

Catalytic reduction of nitric oxide over copper Part III: Influence of water vapour

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Abstract

This paper reports on the effect of water vapour on the reduction of NO over copper in the presence of oxygen and isobutene. Reactions were studied at 700 K and at 770 K. Mass spectroscopy (MS) and X-ray photoelectron spectroscopy (XPS) were used to monitor the gas phase composition during reaction and to analyse the catalyst surface, respectively. XPS spectra show that the presence of water vapour influences the Cu oxidation state. At 700 K adsorption of aldehyde is partly blocked by copper oxide resulting in a decrease in the activity of the reaction, although the main mechanism is not changed. At 770 K, water vapour generates an even more oxidised surface, which promotes a complete oxidation of hydrocarbon, the main mechanism of NO reduction is changed, and the activity of the reaction is slightly increased. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

As a result of the strict legislation concerning exhaust gas emissions from automobiles, catalytic reduction of NO has received increased attention. Since 1990, when Held et al. [1] and Iwamoto [2] reported that Cu-ZSM-5 shows high activity in the reduction of NO with hydrocarbon in an oxygen-rich condition, copper-based oxides and copper-ion-exchanged zeolites have been extensively explored for the purpose of

controlling NO emission from diesel and lean-burn gasoline engines [3,4]. The ultimate aim of these studies was to reveal the surface process and reactivity of the copper-containing catalysts under real exhaust conditions, but, most of the studies were made in the absence of water vapour. This is unrealistic, since there is about 10% water vapour in the real automobile emission gases, and water vapour is also a product of the reaction when a hydrocarbon is chosen as the reductant. In fact, the presence of steam severely poisons the NO reduction reaction, and this poisoning by water vapour is a main obstacle for Cu-ZSM-5 to be commercialised as a

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catalyst for the reduction of NO by a hydrocarbon (cf. recent reviews by Armor [5] and Walker [6]). It was suggested that dealumination within Cu-ZSM-5 or substantial sintering of the Cu species in the presence of water vapour is the possible deactivation pathway [6]. The influence of water vapour on the NO reduction was also studied on Co-ZSM-5 [5,7]. Irreversible deactivation, such as that occurring within Cu-ZSM-5 was not observed with the Co-ZSM-5 catalyst used, instead it was suggested that the effect of water vapour on this type of catalyst is mainly a kinetic phenomenon, and that adsorption competition between water vapour and NO inhibits the reaction [7]. It was also suggested that the deactivation by water vapour of a metal-exchanged zeolite catalyst depends not only on the type of zeolite but also on the type of metal exchanged, and the difference between Cu-ZSM-5 and Co-ZSM-5 catalysts was tentatively explained as being due to the different redox properties of the two metals [7].

Although several studies have been devoted to water, as well as water and NO coadsorption on metal and metal oxide surfaces [8,9], further work is needed to clarify the mechanism of the inhibiting effect of water vapour on different metals in reactions involving NO and a hydrocarbon. The study is of practical importance in order to improve the catalytic activity and durability of metal-based catalysts in the presence of water vapour.

We already reported our results concerning the reduction of NO by hydrocarbon on a copper planar surface [10]. Our work aimed at understanding the reactivity and mechanism of the reaction by correlating the kinetics results to the surface characterisation. It has been established that the catalytic surface is initially in the Cu_2O state. The hydrocarbon is activated on the surface; it withdraws an oxygen from the surface oxide and produces an oxygenated intermediate, $i\text{-C}_4\text{H}_6\text{O}$. At that stage, the conversion of NO is slow and oxygen from the gas phase contributes to restore the copper oxide surface following a Mars and Van Krevelen mecha-

nism. Oxygen is also consumed by hydrogen and carbon coming from the hydrocarbon, producing carbon dioxide and water. At the end of the initial stage of the reaction, the oxygen concentration is low in the gas phase and the copper surface is in a reduced state. At that point, $i\text{-C}_4\text{H}_6\text{O}$ reacts with NO to give N_2 , H_2O and CO_2 . Supplementary experiments of NO reduction by $i\text{-C}_4\text{H}_6\text{O}$ have also been performed, which support our proposal.

In continuation of our work dealing with NO reduction on a copper surface, we again chose a pure copper disc as a model catalyst and we investigated the influence of water vapour upon the mechanism of NO reduction in the presence of a hydrocarbon. By using mass spectroscopy (MS) and photoelectron spectroscopy (XPS), the changes in the reactivity and in the mechanism of the reaction by the addition of water to the reactants will be addressed.

