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New Insights on the Mechanism of the NO Reduction with CO over Alumina-Supported Copper Catalysts

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Carbon monoxide (CO) and nitric oxide (NO) are among the major components of exhaust gases produced from vehicle engines and industrial boilers. Apart from noble metals (Rh, Pt, Pd, ...), which are very active for the simultaneous NO reduction and CO oxidation, copper based catalysts have been widely studied as less expensive alternatives for this reaction. Here we use "in situ" X-ray absorption near edge structure (XANES) to study the state of copper species during the NO + CO reaction. The correlation of copper surface species present on the catalyst with its catalytic performance allows us to deduce that a redox-type mechanism ($\text{Cu}^{2+}/\text{Cu}^+$) is working under reaction conditions and that the NO adsorption and/or dissociation is the slow step of the reaction.

Introduction

The reduction of NO with CO has been extensively studied in recent years in connection with the control of exhaust emission.¹ Present automotive emission control catalysts are rather expensive since they incorporate precious metals such as Rh, Pt, and Pd. In spite of the progress made in the field of these precious metal based systems, the need for more available and less expensive elements is clear. Copper-based catalysts for NO reactions have recently become a subject of great interest; in particular, the decomposition or reduction of NO over $\text{Cu}/\text{Al}_2\text{O}_3$ ^{2–4} and over Cu-exchanged zeolites^{5,6} has been thoroughly studied. The mechanism of reaction is still an open matter, but because a facile $\text{Cu}^{2+}/\text{Cu}^+$ thermal conversion has been noted in inert or oxidizing atmospheres, several investigators have suggested a redox-type mechanism with a cuprous–cupric ion transformation as a relevant reaction step.^{5,7,8}

The principal aim of this paper will be precisely the study of the Cu valence state under a NO:CO = 1:1 atmosphere over a wide range of temperatures, 523–773 K, in an attempt to confirm the existence of a redox mechanism. To reach this goal we will perform a XANES/factor analysis⁹ study of a $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst. With respect to common (surface science) techniques used to characterize the chemical state of a system, XANES has the advantage that it does not require vacuum conditions and allows the analysis of the sample under the direct influence of a reactive atmosphere at elevated temperatures. Moreover, using factor analysis as a tool to interpret "in situ" recorded XANES spectra, it is possible to know the chemical species of Cu present along the reaction coordinate, i.e., it is possible to obtain a chemical description of the active center(s) of the reaction.⁹

Experimental and Computational Details

The 2.1% $\text{CuO}/\text{Al}_2\text{O}_3$ sample was prepared by adsorption of copper, from an aqueous solution of Cu(II) nitrate, on a

suspension of γ -alumina at a pH of 9 (see ref 4 for further details). XANES measurements at the Cu K-edge were performed on line CII at Cornell High Energy Synchrotron Source. A Si(111) double-crystal monochromator was used with 40% detuning to minimize the effects of higher harmonic frequencies. Transmission experiments were carried out using ionization chambers filled with N_2 for detection. The energy scale calibration was monitored by simultaneously measuring a Cu foil (Johnson-Matthey, absorbance 1.5) with the sample under study using a third ionization chamber. Samples were pressed in self-supporting wafers (absorbance 2) and placed in a controlled-atmosphere cell to follow the reaction. In situ calcined (pure O_2 , 773 K, 30 min) samples were contacted with the reaction blend (2 vol % NO, 2 vol % CO in helium) from 523 to 773 K (4 K/min). Catalytic activity measurements were carried out at atmospheric pressure in a quartz flow reactor. A 2 vol % NO, 2 vol % CO reaction mixture was allowed to reach a precalcined (as before) catalyst at a flow rate of $10 \text{ cm}^3 \text{ min}^{-1}$ from 523 to 773 K (2.5 K/min).

As mentioned in the Introduction, factor analysis will be used here to extract chemical information from XANES spectra. In short, principal component factor analysis (PCA) assumes that a variable, the absorbance in a set of XANES spectra, can be modeled as a linear sum of uncorrelated components known as factors or eigenvalues.¹⁰ To decide which factors correspond to signal and which to noise, an F test¹¹ of the variance associated with factor k and the summed variance associated with noise factors ($k + 1, \dots, c$, where c is the number of spectra) is performed. The probability that a F value would be higher than the current value is given by % SL (percentage of significance level). Thus, the k factor is accepted as a principal component (factor associated with signal) if % SL is lower than a test level that previous experience recommends to fix at 5%.⁹ To help in deciding the number of principal components, the ratio between reduced eigenvalues (rev(ratio)) will be used also; this ratio is approximately equal to one when two error eigenvalues are compared and significantly greater than one if one eigenvalue is responsible for the signal.^{10,12} Once the number of principal components is fixed, it is necessary to transform the principal components in XANES spectra corre-

