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NO reduction by isobutene, in the presence of oxygen, on platinum and copper, a comparative study

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Abstract

The reaction of NO, oxygen and isobutene was studied under conditions close to stoichiometric, on a platinum and on a copper disk in order to better understand the role of each metal, free of any support and dispersion effects. The products of the reaction were analysed by mass spectrometry and an XPS characterization of the surface was carried out at different stages of the reaction. A correlation between the catalytic activity for NO conversion and the presence of adsorbed intermediates has been clearly demonstrated on platinum. On copper, a redox cycle of the metal is necessary to activate the catalyst. On platinum, oxygen is necessary to initiate the reaction, clean the surface and form reactive intermediates; the reaction is strongly sensitive to oxygen concentration, whereas on copper, oxygen does not directly participate in the reaction mechanism.

Keywords: NO reduction; Pt catalyst; Cu catalyst

1. Introduction

The catalytic reduction of nitrogen oxide by hydrocarbon is a key reaction for removing nitrogen oxides from automotive emissions. The reaction was primarily studied on catalysts containing noble metals and the three-way automotive catalysts have been successfully used under stoichiometric conditions. Catalysts containing base transition metals and their oxides have received increasing interest during these last ten years [1]. Their activity was shown to be excellent also in the presence of oxygen excess and in the presence of hydrocarbon [2,3]. Copper is one of the most active base transition metals. Not many studies have dealt so far with the mechanism of this reaction on pure, non-supported metals. This paper aims at providing new insights into the reaction mechanism by comparing the reactivities and the surface states of platinum and copper in the reaction of NO reduction by isobutene. The role of oxygen will be addressed on both catalysts.

2. Experimental

The catalyst samples used in these experiments consisted of planar polycrystalline disks of pure metal. The area of the copper sample was 70 cm^2 and the platinum one was 8 cm^2.

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The samples were reduced under hydrogen at 10 Torr at appropriate temperature for 2 h before every catalytic test. The level of contamination of the surfaces after this treatment was checked by Auger electron spectroscopy. No oxygen could be detected and the residual carbon level was in the low submonolayer range.

The experiments were performed in a 18 dm^3 quartz reactor in a static mode. The catalyst sample and the reaction gaess were uniformly heated by an external furnace. A small leak was constantly maintained to a mass spectrometer (MS) to enable the analysis of the gas composition during the reaction.

At different stages in the reactions, the sample was cooled, the reaction gases were pumped away and the catalyst was then transferred under UHV to the surface analysis system. Auger and XPS analyses of the sample were performed. In the XPS mode, Mg Kα (1253.6 eV) radiation was used as excitation source and the electron kinetic energies were analysed by a CLAM 2 hemispherical energy analyser utilising a pass energy of 20 eV.

Isobutene was chosen as a 'simple' representative of unsaturated hydrocarbons present in exhaust gases and the reactions were performed in the presence of oxygen in the gas phase. The reaction procedure and product identification are described in Refs. [4,5] in detail.

3. Results and discussion

3.1. Catalytic activity

The conversion of NO exhibits two different time courses on platinum and copper catalysts (see Fig. 1).

On platinum, a monotonous decrease of NO was observed, together with a consumption of oxygen and isobutene in the gas phase. The reaction rate decreases when little or no oxygen is left in the gas phase.

In the presence of isobutene and oxygen, the copper catalyst undergoes an induction period corresponding to the total consumption of oxygen and to a low rate of NO conversion. The rate of NO conversion increases and remains high until almost the whole amount of NO has been converted. A final stage of the reaction is characterised by a low rate of NO and isobutene conversion. On both catalysts, the main reaction products are identical: H_2O, CO, CO_2, N_2 and very little N_2O and NO_2. Worth noting is a C_4 unsaturated aldehyde traced by amu 70 and 39, resulting from a partial oxidation of isobutene, evolved in the gas phase; it was then consumed at the same time as NO. The conversion rate was maximum at corresponding temperatures on both metals, 773 K on platinum and 693 K on copper, respectively.