2. Experimental

The catalyst sample used in the experiments was a polycrystalline copper disc with a surface area of 70 cm^2 ; it was reduced in hydrogen with a pressure of 10 Torr at 870 K for 2 h before each catalytic test.

The gas mixture used in the experiments consisted of 1.0 Torr NO, 1.0 Torr O_2 , 0.5 Torr $i\text{-C}_4\text{H}_8$ and 2.5 Torr H_2O in the case of a 'wet' gas mixture. In the 'dry' gas mixture, the H_2O was replaced by Ar, keeping an initial pressure of 5 Torr.

In Fig. 1, a schematic outline of the experimental system is presented. Part (A) is a batch

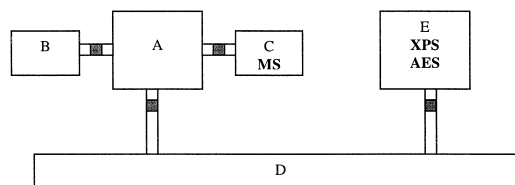


Fig. 1. Schematic outline of the experimental system. (A) Reactor; (B) gas handling system; (C) MS; (D) transfer line; (E) surface analysis chamber.

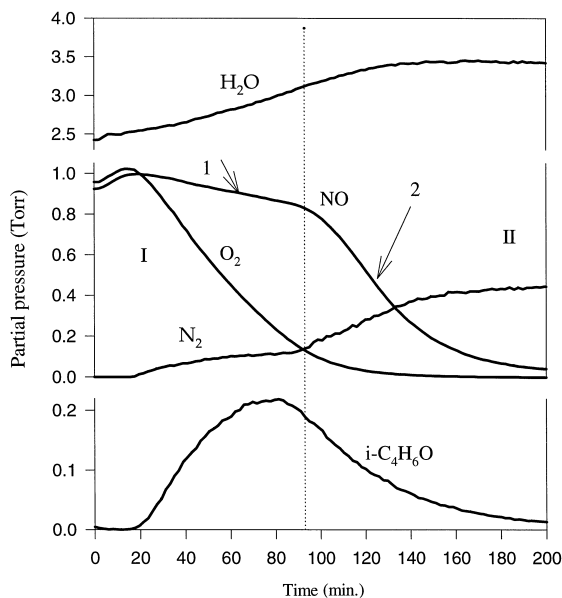


Fig. 2. Development of NO, O₂, *i*-C₄H₆O in the reaction at 700 K. $P_{\text{NO}} = P_{\text{O}_2} = 1.0$ Torr, $P_{i\text{-C}_4\text{H}_8} = 0.5$ Torr, $P_{\text{H}_2\text{O}} = 2.5$ Torr. The numbers I and II correspond to the slow and rapid NO conversion stages respectively, 1 and 2 show the instants when the reaction was interrupted for XPS measurements.

reactor as described previously [10], equipped with gas handling (B) and MS systems (C). A needle valve between the MS chamber and the reactor is used, ensuring a constant sampling of the gas phase during the reaction process. Part (E) is a surface analysis chamber equipped with XPS and Auger electron spectrometry (AES) facilities. Between (A) and (E), is an ultra high vacuum (UHV) transfer line (D). When characterisation of the catalytic surface is needed, the whole reaction system is cooled to room temperature, the reactor is evacuated to high vacuum by a turbo pump, then the sample can be transferred into the surface analysis chamber. Such a transfer process avoids contamination of the catalyst by the air.

During the catalytic tests, the gas phase composition was monitored by MS. Quantitative MS data were obtained using the fragmentation patterns determined experimentally from calibration measurements with pure gas known mixtures [11].

At certain stages of the reaction, XPS was used to characterise the catalyst surface. In the XPS measurement, an AlK_α (1486.6 eV) X-ray source was used, and the electrons were energy analysed with a CLAM 2 hemispherical energy analyser. A small gold foil attached to the copper sample provided an internal reference for the binding energy of Au4f_{7/2} at 84 eV. All peak intensities have been normalised to the one of the Cu2p_{3/2} level. The overall resolution was set to 1 eV.

