Catalytic reduction of nitric oxide on copper. Part I

H. Lu [a], C-M. Pradier [b,*], A.S. Flodström [a]

[a] *Materials Physics, Royal Institute of Technology / KTH, 100 44 Stockholm, Sweden*
[b] *Laboratoire de Physico-Chimie des Surfaces, CNRS-URA 425, Ecole Nationale Supérieure de Chimie de Paris, 11 Rue Pierre et Marie Curie 75005 Paris, France*

Abstract

The mechanism of NO reduction on copper in the presence of oxygen and isobutene was studied at T = 770 K, under reducing conditions. Mass spectroscopy was used to identify gas-phase intermediates and reaction products. One intermediate species resulting from the partial oxidation of isobutene was shown to be active in the NO conversion. X-ray photoelectron spectroscopy was used to analyze the copper surface at different stages of the reaction. Our conclusion is that oxygen first activates the surface, by forming coexisting phases of Cu_2O and CuO. The copper surface is then reduced by the hydrocarbon, leading to Cu^+ in majority, and to the formation of an active intermediate. At last, the reduction of NO proceeds rapidly on a zero-valent copper surface together with consumption of the previously formed intermediate. At the end of the reaction, the surface is poisoned by carbon.

1. Introduction

Copper dispersed on oxidic supports, copper ion-exchanged zeolites, are known for their catalytic activity in selective catalytic reduction (SCR) of nitric oxide [1]. Besides ammonia and hydrogen, which are commonly used reductants for stationary sources, but not easily applicable for automobiles, hydrocarbons, in the presence of oxygen, were also shown to react with NO on a copper based catalyst [2–4]. In that respect, C_2 and C_3 are the most currently studied hydrocarbons [5–7] and copper on zeolite is among the most active catalysts [8]. Iwamoto and Hamada have reported that propene and propane are better reductants for NO than carbon monoxide [2]. On Cu-ZSM-5 zeolites, it has been established that the direct reductant of NO is not the hydrocarbon but a reactive intermediate resulting from a partial oxidation of hydrocarbon [5]. As a matter of fact, there have been many proposals for the nature of the reactive intermediate, oxygenates [5,6], isocyanate [8], and NO_2 [9–11], and it appears that the main pathway of the reaction is strongly dependent on the reaction conditions $(T, P(O_2)/P(HC)$ ratio).

The determining role of copper atoms or copper ions in this catalytic system has also

* Corresponding author. Fax: +33-1-46340753.

given rise to numerous interpretations. It is generally assumed that the reduction of NO proceeds by an oxidation–reduction mechanism of the catalyst but, still, divergent views exist about the oxidation state of copper required in the subsequent steps of the reaction. On Cu-ZSM-5, the NO decomposition rate, measured at elevated temperature, was shown to be related to the cuprous ion concentration [12]. The controversy about the oxidation state of the copper active sites, both in the decomposition and in the reaction of NO with a reductant, has been well documented by Hall and Valyon [13]. Some studies make clear the role of the support-to-metal interactions in relation to the reducibility of supported Cu^{2+} ions [14]. In particular, modifications of the copper oxidation state are often related to the ability of the support to store or release oxygen throughout the catalytic process.

A more limited number of studies, dealing with NO and its reduction, have been reported on non-supported copper samples. The extensive work of Geus and his team on copper single crystals has to be mentioned. They, in particular, investigated the kinetics of the interaction of NO and O_2, NO and CO on copper single crystal surfaces [15]. These studies, carried out up to 0.1 Pa, proved that reduction of a copper oxidized surface occurs by reaction between the reductant (CO in their case) and adsorbed oxygen. In a recent study of the reactivity of a O_2/C_3H_6 mixture on Cu(111), authors from the same group propose a model involving ' assisted sticking' to explain the enlargement of the sticking probability for oxygen in the presence of propene at 750 K. We will retain in memory that a product RO, where R is the reductant is assumed to explain the influence of propene on the reactivity of oxygen on copper [16]. This type of surface science studies are very useful for the understanding of reaction mechanisms involving O_2, NO and a hydrocarbon on copper-based catalysts.

We chose a similar approach, we used a disk of copper as a model catalyst, in order to focus on the activity and electronic changes of the

pure metal, isolated, in the presence of gas mixtures containing NO, oxygen and isobutene. Our purpose was (i) to show the feasibility of the reduction of NO on pure copper, as a model catalytic surface, and (ii) to correlate the various steps of the catalytic process to an XPS characterization of the copper surface.

Measurements were undertaken of the reaction kinetics in a static mode; this allowed the investigation of the catalytic surface at various stages of the reaction at low or high NO conversion corresponding to various concentrations of products of the reaction. The surface characterization and kinetics data were correlated to each other in order to propose a possible reaction mechanism.

2. Experimental

The investigated catalytic substrate was a planar polycrystalline, 70 cm^2 area, copper disk; it was mechanically polished and rinsed in alcohol before the in situ cleaning procedure. In the catalytic reactor, the copper sample was reduced for two hours under $P = 10$ Torr of hydrogen at 870 K before each catalytic test. The cleanliness of the copper surface after the hydrogen reduction was checked by Auger electron spectroscopy (AES). No oxygen could be detected and the level of residual carbon was in the low submonolayer range.

