Catalytic reduction of nitric oxide over copper.
Part II: Influence of sulfur dioxide

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Abstract

The influence of sulfur dioxide on the reduction of nitric oxide over copper, in the presence of isobutene and oxygen, has been examined under reducing conditions in the 720 to 820 K temperature range. The catalytic activity of NO conversion was drastically decreased by the presence of a few ppm of SO_2 in the gas phase, and the toxicity of sulfur was reduced when the temperature was increased. The Cu sample was characterized by X-ray photoelectron spectroscopy, at different stages of the reaction. It was demonstrated that sulfur dioxide poisoned NO conversion by hindering the partial oxidation of the hydrocarbon and by occupying the active sites, both factors contributing to a decrease in the surface concentration of the active intermediate (oxygenated product). Two kinds of adsorbed sulfided species, SO_4^{2-} and S^{2-}, were identified on the Cu surface. At the end of the reaction, the catalyst surface was poisoned both by carbon and sulfur species.

Keywords: Nitric oxide reduction; Sulfur dioxide; Copper; Isobutene; X-ray photoelectron spectroscopy; Environment

1. Introduction

Activity of a model copper catalyst was reported in the first part of this study [1]. A disk of pure copper was shown to be active in the reduction of NO by isobutene in the presence of oxygen. Under reducing conditions and at $T = 770$ K, the reduction of nitric oxide proceeds via a partial oxidation of isobutene, leading to isobutenal as an active intermediate.

Compared with noble metals, copper based catalysts are very sensitive to sulfur poisoning [2]. There has been so far a limited number of studies devoted to SO_2 deactivation of copper-ion-exchanged zeolite catalysts in NO reduction processes. Iwamoto et al. showed that sulfur dioxide can completely block nitric oxide decomposition but only slightly poisons its selective reduction by propene; the authors attributed this poisoning phenomenon to a change in the electronic state of the copper ions [3]. In some other studies, the deactivation was attributed to pore blocking by species resulting from an SO_2–NH_3 interaction when NH_3 was used as

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reductant [4], or by strong interactions between SO_4 and copper ions in the direct decomposition of NO [5]. IR studies of SO_2 adsorption on Cu/Al_2O_3 catalysts have demonstrated that, in the presence of an organic compound, SO_2 decomposes on the surface to give adsorbed sulfur species and two types of new surface sites, Cu^0–S and Cu^+–S [6]. It was shown by Lavalley et al. that copper on alumina acts as a catalyst for oxidation of SO_2 to SO_3 which then forms a surface sulfate at the copper sites. These $CuSO_4$ were also shown to be easily decomposed by H_2 at 693 K [7]. Adsorption of NO as a probe molecule, tested on sulfated CuO surfaces, indicated that SO_4 anions on the surface increase the positive charge of the copper sites [8].

These results from recent literature clearly show that the nature of the poison species, and their induced toxicity are highly dependent upon the reducing agent and on the type of copper–sulfur dioxide interactions. In order to obtain new insights into the mechanism of copper deactivation by SO_2, in the reduction of NO by a hydrocarbon, our approach consisted in adding controlled amounts of sulfur dioxide into the catalytic system which has been well characterized in the first part of this work. In this second part of our study, traces of sulfur dioxide were admitted together with the reactants, NO, O_2 and i-C_4H_8, in the gas phase, and attention was paid to the effects of sulfur dioxide upon (i) the copper surface (electronic state of copper and nature of adsorbed species), and upon (ii) the catalytic activity.

This study is of practical importance because of the presence of SO_2 in exhaust emissions containing NO_x, especially in diesel exhaust gases.

The catalytic activity was tested first at 770 K, standard temperature defined in Part I, and also between 720 and 820 K in order to investigate the effect of temperature upon the SO_2 poisoning phenomenon.

The catalytic activity and the surface will be examined in a similar way as in the previous

work. Experimental conditions will be shortly described in this paper.

