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A transient kinetic study of carbon monoxide oxidation over copper-based catalysts for automotive pollution control

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Abstract

CO oxidation over an alumina supported copper–chromium oxide has been studied by the step-response method. In this study the response of the catalyst is measured after step changes in the CO, ¹³CO and O₂ concentration in order to reveal the reaction mechanism and the concentration of active sites. Special attention was given to the behaviour of the catalyst under conditions changing from net oxidization to net reduction, as this is representative for realistic exhaust gas conditions. It was found that the catalyst goes through an oxidation/reduction cycle under these conditions. The activity of the catalyst in an oxidizing gas feed following the reducing gas feed is initially higher than the steady-state activity. The surface reaction is rate determining under oxidizing and reducing conditions, but the removal of CO₂ from the catalyst surface also affects the overall rate of the reaction. It is found that 27% of the surface copper is covered with CO and CO₂ in a reducing reaction mixture, i.e., 5% CO and 1.5% O₂ in He. This amount is 18% in an oxidizing reaction mixture. CO readsorbs rapidly at the catalyst surface, but CO₂, which desorbs via a concerted reaction mechanism with O₂, hardly readsorbs at the catalyst surface.

1. Introduction

The catalytic oxidation of CO to CO₂ is of great importance in decreasing the release of CO from automobiles. Previous research [1–3] has shown that the combination of Cu- and Cr-oxides constitutes a catalyst with a relatively high activity for the conversion of CO by

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O₂, N₂O and NO. In this way the use of precious metals may be avoided in exhaust catalysis.

The use of Cu–Cr as an active phase for CO oxidation was reported as early as 1933 [4] and a number of papers have appeared since then. However, little is still known about the behaviour of the Cu–Cr catalyst under dynamic conditions, although the catalyst has to work in an environment in which the composition changes continuously between oxidizing and reducing conditions. Furthermore, the reaction mechanism and the identity and concentrations of active species at the catalyst under realistic reaction conditions is still not unequivocally established, although attempts have been made based on steady-state kinetic measurements [1,3,5].

The transient response method using step changes in feed concentrations is a fast, simple and sensitive method that gives information related to reaction sequences, reaction rates and adsorption/desorption rates, especially when isotopes are used [6–10]. Therefore, the step–response method is used in order to reveal the reaction mechanism of the CO oxidation over the Cu–Cr catalyst under realistic reaction conditions and to determine surface concentrations of the species involved.

2. Experimental

Throughout this paper all isotopically labelled species are addressed with a prefix, viz. ¹³C, whereas the unlabelled species are addressed without a prefix, viz. C for ¹²C.

2.1. Gases and catalyst

All gases were of HP or UHP grade and were purified (O₂ and/or H₂O removal) before use (UCAR). All gas mixtures, including the ¹³CO (Thamer Diagnostica, 99%) mixture, were prepared in a separate gas mixing system and were stored in lecture bottles.

The catalyst was prepared by pore volume impregnation of γ -Al₂O₃ [Ketjen 000-1.5E (CK300), $V_p = 0.5$ ml/g, $S_a = 200$ m²/g, and $d_p = 0.15 - 0.25$ mm] with an aqueous solution of copper(II) nitrate and chromium(III) nitrate. The catalyst was dried for 2 h at 393 K and subsequently calcined in air up to 773 K (5 K/min, 2 h isothermal), resulting in a 10 wt.-% Cu–Cr/Al₂O₃ catalyst with a Cu/Cr ratio of 1.

2.2. Apparatus

The apparatus used for the step–response experiments is represented schematically in Fig. 1. The apparatus consisted of a gas feed selection section, a reactor section and a gas analysis section. The gas feed selection section consisted of three low-volume four-way valves. The four-way valves were connected in such a way that step changes between three different gas mixtures were possible. One of the four-way valves was pneumatically operated (SV), which permitted an instantaneous exchange of two selected gas feed lines. To minimize pressure disturbances during the step changes, the pressure in these flow lines was monitored by a differential pressure transducer and equalized and controlled by back-pressure controllers.

Fig. 1. Flow scheme of the step-response equipment. A,B,C, gas feed; BPC, back-pressure controller; CAP, capillary; COMP, computer; MS, mass spectrometer; PI, pressure indicator; SV, switching valve; TIC, temperature indicator and controller.

