X-ray Photoelectron Spectroscopy and Infrared Study of the Nature of Cu Species in Cu/ZrO₂ de-NOx Catalysts

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The present paper aims to clarify some of the still controversial aspects of the chemistry of copper in Cu-based catalytic systems active for de-NO_x processes by using hydrocarbons as reductants. Reactivity tests, X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) experiments have been carried out with Cu/ZrO₂ catalysts (3% copper). With no oxygen in the reaction flow, complete reduction of NO to N_2 occurs at $T > 623$ K with C_3H_8. In the presence of oxygen, complete oxidation of the hydrocarbon occurs without any significant conversion of NO. XPS shows that Cu^+ species can be formed at $423 < T \leq 623$ K when heating with a NO + C_3H_8 mixture, provided that carbonaceous species are previously formed by heating the catalyst with C_3H_8 at 773 K. To clarify the chemical interaction occurring between carbonaceous residues, copper and NO on the surface of real catalysts, experiments have been carried out with a model system consisting of copper particles deposited by evaporation on the surface of graphite. It was found that 100% Cu^+ is obtained when the Cu−graphite system is exposed to NO between 298 and 773 K. Simultaneously, it was found that C−NO (N1s binding energy, BE 403.3−404.8 eV), C−N (N1s BE 398.5 eV), and different C−O species are formed on the surface of graphite. −C−N and −C−O species are stable up to 773 K, whereras the −C−NO features disappear from the spectra at $T > 473$ K. To understand the chemical processes that occur on the Cu/ZrO₂ catalysts, an FTIR experiment has been carried out. Exposure of the catalyst to C_3H_8 at 773 K leads to the appearance of a series of bands between 1300 and 1600 cm^{-1} attributed to adsorbed carbonaceous species. Also, a very little band coming from −CN species is detected in these conditions. These species were stable when contacting the sample with NO at $T \leq 623$ K. Above this temperature, the bands decreased in intensity to disappear at $T = 723$ K. The implications of the formation of Cu^+ and Cu^{2+} states and that of the adsorbed oxygenated carbonaceous species in de-NO_x processes over Cu/ZrO₂ catalysts are discussed.

Introduction

Since the discovery by Iwamoto[1] that Cu−ZSM5 systems are effective catalysts for de-NO_x reduction processes with hydrocarbons (selective catalytic reduction (SCR) reactions), much work has been dedicated to both understand the reaction mechanism and develop catalysts that are active under real outlet conditions (i.e., in the presence of O₂, H₂O, SO₂, and other gases present in the outlets of burning installations). A point of much interest for many fundamental studies on this subject has been the determination of the role of copper in this reaction. For this purpose, different methods such as electron spin resonance (ESR), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and other techniques have been used.[2−8] A recent review by Parvulescu et al.[9] summarizes most of the progresses made on this subject during the last years.

Different interpretations have been proposed to explain the reactivity of Cu-based catalysts. Thus, it has been claimed that the formation of intermediate Cu^+−NO adsorbed states is critical for the activation of the NO molecule.[2−10] According to this model, the stabilization of the Cu^+ state of copper would

be crucial for such a process. In other interpretations, a direct interaction between NO and carbonaceous species adsorbed on the surface of the catalyst would constitute the limiting step for the reduction of NO.[11] Owing to the complexity of the reaction, it is reasonable that none of these interpretations can be taken as definitive and that more complex reaction pathways may control the overall de-NO_x reaction. It is also likely that, depending on the catalyst system and/or hydrocarbon used, different intermediate processes may be involved in the reaction.

Many studies in the literature over Cu-based de-NO_x catalysts have been carried out with copper exchanged zeolites.[1−11] Oxide-based catalysts have been proposed as an alternative to zeolites owing to their generally higher stability under the hydrothermal conditions existing in this type of processes.[12] With the present paper, we want to contribute to the discussion over intermediate species by studying by XPS and FTIR the behavior of copper in a Cu/ZrO₂ catalysts used for the SCR reaction by using C_3H_8 as hydrocarbon. Cu/ZrO₂ catalysts have been previously reported to be active for this type of processes, although only some papers devoted to the analysis of the state of copper have been published.[13,14] Therefore, our purpose here is to bring some light about the conditions favoring the formation of the different valence states of copper in this type of systems and, if possible, to draw some conclusions about the participation

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of either Cu^+ and Cu^{2+} in the SCR reactions. The role of carbonaceous species in stabilizing the different states of copper and its eventual reaction with NO are also addressed.

The results are discussed in relation with the behavior of copper and carbonaceous species adsorbed on the catalyst surface under NO + C_3H_8 (O_2) mixtures. The choice of this reaction mixture is due to the fact that C_3H_8 and C_3H_6 are hydrocarbons well-known for yielding carbonaceous residues on the surface of oxides when heated in their presence. A model experiment by XPS with Cu deposited on graphite and then exposed to NO has been carried out to clarify the effect of certain reaction conditions in stabilizing Cu^+ species.

