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NO Reduction over Alumina-Supported Cu and Cu–Cr Studied with the Step–Response Method

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The NO reduction by CO over alumina-supported Cu and Cu–Cr has been investigated by means of transient experiments using step changes in the feed concentration. First, the isothermal reduction by CO and oxidation by NO of the catalysts was studied. Next, the influence of oxygen on the NO conversion was determined. NO is adsorbed on the oxidized catalysts as nitrite/nitrate complexes and as Cu^{2+}–NO. The nitrite/nitrate complexes decompose only in a reducing atmosphere, whereas NO readily desorbs from Cu^{2+} in He. CO is retained on the catalysts in a CO/NO/He atmosphere. It was found that the conversion of NO is not only limited by O_2 in the gas phase, but that NO also competes with subsurface oxygen to oxidize the surface of the catalysts. In other words, NO is only converted when the catalysts are in a reduced state. Since the activity of the Cu–Cr catalyst in NO reduction was found to be higher than that of the Cu catalyst, it is concluded that Cr helps to keep the Cu in a more reduced state. N_2O may be formed under dynamic conditions even when it is not observed in the steady state. It was nicely demonstrated that the step–response experiments allow the calculation of the concentrations of the different surface species. These concentrations strongly depend on the reaction conditions. © 1997 Academic Press

INTRODUCTION

The reaction between NO and CO is an important process in the catalytic control of exhaust emissions. Most studies focus on the use of noble metals for this reaction. Cu-based catalysts might be of interest for fuels with a low or negligible sulfur content. Extensive research on the use of Cu-based catalysts in the NO reduction was performed in the 1960s and early 1970s. This research has been reviewed by Shelef in 1975 (1). As the sulfur levels in fuels are continuously decreasing, Cu-based catalysts still receive much attention (2–6). Cu-exchanged zeolites seem especially promising, as their activity in the decomposition of NO is high (7, 8).

Information on the mechanism, kinetics, and structure sensitivity of the NO reduction over Cu-based catalysts is necessary to improve our insight into the working of catalysts in emission control. Therefore, Cu-based catalysts have been studied at our laboratory by means of steady-state (2, 9, 10) and FT-IR experiments (11, 12). The Cu–Cr catalyst was found to be particularly active in the CO oxidation and NO reduction (2). As an exhaust gas catalyst typically operates under dynamic conditions, information on the behavior of the catalyst in a periodically changing feed gas composition is essential. Recently, the dynamic behavior over Cu-based catalysts was investigated by means of step–response experiments (13–16). In the present study step–response analysis employing labeled and unlabeled compounds is used to obtain information on the NO reduction over Cu and Cu–Cr. First, the oxidizing potential of NO is examined. As it is known that O_2 and NO compete to react with CO (2, 10), secondly the influence of O_2 on the NO reduction is investigated.

METHODS

Gases and Catalyst

Throughout this paper all isotopically labeled species are addressed with a prefix, viz. ^{13}C, whereas the unlabeled species are addressed without a prefix, viz. C for ^{12}C.

All gases were of HP or UHP grade (UCAR) and were purified (O_2 and/or H_2O removal) before use. The gas mixtures, including the ^{13}CO (Thamer Diagnostica, 99%) mixture, have been prepared in a separate gas mixture system.

The NO reduction was investigated over 10 wt% CuO/Al_2O_3 ($d_p = 0.105–0.140$ mm) and 10 wt% CuO–Cr_2O_3/Al_2O_3 (Cu/Cr molar ratio of 1, $d_p = 0.15–0.25$ mm). A description of the catalyst preparation is given elsewhere (11, 12). In the experiments 50 mg of the Cu catalyst or 100 mg of the Cu–Cr catalyst was used (i.e., similar amounts of Cu).

Apparatus

The apparatus used for step–response analysis consisted basically of a gas feed section, a reactor section, and a gas

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analysis section. In order to assure isothermal operation, the reactor was surrounded by an aluminum cylinder and the catalyst bed was diluted with SiC ($d_p = 0.2–0.5$ mm, volume ratio catalyst : SiC = 1 : 1.1). The product gas was analyzed by a 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, and mass spectrometer sensitivity for the different molecules. Finally, the corrected data were presented as molar fraction in the product gas mixture. The apparatus has previously been described in more detail (13, 14, 16).

Procedures

In the experiments a flow rate of 30 ml $\min^{-1}$ (STP) and atmospheric pressure was used. Two series of experiments were performed at 473, 493, and 513 K. In series (I) the oxidation performance of NO was investigated by subjecting the catalysts subsequently to an NO-, CO-, and NO-containing gas phase at reaction temperature (Fig. 1). The first step, step (I.i), is regarded as an oxidizing pretreatment and therefore will not be discussed in this paper. The NO- or CO-containing mixture was led over the catalyst for 300 s. In between the step changes inert gas (He) was passed over the catalyst for 240 s. In series (II) the influence of oxygen on the NO reduction was investigated (Fig. 1). Here, a net reducing mixture containing NO and CO in a ratio of 1/1.5 was introduced over the catalyst until the steady state was reached. Then, the gas phase was changed to an O_2 containing mixture, followed by a switch back to the NO/CO/He mixture after 240 s. All experiments were found to be well reproducible.

To be able to discriminate between the responses of CO_2 and N_2O and the responses of CO and N_2 in the mass spectrometer, ^{13}CO was used in all experiments over Cu–Cr and in series (II) over Cu. The use of labeled ^{13}CO was unnecessary in series (I) over Cu, since it was found that CO_2/N_2O and CO/N_2 are not formed simultaneously under the applied conditions.

To some of the gas mixtures 0.5% Ar was added. Not adsorbing on the catalyst, Ar illustrates the undelayed gas phase response upon a step change. Step changes performed over SiC and Al_2O_3 have shown that SiC and Al_2O_3 do not influence the shape of the response curves and that adsorption of the reactants and products on Al_2O_3 can be disregarded. Calculations have shown that the steady-state mass and heat transfer criteria are fulfilled and that the unsteady-state mass and heat transfer do not influence the shape of the response curves (16, 17).

The amount of a certain component produced during an experiment was calculated by integrating the area under the production curve. The amount of a certain component adsorbed during an experiment was calculated by subtracting the amount of the component that left the reactor from the amount that was fed. The maximum error in the determination of these amounts is estimated to be about 15%.

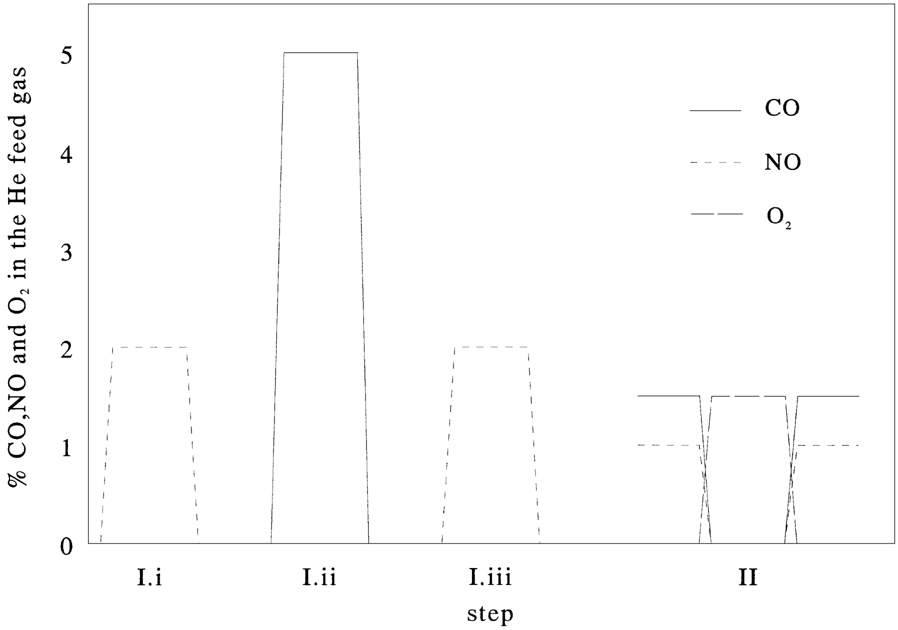

FIG. 1. Visualization of the concentration step sequences in series (I) and (II) performed over the Cu and Cu–Cr catalyst.