A 18 dm^3 quartz tube was used as a reactor; it was connected to a UHV chamber equipped with conventional surface analysis tools. The sample was transferred under vacuum between the two chambers.

The catalysis experiments were performed in a static mode in the reactor. Argon was used as a balance gas to maintain a 5.0 Torr total pressure in the reactor. The copper substrate was inside the quartz reactor heated by an external furnace. In order to measure the reaction temperature, a chromel–alumel thermocouple was in contact with the walls of the reactor.

Standard catalytic conditions have been de-

fined after several trials. The purpose of this work was rather to be able to observe and characterize various surface states throughout a catalytic process than to keep conditions relevant to real catalysis.

A small constant leak was maintained from the reactor to a mass spectrometer, to enable the gas composition to be analyzed during the reaction.

Photoelectron spectroscopy was applied at different stages of the reaction. The Cu sample was cooled down to room temperature, the reaction gases pumped away, and the sample transferred to the surface analysis system. The sample was then subjected to XPS (X-ray photoelectron spectroscopy) studies. In the XPS mode, MgK α (1253.6 eV) radiation was used as excitation source, and the electron kinetic energies were determined by a CLAM 2 hemispherical energy analyzer at a pass energy of 20 eV. A small gold foil was attached to the copper sample to provide an internal reference for the binding energies. Au-4f$_{7/2}$ was taken at 84 eV. The accuracy of the binding energy values was better than 0.3 eV.

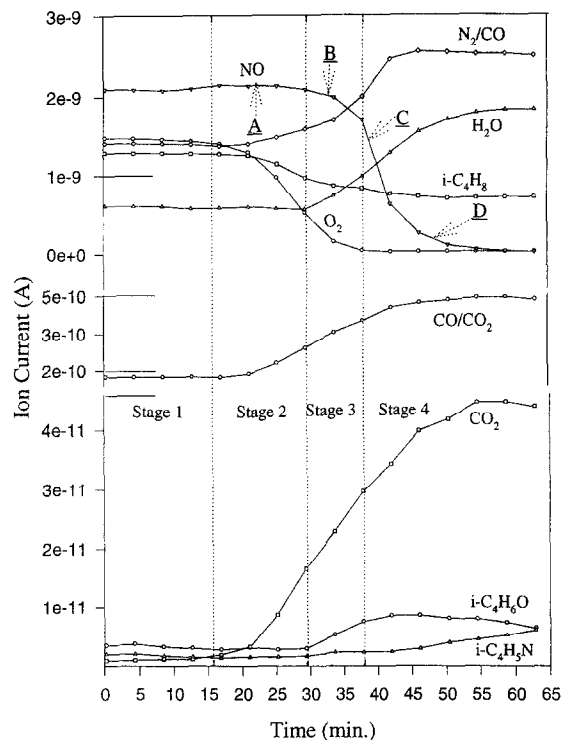Fig. 1. A typical time course of a reaction run at 770 K, $P(i\text{-}C_4H_8) = 0.5$ Torr, $P(\text{NO}) = 1.0$ Torr, $P(O_2) = 1.0$ Torr, Ar as balance gas, and total pressure 5.0 Torr. Note that, during the initial stage of the reaction, the temperature increases from 300 to 770 K. The letters A–D correspond to the stages when XPS measurements were performed.

3. Results

3.1. NO, O_2, i-C_4H_8 on copper, standard conditions

3.1.1. Kinetics data

Fig. 1a shows a typical time course of a reaction run at 770 K with $P(O_2) = 1.0$ Torr, $P(i\text{-}C_4H_8) = 0.5$ Torr and $P(\text{NO}) = 1.0$ Torr, i.e., reducing conditions regarding the total oxidation of the hydrocarbon. The temperature, 770 K, was chosen to lead to the highest activity, after a screening in the 700 to 800 K range. This is also the temperature reported for the maximum activity in NO conversion on Cu-ZSM5 [2,17]. We will call these conditions 'standard' in the rest of the text. The main products resulting from the conversion of NO and i-C_4H_8 were N_2, CO and H_2O. Note that

CO_2 is not a major product of the reaction; assuming similar sensitivities, at maximum, it is only 2% of the N_2/CO signal. Mass peaks at respectively 67 and 70 amu, detected at certain stages, were unambiguously assigned to CH_2=CCH_3CN (2-methyl-2-propenenitrile) and CH_2=CCH_3CHO (i-C_4H_6O or 2-methyl-2-propenal) after having checked their fragment peaks. After mass calibration, NO_2 and N_2O were found to be at negligible concentrations in the gas phase.

The curves in Fig. 1a clearly show four domains of catalytic activity corresponding to different compositions of the gas phase: a first stage (0–16 min) during which the temperature is raised from 300 to 770 K, and no reaction takes place; a second stage (16–30 min) corresponding to the conversion of oxygen and

isobutene into CO_2 and CO; a third stage (30–38 min) during which the NO signal decreases slowly, together with that of other reactants, to the benefit of CO, CO_2, H_2O, N_2, and i-C_4H_6O; finally, an 'active' stage takes place (after 38 min) characterized by a very small amount of oxygen in the gas phase and the highest rate of NO conversion. During the latter stage, the main products are N_2, CO, H_2O, and also small amounts of CO_2 and i-C_4H_5N. It is worth noting that the amount of produced unsaturated

aldehyde (i-C_4H_6O) decreases in the transition between the third and the final stage. Finally, the rate of NO conversion decreases.