2. Experimental

For the catalytic experiments, a high purity polycrystalline, Cu disk, 70 cm^2 in area, was placed in a quartz tube reactor, immersed in an external oven, and the reaction temperature was measured by a thermocouple in the reactor bed. Reactions were carried out in a static mode. Before each test, the catalyst was reduced with hydrogen, $P_{H_2} = 10$ Torr, at 1000 K for two hours. The reactants were introduced into the reactor in the following sequence and concentration: SO_2, 0 to 1×10^{-4} Torr (0–20 ppm), NO, 1.0 Torr, O_2, 1.0 Torr, i-C_4H_8, 0.5 Torr, and Ar, 2.5 Torr. The catalytic test was monitored by mass spectroscopy (MS) as a function of reaction time. The use of a closed, static mode reactor was chosen in order to have access to the surface characterization of the catalyst at various stages of the reaction. For comparing experiments performed with various amounts of poison, or at different temperatures, the catalytic activity will be defined as the rate of NO conversion when it is highest. The loss of catalytic activity due to SO_2 poisoning will be calculated as $(R_0 - R(SO_2))/R_0$ in %, where R_0 and $R(SO_2)$ represent the catalytic activity when SO_2 is respectively absent and present in the reactants.

The catalyst surface was studied by X-ray photoelectron spectroscopy (XPS) using a Mg $K\alpha$ (1253.6 eV) X-ray source. Spectra were measured in a fixed analyzer transmission mode with a pass energy of 20 eV. The binding energies were corrected by using the value of 84 eV for Au-$4f_{7/2}$, a gold small piece being attached to the copper surface. Before every measurement, the whole reaction system was quenched to room temperature, and the gas mixture was pumped away. The catalyst sample was then transferred under UHV to the XPS chamber. Those measurements enabled us to

examine the adsorbates and the surface oxidation states of the catalyst at various steps of the reaction of NO reduction and to compare the data to the ones obtained in the absence of sulfur dioxide.

3. Results

3.1. Products and reaction process

Conversion of i-C_4H_8 and NO in the NO + O_2 + i-C_4H_8 + SO_2 gas mixture over Cu was tested at 770 K. Fig. 1 (top) shows a typical time course of the main products and Fig. 1 (bottom) details the NO, O_2, i-C_4H_8, i-C_4H_6O and SO_2 signals in the catalytic reaction over Cu, where the reaction conditions were initially as follows: $P_{NO} = P_{O_2} = 1.0$ Torr, $P_{i\text{-}C_4H_8} = 0.5$ Torr, $P_{Ar} = 2.5$ Torr, $P_{SO_2} = 1 \times 10^{-6}$ Torr, i.e. 0.2 ppm SO_2 in the gas mixture. It is apparent that the reaction proceeds in two stages. During the first stage NO is slowly converted, the concentration of SO_2 in the gas phase is rapidly dropped to a negligible level; oxygen is almost totally consumed to the benefit of CO_2, H_2O and low levels of i-C_4H_6O. In the second stage, the rate of NO conversion drastically increases. The reaction products are the same as those obtained when the reaction is run in the absence of poison, i.e. H_2O, CO_2, N_2 and CO together with low levels of i-C_4H_5N and i-C_4H_6O. Noticeable is the absence of NO_2, the mass 46 signal being ascribed to a CO_2 isotope after having made a mass calibration. The concentration of N_2O, also evaluated by mass calibration, is negligible throughout the reaction. The unsaturated aldehyde, i-C_4H_6O, formed during the first stage of the reaction, decreases together with NO. The interrelated behaviors of NO and i-C_4H_6O in this reaction are similar to those observed in the absence of sulfur for the same system [1] (see also in [1] the identification of the mass peaks). Note that no sulfur compounds, sulfides or sulfates, resulting from a reaction with hydrocarbon or oxygen, can be detected in the gas phase.
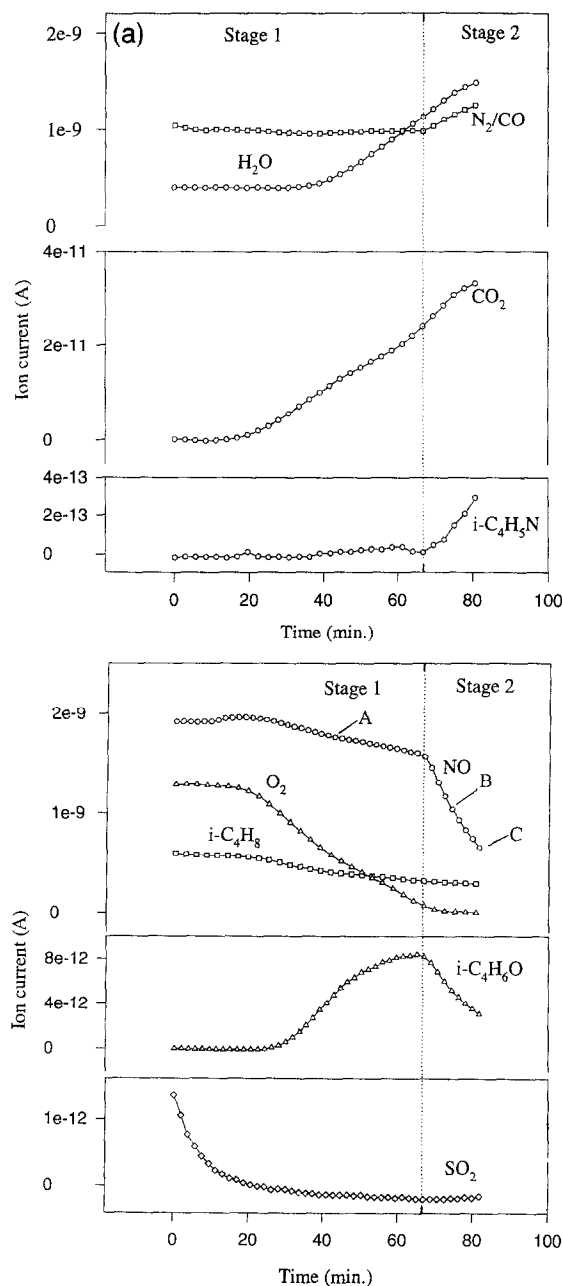