3. Results

3.1. Kinetics data

The effect of water vapour on the reduction of NO over Cu was first studied at 700 K. Fig. 2 shows the H₂O, NO, O₂, N₂ and *i*-C₄H₆O partial pressures in the gas phase, the initial reactant pressures being: $P_{\text{NO}} = P_{\text{O}_2} = 1.0$ Torr, $P_{i\text{-C}_4\text{H}_8} = 0.5$ Torr, $P_{\text{H}_2\text{O}} = 2.5$ Torr. The main

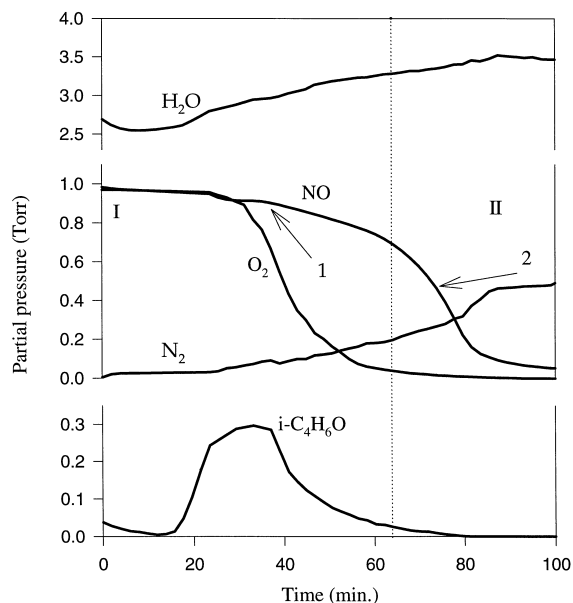


Fig. 3. Development of NO, O₂, *i*-C₄H₆O in the reaction at 770 K. $P_{\text{NO}} = P_{\text{O}_2} = 1.0$ Torr, $P_{i\text{-C}_4\text{H}_8} = 0.5$ Torr, $P_{\text{H}_2\text{O}} = 2.5$ Torr. The numbers I and II correspond to the slow and rapid NO conversion stages respectively, 1 and 2 show the instants when the reaction was interrupted for XPS measurements.

features of the reaction process are not altered by the addition of water vapour to the reactants: NO conversion proceeds in two stages under both conditions, a slow conversion (together with partial oxidation of $i\text{-C}_4\text{H}_8$ to $i\text{-C}_4\text{H}_6\text{O}$) followed by a rapid conversion (associated with consumption of $i\text{-C}_4\text{H}_6\text{O}$), and the main products of the reaction, N_2 , CO_2 , H_2O , $i\text{-C}_4\text{H}_6\text{O}$, are not influenced by the presence of water

vapour. Under these conditions, it may be said that the addition of water vapour does not change the main path of the reaction of $i\text{-C}_4\text{H}_6\text{O}$ with NO [10]. However, it is observed that the presence of 2.5 Torr water vapour decreased both the rate of $i\text{-C}_4\text{H}_6\text{O}$ consumption and the rate of NO conversion, the latter by a factor of 30%: a maximum activity of $1.6 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ is reached with a ‘dry’ gas mixture com-