Experimental Section

Cu/ZrO_2 (3% of Cu) has been prepared by wetting impregnation of a ZrO_2 powder prepared by forced hydrolysis according to a procedure previously described.[15] Reaction tests were carried out on a conventional reaction setup where reaction analysis was done on a gas chromatograph (Varian GC3800) supplied with a TCD detector, a Porapack N column, and a 5 A molecular sieve column. Data are collected and analyzed in a chromatographic workstation. For the reaction tests, NO and C_3H_8 were diluted in He (1000 and 2500 ppm, respectively), whereas O_2 was supplied directly to the gas mixture (3%). Mass flow controllers were used for dosing the gases to the reactor, with a total flow of 100 mL min^{-1}. After the catalysts were heated in the reactor at 673 K in a mixture He/O_2 (3%) for 3 h, the reactor tests were performed using an ascendant heating ramp of 1 K min^{-1}, followed by a temperature constant period (3 h) and then a descendent cooling ramp (1 K min^{-1}). Sample injections were taken into the GC every 20 min. The results presented here were taken from the cooling side of the reaction protocol. Catalytic tests were carried out with approximately 200 mg catalyst.

XPS spectra have been recorded with a Leybold-Heraeus LHS-10 spectrometer (base pressure 3×10^{-10} Torr) working in the constant pass energy mode at a value of 40 eV. The Al $K\alpha$ radiation ($h\nu = 1486.6$ eV) was used as excitation source. Binding energy (BE) reference was taken at the C1s peak of the carbon contaminating the surface of the samples at a value of 284.6 eV.

Thermal treatments under conditions simulating the reaction mixture were carried out in the pretreatment chamber of the XPS spectrometer (base pressure 3×10^{-10} Torr). The samples were heated under mixtures of gases, subjected to Ar^+ bombardment for cleaning, or exposed to a copper evaporation source for deposition of Cu particles by evaporation. The samples were transferred to the analysis chamber without exposure to the air.

The Cu/ZrO_2 catalyst was subjected to thermal treatments for 30 min under NO (0.1 Torr), C_3H_8 (0.1 Torr), or mixtures NO + C_3H_8 (0.1 + 0.1 Torr). Eventually, O_2 (1 Torr) was added to the reaction mixture. H_2 treatments were done with 2 Torr of this gas. The selected gas partial pressures tried to reproduce the reaction conditions used for the catalytic tests.

For the model experiment, a flat graphite plate was used. Prior to any other manipulation, this sample was sputtered cleaned with Ar^+ ions of 2 keV. These ions were provided by a IQP10 source attached to pretreatment chamber. Copper evaporation on the graphite phase was done by resistively heating a thin Cu wire wrapped around a W wire (0.1 mm thick). Graphite and the copper graphite samples were heated in NO (10^{-1} Torr) for 30 min at increasing higher temperatures up to 723 K.
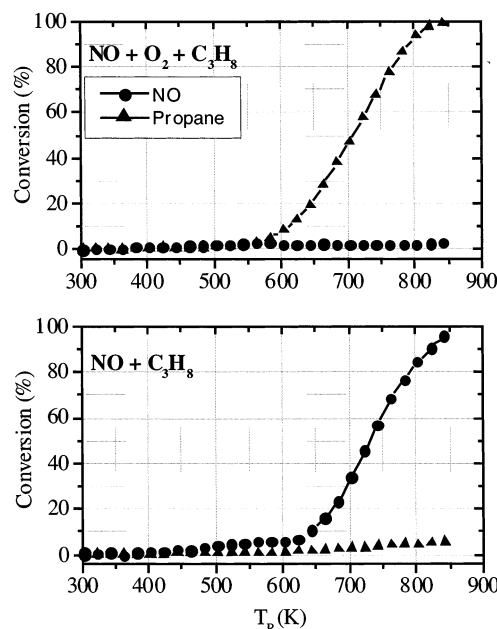

Figure 1. NO and C_3H_4 conversion degrees over a Cu/ZrO_2 catalysts with (right) and without (left) oxygen in the reaction mixture.

IR measurements were recorded in a Nicolet 510 FTIR spectrometer at a resolution of 4 cm^{-1}. The Cu/ZrO_2 catalyst powder was pressed into a very thin, self-supported pellet that was placed in a SPECAC IR cell where thermal treatments under gas flow conditions could be carried out. For the performed experiments, C_3H_8 (500 ppm) and NO (1000 ppm) diluted in He were used as reactant gases. Treatments were carried out for 30 min and spectra were recorded in transmission mode at 298 K with or without the reactants in the reaction cell.