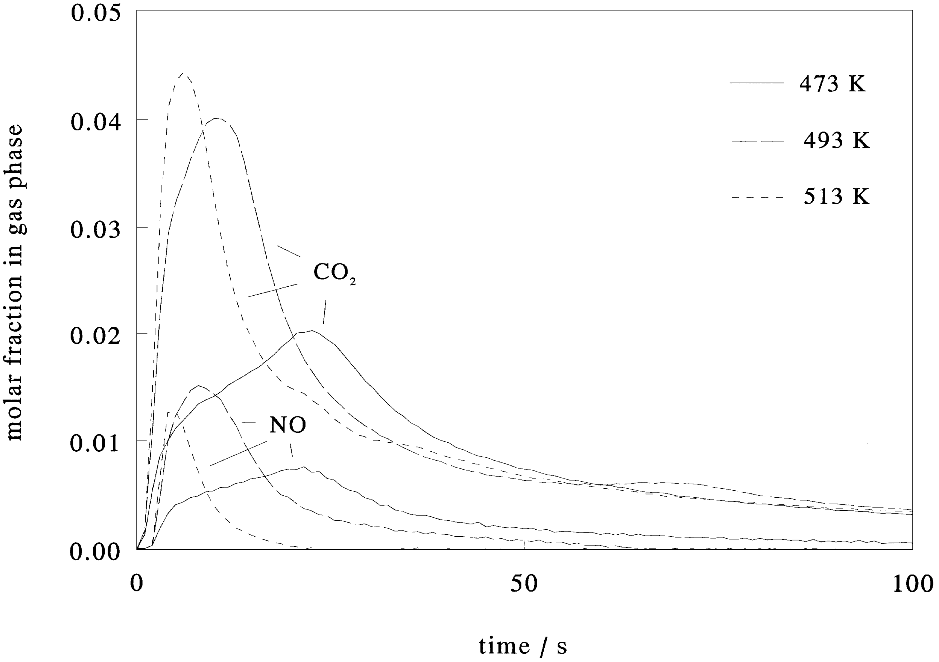

FIG. 2. Response curves of CO_2 and NO after a step change from He to 5%CO/He over Cu/Al_2O_3 preoxidized by NO, step (I.ii).

RESULTS

Cu Catalyst

Series (I). Figure 2 gives the CO_2 and NO responses after a step change from He to 5%CO/He over Cu preoxidized by NO, step (I.ii). Figure 2 shows that directly after the step change CO_2 is formed. The CO_2 signal increases, passes through a maximum, and slowly declines; the signal seems to be a convolution of two peaks. When the temperature increases from 473 to 513 K, the position of the maximum shifts to shorter times, the height of the maximum increases, and the width of the maximum decreases. The total amount of CO_2 produced is found to increase from 473 to 493 K (Table 1) and then decreases at 513 K. This amount is expected to increase with temperature (15, 16), but can be explained by the more reduced state of the catalyst at 513 K due to the preceding experiments at 473 and 493 K. The CO response is about complementary to the CO_2 response, except for a small amount of CO that is retained at the catalyst surface. This amount desorbs when the gas phase is switched back to He, corresponding with previous studies (13–16). With a short delay, NO desorbs from the catalyst during the reduction, but N_2 and N_2O are not observed. The shape of the NO and CO_2 response curve are highly correlated, implying that CO_2 production and NO desorption take place simultaneously. Similar to the CO_2 responses, the NO response at 473 K seems to be a convolution of two peaks. The amount of NO that desorbs is about equal at 473 and 493 K, but is much smaller at 513 K. When the NO response has reached zero a second maximum is formed in the CO_2 response curve of 493 K.

The subsequent oxidation by NO, step (I.iii), is displayed in Fig. 3. A sharp N_2 evolution peak is observed near the breakthrough front of NO. At all temperatures a slowly declining N_2O production is observed. At 513 K it is preceded by a small maximum in the N_2O production. The amount of N_2 produced increases with temperature, whereas the amount of N_2O formed remains constant (Table 1). The N_2O production, however, still continued at the moment that the total amount of N_2O formed was calculated. It is found that NO adsorbs on the catalyst during the passage of NO/Ar/He, but due to the slow adsorption rate a reliable value for the amount is impossible to derive. Some of the adsorbed NO desorbs when the gas phase is switched back to He, as was indicated by comparison of the NO response with the Ar response.

TABLE 1

Amount of CO_2 Produced, NO Desorbed, N_2 Produced, and N_2O Produced in Steps (I.ii) and (I.iii) over Cu/Al_2O_3, Expressed in Moles per Mole of Cu

	Step (I.ii) He → 5%CO/He		Step (I.iii) He → 2%NO/He	
T (K)	CO_2 produced	NO desorbed	N_2 produced	N_2O produced
473	0.34	0.07	0.005	0.03
493	0.42	0.06	0.008	0.03
513	0.37	0.02	0.009	0.03

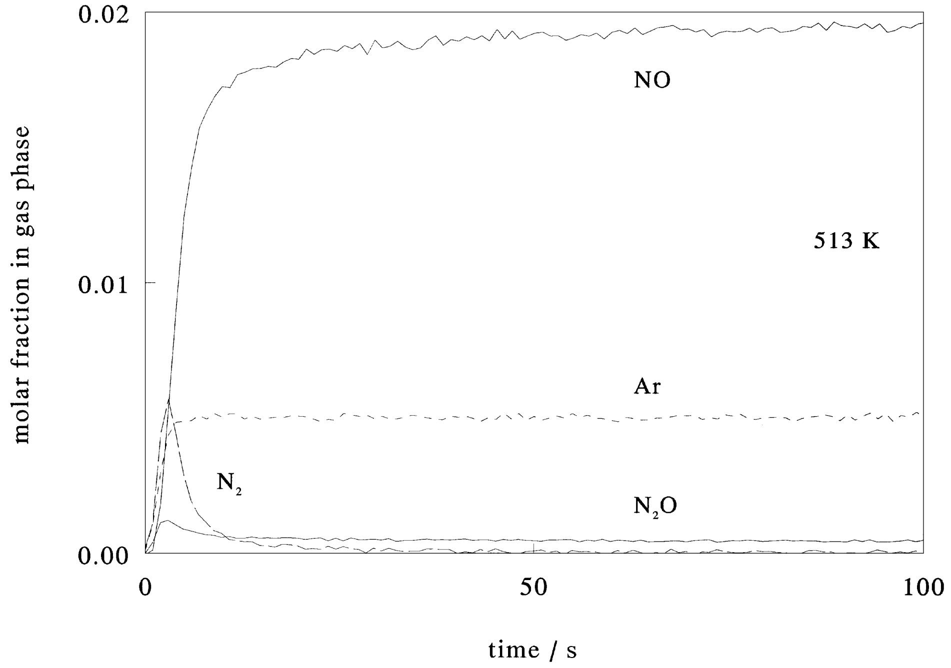

FIG. 3. Response curves of NO, N_2, N_2O, and Ar after a step change from He to 2%NO/0.5%Ar/He over Cu/Al_2O_3 prereduced by CO, step (I.iii).

