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Adsorption and Reactivity of NO on Copper-on-Alumina Catalysts

II. Adsorbed Species and Competitive Pathways in the Reaction of NO with NH_3 and O_2

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The surface reactivity in NO conversion to N_2 in the presence or absence of ammonia and oxygen of a copper-on-alumina catalyst was studied by pulse and step-change transient catalytic experiments. In the absence of ammonia, chemisorption of NO on the copper sites of the catalyst is significant and the chemisorption is enhanced by the presence of oxygen. However, gaseous O_2 also promotes the formation of small, but not negligible, amounts of N_2 from NO when no reducing agent is present, probably through the formation of an intermediate copper–nitrite complex which further reacts with NO. In the presence of ammonia, chemisorption of NO still occurs but to a lesser extent. It is shown that the initial rate of NO depletion and N_2 formation in NO or O_2 concentration step-change experiments is higher than that observed in stationary conditions. These results indicate that the mechanism of NO conversion over copper-on-alumina in the presence of chemisorbed ammonia involves the preliminary oxidation of NO to a NO_2 or nitrite adspecies which then reacts with chemisorbed ammonia. The formation of N_2O is observed only when gaseous O_2 is present and it is suggested that N_2O derives from a parallel side reaction involving the decomposition of an ammonium nitrate surface intermediate. © 1995 Academic Press, Inc.

INTRODUCTION

The mechanism of surface transformation of NO on mixed oxide catalysts has been widely studied in the past, in particular with reference to the reaction of NO with NH_3 and O_2 on $V-TiO_2$ based catalysts (1,2 and references therein), but also using alternative catalysts such as Fe-Cr-oxides on alumina (3). Different hypotheses have been reported for the mechanism of reaction, including (i) the reaction between ammonium ion and adsorbed NO_2 derived from the reaction of NO with adsorbed O_2 (4), (ii) the reaction between ammonium ion and gaseous NO (5–7), (iii) the reaction between an amide species generated by dissociative chemisorption of ammonia and gaseous NO (8) and (iv) the reaction between coordinated ammonia and a species generated by spillover of NO on the support (9). Despite the extensive effort in the study of the reaction mechanism and the use of several physicochemical methods of investigation, conclusive evidence in favor of a specific mechanism of reaction has not been reported. It should be noted, however, that in all cases little attention was devoted to the possibility of multiple competitive pathways of reaction and to the role of adsorbed species formed during the catalytic reaction in determining the surface reactivity.

Few data are available for copper-based catalysts. Otto and Shelef (10) studied the reaction of NO and NH_3 in the absence of O_2 over unsupported CuO, concluding that the dissociative chemisorption of ammonia is the rate-controlling step and that the amide species formed reacts with NO forming exclusively N_2. A side reaction leading to N_2O is also present, but derives from the consecutive transformation of a surface complex containing two NO molecules. Hierl *et al.* (11) also agree that the formation of a dinitrosyl complex may be involved in N_2O formation, but the resulting Cu–(O) species may subsequently react with an NO molecule to form a surface nitrite complex which then can be transformed to a nitrate complex. The formation of dinitrosyl species has been extensively addressed with respect to the mechanism of NO decomposition over Cu-ZSM-5 catalysts (12, 13). It has been suggested, however, that the Cu–(O) species generated by decomposition of the dinitrosylic complex to give N_2O reacts with two further NO molecules forming a nitrosyl–nitrite copper complex which is the active species in the mechanism of NO decomposition to N_2 and O_2. In contrast, in their studies of the catalytic reduction of NO with ammonia in the absence of O_2 over Cu(II)–NaY Mizumoto *et al.* (14) concluded that N_2O derives from the reaction of NO with an ammonia–copper complex to give adsorbed N_2O and an ammonia–nitrite copper complex which, in turn, reacts with an ammonium ion to form N_2, thus reforming the starting ammonia-copper complex. Amine–copper complexes catalyze the reduction of NO by NH_3 also in aqueous solution, but Oates and Lunsford (15) have suggested that the mechanism is

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different from that reported for copper-zeolite since the presence of nitrite ions is not important.

In Part I of this work (16) we have also discussed the possible role of nitrite–nitrate species regarding the mechanism of reaction of NO with NH_3 and O_2 over copper-on-alumina, suggesting that they are responsible for the formation of by-product N_2O via the formation of an ammonium nitrate species, and the nitrate species also induce a self-poisoning of the surface reactivity of the catalyst. The presence of competitive pathways of transformation of NO to N_2 was also suggested, but not proven.

The aim of this work, therefore, was to analyze in more detail the mechanism of reaction of NO with NH_3 and O_2 over copper-on-alumina and in particular to investigate the possible presence of multiple pathways of reaction and the role of the presence of adsorbed species in determining the surface reactivity. For this purpose, pulse- and step-change transient catalytic studies were used as a tool to obtain information on the time-dependent modification of the surface reactivity when the concentration of one or more reactants (NO, NH_3, or O_2) is changed while maintaining the concentration of the others constant.

The reference sample used in this study was a copper-on-alumina catalyst containing 5 wt% copper (as CuO). As reported in Part I of this work (16), no crystalline CuO is detected in this sample and characterization data, in agreement with literature data, indicate complete saturation by copper ions of the defect sites of the spinel-type surface structure of γ-Al_2O_3, forming a surface $CuAl_2O_4$ spinel-type compound.

EXPERIMENTAL

Copper-on-alumina was prepared by an incipient wet impregnation method using an aqueous copper acetate solution as described in Part I of this study (16). The final copper content was 5 wt% (expressed as CuO). γ-Al_2O_3 from Rhône–Poulenc (RP535A) with a surface area of 117 m^2g^{-1} was used as the support. Before the addition of copper, the alumina pellets were ground to grain size in the 0.1–0.2-mm diameter range and used in this form for the catalytic tests.