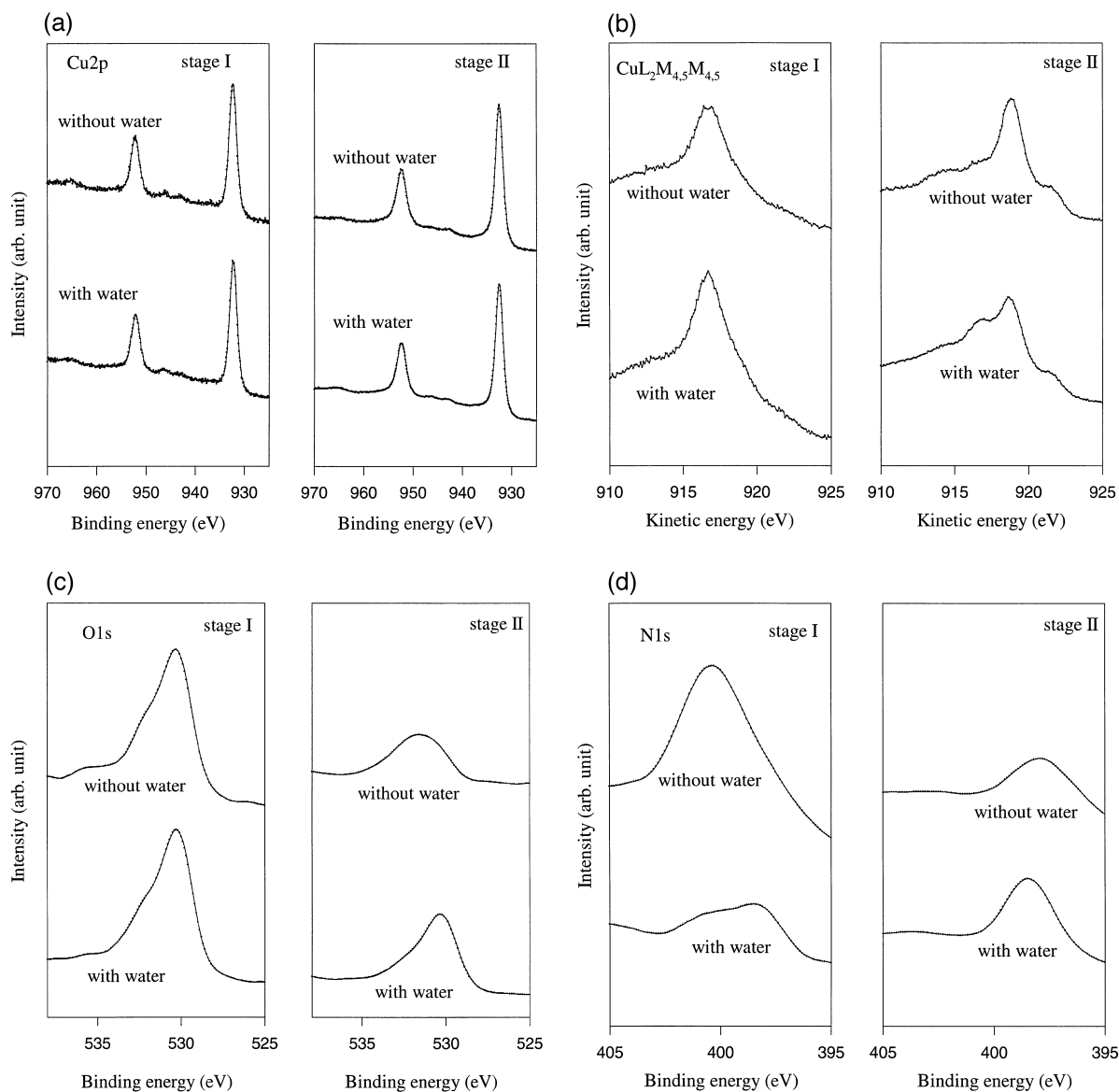


Fig. 4. XPS spectra from Cu surfaces at 700 K. Same reaction conditions as in Fig. 2. (a) Cu 2p_{3/2}, (b) Cu L₂M_{4.5}M_{4.5}, (c) O 1s, (d) N 1s.