Fig. 1. NO reduction under the following conditions: $T = 770$ K, $P_{SO_2} = 1 \times 10^{-6}$ Torr, $P_{i\text{-}C_4H_8} = 0.5$ Torr, $P(NO) = 1.0$ Torr, $P_{O_2} = 1.0$ Torr, Ar as balance gas, total pressure 5.0 Torr. (top) Main products, (bottom) reactants and oxygenated intermediate.

3.2. Influence of SO_2 partial pressure

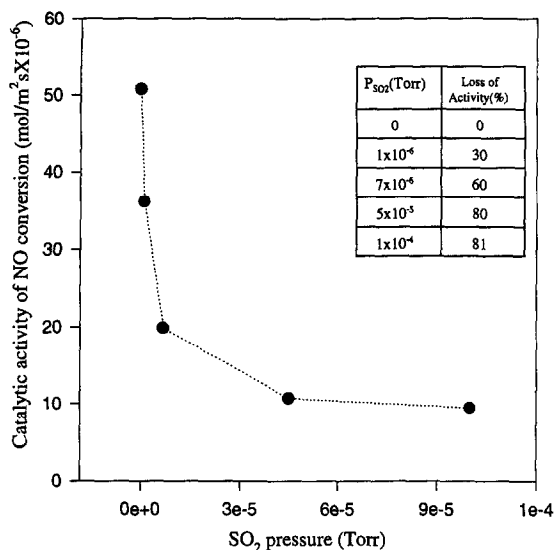The initial partial pressure of SO_2 was varied in a series of catalytic tests. Changes in the

P_{SO_2}(Torr)	Loss of Activity(%)
0	0
1×10^{-6}	30
7×10^{-6}	60
5×10^{-5}	80
1×10^{-4}	81

Fig. 2. Catalytic activity as a function of SO_2 pressure; $P_{SO_2} = 0$ to 1×10^{-4} Torr, other conditions are the same as in Fig. 1. The inset table shows the decrement of the catalytic activity with changing SO_2 pressure.