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TABLE 1: Principal Component Analysis Results

factor	eigenvalue	% SL	rev (ratio)	variance ^a
1	638.420	0.00	968.0	99.900
2	0.610 39	0.00	27.4	0.096
3	0.020 57	0.02	10.1	0.004
4	0.001 87	8.96	1.38	
5	0.001 23	9.47	1.10	
6	0.001 02	5.83	1.87	
7	0.000 44	9.66	1.67	
8	0.000 23	13.80	1.55	
9	0.000 13	18.36	1.83	
10	0.000 06	30.70	1.07	

^a Variances lower than 10^{-3} are not reported.

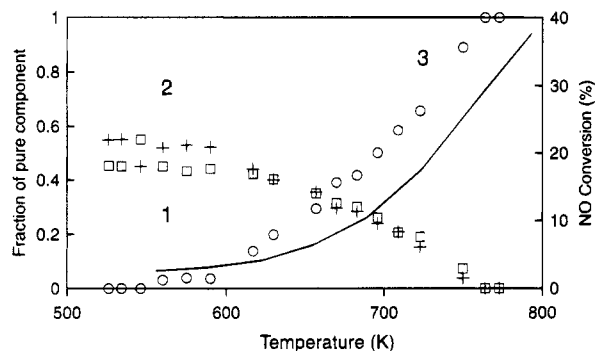


Figure 1. Concentration profiles of the pure components along the reaction coordinate (\square , $+$, \circ) and percentage of NO conversion (full line).

sponding to the Cu chemical species present in the sample. To do this, a rotation of the concentration profiles, the amount of each chemical species along the reaction coordinate, is performed using the varimax method followed by iterative transformation factor analysis (ITFA).¹³ The rotation matrix obtained in this way is then used to generate the XANES spectra of pure Cu components.⁹

Results and Discussion

The factor analysis results obtained for 17 spectra taken during the temperature ramp are presented in Table 1. Both the reduced eigenvalue ratio and the F test conclusively show the existence of three principal components. The concentration profiles of the corresponding three pure Cu species (Figure 1) point out that two of them are observed at the beginning of the ramp while the remaining one is present only at high temperature. Because the first spectrum of this series is identical to the one obtained after calcination at 773 K (not shown), the two initial Cu species should correspond to Cu^{2+} compounds. The XANES spectra associated with these pure Cu components are given in Figure 2. On the basis of a previous XPS study,⁴ the two oxidic species can be ascribed to CuO-like and superficial copper aluminate. In order to determine which spectrum corresponds to superficial copper aluminate, the XANES of an "in situ" calcined 0.8% $\text{CuO}/\text{Al}_2\text{O}_3$ (which contains only superficial Cu^{2+} aluminate⁴) has been obtained and included in Figure 2. Using this XANES spectrum as a reference, species 2 can be identified as superficial Cu^{2+} aluminate; the overall spectrum shape is quite similar to that of the reference although a small shift (of less than 1 eV) is observed in the maximum of the ≈ 8997 eV continuum resonance. In view of the strong bond length dependence of this resonance,¹⁴ this shift can be attributed to small differences in coordination distances, probably generated by a distinct degree of disorder in the aluminates. Assuming this assignment, species 1 may then be ascribed to CuO-like species; however,

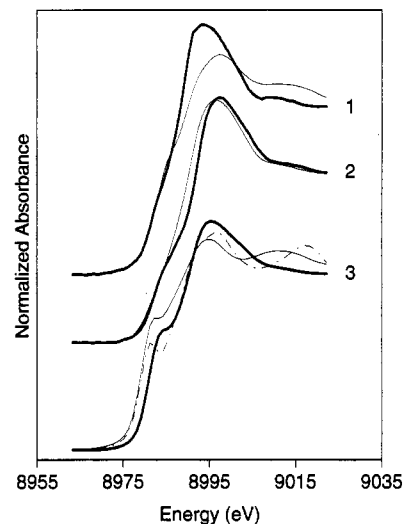
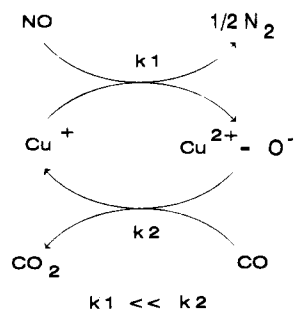


