.42	0.17	0.37	0.09	0.31	0.09
573	0.44	0.18	0.40	0.11	0.32	0.11
593	0.44	0.18	0.46	0.11	0.35	0.10
613	0.44	0.19	0.46	0.11	0.36	0.12

increase of the reaction rate until no removable oxygen is available anymore. The maximum in the CO_2 and the minimum in the CO response shift to shorter times and become more pronounced at increasing temperatures. This is caused by an increase in the surface reaction rate. However, the total amount of CO_2 produced and CO retained are independent of the temperature (Table 1). At 533 K these amounts are somewhat less, as the reaction rate is too low at this temperature to reach complete reduction of the catalyst within 240 s (Fig. 2). After 240 s the gas phase is switched back to He. Here, the CO and CO_2 responses are identical to those measured when the gas phase over $\text{SiC}/\text{Al}_2\text{O}_3$ is switched from CO/ CO_2 to He. This means that neither CO nor CO_2 desorbs from the Cr catalyst in an inert atmosphere.

The reoxidation process, step (ii), of the catalyst is displayed in Fig. 3. It is found that CO_2 is produced during the reoxidation, whereas CO desorption is not observed. Table 1 shows that only a fraction of CO retained in step (i) leaves the catalyst as CO_2 , indicating that the catalyst is only partly reoxidized. CO_2 production does not start instantaneously after the step change; it is slightly delayed. Since oxygen is consumed directly after the step change this means that reoxidation is not the limiting stage in the CO oxidation over chromium, in agreement with a kinetic study over a Cu–Cr catalyst (Dekker *et al.*, 1992; Kapteijn *et al.*, 1993). The oxygen appears when the CO_2 declines. The amount of CO_2 produced and oxygen consumed are found to be independent of temperature above 533 K (Table 1).

Fig. 3. Response curves of CO_2 and O_2 after a step change from He to 2.5% O_2/He over reduced $\text{Cr}/\text{Al}_2\text{O}_3$, step (ii), at 533 K and 573 K.

The CO_2 and CO responses measured during reduction of the partly oxidized catalyst are given in Fig. 4, step (iii). The reduction patterns are almost identical to the ones obtained for the fully oxidized catalyst. The only difference is that the maximum has shifted to shorter times (compare Fig. 2 with Fig. 4a and Fig. 4b), which indicates that initially more sites are available for CO adsorption. The amount of CO_2 that has desorbed during reoxidation is retained again during this second reduction step (Table 1). Hence, it can be concluded that CO is retained on the catalyst in two forms: one form is liberated as CO_2 only when the catalyst is fully oxidized (100% O_2 , 1 h, 773 K), whereas the other type is already liberated as CO_2 when the catalyst is partly reoxidized (2.5% O_2 , 240 s, 533–613 K). Based on literature, the first type is addressed to a carbonate species and the second type to CO adsorbed on coordinatively unsaturated surface (cus) Cr^{3+} sites (Little and Amberg, 1962; Shelef *et al.*, 1968; Burwell *et al.*, 1969; Zecchina *et al.*, 1969; Bijsterbosch *et al.*, 1992). Assuming that each chromium atom present at the catalyst surface is occupied by one CO after complete reduction, the total amount of retained CO gives the Cr dispersion of the catalyst, i.e. 20%. The amount of CO retained during the second reduction treatment, step (iii), corresponds to the number of sites really available for the surface reaction, i.e. 10%.

When the reoxidation process is performed for the second time, step (iv), exactly the same responses as found for step (ii) are obtained. Thus,

the oxidation and reduction of the chromium catalyst is completely reversible once the fully oxidized catalyst has been reduced.

Previous research has shown that the surface chromium of the catalyst is converted to Cr^{5+} and Cr^{6+} (CrO_3) during oxidation (Shelef *et al.*, 1968; Burwell *et al.*, 1969). Furthermore it was found that CrO_3 reduces in one step to Cr_2O_3 at 580 K but that Cr_2O_3 is hardly reduced further (Burwell *et al.*, 1969; Stegenga *et al.*, 1990; Bijsterbosch, 1993). If in our experiments CO adsorption takes place at Cr^{3+} surface ions due to reduction of only surface CrO_3 to Cr_2O_3 , then the expected ratio of CO_2 produced to CO retained would be 1.5. The amount of CO_2 produced, however, is twice as large, Table 1, step (iii), indicating that not only reaction of surface oxygen but also reaction of subsurface oxygen takes place, as has been suggested before (Burwell *et al.*, 1969; Zecchina *et al.*, 1969). The tail in the response curves of CO_2 can be explained by a slower reaction of these subsurface oxygen atoms. Although some subsurface oxygen reacts, the amount of CO_2 produced during reduction indicates that the catalyst is not completely reduced from CrO_3 to Cr_2O_3 ($\text{CO}_2/\text{Cr} = 0.4$ instead of 1.5). Furthermore, the total amount of CO_2 produced is constant with temperature. Apparently only oxygen atoms very close to surface Cr sites are able to move towards the surface.