Pulse- and step-change transient catalytic studies were carried out in an apparatus equipped with an on-line VG SX200 mass quadrupole apparatus equipped with a double turbomolecular vacuum pump system. Individual gases (He, O_2, NO, or NH_3), stored in cylinders in already calibrated mixtures in helium, can be sent to a quick-switch four-way valve (Whitey 43YE2) or to a six-way valve (Valco C6UWT) after regulation of the flow to generate the step- or pulse-changes in the concentration of one or more reactants while maintaining constant the concentration of the others. This is realized by substituting an independent flow of helium with that of an equal flow of helium containing the desired reactants. In this way it is possible to maintain the catalyst in a continuous flow of one or more reactants and induce at selected times a pulse- or step-change in the concentrations of one or more of the other reactants.

The time-resolved change in the reactor outlet concentration of the reactants or reaction products was monitored through the mass quadrupole apparatus and the results were compared with those obtained from the same experiments done by substituting the catalyst with an equivalent volume of quartz microspheres having the same mean diameter as the catalyst particles. A 5-cm^3 quartz catalytic reactor filled with quartz balls to decrease the dead volume was used. The continous flow reactor operates at atmospheric pressure. A calibrated and heated capillary tube connects the reactor outlet to the mass quadrupole apparatus, whereas the excess flow from the reactor is sent to vent. This arrangement prevents changes in the operating pressure of the reactor. All connection lines are maintained at around 80–100°C in order to limit adsorption phenomena.

The quantification of the concentration of the various components in the inlet and outlet stream of the reactor was achieved by calibration of the mass quadrupole response using calibrated mixtures in helium of the single components of the feed. To minimize errors associated with day-to-day changes in sensitivity the mass quadrupole apparatus was recalibrated periodically. Fluctuations in the operating pressure were compensated for by using the helium pressure as an internal standard for total vacuum pressure. The mass quadrupole data, after correction for total pressure changes, were then corrected to take into account the possible presence of multiple fragmentations on a single mass intensity (16). The correctness of the analytical approach was verified in several steady-state catalytic experiments; agreement of the total nitrogen balance was ±8%.

The experiments were usually made with 0.5 g of catalyst. The total flow rate as 12 liter · h^{-1}, unless otherwise indicated. The quartz reactor inlet diameter was 10 mm in order to reduce the catalyst bed length and thus reduce the possible readsorption phemomena. It was verified that in stationary conditions (feed: 800 ppm NO, 835 ppm NH_3, 3% O_2, total flow rate 12 liter · h^{-1}, 0.5 g sample) the conversion of NO and ammonia remained constant when the amount of catalyst and the total flow rate was doubled. In addition, the conversions do not vary significantly when catalyst particles with larger dimensions are used (0.2–0.4 mm as compared with the 0.1–0.2 mm usually employed). The results of these tests make it possible to conclude that inter- and intraphase mass diffusional limitations are absent in our experimental conditions. The low concentration of the reactants allows heat transfer limitations to be regarded as negligible. The temperature of the catalyst bed was determined by a 0.5-mm axial thermocouple in direct contact with the catalytic bed.

The analysis of nonstationary behavior of the surface reactivity of copper-on-alumina in NO adsorption and conversion was made using both pulse- and step-changes in the concentration of one or more reactants while the concentration of the other was maintained constant. In these experiments a continuous flow of (NH_3) + (O_2) + He was sent to the reactor containing the catalyst and a pulse or a step-change in the concentration of NO or of O_2 was made while monitoring the change in the reactor outlet concentration using the mass quadrupole detector. The comparison of the difference in the time response obtained in the same conditions, but substituting the catalyst with quartz pellets made it possible to determine the specific contribution of the catalyst. This procedure avoids the necessity of correcting the response to take into account the dead volume of the catalytic apparatus, becasue both the instrumental response and the delay in the response due to the dead volume of the apparatus determine the time response of the system without the catalyst and are thus subtracted in the differential response obtained from the comparison of the results with and without the catalyst.

The use of both pulse- and step-change experiments is due to the different information that can be obtained from the combination of the two methods. In fact, in blank experiments it was shown that the time response of the system (mass quadrupole detector plus catalytic apparatus) to changes in reactant concentrations is rapid when the concentration of NO or O_2 is increased from nearly zero to a fixed value, whereas the time required to return to zero when the introduction of the probe molecule is stopped is much slower. This is caused by both mass-quadrupole detector memory effects and the dead spaces of the system (valves, valve switching, reactor, transport lines) estimated to be about 5–6 cm^3. The first factor, in particular, is the more critical, because experiments with different dead volumes do not show any marked effects. In fact, the time response of the system to a stop of NO or O_2 feed is about 20–30 s for a 95% decrease in initial concentration and of the order of 5–10 min for a further decrease to 99% of initial concentration. In our conditions, the characteristic dead-volume filling time is only about 2 s. A reliable analysis of desorption phenomena in step-change experiments in our experimental apparatus is thus not possible. On the contrary, the instrumental response time when the concentration of the probe molecule was increased was shorter than the characteristic time of change in the surface reactivity due to the combination of adsorption–reaction phenomena, as shown in the various figures which always report the system time-response in absence of the catalyst. This base response is the reference to evaluate the effect of the catalyst and allows problems connected with the system lag to be circumvented. The different mass quadrupole response time to increases and decreases in the inlet concentration also explains why the pulse shape in blank experiments is not Gaussian, but rather shows a significant tail on the right side (see curve a in Fig. 1).

Information on desorption phenomena can be obtained using the pulse method due to the lower amount of probe molecule introduced in the quadrupole chamber which minimizes the delay. Therefore, experiments were usually made using both types of transient reactivity tests. For clarity, however, only the results more relevant for the scope of the work are discussed here. Since the pulse experiments were focused on the study of desorption phenomena, data for the pulse tests are reported only for a reaction temperature (250°C) slightly lower than that of the step-change experiments (300°C). No remarkable differences were observed in pulse tests at 300°C, but the data at 250°C more clearly show the presence of slow desorptions of reactants or reaction products.

It should also be noted that the instrumental response time to changes in the ammonia concentration was very slow in all cases. Consequently the experiments with ammonia were carried out only with a continuous flow of ammonia plus helium and in some cases O_2.