Series (II). The response curves obtained after a step change from ^{13}CO/NO/He to O_2/He are given in Fig. 4. Figure 4 shows that the steady-state N_2 and N_2O productions are very low under the applied conditions and that the selectivity to N_2 formation is about 70%. Directly after the step change ^{13}CO and $^{13}CO_2$ desorb from the catalyst. The amount of ^{13}CO desorbed appears to decrease slightly when the temperature increases (Table 2), whereas the value for $^{13}CO_2$ remains constant. The O_2 breakthrough only appears after the decrease of the $^{13}CO_2$ signal. The O_2 delay time

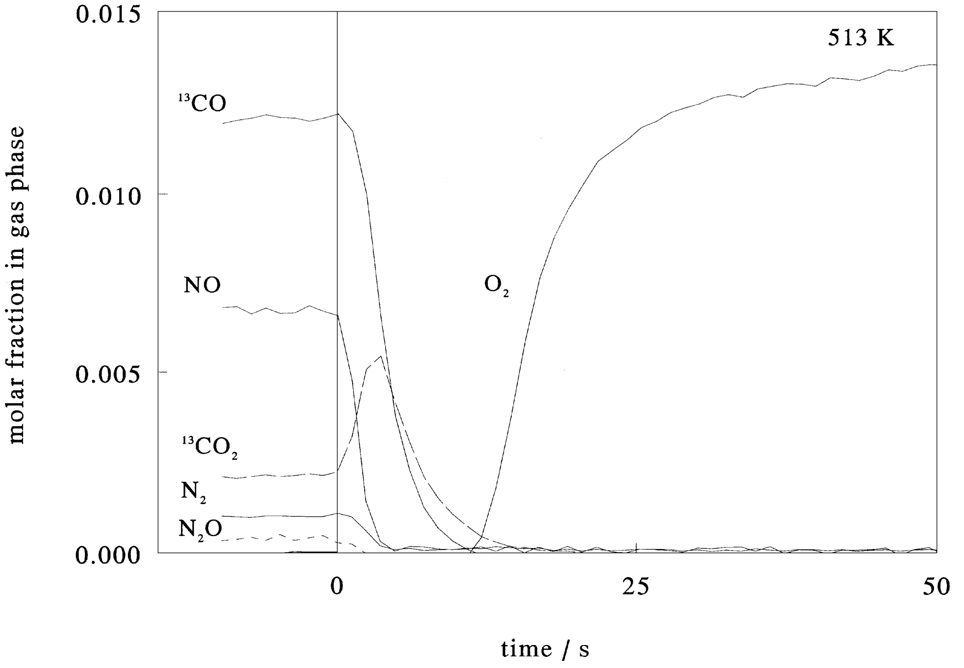

FIG. 4. Response curves of $^{13}CO_2$, ^{13}CO, NO, N_2, N_2O, and O_2 after a step change from 1.5%^{13}CO/1%NO/He to 1.5%O_2/He over Cu/Al_2O_3, series (II).

TABLE 2

Amount of $^{13}CO_2$ Produced, ^{13}CO Desorbed, O Consumed from the O_2/He Feed, and O Abstracted from the Catalyst in Series (II) over Cu/Al_2O_3, Expressed in Moles per Mole of Cu

	1%NO/1.5%^{13}CO/He → 1.5%O_2/He			1.5%O_2/He → 1%NO/1.5%^{13}CO/He
T (K)	$^{13}CO_2$ produced	^{13}CO desorbed	O consumed	O abstracted
473	0.008	0.013	0.09	0.09
493	0.009	0.012	0.11	0.12
513	0.008	0.009	0.14	0.16

increases with temperature which means that the oxygen consumption from the O_2/He feed (used for catalyst oxidation and possibly for CO_2 production) increases with temperature (Table 2).

After switching the gas phase back to ^{13}CO/NO/He, instantaneously $^{13}CO_2$ is produced (Fig. 5). The $^{13}CO_2$ production gives a broad maximum before it declines to the steady-state production. This maximum becomes lower and narrower at decreasing temperatures. ^{13}CO is observed only after the maximum in the $^{13}CO_2$ response has been reached. Some ^{13}CO is retained at the catalyst. The NO response displays a small delay, after which it rapidly rises and then gradually decreases to the steady-state value. At the maximum of the NO signal, the total nitrogen fraction in the outlet ΣN, i.e., $NO + 2N_2 + 2N_2O$, exceeds the fraction NO in the feed. N_2O production starts directly after the step change and slightly increases in time. A small peak in the N_2 response is found after which it slowly increases to the steady-state value. The steady-state values that are eventually reached are displayed at the left side of Fig. 4. The amount of oxygen abstracted from the catalyst during the reduction (i.e., the oxygen evolving as CO_2 minus the oxygen consumption from NO and calculated as $CO_2-2N_2-N_2O$) (Table 2) is about equal to the amount that was consumed from the gas phase after the step from ^{13}CO/NO/He to O_2/He.

Cu–Cr Catalyst

Series (I). Figure 6 displays the step change from He to 5%^{13}CO/He, step (I.ii), over Cu–Cr preoxidized by NO. As shown, the $^{13}CO_2$ production instantaneously reaches a maximum and then slowly decreases. Again the CO_2 signal seems to be a convolution of two peaks; it clearly declines in two stages at 493 K. The $^{13}CO_2$ production is smaller at 513 K than at 493 K (Table 3), deviating from earlier experiments (13, 16). Similar to the Cu catalyst, it can be explained by the more reduced state of the catalyst at 513 K due to the preceding experiments. The fraction ^{13}CO in the outlet is initially zero, but after a while it starts to increase. The sum of the ^{13}CO and $^{13}CO_2$ response is smaller than the fraction ^{13}CO in the feed gas, which means that ^{13}CO is retained at the catalyst. As found previously (14, 16), part of the retained CO desorbs when the gas phase is switched to He. NO desorbs, but only after the maximum in the $^{13}CO_2$ production. N_2 and N_2O production are not observed. The

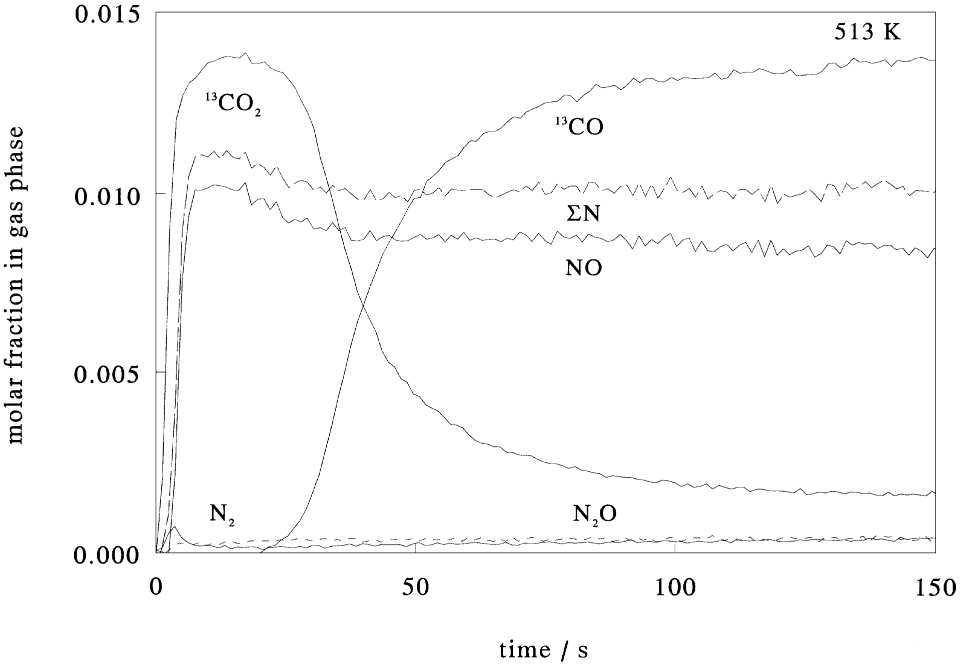

FIG. 5. Response curves of $^{13}CO_2$, ^{13}CO, NO, N_2, N_2O, and ΣN (i.e., $NO + 2N_2 + 2N_2O$) after a step change from 1.5%O_2/He to 1.5%^{13}CO/1%NO/He over Cu/Al_2O_3, series (II).