The catalyst (100 mg) was placed in a quartz reactor with a 5 mm internal diameter at the sample location and with a 1.5 mm capillary below the sample. A stainless steel frit was placed at the end of this capillary for protection of the gas analysis section. The system volume downstream the sample was minimized in order to minimize dispersion effects. The reactor was surrounded by an aluminum cylinder, which contained the thermocouple to control the oven temperature. To improve heat transfer from the particles to the surroundings the catalyst bed was diluted with SiC (279 mg, $d_p = 0.2\text{--}0.5$ mm, volume ratio catalyst:SiC = 1:1.1).

Product gas analysis was performed by a quadrupole mass spectrometer (Balzers, QMG 420), which was placed in a temperature-controlled oven ($T = 398$ K). Gas introduction into the mass spectrometer was achieved by differential pumping via a heated fused silica capillary ($T = 383$ K) and a variable leak valve. The capillary was positioned within the gas flow line without creating any dead volume. Signal analysis, mass selection, and sample rates were controlled by a personal computer equipped with the Balzers software program Quadstar 420 V3.0 that collects the data and stores it for further analysis. The raw data were corrected for background levels, fragmentation contributions (CO_2 to CO) and mass spectrometer sensitivity for the different molecules.

2.3. Experimental procedures

Several step sequences were performed with a gas flow of 45 ml min^{-1} , at a temperature of 473 K and at a pressure of 1 bar. To obtain reproducible results the catalyst was subjected to an oxidation, reduction, and oxidation pretreatment before the step sequences. In these pretreatments the temperature was raised to 773 K with a temperature increase of 5 K min^{-1} .

in a O₂, CO and O₂ flow (30 ml min⁻¹), respectively. The catalyst was kept at 773 K for half an hour followed by cooling to room temperature. In the second oxidation pretreatment the catalyst was cooled to reaction temperature. A reduction pretreatment was performed since it caused an increase in catalyst activity [11]. The oxidation pretreatment was repeated after each step sequence. The step sequences were performed after steady-state conversion had been reached in the initial feed mixture of the sequence. All step sequences were performed several times and were found to be easily reproducible.

The following step sequences were made:

- I a (5% CO + 3.5% O₂) / He $\longleftrightarrow$ He
- b (5% CO + 3.5% O₂) / He $\longleftrightarrow$ 3.5% O₂ / He
- II a (5% CO + 2.5% O₂) / He $\longleftrightarrow$ He
- b (5% CO + 2.5% O₂) / He $\longleftrightarrow$ 2.5% O₂ / He
- III a (5% CO + 1.5% O₂) / He $\longleftrightarrow$ He
- b (5% CO + 1.5% O₂) / He $\longleftrightarrow$ 1.5% O₂ / He
- IV (5% CO + 2.5% O₂) / He $\longleftrightarrow$ (4.5% ¹³CO + 2.5% O₂) / He
- V (5% CO + 1.5% O₂) / He $\longleftrightarrow$ (4.5% ¹³CO + 2.5% O₂) / He

The initial feed mixture of CO and O₂ in He was net oxidizing in step sequence I. Both CO and O₂ were withdrawn and introduced again in step sequence Ia, whereas only CO was withdrawn and introduced again in step sequence Ib. The same procedure was followed when starting with a stoichiometric feed mixture of CO and O₂ in He (step sequence IIa and IIb) and when starting with a net reducing feed mixture of CO and O₂ in He (step sequence IIIa and IIIb). The mixture of CO and O₂ in He changed from stoichiometric to almost stoichiometric in step sequence IV. Step sequence V exhibited a change in the feed mixture of CO and O₂ in He from net reducing to almost stoichiometric and reverse. CO was exchanged by ¹³CO in step sequence IV and V in order to separate the responses of both feed mixtures.

For the interpretation, the step-response curves were compared with a gas phase step change performed over 279 mg SiC and 100 mg γ-Al₂O₃ at the same experimental conditions as the step sequences. These blank runs were performed with only one component in He, i.e., 5% CO/He, 5% CO₂/He and 3.5% O₂/He. For comparison the level of these blank runs was adjusted to the steady-state level of CO, CO₂ or O₂ in the experiments. It was assumed that the blank runs of ¹³CO₂ and ¹³CO equalled the blank runs of CO₂ and CO, respectively. The amount of CO₂, ¹³CO₂, CO or ¹³CO desorbing from the catalyst after a step change was calculated by subtracting the area under the blank run from the area under the response curve, and converting this value to moles. The amount of ΣCO_x (or Σ¹³CO_x) adsorbing after a step change was calculated by subtracting the amounts of CO and CO₂ (or ¹³CO and ¹³CO₂) measured in the outlet from the amount of CO (or ¹³CO) led over the catalyst.