RESULTS

Pulse Experiments

Reported in Fig. 1 is the comparison of the behavior of copper-on-alumina maintained under a continuous flow of He (b) or of He + 5% O_2 (c) during three consecutive pulses of NO. The signal (a) refers to that observed in the same conditions, but without the catalyst. The behavior was followed up to about 20 consecutive pulses, but markedly different results were not observed. The change in time between consecutive pulses was also found not to cause significant differences in the observed phenomenology.

In the absence of the catalyst (curve a) a non-Gaussian signal shape with a tail on the right side is observed for the reasons discussed under Experimental. When the catalyst is present (curve b) the intensity of the maximum in NO concentration decreases, but a much longer tail on the right side is observed. This indicates that a large fraction of NO is initially adsorbed by the catalyst and then slowly released. When oxygen is present (curve c), the adsorption is greater and the desorption process even slower. In the latter case, in particular, after 3–5 pulses of NO, no longer can any distinct signal of the pulse be observed, but rather only a broad unstructured signal which indicates the occurrence of very slow desorption. N_2 is the only reaction product observed, but only in small

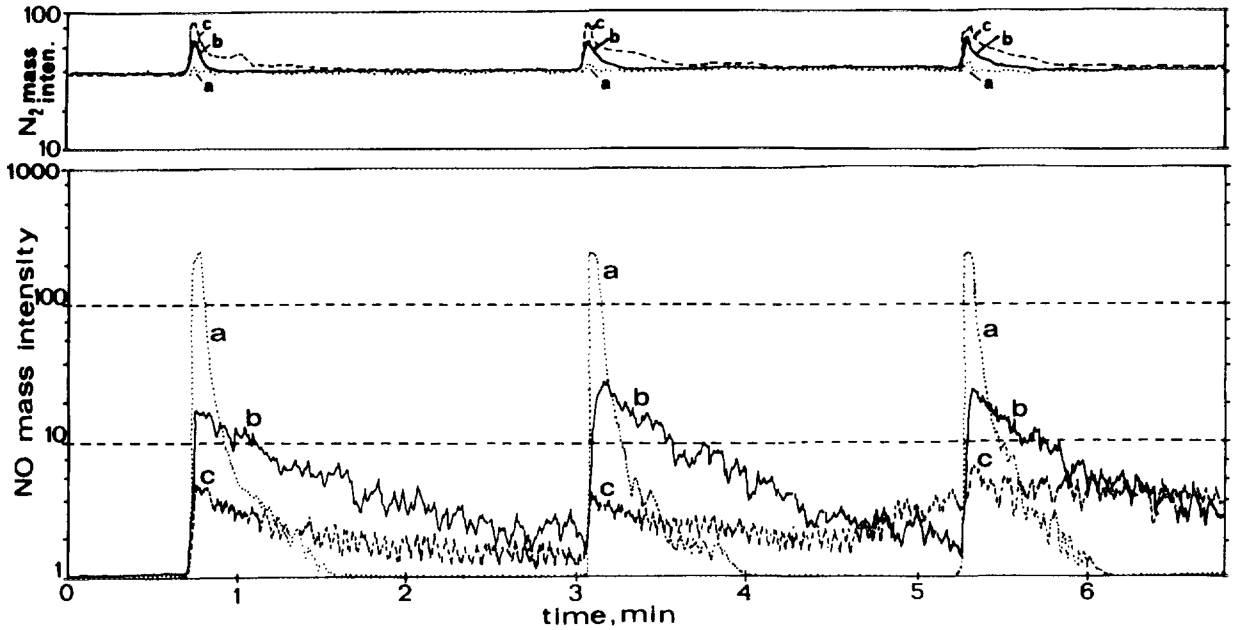

FIG. 1. Pulse experiments using copper-on-alumina catalyst (5 wt% as CuO) at 250°C in comparison with the mass response observed in the absence of the catalyst (curve a). Curves b and c refer to pulses of NO while the catalyst is maintained in a continuous flow of helium (6 L · h^{-1}) or helium containing 5% O_2, respectively. Bottom of the figure: intensity of the mass ($\times 10^{11}$) at 30 for NO response. Top: intensity of the mass ($\times 10^{11}$) at 28 for N_2. Each pulse is about 4.1×10^{-7} mol of NO. Tests with 0.3 g of catalyst.

amounts. It should be pointed out that the base signal of N_2 in the absence of the catalyst (curve a) is due to N_2 leaked from the atmosphere, but the comparison of the response of N_2 with (curve a) or without the catalyst (curves b and c) shows that small, but not negligible, amounts of N_2 form when the pulse of NO is fed over the catalyst.

Summarized in Fig. 2 is the behavior of the catalyst during pulses of NO in the presence of ammonia. Figure 2A reports the behavior in a series of consecutive pulses on the catalyst on which NH_3 was preadsorbed at 250°C followed by removal of gaseous or weakly adsorbed species with a flow of helium (15 min at 250°C). Figure 2B reports, on the other hand, the behavior observed in the series of pulses while sending a flow of He + 1% NH_3 (curves a and b) or a flow of He + 1% NH_3 + 5% O_2 (curves a', b', and c'). Curves a, b, and c refer to the mass intensity signal for N_2, NO, and N_2O, respectively. The latter product was observed only when O_2 was present. No other reaction products such as NO_2 were observed. The initial base signal of N_2 (before the first NO pulse) (curve a in Fig. 2A; curves a and a' in Fig. 2B) is due to small amounts of N_2 leaked from the atmosphere, but the higher value which occurred when O_2 was present indicates the presence of a side reaction of oxidation of NH_3 to N_2.

In the series of pulses of NO on the catalyst with preadsorbed ammonia (Fig. 2A), the conversion of NO progressively decreased as shown by the parallel increase in the unreacted NO. It is worth noting that the slow desorption phenomena observed in the absence of ammonia are no longer present and the pulse shape of unreacted NO remains narrow (compare pulse shape in curve b in Fig. 2A with that in curve b in Fig. 1). N_2 is the only product observed in this reaction.