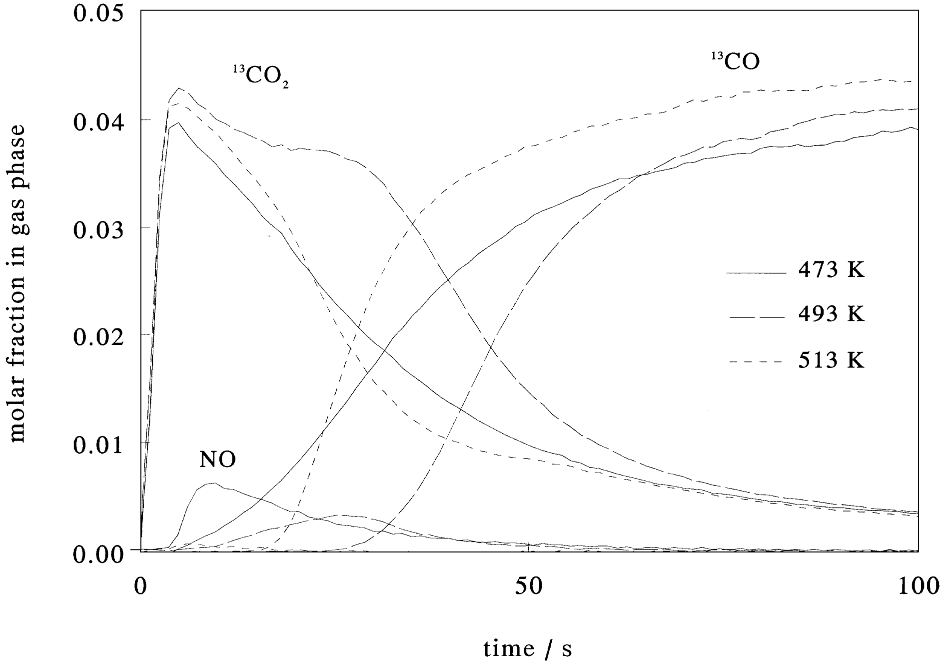

FIG. 6. Response curves of $^{13}CO_2$, ^{13}CO, and NO after a step change from He to 5%^{13}CO/He over Cu–Cr/Al_2O_3 preoxidized by NO, step (I.ii).

amount of NO desorbing is about equal at 473 and 493 K, but is almost zero at 513 K.

Reoxidizing reduced Cu–Cr by NO, step (I.iii), results in N_2 and N_2O production and a delayed $^{13}CO_2$ desorption (Fig. 7). A maximum is observed in the broad N_2 response. When the N_2 production starts to decrease, the NO breaks through. Around this point also N_2O production may start. The ΣN response curve, i.e., $NO + 2N_2 + 2N_2O$, shows that the amount of nitrogen in the exit is smaller than the amount of nitrogen fed as NO, indicating that NO is retained at the catalyst. The amount of NO retained is about 0.07 mol NO per mol Cu at 513 K. Reliable values at the other temperatures could not be obtained, as the NO retention takes place very slowly. Part of the retained NO desorbs when the gas phase is switched back to He. The amounts of N_2 and N_2O produced and CO_2 desorbed are included in Table 3. Table 3 shows that the selectivity for N_2 production increases with temperature. Comparison of Fig. 7 and Table 3 with Fig. 3 and Table 1 clearly demonstrates that reduced Cu–Cr is much easier oxidized by NO than reduced Cu.

Series (II). The steady-state activity of Cu–Cr in the NO reduction by CO (Figs. 8a and 8b) is much higher than that of Cu. However, both catalysts give similar responses after the step change from ^{13}CO/NO/He to O_2/He : ^{13}CO desorption, $^{13}CO_2$ production, and oxygen consumption. Also over Cu–Cr the $^{13}CO_2$ production initially increases, at 473 K more than at 513 K. At both temperatures, the $^{13}CO_2$ response seems to display two convoluted processes and the ^{13}CO response a shoulder. When oxygen breaks through the fractions ^{13}CO and $^{13}CO_2$ rapidly drop to zero. Table 4 gives the amounts of $^{13}CO_2$ produced, ^{13}CO desorbed, NO

TABLE 3

Amount of $^{13}CO_2$ Produced, ^{13}CO Retained, NO Desorbed, N_2 Produced, and N_2O Produced in Step (I.ii) and (I.iii) over Cu–Cr/Al_2O_3, Expressed in Moles per Mole of Cu

	Step (I.ii) He → 5%^{13}CO/He			Step (I.iii) He → 2%NO/He		
T (K)	$^{13}CO_2$ produced	^{13}CO retained	NO desorbed	$^{13}CO_2$ produced	N_2 produced	N_2O produced
473	0.42	0.10	0.03	0.03	0.02	0.12
493	0.54	0.13	0.02	0.04	0.05	0.10
513	0.39	0.09	0.002	0.02	0.05	0.07

TABLE 4

Amount of $^{13}CO_2$ Produced, ^{13}CO Desorbed, NO Desorbed, O Consumed from the O_2/He Feed, ^{13}CO Retained and O Abstracted from the Catalyst in Series (II) over Cu–Cr/Al_2O_3, Expressed in Moles per Mole of Cu

	1%NO/1.5%^{13}CO/He → 1.5%O_2/He				1.5%O_2/He → 1%NO/1.5%^{13}CO/He	
T (K)	$^{13}CO_2$ produced	^{13}CO desorbed	NO desorbed	O consumed	^{13}CO retained	O abstracted
473	0.039	0.029	0.006	0.22	0.074	0.17
493	0.045	0.024	0.004	0.22	0.077	0.19
513	0.039	0.015	0.001	0.28	0.074	0.21

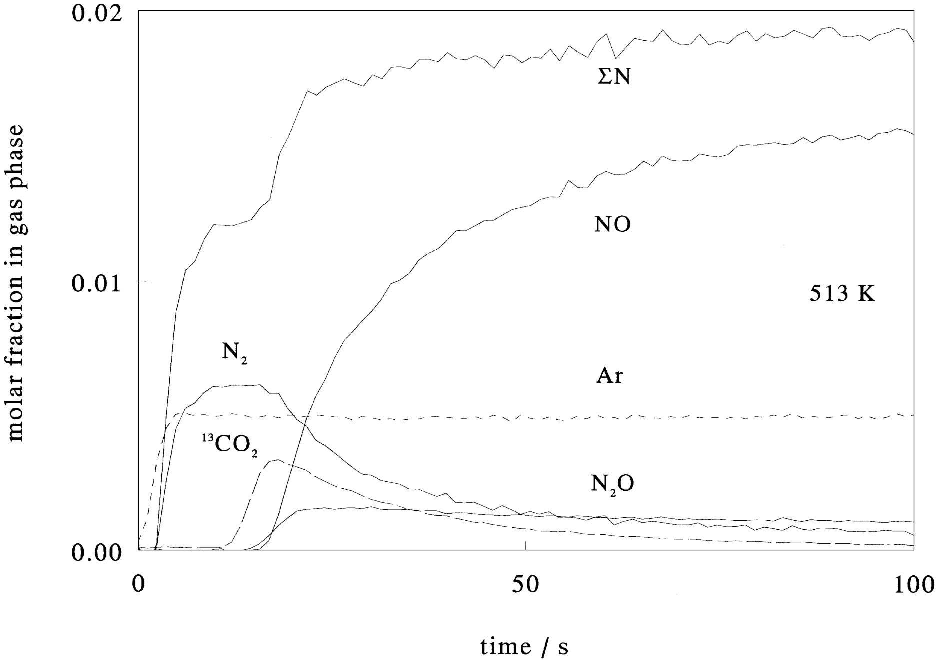

FIG. 7. Response curves of $^{13}CO_2$, NO, N_2, N_2O, ΣN (i.e., $NO + 2N_2 + 2N_2O$), and Ar after a step change from He to 2%NO/0.5%Ar/He over Cu–Cr/Al_2O_3 prereduced by ^{13}CO, step (I.iii).

desorbed, and oxygen consumed from the O_2/He feed (used for catalyst oxidation and possibly or CO_2 production).