Results

Catalytic Tests. Figure 1 shows NO and C_3H_8 removal conversion yields for the reaction $C_3H_8 + NO$ (O_2) $\rightarrow$ N_2 + $CO_2 + H_2O$ [1] over the Cu/ZrO_2 catalyst in the presence and absence of oxygen. In all cases, N_2, CO_2, and H_2O were the sole reaction products detected. The figure shows that in the absence of oxygen NO is reduced to N_2 at $T > 623$ K, a process that is accompanied by the removal of the stoichiometric amount of C_3H_8 according to $C_3H_8 + 10NO \rightarrow 5N_2 + 3CO_2 + 4H_2O$. In the presence of O_2, C_3H_8 becomes oxidized at $T > 623$ K, although practically no NO is reduced under these conditions. This behavior suggests, as previously observed by Kung and co-workers[12] that with oxygen the Cu/ZrO_2 is an efficient oxidation catalyst of C_3H_8, but no reaction routes are available for reduction of NO. This behavior was different with CH_4 where even in the presence of O_2 ca. 50% reduction of NO was achieved.[16] For the present study, aiming at dilucidating the chemical state of copper in Cu/ZrO_2 catalysts and the influence of organic residues for the stabilization of different oxidation states of this element, we have selected C_3H_8 as the hydrocarbon because it yields readily carbonaceous species on the catalyst surface. It is worth noting that similar results were obtained when using C_3H_6 which is well-known for its ease cracking on oxide surfaces.

XPS Study of the NO−Graphite Interaction. A reasonable hypothesis to account for by the previous catalytic results is that some intermediate carbonaceous species formed on the surface of the Cu/ZrO_2 catalyst might be involved in the reduction of NO. In the presence of oxygen, these species could be totally eliminated from the surface. Under this previous
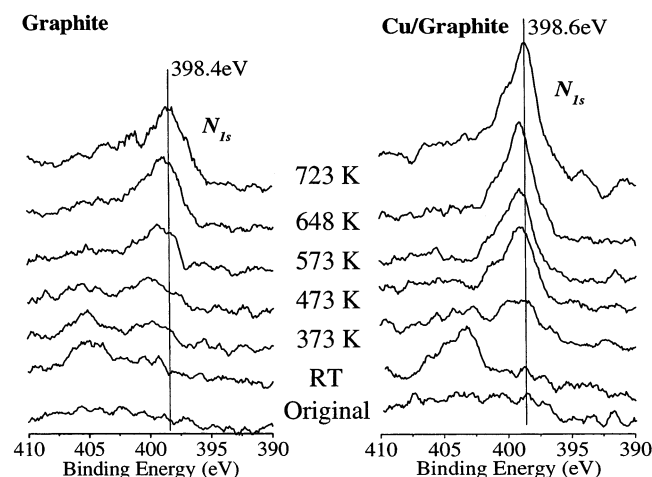
XPS and IR study of Cu−Zirconia

J. Phys. Chem. B, Vol. 106, No. 39, 2002 **10187**

Graphite

Cu/Graphite |398.6eV

|398.4eV

N_{1s}

N_{1s}

723 K

648 K

573 K

473 K

373 K

RT

Original

410 405 400 395 390
Binding Energy (eV)

410 405 400 395 390
Binding Energy (eV)

Figure 2. N1s photoelectron spectra recorded after adsorption of NO on graphite (left) or Cu/graphite (right) systems at the indicated temperatures.

assumption, it seems interesting to study the direct interaction of NO with carbon formed at the surface of the catalyst. An experiment was intended over a Cu/ZrO_2 catalyst after prolonged heating with C_3H_8 or C_3H_6 at $T > 623$ K to generate graphitic-like species on the surface. However, although the amount of carbonaceous species detected by XPS significantly increased after these treatments with the hydrocarbons, the N1s signal intensity after adsorption of NO was below the sensitivity limit of the spectrometer. Therefore, we studied the interaction of NO with pure graphite. The reaction of NO with the basal plane of graphite has been previously studied by STM.[17] Here, such a reaction has been studied by XPS. Figure 2 shows N1s spectra recorded after adsorption of NO on the graphite surface at increasing temperatures. Two experiments are reported. In the first one, a clean graphite plate was used; in the second, metallic copper was deposited by evaporation on the surface of graphite. It is known that deposition of copper on graphite by evaporation leads to the formation of small three-dimensional copper particles.[18] Thus, in our experiment, a considerable extent of the graphite surface should be free from copper, as the surface coverage expressed in terms of equivalent monolayers was ca. 1.2. (This means that the intensity of the Cu 2p photoemission line in our experiment would be equivalent to that eventually obtained when 1.2 monolayers of copper would spread on the whole graphite surface according to a two-dimensional growth mechanism.)