3. Results

3.1. Step sequence I

In order to investigate the state of the catalyst under oxidizing conditions, a step change was made from a net oxidizing mixture to He (Ia) and to O₂/He (Ib). Fig. 2A gives the

Fig. 2. Responses of CO, CO₂ and O₂ after the following step changes: A: (5% CO + 3.5% O₂)/He → He (Ia); (5% CO + 3.5% O₂)/He → 3.5% O₂/He (Ib). B: He → (5% CO + 3.5% O₂)/He (Ia); 3.5% O₂/He → (5% CO + 3.5% O₂)/He (Ib). Bold lines, blank run, dashed lines, steady-state.

CO₂, O₂ and CO responses after these step changes. The figure shows that the CO₂ response after the step change to He (CO₂(Ia)) is equal to the blank run. However, the CO₂ response after the step change to O₂/He (CO₂(Ib)) is slower and thus indicates that CO₂ desorbs from the catalyst. The O₂ response after this step change (O₂(Ib)) is not instantaneous, which means that the catalyst consumes some oxygen.

Fig. 2B displays the CO₂, O₂ and CO responses after the reverse step changes from He (Ia) and O₂/He (Ib) to the net oxidizing mixture. Here, the results of the CO and CO₂ responses are similar for both step changes. The CO₂ responses are instantaneous, but the CO responses are slower and thus indicate that CO (or CO₂) is retained at the catalyst. The O₂ response after the step change from O₂/He (O₂(Ib)) is not instantaneous and shows that the catalyst is slightly reduced.

The oxygen responses of step sequence Ia are not given in Fig. 2A and 2B since they were instantaneously steady-state.

3.2. Step sequence II

The step changes from a stoichiometric mixture to He (IIa) and to O₂/He (IIb) (and reverse) lead to responses that are essentially equal to the responses for the oxidizing mixture which are shown in Fig. 2A and 2B.

3.3. Step sequence III

The state of the catalyst under reducing conditions can be determined by measuring the response of the catalyst after a step change from a net reducing mixture to He (IIIa) and to

Fig. 3. (a) Responses of CO_2 , O_2 (left) and CO (right) after the following step changes: (5% CO + 1.5% O_2)/He $\rightarrow$ He (IIIa), (5% CO + 1.5% O_2)/He $\rightarrow$ 1.5% O_2 /He (IIIb). Bold lines, blank run; dashed lines, steady-state (b) Responses of CO and CO_2 after the following step changes: He $\rightarrow$ (5% CO + 1.5% O_2)/He (IIIa), 1.5% O_2 /He $\rightarrow$ (5% CO + 1.5% O_2)/He (IIIb). Bold lines, blank run

Table 1

Amount of CO₂, CO and Σ CO_x desorbing and Σ CO_x adsorbing per mol of Cu in the catalyst in step sequence IIIb. (5% CO + 1.5% O₂)/He $\longleftrightarrow$ 1.5% O₂/He

Species	Desorption (mol/mol)	Adsorption (mol/mol)
Σ CO _x	0.040	0.053
CO ₂	0.029	
CO	0.011	

O₂/He (IIIb). The left side of Fig. 3a gives the CO₂ and O₂ responses after the step changes and the right side gives the CO responses. The CO₂ response upon the step change to He (CO₂(IIIa)) is almost equal to the blank run, but desorption of CO₂ is observed upon the step change to O₂/He (CO₂(IIIb)). The CO desorption is about the same in both cases. The fraction of O₂ in the outlet after the step change to O₂/He (O₂(IIIb)) shows that initially some O₂ is still consumed.

The reverse step changes from He (IIIa) and from O₂/He (IIIb) to the net reducing mixture are given in Fig. 3b. The CO₂ responses are instantaneous in both cases, but an extra production ('overshoot') of CO₂ is measured after the step change from O₂/He (CO₂(IIIb)). The CO responses exhibit a delay in both cases. The CO response after the step change from He (CO(IIIa)) increases faster to its steady-state level and is more delayed.