In the reverse step to ^{13}CO/NO/He (Figs. 9a and 9b), the $^{13}CO_2$ production starts instantaneously and is initially much higher than the steady-state production. The $^{13}CO_2$ production starts to decrease towards its steady-state level after about 50 s at 473 K and 100 s at 513 K and at the same times the ^{13}CO signals appear. The sum of the ^{13}CO and $^{13}CO_2$ signal indicates that ^{13}CO is retained on the catalyst during the step (Table 4). The appearance of NO is delayed, but as soon as NO appears it rapidly rises and then slowly declines to the steady state. The NO response exhibited the same behavior over Cu, but less pronounced. The total fraction nitrogen in the outlet ΣN, i.e., $NO + 2N_2 + 2N_2O$, again temporarily reaches a value above the fraction NO in the feed. The N_2 response is also similar to that over Cu; it displays a local maximum and then a local minimum after which a period of monotonous increase is observed. The minimum in the N_2 curve is located at the same position as the maximum in NO. The maximum of the N_2 peak lies in the breakthrough front of NO. The N_2O production gradually increases after the step change at 473 K but displays a maximum at 493 and 513 K. The amount of N_2O produced at the steady-state level decreases when the temperature increases above 473 K and is close to zero at 513 K. The amount of oxygen abstracted from the catalyst after the step change (i.e., the oxygen evolving as CO_2 minus the oxygen consumption from NO and calculated as CO_2–$2N_2$–N_2O) is included in Table 4 and is about equal to the amount consumed after the preceding step from ^{13}CO/NO/He to O_2/He. The steady-state values ultimately obtained can be found in the left side of Figs. 8a and 8b.

DISCUSSION

Series (I)

In previous studies a similar series of experiments as series (I) was performed over the Cu catalyst but O_2 instead of NO was used (13–16). In those studies the reduction of fully oxidized Cu (i.e., Cu treated with 100% O_2 for 1 h at 773 K) was found to take place in two steps. In the first step CO reacted from the gas phase with adsorbed oxygen to CO_2. The second step involved reaction of reversibly adsorbed CO on Cu^{1+} with oxygen that has migrated from the bulk to the surface of the catalyst. Modeling of the response curves (15, 16) has revealed the reaction rate constants, activation energies and the Cu dispersion (viz. 14%). The same steps were found to take place over partly oxidized Cu (i.e., Cu treated with 2.5% O_2 for 5 min at 473 K); however, due to the lower oxidation state of the catalyst both steps occurred simultaneously and could hardly be distinguished anymore (16). The shape of the response curves after step (I.ii) (Fig. 2) reveal indeed a convoluted process for the CO_2 formation after oxidation by NO. In the presence of NO, however, the diffusion/reaction of subsurface oxygen is hindered by adsorbed NO, as the CO_2 production maximum is retarded compared to the NO maximum and a small peak in the CO_2 response at 473 K appears as soon as the NO concentration reaches zero.

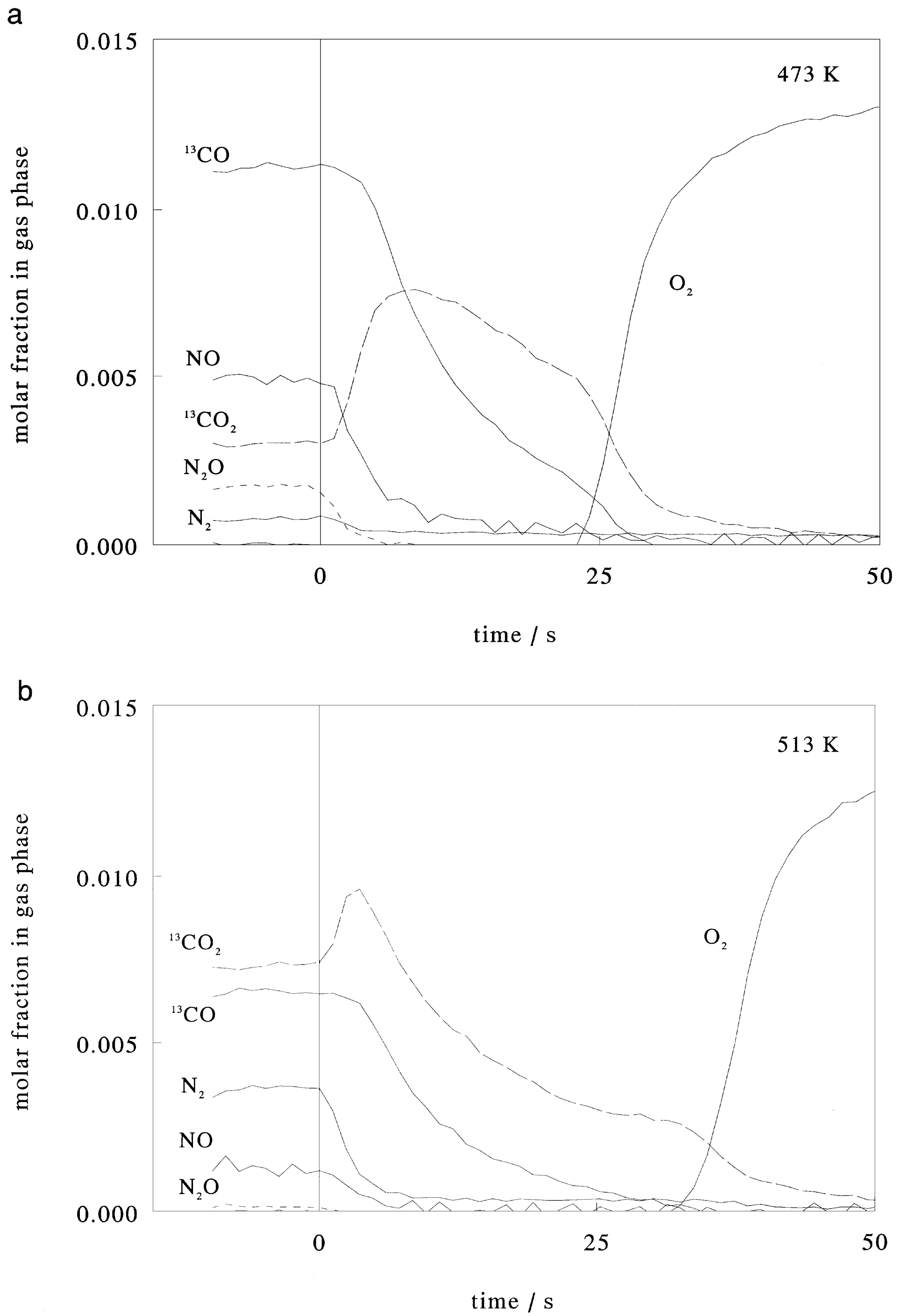

FIG. 8. Response curves of $^{13}CO_2$, ^{13}CO, NO, N_2, N_2O, and O_2 after a step change from 1.5% ^{13}CO/1% NO/He to 1.5% O_2/He over Cu–Cr/Al_2O_3, series (II). (a) 473 K; (b) 513 K.