When NH_3 was present in the gas phase (Fig. 2B), the conversion of NO was complete in all cases (in the absence or presence of O_2), but in the latter case small amounts of N_2O also formed (curve c'). The pulse shape for N_2 formation is larger when O_2 is present in the feed as compared to the case without oxygen (compare curves a' and a of Fig. 2B), suggesting the possible presence of an additional slower process of N_2 formation in the presence of gaseous O_2.

Figure 3 reports the behavior of the γ-Al_2O_3 support in similar experiments of pulses of NO in a flow of He (A), in a flow of He + O_2 (B) or using an alumina on which NH_3 was preadsorbed. The reference response for the pulses of NO in the absence of the catalyst nearly coincides with the pulse shape of curve A. The similar shape in a flow of He with and without the catalyst indicates the absence on pure alumina of significant chemisorption phemomena. Furthermore, no formation of N_2 is observed (Fig. 3), in contrast with the case of copper-on-alumina (Fig. 1). Similar results to those in a flow of He were observed in a flow of He + O_2. These results thus indicate

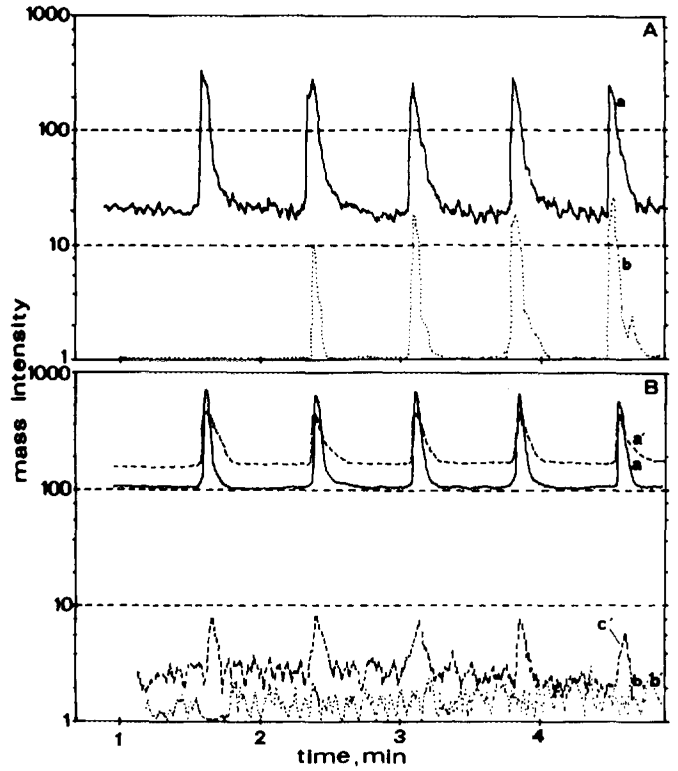

FIG. 2. Mass intensity ($\times 10^{11}$) for N_2 (a), NO (b), and N_2O (c) in pulses of NO on copper-on-alumina at 250°C. (A) on the catalyst in a flow of He, but on which NH_3 was preadsorbed at 250°C; gaseous or weakly adsorbed species were then removed with a flow of He at the same temperature for 15 min. For the sake of clarity, the background noise in curve b was omitted. (B) on the catalyst maintained in a flow of He + 1% NH_3 (curves a and b) or in a flow of He + 1% NH_3 + 5% O_2 (curves a', b', and c'). Other conditions as in Fig. 1.

that surface copper ions on alumina are responsible for both strong chemisorption of NO and its surface transformations. When preadsorbed ammonia is present on the catalyst, a small formation of N_2 was observed, but in much lower amounts than that formed in similar experiments over copper-on-alumina (compare Fig. 3C with Fig. 2B). The reaction of NO with chemisorbed ammonia also explains why the pulse shape of NO over the catalyst with preadsorbed ammonia (curve C) is narrower than that observed for curves A and B. Surface copper ions are thus important not only for NO chemisorption, but also for the reaction of chemisorbed ammonia to give N_2.

Step-Change Experiments

Reported in Fig. 4a is the system response to a step-change in the concentration of NO in the absence (dashed line) and presence (dotted line) of the catalyst. As reported in the experimental part, the difference in the response between the NO signal with or without the catalyst is due to chemisorption of NO on the catalyst surface or the conversion of NO to reaction products. The difference between the two signals (reported also in Fig. 4a) allows the moles of NO converted (about 2.3×10^{-6} mol of NO per g of catalyst) to be quantified: 50–60% of converted moles remain strongly chemisorbed on the catalyst, while the remaining part transforms to N_2. In these experiments, O_2 did not form, indicating that the formation of N_2 from NO is due to the reoxidation by NO of the reduced copper sites generated by the spontaneous reduction in a flow of He. At higher reaction temperature (450°C), however, a different reactivity pattern was found (Fig. 4b). In this case the formation of N_2 progressively increased reaching a constant value after 50 s. The formation of O_2 also is detected. At this temperature, the amount of adsorbed NO decreased significantly to around 30–40% of that remaining adsorbed at 300°C. This suggests that at higher reaction temperature, the amount of chemisorbed NO decreases, but probably changes the mechanism of transformation of NO to N_2.