Table 1 gives the amount CO₂, CO and Σ CO_x (the sum of the amount CO₂ and CO) desorbing per mol Cu present in the catalyst after the step change to O₂/He (with an error of about 15%). This amount is expressed per mol of Cu in the catalyst, because the activity of a Cr catalyst is, in contrast to a Cu catalyst, very low under the conditions used [3,11–14]. Therefore Cu is regarded as active phase for this catalyst. Also the amount Σ CO_x adsorbing at the catalyst after the step change from O₂/He to the net reducing mixture is included in Table 1. The table shows that the amount of Σ CO_x adsorbing is higher than the amount which has desorbed. An explanation might be that a considerable part of the desorption is reflected in the tail of the response curve and cannot be accurately determined.

3.4. Step sequence IV

In the above described experiments the Cu–Cr catalyst is studied under oxidizing and reducing conditions by changing the gas phase composition to (or from) He and O₂/He. However, the behaviour of the catalyst may alter by changing the gas phase composition [9] and the step sequences might not be representative for the catalyst behaviour. Therefore, a step change is made from a stoichiometric reaction mixture of (CO + O₂)/He to almost the same mixture but containing labelled ¹³CO instead of CO, i.e. (¹³CO + O₂)/He. The latter mixture is slightly oxidizing, but the overall conditions in this experiment can still be considered steady-state since the responses in step sequence I (oxidizing mixture) are essentially the same as the responses in step sequence II (stoichiometric mixture). The left side of Fig. 4 gives the CO₂, ¹³CO₂, and O₂ responses after the step change, and the right side gives the CO and ¹³CO responses. The figure shows that CO₂ desorbs from the catalyst after the step change and that the fraction ¹³CO₂ gradually increases after the step change.

Fig. 4 Responses of CO_2 , $^{13}\text{CO}_2$, O_2 (left), ^{13}CO and CO (right) after the following step change: (5% CO + 2.5% O_2)/He $\rightarrow$ (4.5% ^{13}CO + 2.5% O_2)/He (IV). Bold lines, blank run; dashed lines, steady-state.

Table 2

Amount of CO_2 , CO , ΣCO_x and $\Sigma^{13}\text{CO}_x$ adsorbing/desorbing per mol of Cu in the catalyst in step sequence IV: (5% CO + 2.5% O_2)/He $\rightarrow$ (4.5% ^{13}CO + 2.5% O_2)/He

Species	Desorption (mol/mol)	Adsorption (mol/mol)
ΣCO_x	0.031	
CO_2	0.013	
CO	0.018	
$\Sigma^{13}\text{CO}_x$		0.033

The fraction O_2 in the outlet is 0.01 for both gas mixtures. The CO response continues for a few seconds after which it decreases and the ^{13}CO response increases. The amount CO_2 , CO and ΣCO_x (the sum of the amount CO_2 and CO) desorbing and the amount $\Sigma^{13}\text{CO}_x$ adsorbing after the step change are given in Table 2 which shows that the amount of ΣCO_x desorbing is about equal to the amount of $^{13}\text{CO}_x$ adsorbing, as is expected.

3.5. Step sequence V

Finally the behaviour of the catalyst under dynamic conditions, which are characteristic for realistic exhaust gas conditions, is measured. A step change is made from a reducing mixture of (CO + O_2)/He to a slightly oxidizing mixture of (^{13}CO + O_2)/He. In the former mixture all the O_2 is consumed whereas in the second some O_2 is still left. The left side of Fig. 5a gives the CO_2 , $^{13}\text{CO}_2$ and O_2 responses. The figure shows that CO_2 desorbs from

Fig. 5. Responses of CO_2 , $^{13}\text{CO}_2$, and O_2 (left), ^{13}CO and CO (right) after the following step change. (a) $(5\% \text{ CO} + 1.5\% \text{ O}_2)/\text{He} \rightarrow (4.5\% \text{ }^{13}\text{CO} + 2.5\% \text{ O}_2)/\text{He}$ (V) (b) $(4.5\% \text{ }^{13}\text{CO} + 1.5\% \text{ O}_2)/\text{He} \rightarrow (5\% \text{ CO} + 1.5\% \text{ O}_2)/\text{He}$ (V) Bold lines, blank run; dashed lines, steady-state.