The reduction of the Cu–Cr catalyst, either fully or partially oxidized with O_2, was found to proceed via reaction of adsorbed CO with adsorbed oxygen at temperatures below about 453 K (13, 16). At higher temperatures the reaction of CO from the gas phase dominates. Subsurface oxygen again forms an additional source of oxygen. CO is found to be retained at Cu and Cr surface sites as a carbonyl and a carbonate species, respectively. Retained CO easily desorbs from the Cu sites in He, whereas oxygen is needed to convert the carbonate species at the Cr sites. The amounts of CO and CO_2 evolving indicated that the Cu and Cr dispersion of the catalyst is 15%. The shape of the $^{13}CO_2$ and ^{13}CO

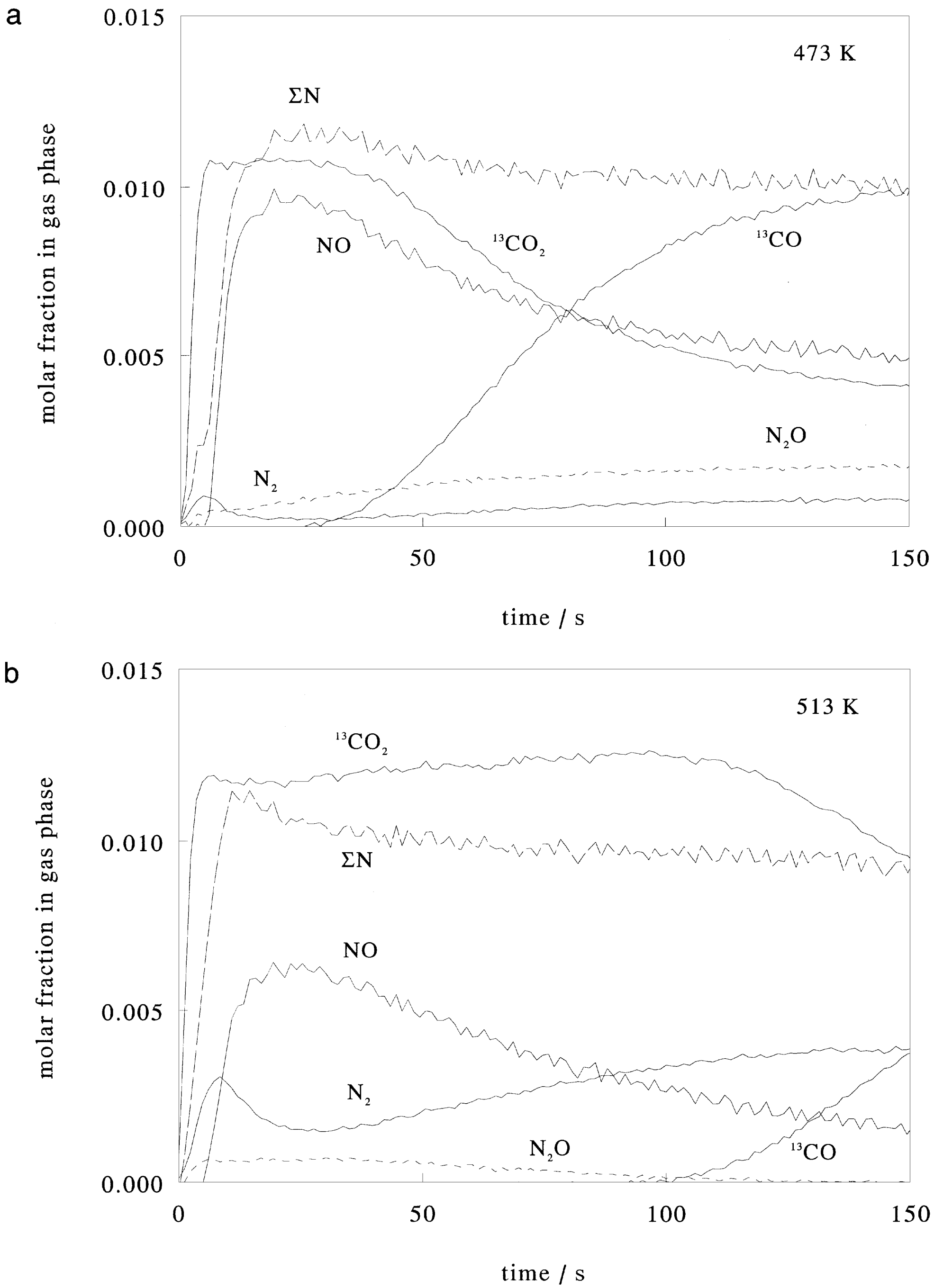

FIG. 9. Response curves of $^{13}CO_2$, ^{13}CO, NO, N_2, N_2O, and ΣN (i.e., $NO + 2N_2 + 2N_2O$) after a step change from 1.5% O_2/He to 1.5% ^{13}CO/1% NO/He over Cu–Cr/Al_2O_3, series (II). (a) 473 K; (b) 513 K.

responses in steps (I.ii) and (I.iii) (Figs. 6 and 7) indicate that the same mechanism applies in the present study. The amount of ^{13}CO retained and $^{13}CO_2$ produced, however, is smaller during oxidation by NO than during oxidation by O_2 (16). The total amount of carbonate and carbonyl groups must be the same in both cases, indicating that NO has converted only part of the carbonate species. In other words, 2% NO/He does not oxidize the catalyst as good as 2.5% O_2/He, which agrees with results showing that reduction of NO in a $NO + CO + O_2$ mixture only occurs when all O_2 is consumed (2, 9, 10).

Two types of NO are found to be adsorbed on the catalysts. The first type desorbs when the gas phase is switched from NO to He, and the second type when CO is led over the catalyst. The latter evolution of NO is related to the CO_2 production. Both types of adsorbed NO must be associated with Cu, since hardly any NO adsorbs on alumina (4, 12) and only a very small peak of $Cr^{2+/3+}$–NO (or Cu^{1+}–NO) was identified in a FT-IR study on the Cu–Cr catalyst (12). In previous work (4, 12, 18) a nitrosyl (Cu^{2+}–NO) complex and nitrite/nitrate complexes were identified on Cu and Cu–Cr catalysts. Bijsterbosch (12) performed a FT-IR study over the same catalysts as used in the present study and observed that Cu^{2+}–NO is held less strongly than nitrite/nitrate complexes. This corresponds very well with the results of Hierl *et al.* (4) who combined IR and temperature-programmed desorption (TPD) for alumina-supported CuO. Hierl *et al.* observed that Cu^{2+}–NO decomposes under the evolution of NO between 350 and 450 K, while the nitrite complexes decompose under formation of NO and nitrate complexes between 450 and 600 K. The nitrate complexes finally decompose between 600 and 750 K with the generation of both NO and O_2. Also Shimokawabe *et al.* (18) measured NO desorption combined with O_2 formation in the temperature range 648–753 K in similar TPD experiments as Hierl *et al.* on unsupported and silica-supported CuO. Based on the above-mentioned studies, the NO desorption observed upon a step change from NO/He to He is attributed to NO desorption from Cu^{2+} sites. The NO desorption observed during reduction by CO is ascribed to CO-induced conversion of nitrite/nitrate complexes resulting in CO_2 and NO formation. Since the latter NO desorption does not start instantaneously after the step change and the CO_2 production and NO desorption increase in time, the conversion of nitrite/nitrate groups presumably occurs via adsorbed CO. The absence of N_2 and N_2O formation indicates that desorbed NO does not encounter any reduced sites on which it can dissociate.