3.1.2. Surface analysis

The catalytic test was repeated but stopped at four characteristic times of the reaction, marked A, B, C, and D in Fig. 1a: (A) when the combustion of i-C_4H_8 begins, but NO does not decrease (stage 2); (B) when the conversion of NO is slow (stage 3); (C) when the conversion

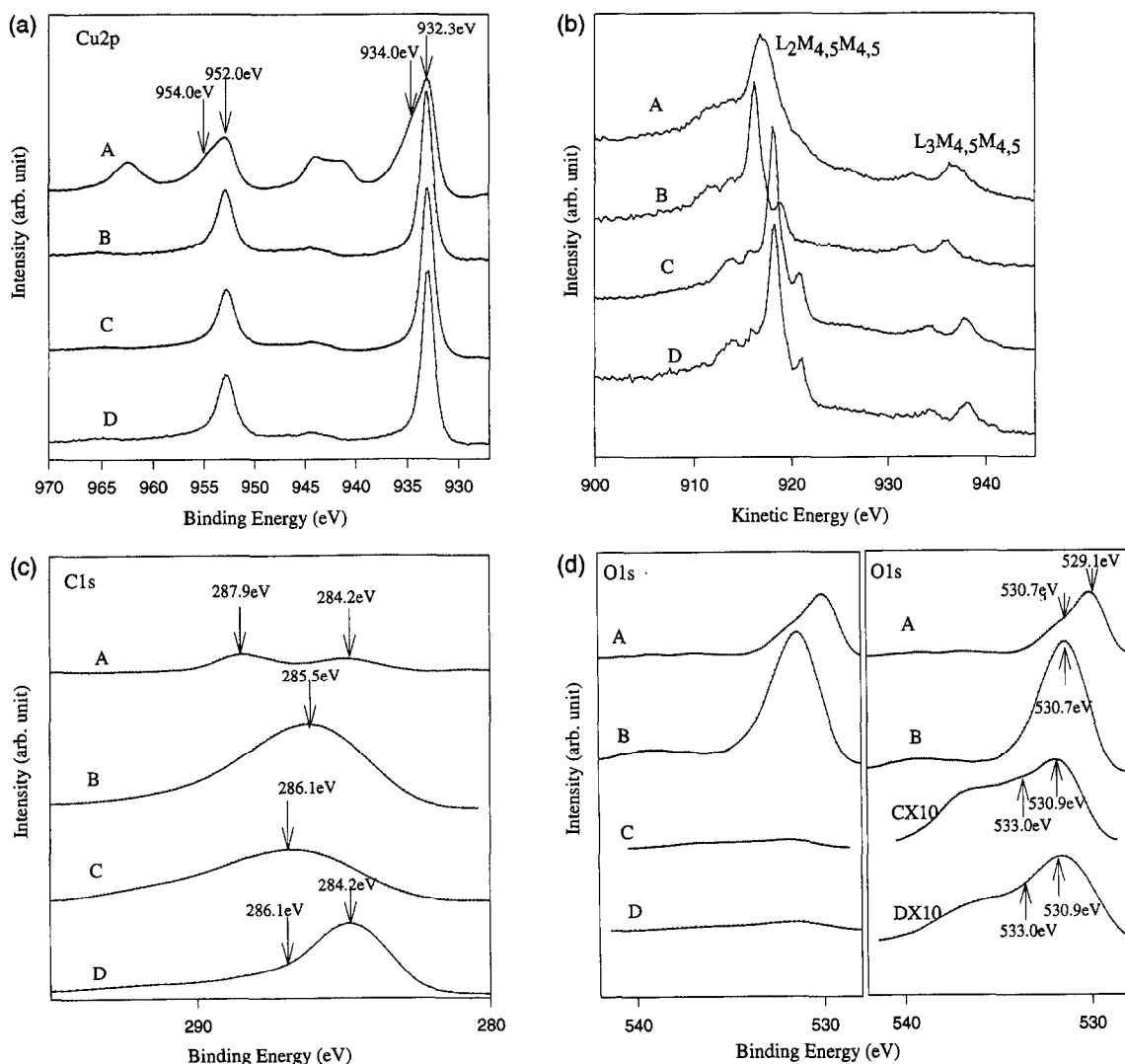Fig. 2. XPS spectra from Cu surface. A: i-C_4H_8 combustion stage; B: slow NO conversion stage; C: maximum NO conversion stage; D: end of reaction. Same reaction conditions as in Fig. 1.

of NO is rapid (early period of stage 4); (D) at the end of the reaction when the conversion of NO is slow again (end of stage 4).

Fig. 2 shows the Cu-2p, C-1s and O-1s XPS peaks, and the Cu-2p $L_{2(3)}M_{4,5}M_{4,5}$ Auger lines in the four stages.