the catalyst after the step change. The fraction CO_2 in the outlet even exceeds the steady-state level of 0.03 before decreasing. The $^{13}\text{CO}_2$ production increases gradually, passes through a maximum and decreases to its steady-state level of 0.03 (not shown). The O_2

Table 3

Amount of CO₂, CO, Σ CO_x, ¹³CO₂, ¹³CO and Σ^{13} CO_x adsorbing/desorbing per mol of Cu in the catalyst after step sequence V: A (5% CO + 1.5% O₂)/He → (4.5% ¹³CO + 2.5% O₂)/He, B (4.5% ¹³CO + 2.5% O₂)/He → (5% CO + 1.5% O₂)/He

Species	A		B	
	Desorption (mol/mol)	Adsorption (mol/mol)	Desorption (mol/mol)	Adsorption (mol/mol)
Σ CO _x	0.051			0.056
CO ₂	0.033			
CO	0.018			
Σ^{13} CO _x		0.035	0.040	
¹³ CO ₂			0.020	
¹³ CO			0.020	

signal slowly increases to the steady-state level after the step change. The CO and ¹³CO responses (right side of Fig. 5a) exhibit a small delay after which they respectively decrease and increase. In Table 3, A gives the amount CO₂, CO and Σ CO_x (the sum of the amount CO₂ and CO) desorbing and the amount of Σ^{13} CO_x adsorbing after the step change.

The responses of the reversed step change are given in Fig. 5b. It is found that ¹³CO and ¹³CO₂ desorb from the catalyst and that the fraction CO (after a delay) and CO₂ gradually increase.

In Table 3, B gives the amount of ¹³CO, ¹³CO₂ and Σ^{13} CO_x (the sum of ¹³CO and ¹³CO₂) desorbing and the amount of Σ CO_x adsorbing after the step change. Table 3 shows that the amount of Σ CO_x desorbing is about equal to the amount of Σ CO_x adsorbing at the reversed step change. The same is true for the amount of Σ^{13} CO_x adsorbing and desorbing. However the amount Σ CO_x adsorbed at the catalyst in a reducing environment is more than the amount of Σ^{13} CO_x adsorbed at the catalyst in the oxidizing environment.

4. Discussion

4.1. Step sequence I

The step change from the net oxidizing mixture to O₂/He (Fig. 2A) shows that CO₂ desorbs from the catalyst. In-situ FT-IR measurements [15] have indicated that both CO and CO₂ are adsorbed at this catalyst in the presence of CO and O₂. Therefore, the measured CO₂ can either be CO₂ desorbing from the catalyst or adsorbed CO which has reacted to CO₂. O₂ plays a major role in the CO₂ desorption, because O₂ is consumed after the step change and because neither CO₂ nor CO desorption is observed after the step change to He. According to Sokolovskii [16], who follows Boreskov's terminology, a concerted mechanism is accomplished when a reaction rate in the presence of a reactant differs from the reaction rate in the absence of this reactant. Otherwise a so-called step-wise mechanism is established. As the desorption rates in a He and O₂/He atmosphere differ, it can be concluded that desorption of CO₂ proceeds via a concerted and not via a step-wise reaction mechanism, i.e. the desorption of CO₂ and the adsorption of O₂ occur simultaneously.

The reverse step changes to He and to O₂/He (Fig. 2B) give instantaneously a steady-state CO₂ production. This was also found for the fully oxidized catalyst used in this study [17] and for a CuO catalyst [18]. The instantaneous steady-state production indicates that surface reaction or reactant adsorption is the rate determining step in the CO oxidation under the conditions used [8]. The oxidation is a very rapid reaction, as the CO oxidation was found to be zero order in O₂ even at very low O₂ concentrations [5,13,19,20]. The adsorption of CO can be excluded as rate determining step too, because in-situ FT-IR experiments have indicated that adsorbed CO₂ can be formed at this catalyst without an observable formation of the Cu¹⁺–CO complex [15]. Therefore, the surface reaction must be the rate determining step. This confirms a steady-state kinetic study of this catalyst [3,5]. This study has also indicated that the surface reaction is rate determining, while desorption of the CO₂ intermediate was found to proceed at comparable rate. Furthermore, Shelef et al. [21] and Boreskov [22] also concluded that the limiting stage of the CO oxidation is associated with scission of the catalyst–oxygen bond, i.e. the reduction of the catalyst surface by CO. Their conclusion was based on the correlation of decreasing activity of transition metal oxides with increasing surface–oxygen bond strength.