3.2. Role of oxygen in the reaction

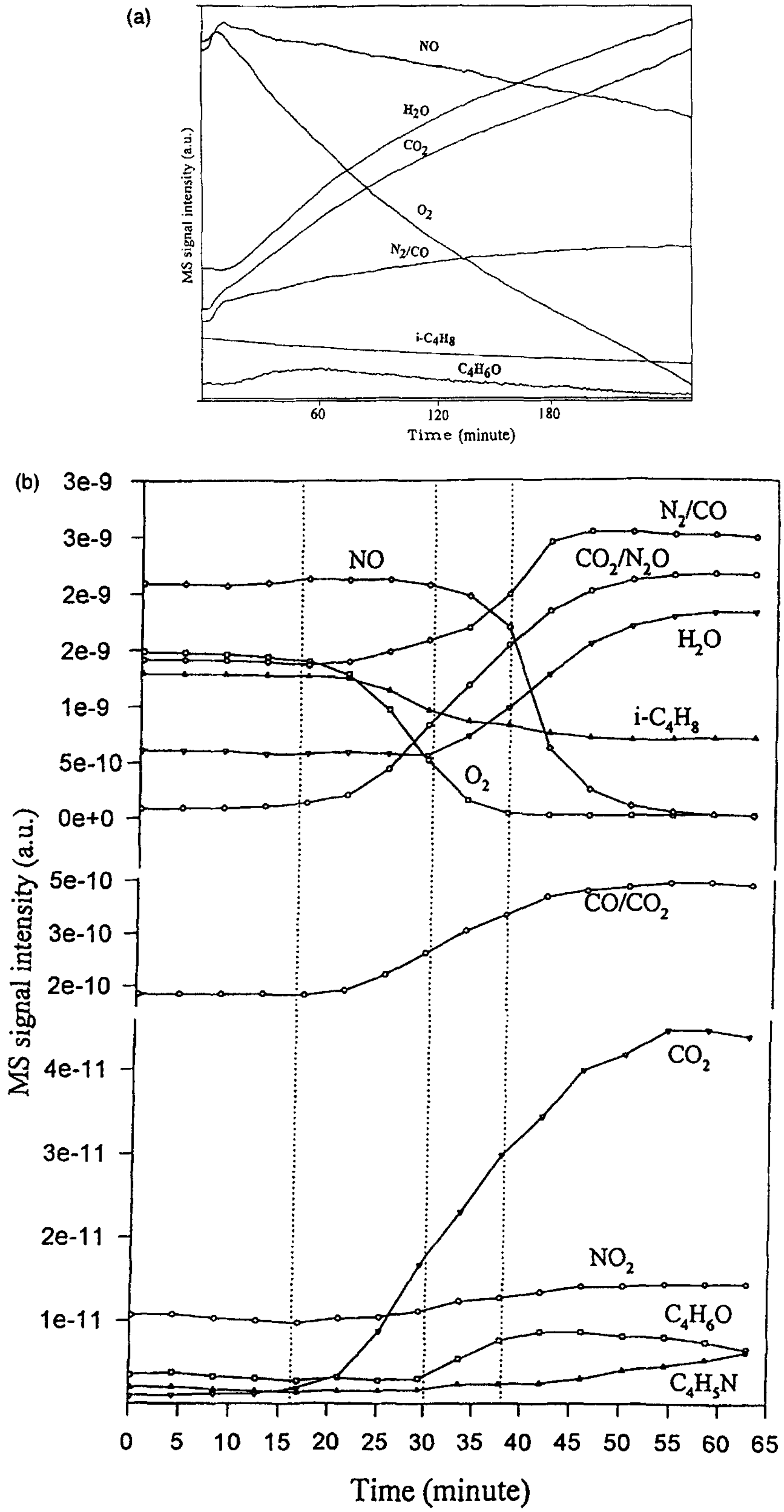
3.2.1. NO + isobutene reaction in the absence of oxygen

The conversion of NO was tested in the presence of isobutene but without oxygen, on both platinum and copper. Two different behaviours were observed:

On platinum, no reduction of NO by *iso*-C_4H_8 occurs in the absence of O_2. The surface is immediately poisoned by carbonaceous residues.

On copper, the time course of the reaction can be divided into two stages (see Fig. 2); one corresponding to a slow rate of NO conversion and oxidation of the copper disk and a second one corresponding to a high rate of NO conversion. That suggests that, once the copper surface has reached an active stage, the reaction proceeds without inducing a further oxidation of the sample. The main products of the reaction

Fig. 1. NO conversion in the presence of oxygen and isobutene, (a) on platinum, $p_{iso\text{-}C_4H_8} = 0.4$ Torr, $p_{NO} = 1.2$ Torr, $p_{O_2} = 1.5$ Torr, $T = 700$ K, (b) on copper, $p_{iso\text{-}C_4H_8} = 0.5$ Torr, $p_{NO} = 1$ Torr, $p_{O_2} = 1$ Torr, $T = 770$ K.