In spectrum A (stage 2 of the reaction), the Cu surface appears purple–red, and the Cu-2p doublet can be fitted with two components for each line: Cu-$2p_{3/2}$ at 932.3 eV and 934.0 eV, Cu-$2p_{1/2}$ at 952.0 eV and 954.0 eV. Strong satellites are associated with the Cu-2p peaks at higher binding energies, clearly showing that the Cu surface is partially oxidized to Cu^{2+} [18–21]. The $L_{2(3)}M_{4,5}M_{4,5}$ Auger lines of copper are broad and exhibit a shift between 1.0 and 2.0 eV with respect to the kinetic energy of metallic copper $L_{2(3)}M_{4,5}M_{4,5}$ lines. Accordingly, the Cu surface at this stage can be interpreted as supporting the coexistence of Cu^{2+} and Cu^+ [22,23]. The O-1s peak results from a convolution of two peaks, one at 529.1 eV and another at 530.7 eV, which can be attributed to lattice oxygen in CuO and Cu_2O, respectively [24].

In spectrum B (stage 3 of the reaction), the catalyst color is changed to red–orange; the observed Cu $L_{2(3)}M_{4,5}M_{4,5}$ Auger lines are shifted 2.0 eV to lower kinetic energies than those of metallic Cu, whereas the observed Cu-$2p_{3/2,1/2}$ peaks are at the same binding energies as those of metallic Cu. The copper sample at this stage is likely to be Cu_2O [23,24]. The strong O-1s at 530.7 eV can be ascribed to lattice oxygen in Cu_2O, and C-1s at 285.5 eV, slightly shifted to high binding energies compared to hydrocarbon-type carbon on Cu_2O [25], can be attributed to a combination of the carbon from hydrocarbon plus the oxygenated carbon of a surface allyloxy species (CH_2=$C(CH_3)$– CH_2O–) or from aldehydes [24,26]. Oxygen of the latter species would come out at a position close to the one of oxygen from Cu_2O, but with a weak intensity.

In spectrum C (early stage 4 of the reaction, NO conversion at a maximum rate), the Cu-2p

and $L_{2(3)}M_{4,5}M_{4,5}$ spectra appear to be the same as those of reduced Cu, showing the metallic copper state. The broad and weak O-1s peak can be fitted with two contributions at 530.9 eV and 533.0 eV, the latter superimposed on the copper Auger line [27]. The O-1s peak at 533.0 eV and the C-1s peak at 286.1 eV are attributed to carbon from oxygenated active species, probably the aldehyde species [27–29]. However, the existence of a surface intermediate containing C, O and N atoms cannot be excluded. No N-1s peak could be unambiguously detected, due to the overlap with the LMM Auger lines of Cu. Note that the O-1s peak at 530.9 eV is more than ten times lower than the one at 530.7 eV in spectrum B, and can be ascribed to adsorbed oxygen or NO.

In spectrum D (end of stage 4 of the reaction), a new C-1s peak at 284.2 eV is observed and dominating. This peak can be unambiguously attributed to carbon residues [28]. The same two O-1s peaks are present and appear as shoulders to the Cu Auger lines. In comparison with spectrum C, the O-1s peak at 530.9 eV has almost the same intensity, whereas the O-1s peak at 533.0 eV and the C-1s peak at 286.1 eV are weaker, indicating fewer active species on Cu at this stage. The copper is still zero-valent.

Whether these XPS spectra are representative of only a restricted area of the sample, in other words, whether the surface is homogeneous or not, may be questioned. Worth noting is that we changed the sample position several times at each stage of the analysis and obtained identical spectra.

3.2. Influence of oxygen

3.2.1. Kinetics

The reaction of NO + i-C_4H_8 was tested in the absence of oxygen; it is shown in Fig. 3. The rate of reduction of NO progressively increases throughout the reaction, with no clear transitions between slow and rapid stages. The total amount of consumed hydrocarbon is considerably reduced; it essentially leads to CO and
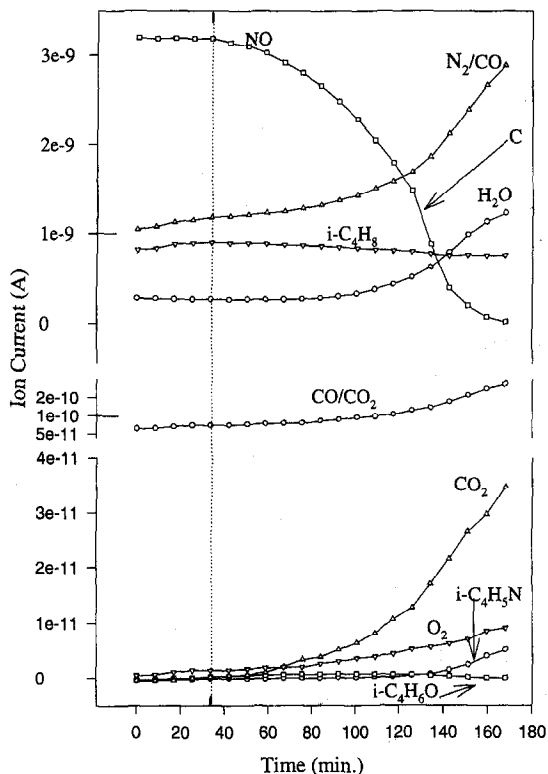
Fig. 3. Time course of a reaction run in the absence of oxygen in the reactant mixture, $T = 770$ K.

Table 1
Catalytic activity for the NO conversion as a function of $P(O_2)$ at 770 K

$P(O_2)$ (Torr)	0.3	0.5	1.0	1.4	1.6
Catal. activity (10^{-5} mol/m^{2}s)	1.3	1.1	1.4	1.4	1.1

conversion of NO and O_2. It appears that the rapid conversion of NO is delayed by a high initial pressure of oxygen.