The step change from O₂/He to the oxidizing mixture (Fig. 2B) shows that CO_x adsorbs at the catalyst and that the O₂ signal is not instantaneous steady-state but slowly decreases towards the steady-state level. As after oxidation by O₂, copper (the active phase) is mainly present as Cu²⁺ [11,23–25], this demonstrates that the oxidation state under working conditions is slightly lowered. This was also found by electrical resistance measurements [26].

4.2. Step sequence III

CO desorbs from the catalyst upon the step change from the net reducing mixture to He and to O₂/He (Fig. 3a). The CO desorption in the He atmosphere is about identical to the CO desorption in the O₂/He atmosphere and thus proceeds via a step-wise mechanism. As much more CO₂ desorbs from the catalyst in the O₂/He atmosphere than in the He atmosphere, it is concluded that CO₂ desorption proceeds mainly via a concerted reaction mechanism. However, it should be mentioned that previous research [17] has indicated that CO₂ production starts instantaneously when exposing the fully oxidized Cu–Cr catalyst to CO/He. Thus, part of the CO₂ desorption proceeds instantaneously without the help of oxygen.

CO desorption is only observed after the step change from the reducing mixture (in which all O₂ is consumed) to He and to O₂/He, but not after the step change from the oxidizing mixture to He and to O₂/He (comparison of Fig. 2A with Fig. 3a). This confirms in-situ FT-IR experiments on this catalyst [15] which have shown that in the absence of O₂ more stable Cu¹⁺–CO complexes are formed than in the presence of O₂. Comparison of Fig. 2A and Fig. 3a also shows that more CO₂ is present on the catalyst under net reducing conditions than under net oxidizing conditions.

Oxygen is consumed after the step change from the net reducing mixture to O₂/He (Fig. 3a). Thus, the catalyst is oxidized. The catalyst is reduced again upon the reverse step change. This reduction of the catalyst temporarily results in a higher CO₂ production ('overshoot') than would be expected from the quantity of O₂ in the feed (Fig. 3b). The step change from He to the net reducing mixture (step sequence IIIa) does not give an

'overshoot' in the CO_2 production. The reason for this is that the catalyst is not oxidized, but has remained in a reduced state in the He flow. This CO_2 overshoot clearly caused the difference in CO responses after the step change from He and from O_2/He (CO(IIIa) and CO(IIIb) in Fig. 3b).

The CO_2 responses for the step changes from He and from O_2/He are both instantaneous, indicating that product desorption is not the rate determining step [8]. For the same reasons as mentioned above (step sequence I) it is concluded that the surface reaction is rate determining.

4.3. Step sequence IV

The $^{13}\text{CO}_2$ production after the step change from the stoichiometric mixture of $(\text{CO} + \text{O}_2)/\text{He}$ to the slightly oxidizing mixture of $(^{13}\text{CO} + \text{O}_2)/\text{He}$ increases nearly linearly. An instantaneous steady-state $^{13}\text{CO}_2$ production is expected in view of the CO_2 production in step sequence I and III. The slower increase in the $^{13}\text{CO}_2$ signal compared to the blank run is attributed to the presence of CO_2 at the catalyst surface which has to be removed before the reaction of ^{13}CO to $^{13}\text{CO}_2$ can take place. Hence, a slower increase of $^{13}\text{CO}_2$ production is observed compared to the CO_2 production in step sequence I and III where the surface did not contain CO_2 . This implies that also the removal of CO_2 from the surface affects the overall rate of the reaction, which is in agreement with steady-state kinetic modelling where the surface reaction and the CO_2 desorption rate were found to be of the same order of magnitude [5].

Although the $^{13}\text{CO}_2$ production is not directly at the steady-state level, it starts instantaneously. However, CO_2 is still present at the catalyst when the $^{13}\text{CO}_2$ production is observed. Obviously the $^{13}\text{CO}_2$ did not exchange with this adsorbed CO_2 . Therefore it is concluded that $^{13}\text{CO}_2$ (and thus CO_2) desorbs rapidly but does not readsorb at the catalyst.