A summary of the reaction mechanism that applies for the reduction and oxidation of the chromium catalyst by respectively O_2 and CO is given in Scheme 1.

Fig. 4. Response curves of CO₂ and CO after a step change from He to 5% CO/He over partly oxidized Cr/Al₂O₃, step (iii), at (a) 533 K, (b) 573 K, (c) 613 K: symbol = experimental, line = simulation.

Fig. 4.—contd..

Scheme 1. Main steps in the reduction and oxidation of Cr/Al₂O₃ by respectively CO and O₂ in the temperature range 533–613 K. (□) surface site, (□_s) subsurface site, (*) site leading to a carbonate species.

Modelling the reduction of partly oxidized Cr/Al₂O₃

The experiments have shown that the isothermal reduction of the oxidized Cr catalyst takes place via a Langmuir–Hinshelwood mechanism (Scheme 1). Furthermore, it was found that two forms of CO are retained at this catalyst, a carbonate and a carbonyl. The carbonate species are only formed once during reduction of the fully oxidized catalyst and cannot be converted during the reoxidation of the catalyst. Thus, the carbonate species will be present at the catalyst but they will not influence the reaction. In order to be able to leave out the formation of the carbonate species from the model,

the data of the second reduction, step (iii), were used for the modelling. Hence, only reactions (a)–(d) of Scheme 1 have to be used to model the reduction of the Cr catalyst by CO.

The response curves show that directly after the step change CO₂ is formed. Kobayashi (1982) has shown that an instantaneous response means that either reactant adsorption or the surface reaction is rate determining. The product desorption, i.e. CO₂ desorption in our case, is therefore not rate determining. So, reaction (d) is much faster than the other reactions and can be left out of the model. Also Shelef *et al.* (1968) reported that in the temperature region above 423–473 K desorption of

Fig. 5. Schematic representation of the reduction of the partly oxidized Cr catalyst.

the oxidized product is considered to be relatively fast over transition metal oxides.

Not only surface oxygen but also subsurface oxygen atoms associated with surface Cr sites are removable. This surface Cr site supposedly adsorbs one CO. Thus, if N_i represents the concentration of active sites (i.e. sites able to hold an oxygen atom) and C represents the number of oxygen atoms that are coordinated to one surface Cr atom, the ratio N_i/C gives the maximum concentration of CO that can be adsorbed at the catalyst. This is schematically represented in Fig. 5 (the carbonate species were also excluded from this scheme). This results in the following reactions to be used for the determination of the kinetic parameters, where now reactions (b) and (c) from Scheme 1 are combined into one:

where

$$\theta_{\square} = 1 - C\theta_{\text{CO}\square} - \theta_{\text{O}\square} \quad (5)$$

It is found that an activity distribution exists between the oxygen atoms associated with the Cr site. In other words, it is easier to remove an oxygen atom from a *full* surface Cr site than from an *empty* surface Cr site. The activity distribution of the oxygen atoms was included in the model by considering a first-order and a second-order dependency of k_2 in the fraction of oxygen present in the catalyst. The distribution of reactivities more often yields this kind of performance of the reaction rate, e.g. desulphurization, in which a second-order behaviour has been found. Both relations account for the different reactivity of the oxygen atoms coordinated to one Cr atom, since the reaction rate constant is high when the fraction of oxygen in the catalyst is close to 1, whereas the reaction rate constant decreases when the fraction of oxygen in the catalyst decreases.

$$k_2 = k_2' \theta_{\text{O}\square} \quad (6a)$$

or

$$k_2 = k_2' \theta_{\text{O}\square}^2 \quad (6b)$$

Finally, the catalyst cannot be fully oxidized but must contain a certain fraction of sites directly available for CO adsorption (i.e. $\theta_{\square}^0$), because otherwise the surface reaction will not start. This is reasonable since the catalyst has been subjected to a treatment that only partially reoxidizes the catalyst.