The presence of O_2 in the feed considerably changes the reactivity of copper-on-alumina in step-change experiments (Fig. 5). The amount of NO converted (chemisorbed and transformed to products of reaction), estimated from the difference in the outlet NO signals in the absence (dashed line) and presence (dotted line) of the catalyst is reported in Fig. 5. The total amount (about 1.1×10^{-5} mol NO g^{-1} catalyst) was considerably higher than in the absence of gaseous oxygen. In addition, N_2 formed according to two pathways, one faster and the second slower, but with a rate that increased with the time-on-

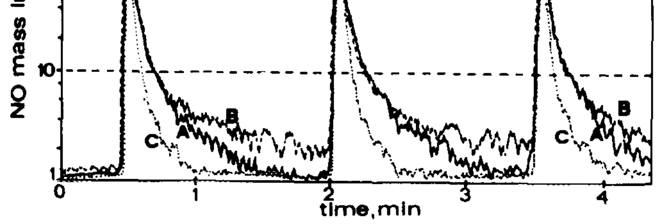

FIG. 3. Pulse experiments using a γ-Al_2O_3 support at 250°C. Pulses of NO while maintaining the catalyst in a flow of He (A), He + 5% O_2 (B) or on the catalyst in flow of He on which NH_3 was preliminarily adsorbed (C). Other conditions as in Fig. 1; mass intensity ($\times 10^{11}$) of NO (bottom) and N_2 (top). The reference signal without the catalyst nearly coincides with that of curve A.

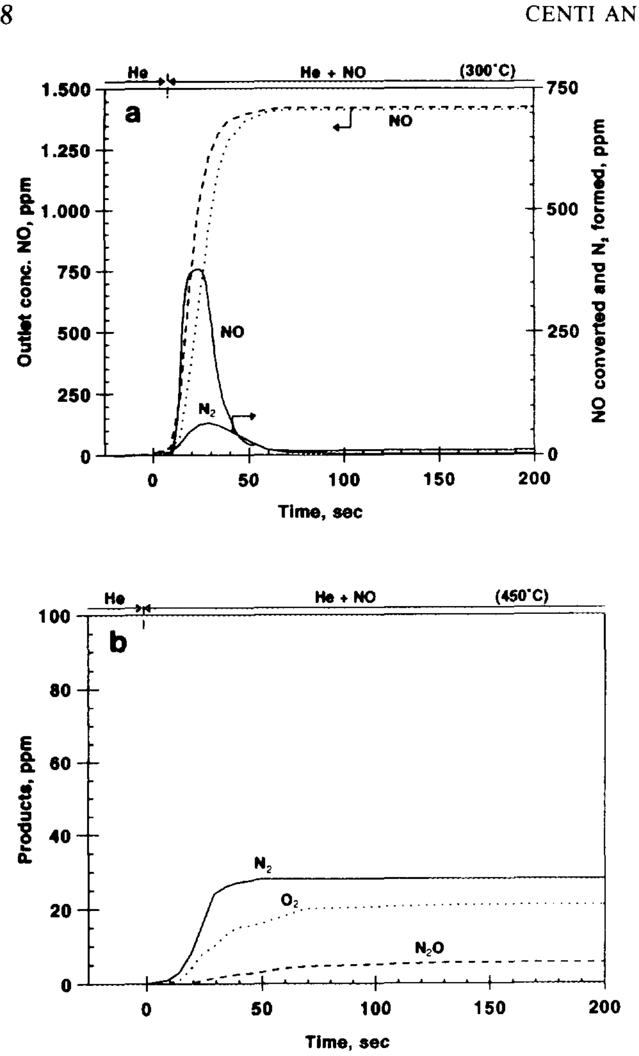

FIG. 4. (a) NO outlet concentration in step-change experiments in a flow of He at 300°C without (dashed line) or with (dotted line) the copper-on-alumina catalyst, and NO converted (determined from the difference between the two above responses) and N_2 formed in the case of the presence of the catalyst. Total flow 12 liter · h^{-1}; 0.5 g of catalyst. (b) Formation of N_2, O_2, and N_2O in NO step-change experiments at 450°C on copper-on-alumina in a flow of He. Other conditions as in (a).

stream. This latter evidence suggests that in this second pathway of transformation to N_2 adspecies formed from the surface transformation of NO in the presence of O_2 are involved. NO_2 or other oxidized nitrogen-oxide species, however, were not detected in the gas phase. N_2O formation also was not observed.

From the difference between the moles of NO converted and the moles of NO transformed to N_2 it can be estimated that the amount of NO remaining chemisorbed on the catalyst at the end of the experiment was about 9×10^{-6} mol NO per gram of catalyst, corresponding to a Cu to NO ratio of around 70 : 1. The Cu : NO ratio is based on the assumption that all copper ions are available at the surface of the catalyst for interaction with NO. Since crystalline or paracrystalline copper oxide is absent in this catalyst (see Introduction), this hypothesis is reasonable.

The effect of the presence of ammonia in the gas phase is summarized in Fig. 6 which reports tests of a step-change in the NO concentration while maintaining the catalyst in a flow of He + 1% NH_3 + 5% O_2 (Fig. 6a) or He + 1% NH_3 (Fig. 6b). No other reaction products were detected, apart from those shown in the figures.

The results both in the presence and absence of O_2 in the feed (Fig. 6a and 6b, respectively) are relatively similar, apart from the additional formation of N_2O when O_2 is present. In addition, the initial amount of N_2 before feeding the NO is higher in the presence of O_2, due to the presence of the reaction of selective conversion of NH_3 to N_2 catalyzed from the copper-on-alumina. The more relevant effect shown in Fig. 6 is that the rate of selective transformation of NO to N_2 initially is higher, progressively decreasing to reach a stationary condition in about 4–5 min of time-on-stream. No remarkable changes in the results were found when the tests were extended up to 1 h of time-on-stream as compared with the results after 5 min. The conversion of NO [difference in the system response for NO with (dotted line) and without (dashed line) the catalyst] is initially complete and then decreases to around 62% after 5 min. In the absence of O_2 the conversion after 5 min is only slightly lower (56%). In parallel with the decrease in the NO conversion, the formation of N_2 passes through a maximum deriving from the combined effect of the step-change in

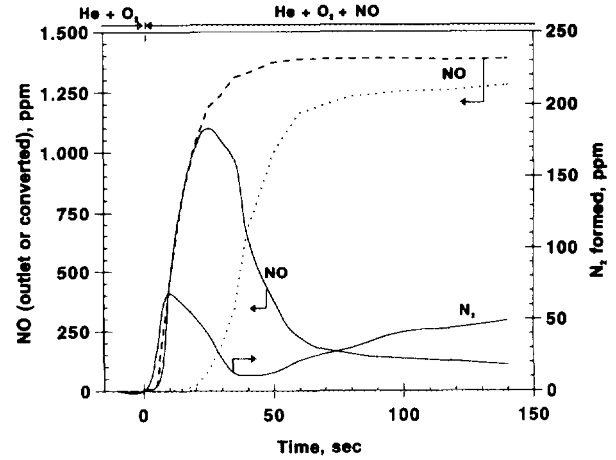

FIG. 5. NO outlet concentration in step-change experiments at 300°C, while maintaining the copper-on-alumina catalyst in a flow of He + 5% O_2. Dashed line: reference signal without the catalyst; dotted line: outlet NO concentration in the presence of the catalyst. Also reported in the figure is the NO converted estimated from the difference between the two above curves, and the formation of N_2. Other experimental conditions as in Fig. 4a.