Furthermore, it can be seen that ^{13}CO exchanges rapidly with CO adsorbed at the catalyst surface. As a consequence of the exchange process in the packed bed reactor, the CO response continues at the initial level and the ^{13}CO response is delayed.

4.4. Step sequence V

The responses after the step change from the net reducing mixture to the slightly oxidizing mixture and reverse (step sequence V) give essentially identical responses as after step sequence IV (comparison of Fig. 4 with Fig. 5a and 5b). Therefore, it is concluded again that ^{13}CO and CO exchange very rapidly but that $^{13}\text{CO}_2$ and CO_2 readsorption are negligible.

CO_2 clearly desorbs from the catalyst after the step change from the net reducing to the net oxidizing mixture. The fraction CO_2 in the outlet passes through a maximum which exceeds the steady-state level of 0.03. The step change from the same net reducing mixture to O_2/He (IIIb) also showed desorption of CO_2 , but the maximum was not observed in this experiment. The increase in O_2 concentration, 1.5% to 2.5% O_2 , explains an increased rate of CO_2 desorption via a concerted mechanism resulting in a maximum.

The major phenomena after the step change from the net reducing mixture to the slightly oxidizing mixture are completed within 15 seconds, but the CO_2 production is still higher than the steady-state production (Fig. 5a). Previous research has explained an increase in

activity of the Cu–Cr catalyst after a CO pretreatment by a surface Cu enrichment [11,12]. However, the conditions in this experiment are probably too mild for a surface Cu enrichment [27]. It is more likely that the activity increase is caused by the higher concentration of Cu^{1+} sites in a net reducing mixture than in a net oxidizing mixture (see discussion of step sequence III). These Cu^{1+} sites are oxidized when exposing the catalyst to a net oxidizing mixture, which explains the decrease in CO_2 production in time. The presence of Cu^0 sites can be excluded as a cause for the activity increase, since in-situ FT-IR experiments [15] did not show any Cu^0 complexes.

The reduction of the catalyst after the reverse step change from the slightly oxidizing mixture to the net reducing mixture is rather slow. This is also observed after a step change from O_2/He to the reducing mixture (Fig. 3b).

4.5. Quantitative interpretation

Tables 1–3 show that 0.053 mol CO_x (sum of the amount CO and CO_2) is adsorbed at the catalyst per mol Cu under reducing conditions. This amount is 0.035 mol $\text{CO}_x/\text{mol Cu}$ under oxidizing conditions. Previous research [17] has shown that the Cu dispersion of this catalyst is 0.2. This dispersion was determined by calculating the amount CO_x adsorbing per Cu atom in the catalyst after a step change from ($^{13}\text{CO} + \text{O}_2$)/He to CO/He. In this study where O_2 is present, it is shown that 27% of the surface is covered with CO_x under the net reducing conditions and that about 18% of the surface Cu is covered with CO_x under the net oxidizing conditions. This confirms calculations based on steady-state kinetic measurements that showed that about 18% of the active sites are covered with CO_x under oxidizing conditions [5].

5. Conclusions

The described experiments indicate that the step–response method is very useful for the study of heterogeneous catalysts. The use of labelled molecules is essential for the determination of the important features in a reaction mechanism by step–response experiments. In this way the steady-state conditions are maintained while a transient in a labelled species is imposed.

It is shown that both CO and CO_2 are present at the Cu–Cr catalyst in a net reducing and in a net oxidizing mixture. Based on a Cu dispersion of 0.2, the coverage by CO and CO_2 is 27% in a reducing environment and 18% in an oxidizing environment. The catalyst goes through an oxidation/reduction cycle when changing the gas feed composition between net oxidizing and net reducing. The activity of the catalyst is temporarily higher than the steady-state activity after the gas phase composition has changed from net reducing to net oxidizing. The surface reaction of CO with adsorbed oxygen is the rate determining step both under oxidizing and reducing conditions, but the removal of CO_2 from the catalyst surface also affects the overall rate of the reaction. Furthermore, it is found that behaviour of the catalyst in a stoichiometric reaction mixture is identical to that in an oxidizing reaction mixture. Experiments with labelled ^{13}CO have indicated that it exchanges rapidly with adsorbed CO.

CO₂ desorbs rather rapidly via a concerted mechanism with oxygen but is rather slow without oxygen, and does not readsorb at the catalyst.

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