For the Cu catalyst, the total amount of NO evolving in step (I.ii) is about 0.06 mol per mol Cu at 473 and 493 K. About 0.07 mol CO per mol Cu was found to be adsorbed at 473 K (16). The Cu dispersion of the catalyst is about 14% (16), so almost 50% of the metal atoms at the catalyst surface were covered with nitrite/nitrate groups in NO/He and 50% with CO in CO/He (Fig. 10a). On the Cu–Cr catalyst almost 20% of the Cu sites is covered with nitrite/nitrate groups at 473 and 493 K (Fig. 10b) using the Cu dispersion of 15% (16). All Cu and Cr sites are covered with, respectively, carbonyl and carbonate groups in CO/He (16). Over both catalysts much less NO desorption was observed during the reduction by CO at 513 K than at 473 and 493 K. This must mean that all adsorbed NO has desorbed in He (i.e., about 0.07 mol per mol Cu for the Cu–Cr catalyst, which corresponds with 50% of the surface Cu sites) and thus indicates that the nitrite/nitrate complexes are less stable at this temperature.

The amounts of N_2 and N_2O formed during the oxidation by NO, step (I.iii) (Figs. 3 and 7), are small, demonstrating that the catalyst is only partly oxidized by NO and thus that the catalyst is only able to dissociate NO when it is in a reduced state. The N_2O production lasts much longer than the N_2 production. Based on this, Hierl *et al.* (4) concluded that NO dissociation does not take place anymore and that N_2O is formed via a dinitrosyl complex, although they did not find any evidence for the existence of this complex. IR studies (12, 19) indicated that a decrease of the Cu^{1+}–NO band is accompanied by appearance of the N_2O band, implying that N_2O is produced via NO dissociation on Cu^{1+} sites followed by reaction of NO with nitrogen atoms on the surface. Due to oxidation of the catalyst by NO, the amount of Cu^{1+} sites and thus the amount of nitrogen atoms at the surface decreases. Consequently, N_2 is not produced anymore and only a small amount of N_2O can be formed. It can even be envisaged that some of the Cu^{1+} sites are formed via diffusion of oxygen from the surface to the subsurface of the catalyst explaining the prolonged N_2O formation. In this case, the slowly decreasing N_2O formation rate would be the result of the decreasing diffusion rate.

Series (II)

Changing the gas phase from ^{13}CO/NO/He to O_2/He over the Cu catalyst results in ^{13}CO and $^{13}CO_2$ desorption and O_2 consumption (Fig. 4), indicating that the catalyst is oxidized. The $^{13}CO_2$ that evolves is attributed mainly to reaction of adsorbed ^{13}CO, since hardly any carbonate species are formed on the Cu catalyst (11, 12). The total amount of $^{13}CO + ^{13}CO_2$ adsorbed in the ^{13}CO/NO/He mixture is comparable to that in a $CO + O_2$ mixture (Table 2, Fig. 10a) (16). Nitrogenous species are not released; thus nitrosyl and nitrite/nitrate groups are not stable at the catalyst surface under the applied conditions.

The ^{13}CO desorption and $^{13}CO_2$ production observed during the step change from ^{13}CO/NO/He to O_2/He over the Cu–Cr catalyst (Fig. 8) are attributed, respectively, to ^{13}CO desorption from Cu^{1+} sites and to the earlier identified carbonate oxidation (13, 14, 16). Part of the $^{13}CO_2$, however, may originate from ^{13}CO (adsorbed or gas phase) that has reacted with the introduced oxygen. Based on a Cu and a Cr dispersion both of 15% (16), at maximum 25% of the Cr sites are covered by carbonates and at least 17% of the Cu sites are covered by CO in the CO/NO/He mixture (Table 4, Fig. 10b). The amounts are comparable to those in a mixture of CO/O_2/He (14, 16). Only about 5% of the Cu sites is covered by NO in CO/NO/He.

On both catalysts the reversed step from O_2/He to ^{13}CO/NO/He (Figs. 5 and 9) results in a broad maximum in the $^{13}CO_2$ production before it reaches the steady state. NO adsorbs on the catalyst after the step change, as follows from the delayed breakthrough of NO and the small amounts of N_2 and N_2O formed. As the catalyst is in an oxidized state after the oxidation by O_2, probably Cu^{2+}–NO

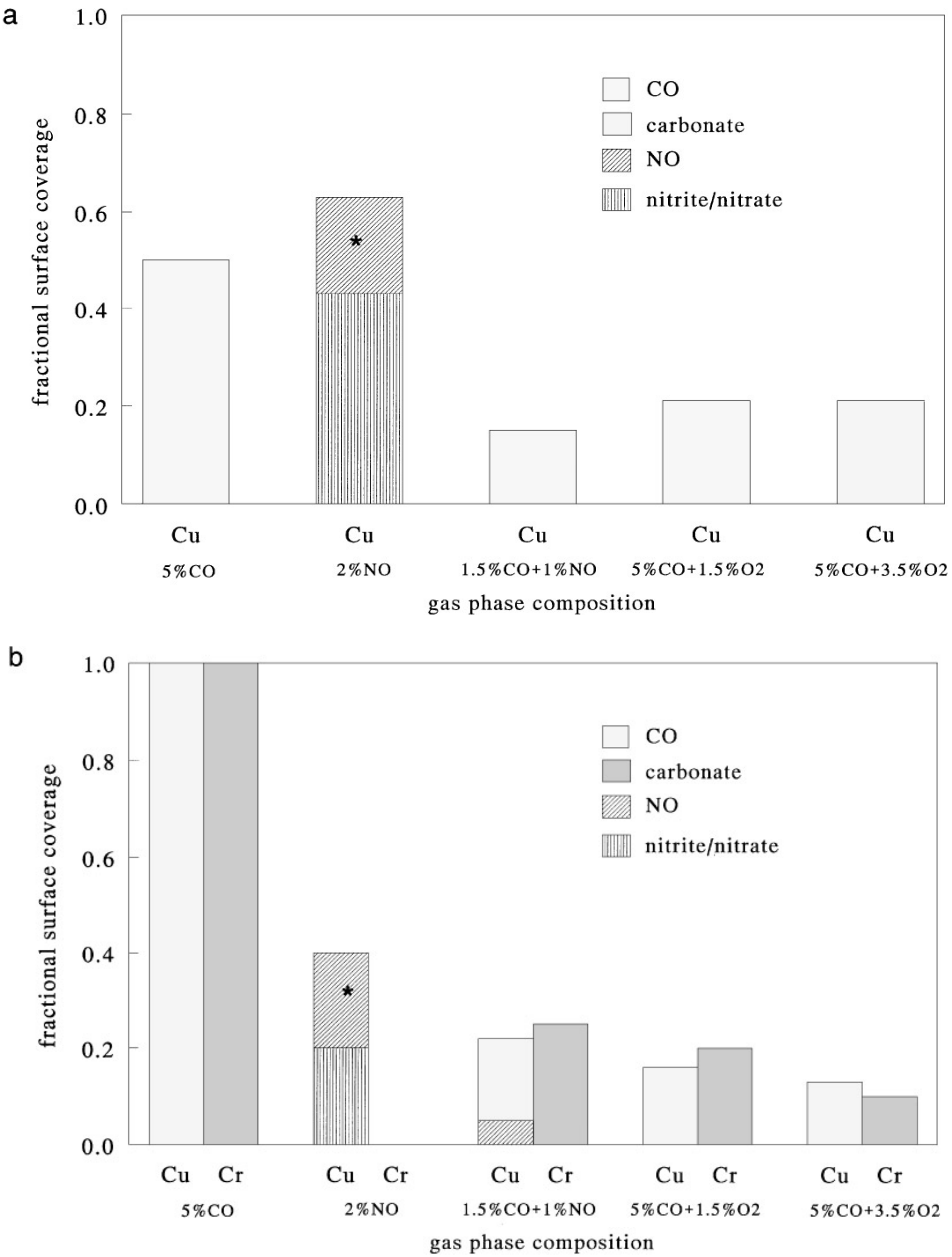

FIG. 10. Composition of the catalyst surface in several gas phases at 473 K (*roughly estimated value). (a) Cu/Al_2O_3, based on the Cu dispersion of 14%. (b) Cu–Cr/Al_2O_3, based on the Cu and the Cr dispersion of 15%.