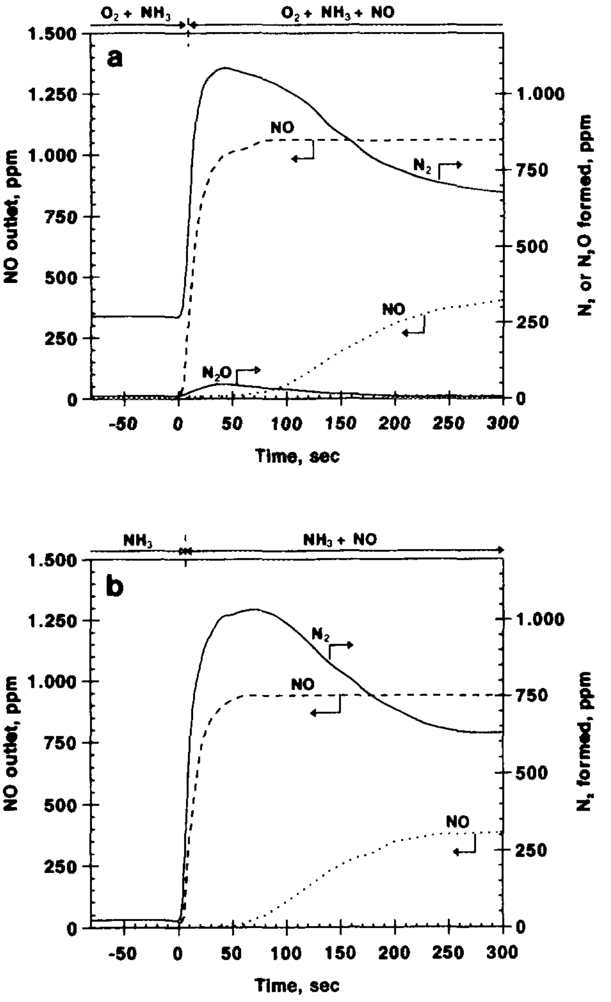

FIG. 6. (a) NO outlet concentration in step-change experiments in a flow of He + 1% NH₃ + 5% O₂ at 300°C without (dashed line) or with (dotted line) the copper-on-alumina catalyst, and N_2 and N_2O formed in the case of the presence of the catalyst. (b) Tests as for a, but maintaining the catalyst in a flow of He + 1% NH₃. Other conditions as in Fig. 4a.

NO concentration and the higher initial surface reactivity of copper-on-alumina.

The results of oxygen step-change experiments carried out while maintaining the catalyst in a flow of helium containing about 900 ppm NO and 1100 ppm NH_3 are shown in Fig. 7. Oxygen was initially largely consumed, as shown from the difference between the oxygen outlet step-profile in the absence of the catalyst (dashed line) and in the presence of the catalyst (dotted line). At the same time, the transient formation of N_2 was initially higher (immediately after the addition of oxygen) and then decreased to a lower stationary value in about 3 min of time-on-stream apparently in a two-step process. This indicates that initially oxygen was converted at a higher rate, due possibly to (i) reoxidation of the catalyst partially reduced in the initial phase in the absence of oxygen and (ii) the higher transient reactivity of surface adspecies. The estimation of the initial N_2 overshoot after oxygen addition indicates that about 6×10^{-6} mol of N_2 form (a larger number of moles as compared with those formed in the hypothesis that the stationary condition observed after 3 min is immediately reached after the admission of oxygen). An initial higher rate of NO depletion is also observed after oxygen admission (Fig. 7). The overshoot in the moles of NO converted (similarly to above, additional moles of NO converted as compared to the number based on the hypothesis of immediate attainment of stationary conditions) is about 4×10^{-6} mol of NO. The difference between the two values, assuming a 1 : 1 reaction between ammonia and NO to form N_2, is due to an initial higher rate of the side reaction of ammonia oxidation to N_2 (which cannot be estimated, however, for the reasons outlined in the experimental part) or to the conversion to N_2 of ammonia and/or nitrogen oxide adspecies formed during the initial treatment in a flow of He + NO + NH_3. Reoxidation of the catalyst or a decrease in the concentration of chemisorbed species leads to a decrease in N_2 formation and in the rate of NO depletion. It should also be noted that after 5 min the amount of N_2 formed is higher in the presence of O_2, notwithstanding the slightly lower NO conversion. This can be attributed to an enhanced rate of the direct oxidation of NH_3 to N_2.