Hence, the parameters in this model are

- N_i maximum concentration of removable oxygen, $\text{mol m}_{\text{cat. bed}}^{-3}$
- k_1 CO adsorption constant, $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
- k_2' surface reaction rate constant, s^{-1}
- $\theta_{\square}^0$ fraction of free sites at $t = 0$
- C oxygen coordination number

The model leads to the following equations to be solved for $z = 0$ to $z = L$:

$$\frac{\partial x_{\text{CO}}}{\partial t} = -v \frac{\partial x_{\text{CO}}}{\partial z} - k_1 N_i x_{\text{CO}} \theta_{\square} \frac{1 - \varepsilon_b}{\varepsilon_b} \quad (7)$$

$$\frac{\partial x_{\text{CO}_2}}{\partial t} = -v \frac{\partial x_{\text{CO}_2}}{\partial z} - C k_2 N_i \theta_{\text{CO}\square} \theta_{\text{O}\square} \frac{RT}{P_i} \frac{1 - \varepsilon_b}{\varepsilon_b} \quad (8)$$

$$\frac{\partial \theta_{\text{CO}\square}}{\partial t} = k_1 x_{\text{CO}} \theta_{\square} \frac{P_i}{RT} - C k_2 \theta_{\text{CO}\square} \theta_{\text{O}\square} \quad (9)$$

$$\frac{\partial \theta_{\text{O}\square}}{\partial t} = -C k_2 \theta_{\text{CO}\square} \theta_{\text{O}\square} \quad (10)$$

The following initial conditions (IC) and boundary conditions (BC) apply:

IC	$x_{\text{CO}} = 0$	at $t < 0 \quad \forall z$
	$x_{\text{CO}_2} = 0$	at $t < 0 \quad \forall z$
	$\theta_{\text{CO}\square} = 0$	at $t < 0 \quad \forall z$
	$\theta_{\text{O}\square} = 1 - \theta_{\square}^0$	at $t < 0 \quad \forall z$
BC	$x_{\text{CO}} = f(t)$	$t \geq 0 \quad \text{and} \quad z = 0$
	$\text{CO}_2 = 0$	$t \geq 0 \quad \text{and} \quad z = 0$

Table 2. Parameter values and 95% error intervals for the elementary processes of the reduction of partly oxidized Cr/Al₂O₃ with CO, step (iii), at several temperatures

T_r (K)	533	553	573	593	613
$10^3 \text{ OF}_{\text{Cr}}$	0.26	0.51	0.13	0.23	0.18
N_r (mol m ⁻³ cat. bed)	382 ± 20	362 ± 18	343 ± 6	362 ± 7	347 ± 6
k_1 (10 ⁻¹ m ³ mol ⁻¹ s ⁻¹)	1.54 ± 0.32	1.7 ± 0.4	1.19 ± 0.19	1.65 ± 0.10	1.01 ± 0.09
k'_2 (10 ⁻¹ s ⁻¹)	0.35 ± 0.02	0.71 ± 0.04	1.56 ± 0.09	2.13 ± 0.05	6.8 ± 0.8
$10 \theta_{\square}^0$	0.76 ± 0.08	0.82 ± 0.09	0.75 ± 0.06	0.73 ± 0.05	1.09 ± 0.09
C	4.8 ± 0.9	4.2 ± 0.8	3.94 ± 0.30	4.2 ± 0.4	4.3 ± 0.30

Fig. 6. Arrhenius plot of calculated rate constants of the elementary steps for the Cr and Cu catalyst.

The solid curves in Fig. 4 give the results of the simulation when using this model with eq. (6b) for k_2 . For a model to represent the measurements satisfactorily the residual distribution should be random with zero mean and not follow a trend with respect to the independent variable. It is found that the model does give a random distribution of all residuals around zero as a function of time and that the error intervals are small. Therefore, it is concluded that the model can describe both the CO and CO₂ response after reduction of a partly oxidized chromium catalyst very well. When using eq. (6a) for k_2 the minimized value for OF_{Cr} was larger than for eq. (6b). Furthermore, the concentration of active sites N_r did not remain constant but was much larger at the two highest temperatures.