Table 1
The time of O_2 disappearance as a function of SO_2 initial pressure

P_{SO_2} (Torr)	0	7×10^{-6}	5×10^{-5}	1×10^{-4}
$T_{O_2 dis.}$ (min)	65	120	230	230

loss of catalytic activity of 30%. 7×10^{-6} Torr of SO_2 (1.4 ppm) leads to 60% deactivation. Further increase of the SO_2 pressure from 5×10^{-5} (9 ppm) to 1×10^{-4} Torr (20 ppm) does not cause any significant additional reduction of activity.

The apparent rate of formation of i-C_4H_8O, measured when it is highest, is also plotted as a function of P_{SO_2} (see Fig. 3). It decreases in a way similar to the rate of NO reduction (Fig. 2). The effect of sulfur dioxide is also marked upon

maximum rate of NO reduction as a function of P_{SO_2} is shown in Fig. 2. The NO reduction rate decreases sharply as soon as a small initial pressure of SO_2 is admitted. The inset table in Fig. 2 indicates that an initial pressure of SO_2 equal to 1×10^{-6} Torr (0.20 ppm) induces a
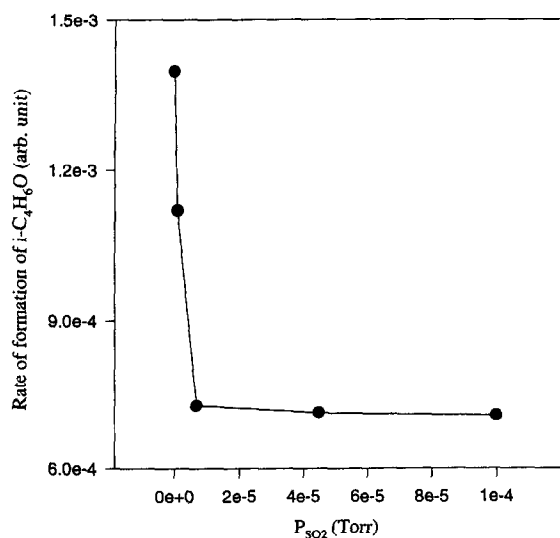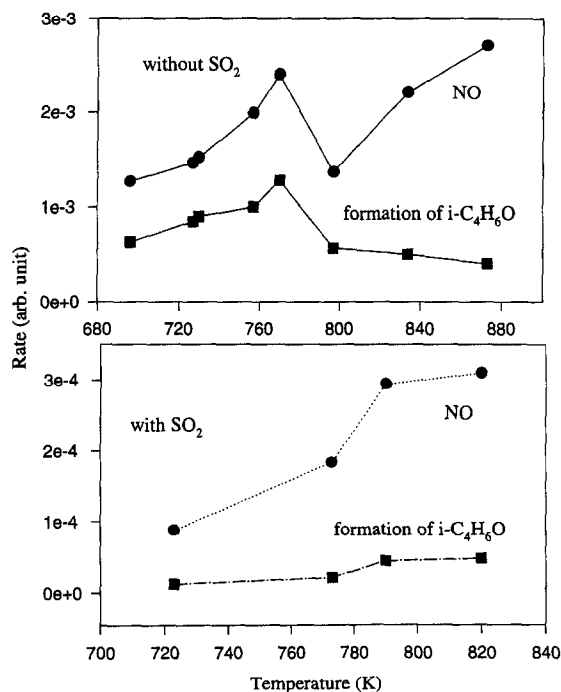

Fig. 3. Rate of formation of i-C_4H_6O, when it is at its maximum, as a function of SO_2 pressure. The conditions are the same as in Fig. 2.