DISCUSSION

Reactivity of NO in the Absence of Ammonia

Both the pulse (Fig. 1) and step-change (Fig. 4) experiments showed that NO is strongly adsorbed on the cata-

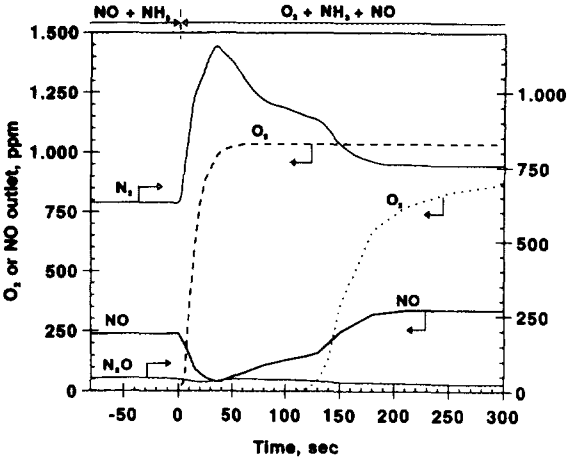

FIG. 7. Step-change in the concentration of O_2 at 300°C while maintaining the catalyst in a flow of He + NO + NH_3 (936 ppm NO and 1098 ppm NH_3). O_2 outlet concentration without (dashed line) or with (dotted line) the copper-on-alumina catalyst, NO outlet concentration, and N_2 and N_2O formed in the case of the presence of the catalyst. Other conditions as in Fig. 4a.

lyst at reaction temperatures of around 250–300°C and only slowly desorbs from it. In the presence of O_2, the adsorption is more pronounced and the total amount of NO adsorbed nearly corresponds to a Cu to NO molar ratio of 70 : 1. The behavior is markedly different from that observed in similar experiments on V-TiO_2 (19), where NO adsorption is negligible. On the other hand, the amount of NO adsorbed by the alumina support (Fig. 3) is also very limited, suggesting that the adsorption must be specifically attributed to the copper surface sites. Infrared characterization of NO adsorption on this catalyst (16) has shown the formation of nitrite–nitrate species, the amount of which significantly increases in the presence of gaseous oxygen. It is thus reasonable to attibute the strong adsorption of NO and its slow release to the formation of oxidized nitrogen-oxide species. Infrared data, in fact, indicate a weak bond of NO with copper ions in the form of a mononitrosyl species, and ESR data further confirm this result (16). In the presence of gaseous oxygen, the amount of NO adsorbed is greater, probably due to a shift from a nitrite to a nitrate species. This can explain the further decrease in the rate of NO desorption in pulse experiments in the presence of O_2 with respect to the same tests without oxygen (Fig. 1). These results in general agree with those reported by Hierl *et al.* (11) who studied the thermodesorption curves of NO on a 10% CuO–Al_2O_3 sample. They suggest, however, that nitrite species form by reaction of NO with a Cu-(O) species generated by the decomposition of a copper–dinitrosyl complex to give N_2O and Cu-(O). The nitrite species can further transform to a nitrate at higher temperatures which then decomposes to NO and O_2.

Our results indicate, on the contrary, a slightly different picture of the surface reactivity and role of adspecies. At 250°C NO interacts with the catalyst according to two main pathways (Fig. 4a). The first one is a dissociative chemisorption on reduced copper sites spontaneously formed during the initial treatment in helium at the same reaction temperature. This reaction is fast and gives rise to the formation of N_2, whereas the oxygen of NO is used for the reoxidation of the reduced sites. A second route involves, on the contrary, the strong adsorption of NO, probably in the form of a nitrite–copper complex as discussed above. At higher temperature (450°C) (Fig. 4b), the mechanism of N_2 formation occurs along a different pathway, as suggested by the comparison of the different time-dependence relationship for the formation of N_2 (compare Fig. 4c and 4b) and the formation of O_2. Reasonably, at this higher temperature the mechanism is analogous to that suggested for NO decomposition over Cu-ZSM-5 (12, 13, 17, 18), even though the copper-on-alumina is comparably much less active for this reaction. In particular, it has been suggested (12, 13, 18) that a key step in the reaction over Cu-ZSM-5 involves the formation of a copper-nitrite–mononitrosyl surface complex which decomposes to $N_2 + O_2$ and Cu–(O). The latter further reacts with two NO molecules reforming the active complex intermediate. Reasonably, a similar mechanism can be suggested also for the formation of N_2 from NO at high temperature on copper-on-alumina. However, in the above mechanism it is suggested that N_2O derives from the decomposition of a dinitrosyl copper complex which forms N_2O and the Cu–(O) species involved in the cyclic mechanism of NO decomposition. According to this mechanism, it is expected that N_2O forms only initially during the formation of the active sites and then its formation decreases, in contrast to that observed (Fig. 4b). This parallel trend with N_2 formation instead suggests an analogous mechanism of formation such as the decomposition of the copper–nitrite–mononitrosyl complex directly to $N_2O + O_2$ and Cu. The precursor copper–nitrite complex is presumably also responsible at lower temperature for the strong adsorption of NO.

In the presence of oxygen (Fig. 5) the mechanism is more complex. In this case, in fact, together with an enhanced strong chemisorption of NO, the formation of N_2 is observed. The time-dependence of formation of N_2 clearly indicates the presence of two pathways of reaction: the first one fast, which rapidly comes to an end, and a second one slower, the rate of which however increases progressively, suggesting a consecutive mechanism involving oxidized nitrogen-oxide adspecies.

It is interesting to note, however, that the presence of oxygen does not inhibit the formation of N_2 from NO at this reaction temperature, as expected on the basis of a mechanism of only reoxidation of reduced copper sites (Fig. 4a), but instead promotes the presence of an additional pathway of reaction.

The first route to N_2 (initial peak in the formation of N_2 in Fig. 5) shows analogies to the mechanism of reoxidation of reduced copper sites suggested for the analogous tests in a flow of helium (Fig. 4a). The mechanism cannot be excluded notwithstanding the presence of O_2 which should inhibit the spontaneous reduction of the catalyst. On the other hand, the oxygen partial pressure in these tests is lower than that of air and it has already been observed (20) that the rate of reoxidation by NO of reduced copper sites is higher than that by O_2. The integral area of the N_2 initial peak in Fig. 5 is around 2.5×10^{-7} mol of N_2 corresponding to about 0.04% of the copper surface sites. In addition, the moles of N_2 formed in this initial step (Fig. 5) are around one third of those formed when O_2 is absent (Fig. 4a). All these data indicate that the initial formation of N_2 can reasonably be attributed to a small amount of reduced copper sites formed in the pretreatment notwithstanding the presence of O_2 in the feed.