Table 2 gives the values of the rate parameters

and their 95% error intervals when using eq. (6b) for k_2 . The table shows that the parameter values have a rather small error distribution. The values for the concentration of active sites N_r , for the oxygen coordination number C and for the initial fraction of empty sites $\theta_{\square}^0$ are found to be independent of temperature, as expected. The latter has an average value of about 0.085 which seems reasonable considering that the catalyst has only been partly oxidized. It shows that the partly oxidizing treatment, step (ii), is able to oxidize more than 90% of the active sites. The oxygen coordination number C has an average value of about 4.3. This agrees with Burwell *et al.* (1969) reporting that at least four molecules of oxygen may react per Cr³⁺ (cus). The oxygen coordination number C differs from the amount of CO₂ produced per CO retained (average value of about 3, Table 1). However, the

Table 3. The amount of CO₂ produced and O consumed in steps (i)–(iv) over Cu/Al₂O₃ at several temperatures, expressed in mol per mol Cu in the catalyst

<i>T</i> , (K)	Step (i), CO ₂ prod.	Step (ii), O cons.	Step (iii), CO ₂ prod.	Step (iv), O cons.
453	0.27	0.11	0.23	0.15
473	0.40	0.19	0.31	0.21
493	0.45	0.22	0.38	0.26
513	0.49	0.28	0.47	0.32
533	0.57	0.34	0.55	
553	0.57	0.35	0.55	0.42

parameter *C* stands for the total amount of oxygen per Cr site, irrespective of whether this site has evolved all oxygen or has retained a CO, while the latter considers only the actually evolved oxygen (as CO₂) and retained CO. The CO adsorption constant *k*₁ is also found to be independent of temperature. Thus, the activation energy for CO adsorption is about zero which is physically acceptable. The surface reaction rate constant *k*₂' was found to increase with temperature (Table 2). Assuming an Arrhenius temperature dependence for *k*₂' the activation energy is found to be *E*_a = 95 ± 19 kJ mol⁻¹ (Fig. 6). This value corresponds well with the value of 80 kJ mol⁻¹ reported by Alkhozov *et al.* (1974) for the CO oxidation over Cr₂O₃ oxide. Furthermore, the Cr–O bond energy was found to be in the same order of magnitude, 109 kJ mol⁻¹, as reported by Borekov (1967). This indicates that the surface reaction reflects the chromium–oxygen bond break.

In conclusion, the modelling of the reduction of the partly oxidized Cr catalyst has led to a model that gives the kinetically most significant reactions under realistic reaction conditions. The model consists of a minimal number of reactions and parameters, but the reactions and the calculated parameter values are still physically acceptable.

Cu/Al₂O₃

Reduction and oxidation of fully oxidized Cu/Al₂O₃

Figure 7 gives the CO₂ responses measured after the step change from He to 5% CO/He over fully oxidized Cu/Al₂O₃ at several temperatures. The curves show that reduction of copper takes place in two stages: CO₂ production is instantaneous then decreases, increases and finally slowly decreases towards zero. The CO response curves display the complementary behavior, except for a very small amount of CO that is retained at the catalyst. The amount of CO₂ produced during the time that CO is passed over the catalyst is given in Table 3. Table 3 shows that the catalyst is only partly reduced, since the ratio CO₂/Cu is not 1 (as in case of full reduction) but less. The CO response curve obtained when the gas phase over the catalyst is switched back to He, is situated above the curve obtained when the gas phase over SiC/Al₂O₃ is switched from CO to He. Therefore, it is concluded that some CO desorbs from this catalyst.

The catalyst is reoxidized in step (ii). During the

reoxidation neither CO nor CO₂ production is measured. Obviously all the CO that was retained during reduction has desorbed when He was passed over the catalyst. The amount of oxygen consumed during the reoxidation is also included in Table 3 and shows that the catalyst was only partly reoxidized.

Reduction of the partly oxidized Cu catalyst, step (iii), also proceeds in two stages. The amount of CO₂ produced is more than the amount of oxygen that was consumed during the reoxidation (Table 3), thus the total degree of reduction of the catalyst has increased after steps (ii) and (iii). The catalyst is again only partly oxidized during the second reoxidation, step (iv). However, the degree of reduction influences the oxidation process, as more oxygen is consumed during the second reoxidation than during the first reoxidation (Table 3).