It should be remembered that the maximum investigated pressure of oxygen, 1.6 Torr, still corresponds to reducing conditions. This is possibly the reason why the increase in oxygen pressure did not favor the NO_2 formation as one would have expected [9,10].

3.2.2. Surface analysis

The carbon and oxygen signals plotted in Fig. 5(a, b) correspond to two reactions, one performed under 'standard' conditions as above and one performed in the absence of oxygen. In these analyses, the reactions were stopped when the rate of NO conversion was maximal (points C in Figs. 1 and 3).
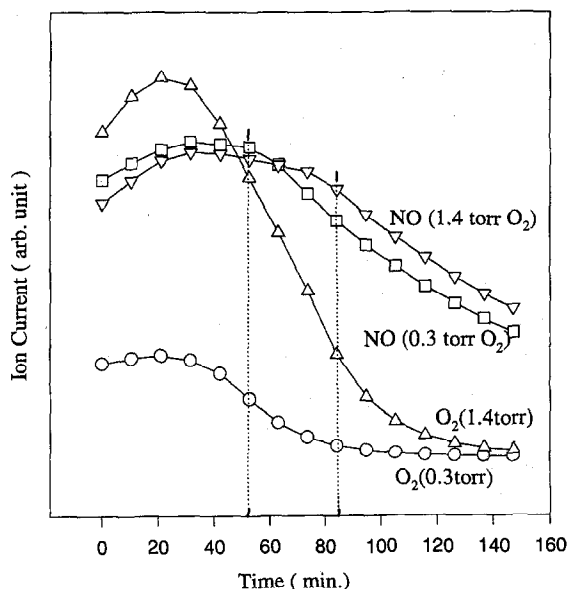
N_2 and to a small fraction of i-C_4H_5N at the end of the reaction. Noticeable is the negligible formation of oxygenate, i-C_4H_6O, without any correlation with the NO conversion profile. This experiment shows that, in the absence of oxygen, NO is mostly decomposed instead of reacting with the hydrocarbon or with an oxygenate.

The influence of $P(O2)$ on the NO reduction was then measured at 770 K, in the 0.3 to 1.6 Torr oxygen pressure range, with $P(NO)$ and $P(i$-C4H8) equal to 1.0 and 1.1 Torr, respectively. In all these reactions, four stages could be identified similarly to what has been observed under standard conditions. The catalytic activity, i.e. highest rate, of NO conversion was not significantly influenced by the oxygen pressure, as is shown in Table 1. The activation period of the reaction was sensitive to $P(O_2)$. This is clear in Fig. 4 which shows the influence of the partial pressure of oxygen upon the

Fig. 4. Time course of NO and O_2 concentrations at different O_2 initial pressures, $P(i$-$C_4H_8) = 1.1$ Torr, $P(NO) = 1.0$ Torr, Ar as balance gas, total pressure 5.0 Torr, $T = 770$ K.
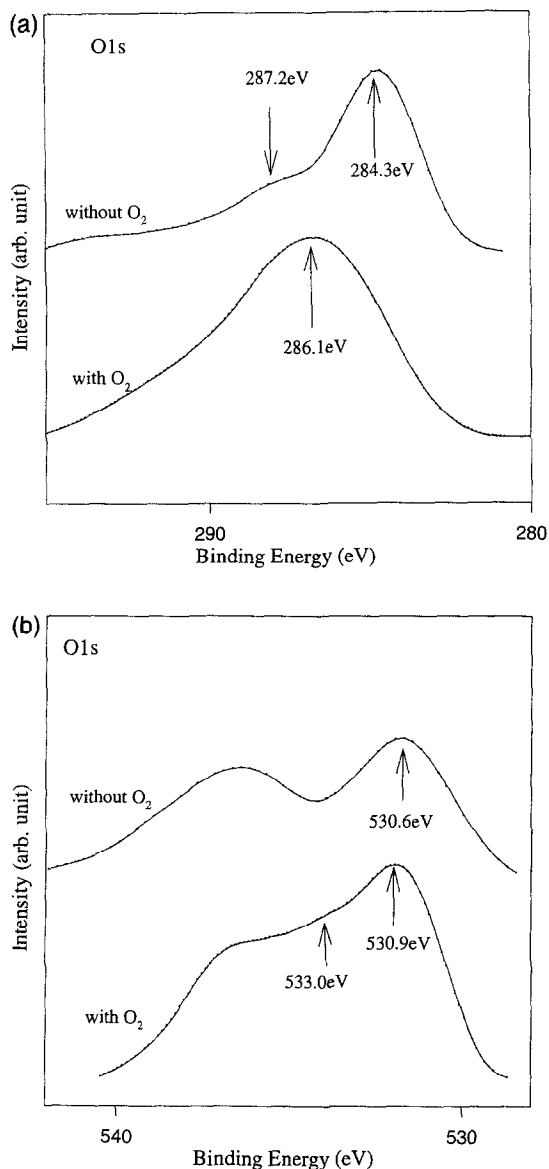
Fig. 5. XPS spectra: C-1s and O-1s lines of the copper surface, reaction run in the absence of oxygen.