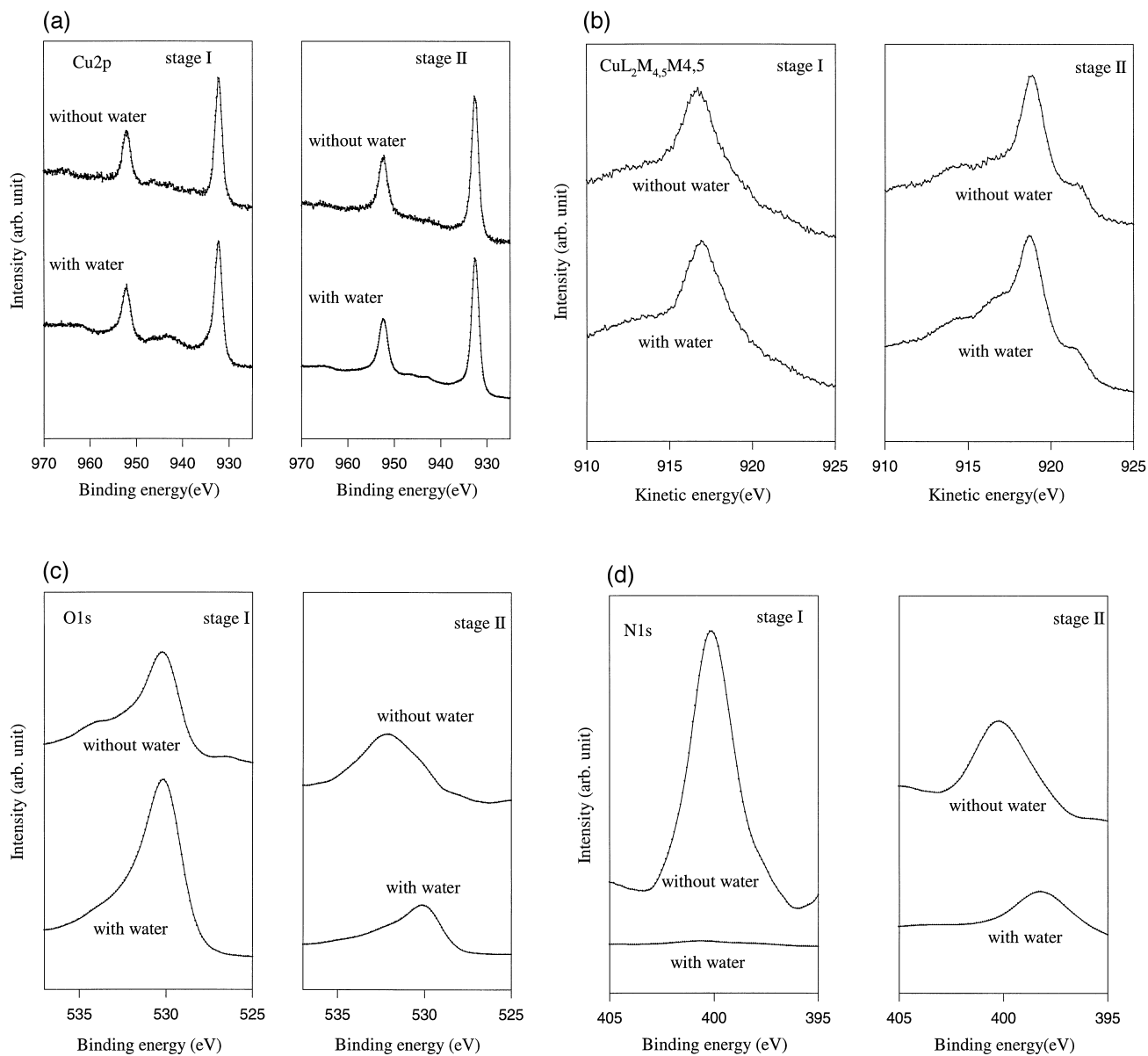


Fig. 5. XPS spectra from Cu surfaces at 770 K. Same reaction conditions as in Fig. 3. (a) Cu 2p_{3/2}, (b) Cu L₂M_{4,5}M_{4,5}, (c) O 1s, (d) N 1s.

Table 1

Binding or kinetic energies of XPS features for the reactions at 700 K (underlined data show the main peaks)

700 K	Cu2p _{3/2} (eV)	Cu L ₂ M _{4,5} M _{4,5} (eV) k.e.	O1s (eV)	N1s (eV)
Stage I without water	<u>933</u>	<u>917</u>	<u>530</u> 532	<u>401</u> 398
Stage I with water	<u>933</u>	<u>917</u>	<u>530</u> 532	<u>401</u> <u>398</u>
Stage II without water	<u>933</u>	<u>919</u>	<u>532</u>	<u>398</u>
Stage II with water	<u>933</u>	<u>919</u> 917	<u>530</u> 532	<u>398</u>

pared to $1.1 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ with a ‘wet’ gas mixture.

The influence of water vapour on NO reduction with isobutene on copper was then investigated at 770 K with the same gas ratio as at 700 K. The H₂O, NO, O₂, N₂ and *i*-C₄H₆O partial pressures throughout the reaction are illustrated in Fig. 3. It must be noted that the variations in *i*-C₄H₆O concentration in the gas phase are no longer related to the rate of reduction of NO. After about 15 min, *i*-C₄H₆O is still produced on stream, but it disappears before the onset of rapid NO reduction. In the most active stage of the NO conversion, there is in fact almost no *i*-C₄H₆O left in the gas phase. It is difficult to propose that the reaction of *i*-C₄H₆O with NO is still the main path of the reaction. It is worth pointing out that the maximum amount of *i*-C₄H₆O is increased and the consumption of *i*-C₄H₆O is more rapid with a ‘wet’ gas mixture than with a ‘dry’ gas mixture. Finally the activity in NO conversion is increased in the presence of water vapour passing from a maximum rate of $2.3 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ with a ‘dry’ gas mixture to $3.2 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ with a ‘wet’ gas mixture.