Fig. 4. NO reduction and i-C_4H_6O formation rates as a function of reaction temperature. $P_{SO_2} = 1 \times 10^{-4}$ Torr. Other conditions are the same as in Fig. 1. Note that, for the sake of clarity, the rate of i-C_4H_6O formation has been multiplied by a factor 10^2 and no scale was indicated. At 820 K, the rate of NO reduction is the same as at 770 K in the absence of SO_2; in the presence of SO_2, passing from 770 K to 820 K, the rate of NO conversion increases by a factor 1.6.

the rate of consumption of oxygen (see Table 1).

3.3. Reaction temperature dependence

The reaction temperature is often an important parameter to control the catalyst deactiva-tion. The influence of the temperature between 720 and 820 K was examined in the absence and in the presence of 10^{-4} Torr of SO_2 at the beginning of the reaction. Results are plotted in Fig. 4. In the absence of sulfur dioxide, the catalytic activity goes through a maximum at $T = 770$ K, slightly decreases, then increases
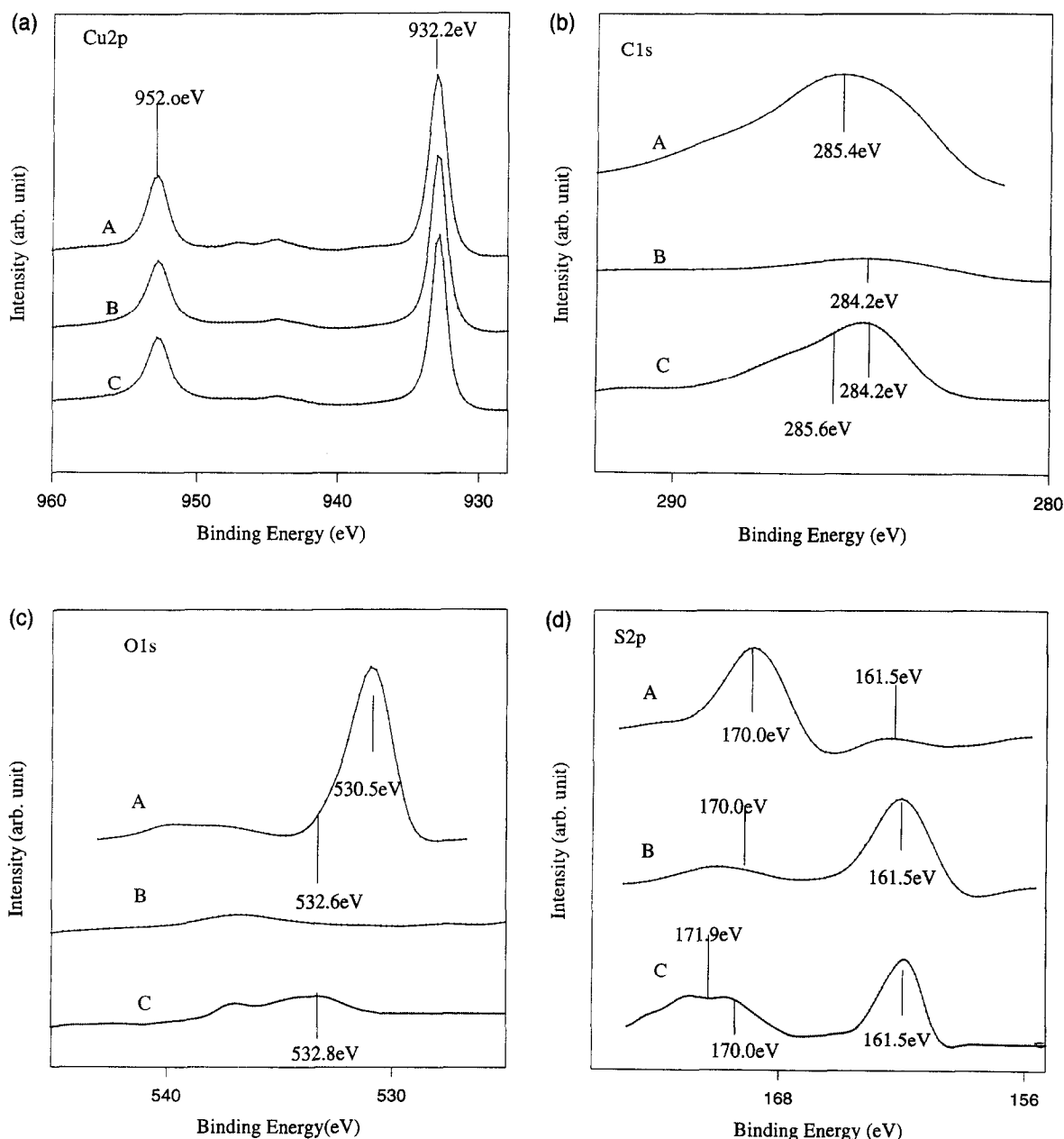