The copper lines (not shown) were identical to the ones in Fig. 2(a, b), indicating also zero-valent copper in the active stage of the reaction. Some differences have to be noticed in the oxygen and carbon spectra: the O-1s line at 533 eV and C-1s line at 286.1 eV, identified in a 'standard' reaction, have almost disappeared when no oxygen was admitted in the reaction mixture. Conversely, an intense carbon peak

was observed at 284.3 eV, assigned to adsorbed isobutene or carbon residues. These findings are in good agreement with the very low amount of aldehydic intermediate detected in the gas phase when the reaction was initiated without oxygen.

3.3. Influence of isobutene

A series of catalytic tests were performed at 770 K, with $P(NO) = P(O_2) = 1.0$ Torr and $P(i\text{-}C_4H_8)$ varying from 0 to 1.6 Torr. When $P(i\text{-}C_4H_8) = 0$, i.e., in the absence of hydrocarbon, no conversion of NO was observed, and the copper sample color immediately changed to dark red. Conversion of NO is inhibited when the copper surface is fully oxidized.

Table 2 shows the influence of the initial pressure of isobutene on the catalytic activity (NO conversion and C_4H_6O formation rates). The catalytic activity passes through a maximum with $P(i\text{-}C_4H_8) = 0.5$ Torr and decreases when the initial pressure of $i\text{-}C_4H_8$ increases further. It is remarkable that strong reducing conditions (from 0.5 to 1.1 Torr of $i\text{-}C_4H_8$) induce a low catalytic activity towards NO conversion, although the rate of formation of $i\text{-}C_4H_6O$ remains roughly constant.

Finally, some NO reduction tests have been performed in the presence of $i\text{-}C_4H_6O$, 2-methyl-2-propenal, or varying mixtures of $i\text{-}C_4H_8$ and $i\text{-}C_4H_6O$ in order to compare the reducing abilities of these two compounds. Since these reactions do not exhibit the same profiles, the catalytic activity was estimated from $T_{1/2}$, the time at which half of the initial amount of NO is converted. The set of data summarized in Table 3 shows that the aldehydic organic com-

Table 2
Catalytic activity of the NO conversion and the $i\text{-}C_4H_6O$ formation rate as a function of $P(i\text{-}C_4H_8)$ at 770 K

$P(i\text{-}C_4H_8)$ (Torr)	0	0.3	0.5	1.1	2.6
Catal. activity (10^{-5} mol/m^{2}s)	0	1.8	6.0	1.4	1.0
$i\text{-}C_4H_6O$ form. rate (ion cur. $\times 10^{-15}$)	—	3.4	13	18	15

Table 3
Time when half of NO amount is reduced, in the presence of various reductant mixtures

Reactants (pressure (Torr))	NO + i-C$_4$H$_8$ + O$_2$ (1/0.2/0.5)	NO + i-C$_4$H$_8$ (1/0.5)	NO + i-C$_4$H$_6$O (1/0.2)	NO + i-C$_4$H$_6$O + i-C$_4$H$_8$ (1/0.2/0.5)
$T_{1/2}$ (min)	40	122	36	36

pound is a better reductant for NO than the corresponding alkene.

4. Discussion

The conversion of NO and isobutene in the presence of oxygen was shown to proceed via an oxido-reduction of the copper surface. Oxygen is necessary to initiate the conversion of NO, the partial oxidation of isobutene being an important step of the reaction.

Note that the direct combustion of i-C$_4$H$_8$, resulting from surface reactions and possibly also from gas-phase reactions, is the main process before the time when NO conversion starts (see stage 2 in Fig. 1). It takes place on a strongly oxidized surface of copper (Cu$^+$ + Cu^{2+}) in agreement with previous results in the literature. In propene oxidation on copper oxide, it was shown that oxygen-rich cuprous oxide or cupric oxide favor complete oxidation of the hydrocarbon to carbon dioxide and water; this is obviously not desired in the NO reduction process [30]. There is, at stage 2, no mild oxidation of isobutene and no, or very little, reaction involving NO, probably because of a too high occupancy of the surface by hydrocarbon and oxygen.

NO reduction starts during stage 3, corresponding to the XPS spectrum B Figs. 1 and 2, i.e. when the catalyst surface is in the Cu$^+$ state. At this stage, the active sites (Cu$^+$) are mainly occupied by adsorbed alkoxide and hydrocarbon species. The blocking of the Cu$^+$ sites, the latter being known to be responsible for the formation of N$_2$O when NO is available in the gas phase [31], accounts for the zero concentration of N$_2$O throughout the reaction.

The lattice oxygen (Cu$_2$O), originating from either O$_2$ or NO dissociation, reacts with the i-C$_4$H$_8$ causing oxidation of the hydrocarbon and reduction of the Cu surface. It is already documented that the lattice oxygen is responsible for the selective oxidation of hydrocarbons [32–34]. This corroborates our conclusion that the aldehydic intermediate is essentially formed during stage 3 of the reaction, when copper is not totally reduced. We tentatively assume that the selective oxidation of isobutene, as the initial step in the reduction reaction, occurs according to the following mechanism: formation of allyloxy species (CH$_2$=C(CH$_3$)–CH$_2$O–), followed by the loss of the second hydrogen. This is consistent with the XPS data. In particular, the C-1s peak, broadened towards high binding energies, which can be related to the oxygenated carbon of such species [26]. In the absence of initial oxygen in the gas phase, the formation of aldehyde could be hardly detected.