Previous studies over several copper crystal surfaces (Habraken *et al.*, 1979; Mesters *et al.*, 1984; Pruissen *et al.*, 1987) have proven that subsurface oxygen atoms can replenish removed surface oxygen atoms. Based on these results, the observed two-stage reduction mechanism can be explained by a fast reaction of surface oxygen atoms in the first stage, and reaction of subsurface oxygen that has diffused to the surface in the second stage. The reaction of surface oxygen atoms presumably takes place via a reaction of CO from the gas phase, Eley–Rideal (ER) reaction mechanism, since instantaneously a high CO₂ production is measured after which the reaction rate decreases. During the second stage, reaction of subsurface oxygen accelerates once started. This can be explained by reaction of adsorbed CO, Langmuir–Hinshelwood (LH) reaction mechanism. Initially the surface is completely covered with oxygen, CO adsorption is inhibited and the rate of the CO oxidation is low. However, as the reaction proceeds more sites are generated for CO adsorption, resulting in an increased production rate. As the reduction advances, the amount of subsurface oxygen decreases and the rate of the supplying diffusion process decreases, observed by a decrease in reaction rate.

In summary, the reaction mechanism that applies for the reduction and oxidation of a copper catalyst by respectively CO and O₂ is given in Scheme 2. CO₂ is formed directly after the step change, therefore CO₂ desorption is omitted as a rate-determining step (Kobayashi, 1982) and is not

Fig. 7. Response curves of CO_2 after a step change from He to 5% CO/He over fully oxidized $\text{Cu}/\text{Al}_2\text{O}_3$, step (i), at (a) 473 K and 493 K, (b) 513 K and 533 K: symbol = experimental, line = simulation.

Scheme 2. Main steps in the reduction and oxidation of Cu/Al₂O₃ by respectively CO and O₂ in the temperature range 413–553 K. ($\square$) surface site, ($\square_s$) subsurface site.

included as an individual step in Scheme 2. This was also reported in UHV studies (Habraken *et al.*, 1979; Mesters *et al.*, 1984; Pruissen *et al.*, 1987).

Modelling the reduction of fully oxidized Cu/Al₂O₃

The experiments have shown that the isothermal reduction of the fully oxidized Cu catalyst by CO takes place in two stages (Scheme 2). CO reacts from the gas phase in the first stage, whereas adsorbed CO reacts in the second stage. Furthermore, oxygen diffuses from the bulk to the surface of the catalyst. This solid-state oxygen diffusion is an activated diffusion process, and is represented by a rate equation, just as Pruissen *et al.* (1987) did. Thus, reactions (a)–(d) from Scheme 2 are used in the modelling of the reduction of fully oxidized Cu by CO.

The curves obtained when using these reaction steps did not describe the characteristic features of

This model describes the measured CO₂ response curves very well. However, it was found that the rate constant of CO adsorption k_{ads} cannot be determined accurately on the basis of our experimental data. Therefore, we combined the CO adsorption and the surface reaction to an adjusted LH step.

Although the above reaction step appears to describe an ER reaction, the reaction rate still includes the concentration of empty sites, i.e. sites at which CO can adsorb. The reaction rate is proportional to $x_{\text{CO}}\theta_{\square}\theta_{\text{O}_{\text{LH}}\square}$ in the adjusted LH reaction. A true LH reaction rate is proportional to $\theta_{\text{CO}}\theta_{\text{O}_{\text{LH}}\square}$, but since $\theta_{\text{CO}}\theta_{\square}$ eventually a similar relation is found.

In summary, the following reactions were used for the simulation of the reduction of fully oxidized Cu/Al₂O₃ by CO:

the CO₂ response curves at all. Simulations produce the first maximum (ER mechanism), but subsequently the calculated CO₂ response decreases without giving the second maximum. In order to be able to describe the two-stage reduction, it was necessary to distinguish two oxygen species at the catalyst. The first type reacts via an ER mechanism. It can only be formed by oxidizing the catalyst and might be situated on top of the catalyst surface (schematically represented in Fig. 8a). The second type is held much stronger and is probably situated in the catalyst surface. This type only reacts via an LH mechanism. This layer of oxygen comes available when the ER reaction progresses and it is refilled by diffusion of oxygen from the bulk towards the surface of the catalyst. Initially this layer cannot be completely filled with oxygen, but must contain some sites that can adsorb CO (a fraction $1-y$) and initiate the LH reaction. The LH reaction and the diffusion are schematically represented in Fig. 8b. This gives

The parameters to be determined are

- N_s concentration of surface sites, $\text{mol m}_{\text{cat. bed}}^{-3}$
- N_{ss} concentration of subsurface sites, $\text{mol m}_{\text{cat. bed}}^{-3}$
- k_{ER} Eley-Rideal reaction rate constant, $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
- k'_{LH} Langmuir-Hinshelwood reaction rate constant, $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
- k_{dif} oxygen diffusion rate constant, $\text{m}_{\text{cat. bed}}^3 \text{mol}^{-1} \text{s}^{-1}$
- y fraction of oxygen in the surface