Fig. 5. XPS spectra from Cu surface: (a) slow NO conversion step; (b) rapid NO conversion step; (c) end of reaction. $P_{SO_2} = 7 \times 10^{-6}$ Torr. Other conditions are the same as in Fig. 1.

again at $T > 800$ K. Interesting is the different behavior when SO_2 is present: in the latter case, the effect of temperature is a smoothing of the poisoning effect towards the reduction of NO; the activity increases with temperature in the whole 720 to 820 K range.

Fig. 4 also shows that increasing the temperature promotes the formation of i-C_4H_6O, when SO_2 has been added to the reactants.

3.4. Characterization of the catalyst surface

XPS analyses of the Cu surface after evacuation of the NO + O_2 + i-C_4H_8 + SO_2 (7×10^{-6} Torr) reaction mixture at 770 K were carried out at 20, 50 and 80% conversion, i.e. respectively when the reduction of NO is slow, rapid and at the end of the reaction (points A, B and C in Fig. 1). Fig. 5 shows the observed Cu2p, C1s, O1s and S2p XPS spectra. N1s was also checked but could not be detected, because of its overlapping with the Cu LMM Auger lines.

(1) At 20% conversion (slow conversion): The Cu2p peaks appear at 932.2 eV and 952.0 eV; they are not shifted compared to the binding energy of pure copper signals. The Cu $L_{2(3)}M_{4,5}M_{4,5}$ lines (spectrum not shown) are shifted by 2.0 eV towards lower kinetic energies compared to those of Cu(0), indicating that the surface is Cu(I) [9,10]. The O1s peak is intense and asymmetric. It could be deconvoluted into a main peak at 530.5 eV, which is characteristic of lattice oxygen in copper oxide [10], and a fairly weak shoulder at 532.6 eV. A broad C1s peak is observed, centered at 285.4 eV, suggesting the existence of a surface alkoxide species ($CH_2=C(CH3)-CH_2O-$) [11]. Two S2p peaks are detected, a strong one at 170.0 eV and the other, weak one at 161.5 eV, showing the presence of two types of sulfur species, more likely, SO_4^{2-} and S^{2-}, respectively [12,13], and the weak O1s peak at high binding energy being possibly ascribed to oxygen species in sulfate. Oxygen from alkoxide species may also contribute to the O1s peak at high binding energy.

(2) At 50% conversion (rapid conversion): No change of the Cu2p peaks is observed and the Cu $L_{2(3)}M_{4,5}M_{4,5}$ Auger lines are not shifted any longer compared to metallic copper, showing that the surface is in the Cu(0) state. The O1s peak is hardly detectable. A very weak C1s peak appears at 284.2 eV, which originates from deposited carbon. The two S2p peaks are at the same position as those in the former stage, but with drastic changes in the intensities: the intensity of the peak at high binding energy decreases, while the other one increases.

(3) At 80% conversion: The spectra of Cu2p are the same as in the second stage; this shows that the surface is still in the metallic state. A fairly weak O1s signal appears at 532.8 eV, superimposed on the Cu Auger line. A strong and broad C1s peak is observed, fitted with two contributions at 284.2 eV and 285.6 eV respectively, with the peak at low binding energy being stronger than the other one. An intense S2p peak at 161.5 eV is nevertheless observed, along with two weak S2p lines at 170.0 eV and 171.9 eV. We believe that the surface at this stage is poisoned both by carbon and sulfur-containing species.