Kharas suggested, in order to account for the observed requirement of oxygen for the reduction of NO, an oxidative hydrogen abstraction of alkenes which would generate an allyl intermediate; this intermediate would then react with NO [35]. In our case, a mechanism, leading to the formation of an oxidized surface species is preferred in view of C$_4$H$_6$O evolution.

During stage 4 (Fig. 1a), the Cu(I) has been reduced to Cu(0), oxygen has practically disappeared and a certain concentration of i-C$_4$H$_6$O has been reached in the gas phase. The C-1s peak centered at 286.1 eV and associated with a new O-1s peak at a higher binding energy than earlier, 533.0 eV, shows that adsorbed i-C$_4$H$_6$O is now the active species in the NO conversion. The absence of any C-1s peak at 284.4 eV suggests that reduced Cu preferentially attracts

an oxygen-containing species compared to a hydrocarbon species, although the i-C_4H_8 concentration in the gas phase is still high. It is known that aldehydes are more reactive than hydrocarbons [6]. The decrease of i-C_4H_6O in the gas phase is attributed to a reaction of NO with that species rather than with O_2 which is at a low level both in the gas phase and at the catalyst surface (Fig. 2d, spectrum C). The presence of a weak C-1s peak at 286.1 eV (an oxygen-bearing carbon peak) excludes the suggestion that 'coke' deposited on the catalyst becomes the catalytically active surface [36]. During the last stage of the reaction, NO reaction with the aldehyde mainly contributes to NO conversion and leads to N_2, H_2O, i-C_4H_5N, and little CO_2 as products. The direct decomposition of NO into N_2 and O_2 is negligible in view of the low amount of oxygen in the gas phase.

At the end of the reaction, when the concentration of i-C_4H_6O in the gas phase has decreased, the C-1s peak at 286.1 eV and O-1s peak at 533.0 eV, are weaker than in stage C (Fig. 5(c, d), at C and D), and the Cu surface is poisoned by deposited carbon (C-1s at 284.2 eV).

Our results bring evidence of the crucial role of oxygen. It is necessary to initiate the reaction of conversion of NO at an appreciable rate. It induces an oxidation of copper, leaving a surface active for the mild oxidation of the hydrocarbon, a key step of the reaction of NO reduction. Once the rapid stage of NO reduction has been reached, no significant influence of $P(O_2)$ was noticed in the pressure range corresponding to reducing conditions. We also showed that oxygen in excess delays the reaction probably by forming CuO that needs to be reduced to activate the NO reduction process. Excess oxygen also results in a total oxidation of the hydrocarbon (curve not shown) from the beginning of the reaction.

An important consequence is that a non-supported copper catalyst may be oxidized to Cu^{2+} and becomes inactive under slightly oxidizing conditions. It indirectly proves that one role of the support in copper-based catalyst is to facilitate the reaction under net oxidizing conditions, probably by preventing total oxidation of copper, providing an oxygen reservoir and allowing continuous exchanges of oxygen between copper and the support. In order to simulate the role of redox cycles of copper in the reduction of NO with a hydrocarbon, reducing conditions had to be chosen.

In the absence of oxygen, NO dissociation is prevailing; it takes place at a lower rate than its conversion under standard conditions. Though the dissociation of NO provides oxygen, the mechanism via a partial oxidation of the hydrocarbon only slightly contributes to the conversion of NO. This may be ascribed to an initial site-blocking of the surface by carbon as shown by the XPS analysis.

The role of isobutene is connected to the one of oxygen in the formation of a reactive intermediate. In this way, it also prevents the total oxidation of copper. Note that i-C_4H_6O is always at a low concentration, $<$ ca. 0.1 Torr according to our calibration, because precisely, it is a transient intermediate of the reaction. Its formation and its consumption play a determining role in the NO reduction process.

The influence of $P(i$-$C_4H_8)$ can be divided into two ranges: one in which an increase of the pressure promotes the reduction of NO by activating the formation of intermediates, and one where the poisoning of the sample by carbon prevails and induces a loss of activity.

The obvious conclusion is that a rapid conversion of NO can only be observed in a narrow range of the O_2/HC ratio. A too high ratio leads to a deactivation by complete oxidation of the copper surface. A too low ratio blocks both the reaction of oxidation of the hydrocarbon and the conversion of NO.

Our measurements do not permit an absolute differentiation of the fraction of oxidation of isobutene due to oxygen or due to NO. However, in stages 1 and 2 of a standard reaction, the decreases of isobutene and oxygen concen-

trations are the main features of the reaction; moreover, in the absence of oxygen (Fig. 4) the stage of oxidation of i-C_4H_8 to i-C_4H_6O disappears to the benefit of a long, equivalent to stage 3, period during which the consumption of isobutene is extremely slow. These two arguments are in favor of an oxidation of isobutene mainly by oxygen.

Let us remark that, under reducing conditions, the hydrocarbon is not totally oxidized into CO_2 and we do not exclude the possible reduction of NO by CO as a side reaction.

5. Conclusion

The performance of pure copper as a catalyst for NO reduction in the presence of i-C_4H_8 and oxygen was studied by mass spectroscopy, combined with XPS surface analysis at different reaction stages.