The fully oxidized copper catalyst can release during complete reduction a maximum of one oxygen atom per copper atom. Using this value, the concentration of oxygen atoms per catalyst bed volume is at maximum $400 \text{ mol m}_{\text{cat. bed}}^{-3}$. After the fully oxidizing treatment the total concentration of oxygen will be at its maximum value. Since part of the catalyst atoms are situated at the catalyst

- k_{ER}
- $k_{\text{ads}}, k_{\text{des}}$
- k_{LH}
- k_{dif}

Fig. 8. Schematic representation of the reduction of the fully oxidized Cu catalyst: (a) Eley-Rideal reaction process, (b) Langmuir-Hinshelwood reaction process and oxygen diffusion.

surface, this gives for the concentration of oxygen atoms in the subsurface of the catalyst:

$$N_{ss} = 400 - N_s \quad (11)$$

These elementary steps result in the following equations to be solved for $z = 0$ to $z = L$:

$$\frac{\partial x_{CO}}{\partial t} = -v \frac{\partial x_{CO}}{\partial z} - k_{ER} N_s x_{CO} \theta_{O_{ER}\square} \frac{1 - \varepsilon_b}{\varepsilon_b} - k'_{LH} N_s x_{CO} \theta_{\square} \theta_{O_{LH}\square} \frac{1 - \varepsilon_b}{\varepsilon_b} \quad (12)$$

$$\frac{\partial x_{CO_2}}{\partial t} = -v \frac{\partial x_{CO_2}}{\partial z} + k_{ER} N_s x_{CO} \theta_{O_{ER}\square} \frac{1 - \varepsilon_b}{\varepsilon_b} + k'_{LH} N_s x_{CO} \theta_{\square} \theta_{O_{LH}\square} \frac{1 - \varepsilon_b}{\varepsilon_b} \quad (13)$$

$$\frac{\partial \theta_{O_{ER}\square}}{\partial t} = -k_{ER} x_{CO} \theta_{O_{ER}\square} \frac{P_i}{RT} \quad (14)$$

$$\frac{\partial \theta_{O_{LH}\square}}{\partial t} = y k_{ER} x_{CO} \theta_{O_{ER}\square} \frac{P_i}{RT} - k'_{LH} x_{CO} \theta_{\square} \theta_{O_{LH}\square} \frac{P_i}{RT} + k_{dif} N_{ss} \theta_{O_{\square}} \theta_{\square} \quad (15)$$

$$\frac{\partial \theta_{O_{\square}}}{\partial t} = -k_{dif} N_s \theta_{O_{\square}} \theta_{\square} \quad (16)$$

$$\theta_{\square} = 1 - \theta_{O_{ER}\square} - \theta_{O_{LH}\square} \quad (17)$$

The following initial (IC) and boundary (BC) conditions apply:

IC	$x_{CO} = 0$	at $t < 0 \quad \forall z$
	$x_{CO_2} = 0$	at $t < 0 \quad \forall z$
	$\theta_{O_{ER}\square} = 1$	at $t < 0 \quad \forall z$
	$\theta_{O_{LH}\square} = 0$	at $t < 0 \quad \forall z$
	$\theta_{O_{\square}} = 1$	at $t < 0 \quad \forall z$
BC	$x_{CO} = f(t)$	$t \geq 0 \quad \text{and} \quad z = 0$
	$x_{CO_2} = 0$	$t \geq 0 \quad \text{and} \quad z = 0$

The lines in Fig. 7 give the simulated CO_2 responses when using this model. Table 4 gives the estimated values of the parameters and their 95% error intervals. Due to the low reaction rate, the CO_2 production was very low at 453 K. Consequently the CO_2 response curve displayed only one reduction reaction and an extremely small value for N_s was calculated at this temperature. At 553 K the reaction rate was very high and the ER and LH reactions cannot be individually observed anymore in the measured CO_2 response curve. Consequently an extremely large value for N_s was calculated. Therefore, the concentration of active sites at the surface was held on $88 \text{ mol m}^{-3}_{\text{cat. bed}}$ at 453 and 553 K, which is the average of N_s calculated at 473, 493, 513, and 533 K. Now, an extremely small value for y (< 0.1) was estimated at 453 K. Therefore y was kept at 0.93 at 453 K, which is the average of the values found at 473, 493, 513, 533, and 553 K.