(a)
NO
H2O
CO2
O2
N2/CO
i-C4H8
C4H6O
MS signal intensity (a.u.)
60
120
180
Time (minute)
(b)
3e-9
3e-9
2e-9
2e-9
1e-9
5e-10
0e+0
5e-10
3e-10
2e-10
4e-11
3e-11
2e-11
1e-11
N2/CO
CO2/N2O
NO
H2O
i-C4H8
O2
CO/CO2
CO2
NO2
C4H6O
C4H5N
MS signal intensity (a.u.)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
Time (minute)

are N_2 or CO, O_2 and little H_2O. Note that the amount of CO_2 formed in the second stage of the reaction is small. Only the simultaneous increase in the rates of *iso*-C_4H_8 and NO consumptions indicates that the conversion of NO does not exclusively proceed via simple decomposition but also by reaction with the hydrocarbon.

3.2.2. *NO + isobutene reaction in the presence of various* p_{O_2}

On platinum at 700 K, oxygen is necessary to initiate the reaction. The rate of NO conversion increases with p_{O_2}, reaches a maximum under the following conditions: $p_{NO} = 1.2$ Torr, $p_{iso\text{-}C_4H_8} = 0.4$ Torr and $p_{O_2} = 2.5$ Torr. The rate of formation of the unsaturated aldehyde, C_4H_8O, follows exactly the same trend as that of NO conversion. Both reactions slow down but are not totally poisoned in the presence of oxygen excess (slightly oxidizing conditions). A more severe poisoning phenomenon by oxygen was observed on platinum when the reductant was isobutane [4]. Burch at al. explained in a recent paper that oxygen blocks the platinum surface for NO adsorption and that one role of the reductant is to react with the surface oxygen [6].

Fig. 3 shows NO and O_2 evolutions in the gas phase for two reaction runs with 0.3 and 1.4 Torr of oxygen on copper, respectively.

At 770 K in the presence of low pressure oxygen ($p_{O_2} = 0.3$ Torr), the rapid conversion of NO starts earlier than in the presence of a high pressure of oxygen. Note that the delay observed in Fig. 3 for $p_{O_2} = 1.4$ Torr corresponds to an oxygen consumption into CO_2 and H_2O; the selectivity of the reaction is consequently modified (figure not shown). Fig. 3 also shows that, once the rapid stage has been

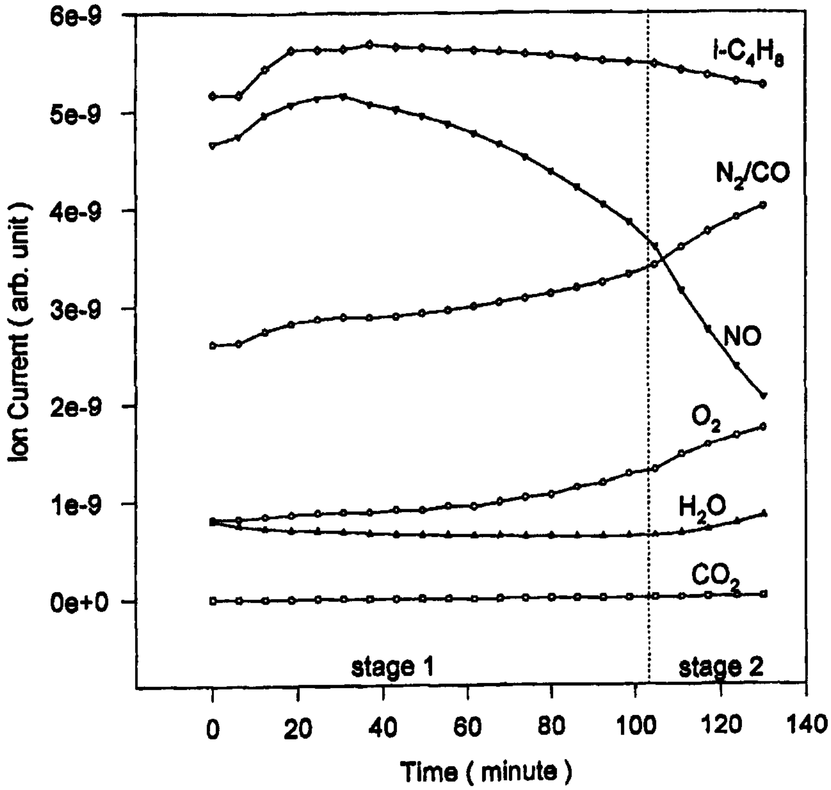


Fig. 2. NO + *iso*-C_4H_8 reaction on copper, $T = 770$ K, $p_{NO} = 1$ Torr, $p_{iso\text{-}C_4H_8} = 1.1$ Torr.