Working on a pure, non-supported copper catalyst brought new insights into the understanding of the reaction mechanism and the role of the metal. The post-reaction surface analysis led us to the following conclusions: when the catalyst surface is in the Cu^+ state, an intermediate (i-C_4H_6O) is produced and the NO conversion is slow. The catalyst is then reduced to metallic Cu in the rapid NO conversion stage. The maximum rate of NO reduction correlates well with a 533.0 eV O-1s peak and a broad C-1s peak centered at 286.1 eV, which identify the active species as being adsorbed i-C_4H_6O on the metallic Cu surface. At the end of the reaction, the catalyst surface is poisoned by deposited carbon.

The conversion of NO reaches an appreciable rate only in the presence of oxygen from the beginning of the reaction.

Oxygen has two major roles: (i) it reacts with the hydrocarbon and forms an oxygenated surface intermediate, (ii) it keeps the surface clean by removing carbon deposits.

We tentatively assume that a similar mechanism accounts for the reactivity of supported copper under slightly oxidizing conditions, provided that the support can continuously exchange oxygen with the metal, thus permitting the redox cycle of the latter.

Acknowledgements

References

[1] F. Mathis, Catal. Lett. 28 (1994) 33.
[2] M. Iwamato and H. Hamada, Catal. Today 10 (1991) 57.
[3] J.L.D. Itri and W.M.H. Sachtler, Catal. Lett. 15 (1992) 289.
[4] J.O. Petunchi, G. Sill and W.K. Hall, Appl. Catal. B 2 (1993) 303.
[5] C.J. Bennett, Appl. Catal. A 86 (1992) L1.
[6] C.N. Montreuil and M. Shelef, Appl. Catal. B 1 (1992) L1–L8.
[7] C. Yokoyama and M. Misono, J. Catal. 150 (1994) 9.
[8] Y. Ukisu, S. Sato, G. Muramatsu and K. Yoshida, Catal. Lett. 16 (1992) 11.
[9] M. Sasaki, H. Hamada, Y. Kintaichi and T. Ito, Catal. Lett. 15 (1992) 297.
[10] J.O. Petunchi, G. Sill and W.K. Hall, Appl. Catal. B 2 (1993) 303.
[11] M. Shelef, C.N. Montreuil and H.W. Jen, Catal. Lett. 26 (1994) 277.
[12] D.-J. Liu and H.J. Robota, Catal. Lett. 21 (1993) 291.
[13] W.K. Hall and J. Valyon, Catal. Lett. 15 (1992) 311, and references therein.
[14] T. Iizuka, H. Ikeda and S. Okazaki, J. Chem. Soc. Faraday Trans. 1 (1986) 61, 82.
[15] A.R. Balkenede, H. den Daas, M. Huisman, O.L.J. Gijzeman and J.W. Geus, Appl. Surf. Sci. 47 (1991) 341.
[16] W.E.J. van Kooten, J.P.C. van Nispen, O.L.J. Gijzeman and J.W. Geus, Appl. Surf. Sci. 90 (1995) 137.
[17] Y. Li and W.K. Hall, J. Catal. 129 (1991) 202.
[18] G. Schön, Surf. Sci. 35 (1973) 96.
[19] G. Ertl, R. Hierl, H. Knözinger, N. Thiele and H.P. Urbach, Appl. Surf. Sci. 5 (1980) 49.
[20] S. Evans, J. Chem. Soc. Faraday Trans. II(71) (1975) 1044.
[21] K.S. Kim, J. Electron. Spectrosc. 3 (1974) 217.
[22] P.E. Larson, J. Electron. Spectrosc. 4 (1974) 213.
[23] K. Sakurai, Y. Okamoto, T. Imanaka and S. Teranishi, Bull. Chem. Soc. Jpn. 49(7) (1976) 1732.
[24] T. Robert, M. Bartel and G. Offergeld, Surf. Sci. 33 (1972) 123.
[25] K.H. Schulz and D.F. Cox, Surf. Sci. 262 (1992) 318.
[26] K.H. Schulz and D.F. Cox, J. Phys. Chem. 97 (1993) 647.
[27] M. Bowker and R.J. Madix, Surf. Sci. 102 (1981) 542.

[28] V. Gellus, P.F. Hedén, J. Hedman, B.J. Lindberg, R. Manne, R. Nordberg, C. Nordling and K. Siegbahn, Phys. Scr. 2 (1970) 70.

[29] K.H. Schulz and D.F. Cox, J. Phys. Chem. 97 (1993) 3555.

[30] B.J. Wood, H. Wise and R.S. Yolles, J. Catal. 15 (1969) 355.

[31] R. Hierl, H.P. Urbach and H. Knözinger, J. Chem. Soc. Faraday Trans. 88(3) (1992) 355.

[32] H.H. Kung, Transition Metal Oxides (Elsevier Science Publ., 1989) p. 200.

[33] K.H. Schulz and D.F. Cox, J. Catal. 143 (1993) 464.

[34] A. Bielanski and J. Haber, J. Catal. Rev. Sci. Eng. 19 1 (1979).

[35] K.C.C. Kharas, Appl. Catal. B(2) (1993) 207.

[36] E. Kikuchi, K. Yogo, S. Tanaka and M. Abe, Chem. Lett. (1991) 1063.