The second pathway to N_2 is instead characteristic of the presence of O_2 and shows that, notwithstanding the limited number of active sites present, an oxidative mechanism of NO reduction is possible. It is, in fact, reasonable to suggest a mechanism analogous to that discussed above for the formation of a copper nitrite surface complex which by further reaction with NO molecules forms an active species that decomposes to N_2 and O_2. The progressive increase in the rate of formation of N_2, in fact, is in agreement with the hypothesis of the formation of an oxidized nitrogen oxide species such as the copper nitrite surface complex as the key step in the reaction.

Reactivity of NO in the Presence of Ammonia

When adsorbed ammonia is present on the surface of the catalyst, the rate of NO conversion to N_2 is obviously enhanced considerably, but pulse experiments (Fig. 2) show that adsorption/desorption phenomena of NO are also influenced. It is interesting to observe that a similar initial behavior is observed when NH_3 is preadsorbed or in the gas phase (Fig. 2), indicating that mainly chemisorbed ammonia is involved in the reaction with nitrogen oxide. This reaction always competes with the direct selective oxidation of ammonia to N_2 which may occur both in the presence and absence of O_2, but with a higher rate in the former case (Figs. 2, 6 and 7). Infrared data for ammonia adsorption and reactivity with O_2 on this catalyst (16) and previous results on unsupported CuO (10) suggest that the mechanism of ammonia conversion to N_2 involves a first step of heterolytic dissociative chemisorption of ammonia to form an OH group and a NH_2 species. The rate of this reaction of ammonia oxidation to N_2, however, is inhibited considerably by the coadsorption of NO, tentatively interpreted as a blockage of the reactivity of copper sites due to the formation of oxidized nitrogen-oxide species (16).

The formation of an NH_2 species has been suggested as the key step in the mechanism of NO reduction on $V-TiO_2$ (8). Gaseous NO reacts with NH_2 to form a nitrosamine species (NH_2NO) that decomposes to N_2 + H_2O. According to this mechanism, it may be expected that the initial transient reactivity of the catalyst in NO step-change experiments in a flow containing ammonia will be higher due to the higher initial availability of these activated ammonia adspecies formed in the initial phase in the absence of NO. Experimental results (Fig. 6) show effectively an initial higher transient reactivity.

Alternative hypotheses also can be proposed to explain this enhanced initial activity. In this respect, it is useful to analyze the results of oxygen step-change experiments (Fig. 7). According to the above mechanism, it is expected that gaseous O_2 plays a role only in the reoxidation of the reduced sites and therefore in O_2 step-change experiments the formation of N_2 and the conversion of NO should only increase progressively to steady state values. On the contrary, a rapid initial increase is observed, but then in about 3 min the formation of N_2 and the conversion of NO returns to values relatively similar to the starting values. In addition, the change in the surface reactivity up to the new steady-state condition in the presence of O_2 apparently involves two different stages. This behavior suggests that adsorbed NO is progressively oxidized in the $NO \rightarrow NO_2 \rightarrow (NO_2)^- \rightarrow (NO_3)^-$ series, according also to the large initial consumption of oxygen (Fig. 7). The different species are characterized by different reactivities with adsorbed ammonia. Tentatively, the NO_2 and nitrite species are the two more reactive and nitrate is the less reactive. Reasonably, these species react with surface copper-amino complexes formed by interaction of ammonia with copper sites, similarly to that proposed to explain the mechanism of NO reduction by ammonia in the absence of O_2 on Cu^{2+}-exchanged NaY zeolite (14). Copper–amino complexes on copper-on-alumina also have been detected by ESR (16).

This mechanism of surface transformation of nitrogen oxide adspecies can well explain the change in the surface reactivity in O_2 step-change experiments (Fig. 7) and similarly also the change in reactivity during NO step-change experiments (Fig. 6). The inhibition of the surface reactivity by formation of nitrate species can also explain the evidence that comparable results of steady-state reactivity are found in NO reaction with NH_3 on copper-on-alumina in the presence and absense of O_2, differently from the $V-TiO_2$ catalysts which show a considerable decrease in the NO conversion in the absence of gaseous O_2. A different effect of oxygen is also shown by other copper-based catalysts such as Cu–ZSM-5 and CuO/SiO_2 which show a decrease or an increase in the conversion of NO by NH_3 in the presence of O_2, respectively (21).

Finally, the formation of N_2O in all these experiments does not parallel that of N_2 formation or of NO depletion, indicating that over copper-on-alumina its formation derives from a parallel side reaction, such as the decomposition of ammonium nitrate species suggested on the basis of infrared data (16).

CONCLUSIONS

The analysis of the transient catalytic response of a 5% copper-oxide on alumina catalyst in pulse and step-change experiments indicates that the transient reactivity may be significantly different from that observed in stationary conditions. This gives useful indications regarding the role of chemisorbed species on the surface reactivity and the possible presence of multiple pathways of reaction.

In the tests in absence of ammonia, it was observed that NO significantly chemisorbs on the copper sites of the catalyst and subsequently is slowly released. The strong chemisorption is enhanced by the presence of gaseous oxygen which also promotes the low-temperature formation of small, but not negligible, amounts of N_2 from NO in the absence of any reducing agent, probably through the formation of a copper nitrite intermediate complex which further reacts with NO.

In the presence of ammonia, NO chemisorption phenomena still exist but to a lesser extent. However, it is also shown that the initial rate of NO depletion and N_2 formation in NO or O_2 concentration step-change experiments is higher than that observed in stationary conditions. These results indicate that the mechanism of NO conversion over copper-on-alumina in the presence of chemisorbed ammonia involves the preliminary oxidation of NO to a NO_2 or nitrite adspecies which then react with chemisorbed ammonia. The further oxidation of NO_2 or nitrite adspecies to a nitrate species leads to a decrease in the surface reactivity.

The formation of N_2O is observed only when gaseous O_2 is present and it is suggested that N_2O derives from a parallel side reaction involving the decomposition of an ammonium nitrate surface intermediate.

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