3.2. Surface characterisation

In order to better elucidate the effect of water vapour upon the reduction of NO, XPS analyses were performed on the copper surface for the reactions run at 700 K and 770 K, after interrupting the reaction either in the slow NO conversion stage (marked as 1 in Figs. 2 and 3) or in the rapid NO conversion stage (marked as 2 in Figs. 2 and 3), with the ‘wet’ and ‘dry’ gas mixtures, respectively. The Cu2p_{3/2}, Cu L₂M_{4,5}M_{4,5} (referring to the kinetic energy), O1s and N1s spectra are shown in Fig. 4a–d and Fig. 5a–d. The corresponding binding or kinetic energies are listed in Tables 1 and 2.

3.2.1. XPS data for reactions at 700 K (Fig. 4a–d; Table 1)

By combining the Cu2p_{3/2} and Cu L₂M_{4,5}M_{4,5} spectra in Fig. 4a and b, with the XPS references for copper and copper oxides [12–16], it can be easily assessed that, in the stage of slow NO conversion, the catalyst is in the Cu(I) state for the reactions both with and without water vapour (Cu2p_{3/2}: 933 eV, Cu L₂M_{4,5}M_{4,5}: 917 eV). The two O1s spectra

Table 2

Binding or kinetic energies of XPS features for the reactions run at 770 K (underlined data show the main peaks)

770 K	Cu2p _{3/2} (eV)	Cu L ₂ M _{4,5} M _{4,5} (eV) k.e.	O1s (eV)	N1s (eV)
Stage I without water	<u>933</u>	<u>917</u>	<u>530</u> 532	<u>401</u>
Stage I with water	<u>933</u> 934	<u>917</u>	<u>530</u> 532	–
Stage II without water	<u>933</u>	<u>919</u>	<u>530</u> <u>532</u>	<u>401</u>
Stage II with water	<u>933</u>	<u>919</u> 917	<u>530</u> 532	<u>398</u>

shown in Fig. 4c are quite similar, with a main peak at 530 eV and a shoulder at 532 eV. Noticeable are the differences in the intensities of the two N1s peaks (Fig. 4d). The total area of the peaks decreases significantly when adding water, the low binding energy peak (398 eV) being the more intense one, while the high binding energy peak (401 eV) is dominating in the absence of water.

For the reactions both with and without water vapour, the Cu2p_{3/2} peak remains at 933 eV at the rapid NO conversion stage. Note that the Cu2p_{3/2} for Cu(I) and Cu(0) are at similar binding energies. However, the main Cu L₂M_{4,5}M_{4,5} line shifted to 919 eV, which suggests that the surface is mostly in the Cu(0) state. With the ‘wet’ reactants, the shoulder at 917 eV together with the main Cu L₂M_{4,5}M_{4,5} line shows that some copper is left on the surface in the +1 oxidation state. The N1s level in both spectra (Fig. 4d, stage II) displays only one component at 398 eV. The main differences lie in the O1s spectra in Fig. 4c: when no water is added in the reactants, the O1s peak is centred at 532 eV, but when water vapour is involved in the reactants, the O1s line can be fitted to two contributions: a main one at 530 eV and a shoulder at 532 eV, the latter having a slightly lower intensity than that observed at 532 eV after a reaction run with a ‘dry’ gas mixture.

3.2.2. XPS data for reactions at 770 K (Fig. 5a–d; Table 2)

When the reactions are run at 770 K and interrupted in the slow NO reduction stage, the positions of the Cu2p_{3/2} and Cu L₂M_{4,5}M_{4,5} lines (Fig. 5a and b) lead to the conclusion that the catalyst surface is mainly in the Cu(I) state both with and without water vapour in the reactants. In the presence of water vapour, a small amount of Cu(II) is also present, as shown by a small contribution to the Cu2p_{3/2} line at 934 eV and its shake up satellite. In both types of experiments, the O1s line can be fitted to two contributions: a small peak at 532 eV and a

main one at 530 eV, the latter being more intense with the ‘wet’ than with the ‘dry’ gas mixture (Fig. 5c). N1s spectra are displayed in Fig. 5d, where it is evident that there is an intense N1s peak centred at 401 eV with a ‘dry’ gas mixture, but that N1s could hardly be detected in the case of a ‘wet’ gas mixture.