Figure 7 shows that the proposed model describes the characteristic features of the CO oxida-

Table 4. Parameter values and 95% error intervals for the elementary processes of the reduction of fully oxidized Cu/Al₂O₃ with CO, step (i), at several temperatures

T_r (K)	453	473	493	513	533	553
$10^3 \text{ OF}_{\text{Cu}}$	0.18	0.26	0.21	0.49	0.26	0.65
N_s (mol m ⁻³ _{cat.bed})	88 [†]	83 ± 9	95 ± 3	82.0 ± 3.0	93.0 ± 2.5	88 [†]
k_{ER} (10 ⁻¹ m ³ mol ⁻¹ s ⁻¹)	0.094 ± 0.006	0.155 ± 0.025	0.307 ± 0.019	0.66 ± 0.06	0.89 ± 0.06	1.55 ± 0.20
k'_{LH} (10 ⁻¹ m ³ mol ⁻¹ s ⁻¹)	0.200 ± 0.013	0.310 ± 0.035	0.65 ± 0.04	0.93 ± 0.07	1.30 ± 0.10	1.68 ± 0.19
k_{dif} (10 ⁻⁴ m ³ _{cat.bed} mol ⁻¹ s ⁻¹)	0.009 ± 0.038	0.36 ± 0.12	0.33 ± 0.04	0.53 ± 0.05	0.64 ± 0.04	0.79 ± 0.06
y	0.93 [†]	0.90 ± 0.05	0.939 ± 0.014	0.970 ± 0.010	0.935 ± 0.017	0.91 ± 0.05

[†]Parameter fixed at this value (see text).

tion over the Cu catalyst very well at all temperatures. This is confirmed by a random distribution of all residuals around zero as a function of time. Furthermore, the obtained parameter values have a high accuracy. The values for N_s and y are independent of temperature, as expected. The average value of N_s is 88 mol m⁻³_{cat.bed}. Since the total amount of oxygen is 400 mol m⁻³_{cat.bed}, this implies a Cu dispersion of about 22%. The average value of y is about 0.93, which indicates that initially the oxygen layer inside the catalyst surface is nearly completely filled. The values of k_{ER} , k'_{LH} and k_{dif} increase with temperature, as expected. Only at lower temperatures k_{dif} is less well determined. This is probably caused by the fact that the response curves at these temperatures are not as characteristic as at the other temperatures. This makes reliable determination of three reaction steps hard.

The activation energy of the three reaction steps were determined by assuming an Arrhenius temperature dependency (Fig. 6).

$$k_{\text{ER}} : E_a = 59 \pm 5 \text{ kJ mol}^{-1}$$

$$k'_{\text{LH}} : E_a = 46 \pm 6 \text{ kJ mol}^{-1}$$

$$k_{\text{dif}} : E_a = 24 \pm 8 \text{ kJ mol}^{-1}$$

A value of about 60 (±8) kJ mol⁻¹ was also reported for the apparent activation energy of the CO oxidation in the presence of both CO and O₂ over supported and bulk copper catalysts (Alkha-zov *et al.*, 1974; Berg *et al.*, 1983; Prokopowicz *et al.*, 1988). Prokopowicz *et al.* (1988) stated that the CO oxidation over supported CuO proceeds via an ER mechanism although CO is present at the surface of the catalyst at the same time. Our observations also indicate that in a CO + O₂ mixture under steady-state conditions the ER reaction will dominate. Furthermore, on the basis of our results one would expect a first-order dependence of the reaction rate on the CO partial pressure. In addition, neither the O₂ nor the CO₂ partial pressure should effect the reaction rate in excess of oxygen. Zeroth-order dependence in O₂ and CO₂ partial pressure has been found; but values between 0.5 and 1 are reported in the literature for the order of CO partial pressure. The latter indicates that some CO might be adsorbed on the

catalyst in the steady state, which agrees with the observations of Prokopowicz *et al.* (1988) and our model. An apparent activation energy of about 30 kJ mol⁻¹ (Habracken *et al.*, 1979, 1980) is found by UHV studies of the reaction of CO with oxygen preadsorbed on several single crystals. If we construct an Arrhenius plot of the maximum CO₂ production level right after the step change, a value of about 35 kJ mol⁻¹ is found. Since this value corresponds so well with the UHV studies this might indicate that in those studies only the apparent activation energy of both surface processes together was determined and not the activation energy of an elementary reaction step.