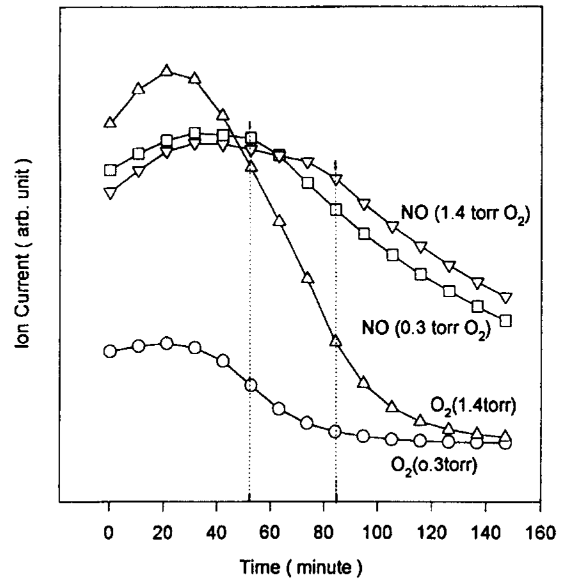


Fig. 3. NO and O_2 traces in the reaction on copper, $p_{NO} = 1$ Torr, $p_{iso\text{-}C_4H_8} = 1$ Torr, $T = 700$ K.

reached, the rate of NO conversion itself is not significantly affected by the initial oxygen pressure.

In the case of a 'high' initial oxygen pressure, NO starts decreasing after a large amount of O_2 has been consumed. The opposite is observed when the initial pressure of oxygen is low. This tends to prove that the role of oxygen in the reaction is only an initial activation of the copper surface; it can also be achieved by NO decomposition itself if there is very little or no oxygen in the gas phase.

The reaction was also performed in the absence of oxygen, it exhibits an induction period 3 times longer than in the presence of 1 Torr O_2, proving that copper has to be activated during this period, oxygen being preferred above NO.

3.3. Surface characterisation

XPS analysis was performed at different stages of the reaction run at 770 K on platinum and at 700 K on copper, (a) initial stage, i.e., before the beginning of the reaction on platinum and when the conversion of NO is slow on copper, (b) when the rate of NO conversion is maximum on both catalysts and (c) at the end of the reaction, when the conversion of NO has become slow again. We will focus on the oxygen signal.

Fig. 4 shows the O 1s region at the three stages of the reaction, on platinum and on cop-

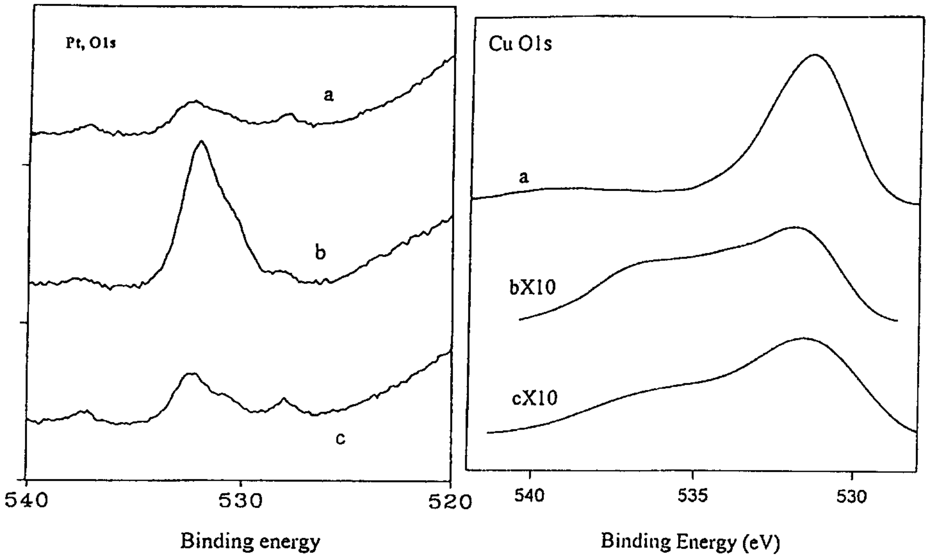


Fig. 4. O 1s signal at various stages of the reaction process, (a) initial stage, (b) high activity, (c) low activity, same conditions as in Fig. 1.

per. On both catalysts, the positions and the intensities of the oxygen signals vary with the reaction time.