When the reaction run with no addition of water is stopped in the rapid stage, the catalyst is in the Cu(0) state according to the positions of the Cu2p_{3/2} and Cu L₂M_{4,5}M_{4,5} peaks. The O1s line is fitted to a main peak at 532 eV and a minor one at 530 eV. The N1s peak still appears at 401 eV, but its intensity is lower than that at the same binding energy in the former stage. When water vapour is added to the reactants, the Cu2p_{3/2} lines are unchanged, but the Cu L₂M_{4,5}M_{4,5} line shows a shoulder at 917 eV, which indicates the existence of a small amount of Cu(I) together with Cu(0). The N1s peak appears at 398 eV, the O1s line is weak and can be deconvoluted into a main one at 530 eV and another at 532 eV.

4. Discussion

Our discussion is based upon a correlation between kinetics results and surface characterisation. It assumes that the species left after cooling and transferring the sample are a good indication of the ones present under reaction conditions.

4.1. Influence of water vapour upon the reaction at 700 K

4.1.1. Stage I

When the reactions are in the slow stage of NO reduction, the catalyst surfaces being in the Cu(I) state whether water vapour is present or absent in the reactants, the 530 eV O1s peak can be unambiguously assigned to oxygen from cuprous oxide [17]. The 532 eV O1s peak is attributed to oxygen in NO and (or) OH species.

This assignment is motivated by the following reasons: (1) molecular adsorption of NO is observed on Cu₂O surface [18–26]; and (2) water dissociates when adsorbed on Cu and Cu₂O surfaces, giving rise to surface hydroxyl groups, which have an O1s binding energy at about 532 eV [27–29]. The N1s peak at 401 eV can be assigned to nitrogen in molecularly adsorbed NO, similar binding energy has been reported previously for the same species [18–21], while the 398 eV N 1s peak is identified as N in Cu nitride resulting from NO dissociation, which is in good agreement with previous studies of NO adsorption on Cu surfaces [21–24]. Note that for reactions run with added water, the 398 eV N1s line dominates while the one at 401 eV significantly decreases compared to what is observed with a ‘dry’ gas mixture. At the same time, the O1s feature does not change much, showing that the peak at 532 eV is in fact mainly due to OH groups. These hydroxyl groups decrease the surface concentration in molecular NO species and facilitate their dissociation. A similar effect has been shown by Au et al. on Cu(111) [29] and also reported by G. Somorjai [30].

We concluded in the previous work [10] that, the first step in the reduction of NO is the partial oxidation of *i*-C₄H₈ to *i*-C₄H₆O. The present work shows that, though the addition of water vapour slightly modifies the nature of the adsorbed species, it has almost no effect on the formation of *i*-C₄H₆O (Fig. 2).

4.1.2. Stage II

In the rapid NO conversion stage, with or without water vapour, the surface is mainly in the zero-valent state.

In the absence of water vapour, the 532 eV O1s peak is attributed to adsorbed aldehyde species, i.e., *i*-C₄H₆O [10], and possibly also to OH. We exclude the possibility of a contribution from adsorbed NO to this O1s peak, because no N1s peak at 401 eV is detected at that stage. The N1s peak is at 398 eV, confirming that NO is completely dissociated on a Cu(0)

surface and probably forms nitride species [21–24].

When water vapour is added to the reactants, the presence of a shoulder to the Cu Auger line at 917 eV, as well as an increased contribution of the O1s at 530 eV shows that water favours Cu₂O on the surface. The O1s peaks at 532 eV is surprisingly weaker than in the above case. Our interpretation is that this high binding energy peak is mainly due to aldehydes and that water in the gas phase partially inhibits adsorption of these species to the benefit of an oxidation of the Cu surface. We suggest that, under our conditions, Cu₂O on the surface decreases the rate of the conversion of NO by inhibiting adsorption of the aldehyde intermediate.

A comparison of the N1s peaks and the O1s lines for ‘dry’ and ‘wet’ gas mixtures indicates that, conversely to the aldehyde adsorption, in the most active stage of the reaction, the presence of water in the gas phase does not alter the adsorption of NO. This conclusion is different from what was observed by Li et al. for a Co-ZSM-5 surface [7]. They suggested that the inhibiting effect of H₂O is due to a blocking of NO adsorption. Such a discrepancy confirms that mechanisms for NO conversion are different on Cu and Co-ZSM-5 surfaces.