complexes and nitrite/nitrate groups complexes are formed (4, 12). Seconds after the step change, however, the total amount of nitrogen in the outlet ΣN, i.e., $NO + 2N_2 + 2N_2O$, temporarily exceeds the amount of nitrogen in the feed, indicating that retained NO is released. The N_2 response after the step change of O_2/He to ^{13}CO/NO/He consists of a N_2 formation peak and a gradually increasing N_2 production. The peak in the N_2 production appears with some delay after the CO_2 production and indicates that NO dissociation initially takes place, but that it becomes restricted thereafter. The maximum in N_2 formation arises concurrently with the NO breakthrough and the increase of the total amount of nitrogen (ΣN), suggesting that initially the adsorbed NO can oxidize the catalyst, but that subsurface oxygen takes over as the oxidizing agent as soon as this adsorbed NO is converted. Only when the catalyst becomes more and more reduced, NO conversion increases and CO_2 production due to catalyst reduction decreases, resulting in an increase in N_2 and N_2O production. This demonstrates that NO reduction is only possible when the catalyst is in a reduced state and that NO reduction is not only limited by oxygen in the gas phase as found previously (2), but also by oxygen in the catalyst itself.

Overall

The N_2 formation is reported to proceed via NO adsorption, dissociation, and recombination of the nitrogen atoms (4, 6), but reaction of originally formed N_2O to N_2 can also explain N_2 formation (20, 21). A kinetic study indicated that the steady-state NO reduction by CO over Cu–Cr proceeds according to both reaction steps (9, 10). The importance of the latter mechanism in the NO reduction over Rh was demonstrated in a kinetic analysis of Cho (22, 23) which showed that reaction between N_2O and CO leading to N_2 can be two or three orders of magnitude faster as an intermediate reaction in a NO + CO-containing gas phase than the isolated $N_2O + CO$ reaction. It can be explained by the combined effect of increased N_2O surface coverage and the decreased inhibition effect on the catalytic surface in the overall NO + CO system compared with that in the isolated $N_2O + CO$ system. The former effect is due to the contribution of surface reactions leading to the production of adsorbed N_2O, while the latter effect is due to the increased repulsive interactions among adsorbed CO and nitrogen species creating more vacant catalytic sites available for N_2O adsorption and dissociation.

Corresponding with previous research (2, 10), the steady-state selectivity of the NO reduction to N_2 is found to increase with temperature (Figs. 4 and 8). It can be explained by the control of the NO reduction by NO dissociation (2, 3, 12, 24). At low temperatures the NO dissociation rate is low and the concentration of nitrogen atoms on the surface is low and that of NO high. The chance of N_2O formation is therefore relatively large. At higher temperatures the concentration of nitrogen atoms adsorbed at the catalyst is higher and the amount of N_2 formed increases. Furthermore, the conversion rate of N_2O to N_2 will increase with temperature. Additionally, it has been found that the activation energy of N_2 formation via recombination of two adsorbed nitrogen atoms is higher than the activation energy of N_2O formation via reaction of NO with adsorbed nitrogen (2). These above-mentioned effects also account for the increase of selectivity in N_2 production with temperature observed when introducing NO over a catalyst reduced by CO, step (I.iii) (Figs. 3 and 7). In the present study the selectivity for N_2 formation also changes in time. For example, after the step change from He to NO/He over Cu–Cr reduced by CO, N_2 is only observed when the N_2 production declines and the NO breaks through (Fig. 6). Thus, initially the N_2O is converted to N_2 but the rate of this reaction decreases when the catalyst is reoxidized.

The changing N_2 production rate as a function of time suggests that the effectiveness of Cu-based catalysts in NO reduction will be influenced by oscillations in the exhaust gas. Additionally, the N_2O production under dynamic conditions may differ from that at steady state. For example, after the step change at 513 K N_2O is produced, whereas it is about zero at the steady state. After the step change at 473 K, however, the N_2O production is initially smaller than that at the steady state.

In summary for both catalysts, the following reaction steps in the NO reduction were identified:

$NO + Cu^{2+} \leftrightarrow NO\text{–}Cu^{2+}$	(a) reversible NO adsorption on Cu^{2+}
$NO + O\otimes \rightarrow ONO\otimes$	(b) nitrite/nitrate formation
$CO\otimes + ONO\otimes \rightarrow CO_2 + NO + 2\otimes$	(c) nitrite/nitrate conversion
$NO + 2\otimes \rightarrow N\otimes + O\otimes$	(d) NO adsorption and dissociation
$NO + N\otimes \rightarrow N_2O + \otimes$	(e) N_2O formation
$N\otimes + N\otimes \rightarrow N_2 + 2\otimes$	(f) N_2 formation
$N_2O + \otimes \rightarrow N_2 + O\otimes$	(g) N_2 formation via N_2O

Here, ⊗ generally represents Cu^{1+}. In the steady-state reduction of NO with CO only steps (d)–(g) will take place, provided that the catalyst is slightly reduced and O_2 is absent. However, in case the catalyst is oxidized or O_2 is present steps (a)–(c) become relevant. The reaction steps in CO oxidation are given in detail elsewhere (13–16).

CONCLUSIONS

The present study demonstrates via the interaction of NO, CO, and O_2 with alumina-supported Cu and Cu–Cr catalysts that step–response experiments employing labeled molecules can provide detailed information on processes occurring at catalytic surfaces and on concentrations of surface species.

NO is adsorbed on the oxidized catalysts as Cu^{2+}–NO and as nitrite/nitrate complexes. NO readily desorbs from Cu^{2+} in He, whereas nitrite/nitrate complexes decompose only in a reducing atmosphere. At 473 and 493 K almost 50 and 13% of the Cu surface sites in, respectively, the Cu and the Cu–Cr catalyst are covered by the nitrite/nitrate complexes; at 513 K this amount is much less.

In a net reducing mixture of CO/NO (1.5/1) about 15% of the Cu sites in the Cu catalysts are covered by CO, NO is not present under the applied conditions. Using the same feed mixture and conditions for the Cu–Cr catalyst demonstrates that about 5% of the Cu sites are covered by NO, about 17% of the Cu sites are covered by CO, while about 25% of the Cr sites are covered by carbonates. Comparison with previous studies has shown that the CO oxidation mechanism and the CO_x coverage are independent of the type of oxidizing component, i.e., oxygen or NO.

The catalysts are only able to convert NO when they are in a reduced state; in other words conversion of NO is not only limited by gas phase O_2 but also by subsurface oxygen. However, directly after a feed composition over the oxidized catalysts has changed to CO/NO/He, a N_2 production peak is observed due to rapid reaction of NO adsorbing on oxidized sites.

As the Cu–Cr catalyst is much more active in the NO reduction by CO and gives less nitrite/nitrate groups in NO/He than the Cu catalyst, it is concluded that Cr assists in keeping the Cu in the Cu–Cr catalyst in a reduced state. No differences between the Cu and Cu–Cr catalyst could be observed in the reaction mechanism of the NO reduction.

The temporal N_2 and N_2O formation under dynamic conditions differs from steady-state conditions, indicating that reaction selectivity and conversion levels are influenced by oscillations in the feed.

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