Figure 2. Predicted pure components: 1, dark line, first pure component, CuO-bulk; 2, dark line, second pure component, light line, superficial Cu^{2+} aluminate; 3, dark line, third pure component, light line, Cu_2O -bulk, dot-dashed line, CuAlO_2 -bulk.

a comparison with CuO-bulk (Figure 2) reveals important differences. This fact may be understood if the CuO-like species corresponds to Cu^{2+} ions or small particles strongly interacting with the alumina surface. This interpretation is supported by the extremely high $I_{\text{Cu}}/I_{\text{Al}}$ XPS ratio obtained for this catalyst.⁴ As mentioned above, the increase of the reaction temperature generates only one reduced species, number 3, that presents the 8983–8984 eV $1s \rightarrow 4p$ transition characteristic of Cu^+ compounds.¹⁵ Again, difficulties are encountered in order to identify this species with certainty, but a comparison with Cu_2O and CuAlO_2 bulk materials (Figure 2) may suggest a Cu_2O -like species on the basis of the preedge and edge regions shapes. It should be noted that Cu^0 was not observed during the experiment; however, we could not have detected it if its contribution was below the detection limit (about 2% of the total Cu).

Although no clear identification is obtained for all the Cu species present during reaction, their oxidation states have been firmly established from the XANES analysis. We will show that this information together with that extracted from the concentration profiles of Figure 1 allows us to interpret several important aspects of the NO + CO reaction. As the first point, it is worth noting that the concentration profiles of Figure 1 show that both Cu^{2+} species start to be reduced around 600 K. This fact was made evident using temperature programmed reduction (followed by thermogravimetric analysis) of the sample under a CO flow. This experiment shows that both Cu^{2+} compounds (oxide and superficial aluminate) begin to lose oxygen near this temperature. Therefore, around 600 K CO initiates the reduction of both Cu^{2+} phases, generating a single Cu^+ compound. Notice that, at the same instant, the NO conversion curve given in Figure 1 reaches light off. After the appearance of this Cu^+ species, its concentration profile (Figure 1) runs approximately parallel to the conversion up to 750 K, being the only Cu species observed at higher temperatures. Considering all these facts together, it is reasonable to conclude that this Cu^+ species is involved in the slow rate step of the reaction, is generated by CO reduction of both Cu^{2+} compounds, and, obviously, is oxidized by the NO dissociation. Therefore, based on this evidence a redox-type mechanism (Scheme 1) is proposed for the NO + CO reaction over this catalyst.

According to Scheme 1, the NO molecule is involved in the slow rate step of the reaction. This conclusion is in agreement

SCHEME 1: Representation of the Redox-Type Mechanism Proposed

with the studies of Balkenende et al.,^{16–18} these authors point out that the NO dissociation on oxidized Cu monocrystals is a structure-insensitive reaction with a probability of 10^{-5} while CO reduction of NO precovered systems can have a maximum probability of about 10^{-3} (only slightly structure sensitive). The oxidation of the Cu monocrystals was carried out by exposure to NO at saturation; under these conditions, the O/Cu Auger ratios reported^{16–18} correspond to surfaces in the Cu^+ state (see, for instance, ref 19). More information about the slow rate step of the reaction can be obtained from a visual inspection of Figure 1. First, we note that the relative positioning of the conversion curve and the catalyst composition is arbitrary. However, a comparison of the slopes of Cu^+ formation and NO conversion shows that approximately below 700 K the first is (always) bigger than the second. This is likely to be interpreted as an effect of the NO coverage, i.e. the NO adsorption, in the reaction rate. Notice that this can be a complex phenomenon as the NO adsorption can be blocked by CO, which is known to adsorb more strongly on cuprous ions than NO .²⁰ This fact comes directly from the nature of the adsorbate/ Cu_2O interaction; while adsorbed NO has an interaction of electrostatic nature,²¹ CO presents strong covalent s-donation and p-back-donation contributions to the bond and an energy of about 4 times greater than NO.²² After 700 K, the NO conversion grows more quickly than the Cu^+ formation, evidencing the effect of the temperature on the NO dissociation, i.e., on the slow rate step of the reaction.

In summary, the correlation of “in situ” XANES studies of catalysts with their catalytic properties allows us to achieve interesting insights about the reaction mechanism. The present data strongly support a redox mechanism for the $\text{NO} + \text{CO}$ reaction in $\text{CuO}/\text{Al}_2\text{O}_3$ systems. This study also shows that the

slow rate step of the reaction is likely to be the NO adsorption and/or dissociation over Cu^+ species.

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