4. Discussion

The deactivation mechanism by sulfur dioxide of the reduction of NO on pure copper is discussed in the light of the kinetics and XPS data. When the reaction is run at 770 K in the presence of 7×10^{-6} Torr of SO_2, the characterization of the catalytic surface leads to the two following conclusions:

(i) The initial NO conversion step is associated with a Cu(I) surface; the binding energy of sulfur, S2p, indicates that sulfur is mainly chemisorbed on the surface as SO_4^{2-}, but no $CuSO_4$ is formed (The Cu2p peaks of $CuSO_4$ would, in that case, exhibit characteristic shake-up satellites) [12,14]; we rather infer the existence of H_2SO_4, adsorbed, dissociated or not, at the surface.

(ii) the rapid NO conversion proceeds on a metallic Cu surface, and here most of the chemisorbed sulfur species are reduced to S^{2-}, but no formation of Cu_2S or CuS (which would lead to a typical Cu(I) or Cu(II) surface) was observed. Such S^{2-} adsorbates could be attributed to chemisorbed H_2S species which are formed by reducing SO^{4-} under rich conditions, showing the reactivity of the hydrocarbon with sulfate ions on a copper surface. This is in agreement with the absence of the O1s signal in spectrum B (Fig. 5c). The Cu_2O to Cu reduction process of the catalyst surface for NO conversion is the same as the one evidenced in the $NO + O_2 + i\text{-}C_4H_8$ system at the same temperature (770 K) [1]. From Ingraham's diagram, which shows the stability regions of the Cu–S–O system in the presence of 10% O_2 and 10 ppm SO_2, $CuSO_4$ is stable and would not decompose to CuO until 853 ± 15 K [15]; Simpson also reported that the desulfiding temperature of Cu_2S under reducing conditions was 922 K [16]. This seems in contradiction with our XPS analyses. It simply indicates that the presence of NO and $i\text{-}C_4H_8$, in addition to SO_2 and O_2 in the gas phase, modifies the phase stability of copper sulfate and sulfide to the benefit of hydrogen sulfide. In fact, it is already reported that natural gas and other reductants such as hydrogen or carbon monoxide can reduce copper sulfate at 720–770 K [17]. Finally, it is clearly demonstrated that SO_2 is a drastic poisoning species for copper, by reacting with oxygen and isobutene and by blocking sites rather than by direct oxidation of the copper surface, as was suggested by Iwamoto [3].

In the reaction process, it was found that SO_2 disappears from the gas phase in the initial NO conversion stage (Fig. 1), suggesting that SO_2 is rapidly converted and/or adsorbed on the catalyst surface. A similar rapid consumption of SO_2 has already been mentioned on Cu/Al_2O_3 by Centi [18]. Note that a non-measurable fraction of SO_2 may be lost by adsorption on the walls of the reactor. Note also that the solubility of sulfur in copper is negligible at temperature

below 870 K and cannot account for the disappearance of SO_2 from the gas phase [19]. Table 1 shows that the initial presence of SO_2 in the gas phase caused a drastic change in the time required for O_2 consumption; this is likely to be due to competitive adsorptions of O_2 and sulfate species on the Cu surface. A similar phenomenon has already been documented for NO reduction by NH_3 over Ni, Pt, Rh, and Pd supported on Al_2O_3 [20].

Compared to the SO_2-free system presented earlier, though the rate of formation of $i\text{-}C_4H_6O$ is reduced in presence of SO_2, the evolution of this intermediate during the reaction is not changed. It is formed when the conversion of NO is slow and decreases during the rapid NO conversion period, as is shown in Fig. 1. Our proposal is that $i\text{-}C_4H_6O$ is also an active intermediate for the reduction of NO in the $NO + O_2 + i\text{-}C_4H_8 + SO_2$ reaction system as it is in the SO_2-free system. Moreover, in the stage of slow NO conversion, the surface sulfate species (SO_4^{2-}), by blocking the active sites, poison the first step of the reaction, i.e. the oxidation of the hydrocarbon.