On platinum, a weak O 1s peak is left at 531 eV binding energy, after reducing treatment due to residual contamination by CO and/or organic compounds. At the most active stage of the reaction, a sharp O 1s line appears at 532.2 eV with a shoulder at 530.9 eV binding energy. The former peak was ascribed to oxygen of aldehydic reactive intermediates [7]. At the less active stage, the O 1s intensity decreases; it could be fitted by two contributions at the same binding energies as in the second stage; note that the one at 532.2 eV is reduced by a factor 5.

Results are totally different on copper. At the first stage of the reaction, corresponding to a low rate of conversion of NO, the XPS analysis shows a strong and broad O 1s line centred at 530.9 eV binding energy. This peak can be ascribed to lattice oxygen from copper oxide and possibly organic compounds containing oxygen, adsorbed on the surface [8]. It is noticeable that the Cu 2p peaks are not shifted with respect to the binding energies of metallic copper signals, but a shift of the Auger lines indicates that copper is likely to be Cu^+ in Cu_2O. CuO would have induced a 1.2 eV shift of the 2p signals [9–11].

At the most active stage of the reaction, the O 1s signal is weak; it is well fitted with three contributions at 530.9 and 533.0 eV plus an Auger line from copper at 537 eV. The peak at 533.4 eV can be attributed to reactive intermediates, methacrolein or compounds derived from, possibly containing C, O and N atoms. We do not exclude isocyanates (–NCO) to be reaction intermediates as already suggested by other authors [12]. Analysis of the carbon and copper regions suggests that the conversion of NO proceeds at a high rate on a clean, metallic copper surface.

At the end of the reaction, when the conversion of NO has become slow; the O 1s is very small and could be fitted with the same contributions as in the active stage but with an important loss of intensity in the 533.0 peak. Copper is in the zero valent state.

Table 1
Binding energy of the Cu $2p_{3/2}$ peak and the kinetic energy of the Cu $L_3M_{23}M_{45}$ transition at different stages of the reaction

	Cu $2p_{3/2}$ peak (eV)	Cu $L_3M_{23}M_{45}$ transition (eV)
Clean surface	933	842.1
Low activity	932.6	844.6
High activity	933	842.6
End of reaction	933	842.1

The Auger spectra of the surface at the end of the reaction exhibits a small nitrogen peak and a strong carbon peak. The surface is essentially poisoned by pure carbon.

In order to identify the oxidation state of copper, possible changes in the Cu $2p_{3/2}$ peak and the Cu LVV Auger lines were checked throughout the reaction. At all stages of the reaction, the Cu $2p_{3/2}$ peak was narrow, not shifted and no increase of the intensity of the satellite peaks was observed, indicating the absence of Cu^{II}. The Auger line Cu $L_3M_{23}M_{45}$, due to an Auger transition appearing when a vacancy in the 2p 3/2 level is filled with a 3p electron with simultaneous ejection of a 3d electron, was carefully analysed at various stages of the reaction. The binding energy of the Cu $2p_{3/2}$ peak and the kinetic energy of the Cu $L_3M_{23}M_{45}$ transition are reported in Table 1.

It is worth noticing that the Auger line was shifted by 2 eV towards higher kinetic energy in one case: at the beginning of the reaction, when the rate of NO conversion is still low. Since, the Cu $2p_{3/2}$ peak is not shifted, we conclude that at the first stage of the reaction, corresponding to a low rate, the copper is in the Cu^I state [7,10]. In the most active state, the copper is totally reduced.

4. Conclusion

Both on pure platinum and pure copper, a compound resulting from a partial oxidation of isobutene was evidenced as an intermediate in the reduction of NO. On platinum, its formation is rate determining; on copper, the rate is limited by the redox cycle of copper.

Under stoichiometric conditions, copper was revealed to be a good candidate to compete with platinum in the deNO$_x$ reactions. Copper is less active but also less poisoned by carbon deposits which may accumulate after repeated catalytic cycles. It undergoes a redox mechanism which is a key step of the reaction. On platinum, the role of oxygen consists of making active intermediates and preventing poisoning of the surface by coking.

Further investigations are in progress to better identify the surface species actually taking part in the reaction.

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