In conclusion, we think that an elegant model has been found that describes very well the complicated CO₂ response curves obtained when reducing a fully oxidized Cu catalyst by CO. Although the model consists of only three elementary steps and a limited number of parameters, it yields physically acceptable parameter values and is able to explain both steady-state and transient kinetic data over a wide range of conditions.

CONCLUSIONS

In this study the step response technique was used to investigate the isothermal reduction (by CO) and oxidation (by CO₂) of an alumina-supported Cr and Cu catalyst. Our evaluation demonstrates that the step response method is a valuable tool in elucidating the reaction mechanism of a heterogeneously catalyzed reaction. The method can give the identity and quantitative contribution of the relevant elementary reaction steps, including steps that can never be resolved in steady-state kinetic research, as for example the migration of subsurface oxygen. Moreover, the total number of active sites and the dispersion of the active metal can be determined. Modelling the response curves yields rate constants and the activation energies of the elementary steps.

The reduction of the Cr catalyst proceeds in a single stage via adsorbed CO. Here, the oxygen atoms that are associated with a surface Cr site are removed. It is found that about four oxygen atoms are associated with a surface Cr site. The reactivity of these oxygen atoms decreases as the reduction proceeds. The activation energy of the reduction is

95 kJ mol⁻¹. The adsorbed CO is released as CO₂ when the catalyst is partly reoxidized. Also a carbonate species is retained at the surface of the catalyst, but this type is liberated as CO₂ only when fully oxidizing the catalyst and does not influence the reduction. The total amount of CO retained yielded a Cr dispersion of 20%, whereas the dispersion of the Cr sites that hold CO and thus participate in the reaction is 10%. The other 10% of surface Cr sites are blocked by carbonate structures.

The Cu catalyst displayed three reduction stages. First, the oxygen situated on the catalyst surface reacts with CO from the gas phase. Second, the oxygen situated in the catalyst surface reacts with adsorbed CO. This oxygen is refilled via diffusion of oxygen from the bulk to the surface of the catalyst. Third, the diffused oxygen reacts. The activation energies of these steps are 59, 46 and 24 kJ mol⁻¹ respectively. The oxygen situated on the catalyst surface is formed via oxidation of the catalyst, therefore the reaction with CO from the gas phase will dominate in a CO + O₂ atmosphere. The dispersion of the Cu catalyst was found to be about 22%.

NOTATION

c_j	concentration of component j , mol m ⁻³
$c_{k\Box}$	concentration adsorbed k , mol m ⁻³ _{cat. bed}
C	oxygen coordination number (Cr catalyst), —
E_a	activation energy, J mol ⁻¹
$f(t)$	polynomial function in time describing the step change, —
k_i, k'_i	reaction rate constant of reaction step i , see text
L	catalyst bed length, m
n	number of data points used in minimization, —
N_s	concentration of surface sites (Cu catalyst), mol m ⁻³ _{cat. bed}
N_{ss}	concentration of subsurface sites (Cu catalyst), mol m ⁻³ _{cat. bed}
N_t	concentration of removable oxygen (Cr catalyst), mol m ⁻³ _{cat. bed}
OF _{Cr}	objective function to be minimized (Cr catalyst), —
OF _{Cu}	objective function to be minimized (Cu catalyst), —
P_t	total pressure, 10 ⁻⁵ Pa
r_j	reaction rate of component j , mol m ⁻³ _{cat. bed} s ⁻¹
$r_{k\Box}$	reaction rate of adsorbed k , mol m ⁻³ _{cat. bed} s ⁻¹
R	gas constant, 8.314 J mol ⁻¹ K ⁻¹
t	time, s
T	temperature (298 K)
T_r	reaction temperature, K
x_j	mole fraction of component j , —
y	fraction oxygen in the catalyst surface (Cu catalyst), —
y_j^{obs}	observed fraction of component j , —

y_j^{cal}	calculated fraction of component j , —
v	flow rate, m s ⁻¹
z	axial distance along the catalyst bed, m

Greek letters

ϵ_b	void fraction of catalyst bed, —
$\theta_{k\Box}$	fractional coverage of adsorbed component k , —
$\theta_{\Box}$	fraction of free sites, —
$\theta_{\Box}^0$	fraction of free sites at $t = 0$ (Cr catalyst), —

Special notation

$\Box$	active site
$\Box_s$	subsurface site
*	carbonate-forming site

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