It is noted that no peaks from carbon or oxygen, characteristic of adsorbed aldehyde, appear in the XPS spectra in the rapid NO conversion stage (Fig. 5, stage B). This suggests that the surface is mainly covered by hydrogen sulfide which blocks a fraction of active sites and considerably reduces the coverage in aldehyde. In addition to a geometric blocking site effect, sulfur may weaken the $i\text{-}C_4H_6O$ adsorption bond on the catalyst surface, through a modification of the electronic density of Cu in the vicinity of the sulfur atom [21–24]. A further weakening of the adsorption of $i\text{-}C_4H_6O$ reduces the catalytic reaction since the reacting molecule would desorb before the surface reaction with NO takes place [22]. Thus the inhibiting effect of sulfur for NO conversion may be twofold: in the reaction of formation of reactive intermediate during the initial step of the reaction and in its coverage and residence time in the second step.

We do not exclude the possibility that the presence of the surface sulfide in the rapid NO conversion stage promotes another pathway for NO conversion, e.g. reaction of adsorbed H_2S reaction with NO ($S^{2-} + NO \rightarrow N_2 + SO_x^{n-}$), or possible direct decomposition of NO promoted in the vicinity of adsorbed sulfur atoms. However, the related evolutions of i-C_4H_6O and NO suggest that the main path for NO conversion is the same as described earlier in the NO + O_2 + i-C_4H_8 system, i.e. the initial NO conversion step is dominated by the formation of i-C_4H_6O and the rapid NO conversion stage is mainly a reaction between NO and i-C_4H_6O.

4.1. Influence of SO_2 partial pressure

It is remarkable that an extremely low concentration of SO_2 in the gas phase (1×10^{-6} Torr) induces a significant drop (30%) in the catalytic activity, showing the high toxicity of sulfur on a copper surface. We also found that, from 5×10^{-5} Torr, an additional increase of SO_2 did not cause further change in the catalytic activity. This is likely to be due to the saturation of the adsorbed sulfur layer. Additional sulfur may be adsorbed on top of the sulfur overlayer forming 3D sulfides [25], having no further influence on the surface reaction. The residual catalytic activity at saturating sulfur coverage can be ascribed to the tolerance of the catalyst [24], i.e. displacement of adsorbed sulfur by reactants or to defects in the adsorbed layer.

4.2. Influence of the temperature

The lower deactivation observed at high temperature can be easily understood: the sulfur adsorption is exothermic [25]; increasing the temperature promotes sulfur compound decomposition and desorption. The main reason for the catalytic activity to be partially recovered at high temperature is the desorption of sulfided compounds. Note that the slight decrease of activity observed in the absence of SO_2 at $T > 773$ K can be ascribed to a total oxidation of hydrocarbon. It is likely to be compensated at $T > 800$ K by the direct decomposition of NO. No maximum is observed in the presence of SO_2, because the main effect is the lower level of site occupancy by sulfided poisons.

5. Conclusion

This paper presents the study of the model catalytic NO reduction with i-C_4H_8 on pure copper using X-ray photoelectron spectroscopy correlated to catalytic measurements. The results provide useful information on the copper–sulfur interactions in the presence of a hydrocarbon and oxygen. It has been found that SO_2, even at an extremely low concentration (0.2 ppm) in the gas phase, can lead to a severe poisoning of the active surface. This poisoning effect can be smoothed by increasing the reaction temperature. A residual catalytic activity exists when the sulfur dioxide content is increased from 5×10^{-5} to 10^{-4} Torr. MS and XPS data have demonstrated that sulfur does not lead to Cu sulfates or sulfides. Although the catalytic activity is considerably decreased, the main mechanism of NO reduction is maintained. Sulfur poisons the reaction by blocking (i) the formation and (ii) the adsorption of i-C_4H_6O, which has been shown to be the active intermediate of the reaction. Note that the sulfur poisoning is reversible; the catalytic activity can be recovered at high temperature. At the end of the reaction, the catalyst surface is poisoned both by carbon and sulfur species.

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