4.2. Water vapour effect on the reaction at 770 K

4.2.1. Stage I

The above description of XPS spectra leads to a straightforward characterisation of the surface after a reaction run at 770 K. In the absence of water vapour, the O1s line at low binding energy, 530 eV, originates from Cu₂O. The main O1s contribution at 532 eV and the N1s peak at 401 eV are due to molecularly adsorbed NO. When water vapour is added to the reactants, adsorbed OH species mainly contribute to the 532 eV peak, since no nitrogen-containing species are detectable. The 530 eV peak, which has a higher intensity with a ‘wet’

than with a ‘dry’ gas mixture, can be assigned to O from Cu_2O and CuO . Obviously, an excess of water in the gas phase induces a deeper oxidation of the surface and blocks the adsorption of molecular NO on the catalyst surface. This strongly oxidised surface is responsible for the total oxidation of $i\text{-C}_4\text{H}_6\text{O}$ occurring before the stage of the rapid NO conversion (see Fig. 3). This is in good agreement with the results of Wise and Yolles who reported that oxygen-enriched Cu_2O and CuO favour a complete oxidation of propylene to CO_2 and H_2O [32].

In the case of the reaction run with a ‘dry’ gas mixture, the effect of temperature on the surface states of the catalyst in the slow stage is interesting: at 770 K, an enhancement of NO adsorption is clear from the intensity of the N1s peak. A similar phenomenon has been observed by Gandhi and Shelef, who claimed that NO adsorption, accompanying an oxidation of the surface, is promoted at high temperature [31]. The influence of water vapour in the slow NO conversion stage also varies with temperature: at 770 K, water vapour inhibits both the reduction of Cu and the adsorption of NO; whereas at 700 K, the reduction of the Cu surface is not influenced by the addition of water vapour, and a slight change in the N1s line is observed.

4.2.2. Stage II

When the reaction is stopped in the most active stage of NO reduction, the copper surface is reduced to $\text{Cu}(0)$. In the absence of added water vapour, we assign the low BE O1s peak to chemisorbed oxygen, and the high BE peak to a combination of OH groups, adsorbed aldehyde species and possibly molecularly adsorbed NO. The absence of the nitride species at 770 K (Fig. 5d, stage II, without water) can be explained by a decomposition of these species at high temperature as it has already been reported [33]. We consider that nitride decomposition at high temperature benefits the conversion of NO because it provides sites for the adsorption of reactive species.

Under ‘wet’ conditions, the 530 eV O1s peak is attributed to cuprous oxide. Considering the rapid consumption of $i\text{-C}_4\text{H}_6\text{O}$, which proves the high reactivity of these species, and the very high concentration of water vapour in the gas phase, we assign the O1s peak at 532 eV to OH species rather than to adsorbed aldehydes. Moreover, MS data, showing no correlation between NO and $i\text{-C}_4\text{H}_6\text{O}$ conversion curves, lead to the conclusion that, under these conditions, $i\text{-C}_4\text{H}_6\text{O}$ is not the active intermediate of the reaction. The presence of OH enhances NO dissociation, which now becomes the main path of the reaction and explains the N1s peak at 398 eV. The role of hydrocarbon is probably to prevent deactivation of the surface by too a deep oxidation.

Our conclusion that NO conversion via dissociation seems is favoured by water at high temperature has to be considered with caution. It is related to the fact that, in the initial stage of the catalytic process, the total oxidation of the hydrocarbon takes place, leaving very reactive, partially reduced, copper sites which will dissociate NO. It does not exclude deactivation effects by water on a copper-supported catalyst. It simply means that deactivation has to be explained by other effects than simply changes in the adsorption and oxidative properties of copper.

5. Conclusion

In the present study, the influence of water vapour on the reduction of NO over copper in the presence of $i\text{-C}_4\text{H}_8$ and O_2 has been investigated at 700 K and 770 K, using MS for the gas phase composition analysis and XPS for surface characterisation in different stages of the reaction.

Partial deactivation by water vapour is observed on copper at 700 K, the activity of the reaction is therefore 30% decreased. The decrease in the amount of adsorbed aldehyde together with the appearance of Cu_2O is responsi-

ble for the deactivation of the reaction. However, the main path of the NO reduction is not changed.

Addition of water vapour to the reactants at 770 K inhibits the reduction of the catalyst surface as it does at 700 K. The oxygen-enriched surface causes, at that temperature, a rapid oxidation of *i*-C₄H₆O to CO₂. We believe that the mechanism of the NO reduction is changed under these conditions, NO dissociation becoming a predominant reaction, promoted by the presence of water vapour.

These results show the temperature sensitivity of the role of water upon the mechanism of NO conversion in the presence of isobutene. They also make clear the importance of the oxidation–reduction process of the copper surface for the main mechanism of NO reduction.

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