Adsorption of NO on clean graphite yields N1s spectra whose evolution with the adsorption temperature is presented in Figure 2. Initially, at 298 K, a broad peak at 404.8−403.5 eV can be detected. This BE value is consistent with the formation of oxidized species of N (i.e., $C-NO_x$).[19] By increasing the temperature, another peak at 398.6 eV develops at $T \geq 473$ K. This peak, whose intensity increases with temperature, is the only one detected at $T \geq 573$K. The BE value of this new nitrogen species is consistent with a nitrogen atom bonded directly to the graphite surface (i.e., $-C\equiv N$ or related species).[19] It must be produced through the reduction of nitrogen of the NO molecule by the graphite followed by the formation of −CN species on its surface, a kind of species that has been previously observed by reaction of NO with soot and other supported catalysts treated with hydrocarbons.[20−22] Obviously, some CO_2 or other carbon oxygenated species must also form as a result of this reaction. When the experiment was carried out on the graphite with copper deposited on the surface of graphite, the recorded N 1s spectra revealed the formation of similar $C-NO_x$

TABLE 1: Atomic Ratios Calculated from the XPS Spectra for NO Adsorbed on Graphite and Cu/Graphite at Increasing Higher Temperature

	graphite		Cu/graphite		
T (K)	N/C	O/C	N/C	O/C	Cu/C
298	0.019	0.044	0.022	0.111	0.117
373	0.017	0.054	0.022	0.125	0.105
473	0.022	0.052	0.024	0.123	0.100
573	0.023	0.084	0.029	0.111	0.101
648	0.034	0.099	0.033	0.138	0.091
723	0.036	0.129	0.044	0.139	0.088

Cu/Graphite

932.6eV

916.5eV |917.9eV

$Cu_{2p_{3/2}}$

Cu_{L3VV}

723 K

648 K

573 K

473 K

373 K

RT

Original

950 945 940 935 930
Binding Energy (eV)
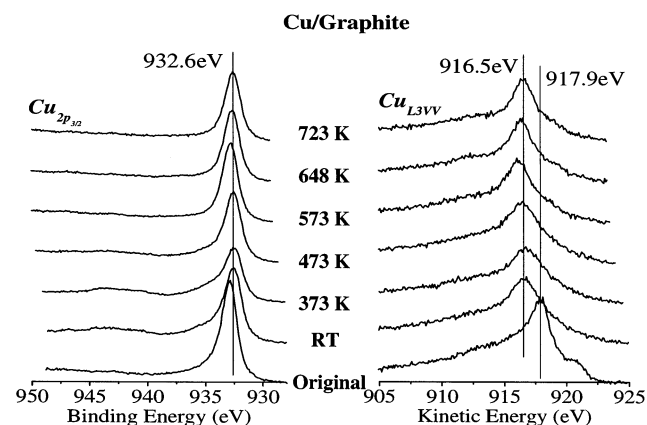
905 910 915 920 925
Kinetic Energy (eV)

Figure 3. Cu2p photoelectrons (left) and CuL₃VV Auger (right) spectra for copper (~1.2 equivalent monolayers) deposited on graphite and then exposed to 0.1 Torr of NO at the indicated temperatures.

and C−N species, although the intensity of the peaks was higher in this case. Table 1 summarizes some atomic ratios deduced from the areas measured by XPS for the different element peaks and their corresponding sensitivity factors. It is apparent from this table and Figure 2 that the overall intensity of the whole N1s spectral region is always higher for NO adsorbed on the Cu−graphite sample than on graphite. A rough estimate of the N/C atomic ratios assuming that, at these high temperatures, nitrogen species adsorb exclusively on the surface of graphite indicates that an equivalent coverage of half a monolayer of nitrogen species is attained at 723 K on the Cu−graphite sample. The higher intensity of the N1s signal on Cu−graphite is an interesting feature of this experiment especially if one takes into account that the actual graphite surface available for NO adsorption is smaller after deposition of copper. This enhancement of the N 1s photoemission intensity suggests that copper is activating the incorporation of nitrogen onto the graphite surface.

From the two sets of spectra in Figure 2, it can be deduced that the transformation of the $C-NO_x$ into the C−N species occurs between 373 and 473 K, although this transformation seems more effective in the experiment on the copper−graphite sample. In this case, spectra were also taken for the Cu 2p and Cu L₃VV Auger peaks. The results, reported in Figure 3, show a clear modification of the shape of spectra after exposure of the sample to NO. The value of the Auger parameter of copper (i.e., 1849.1 eV), a more unambiguous parameter than the Cu $2p_{3/2}$ BE to differentiate between Cu^+ and Cu^0 oxidation states, clearly shows that after NO exposure the Cu^0 particles are transformed into Cu_2O.[8,23,28] It is interesting that heating in the presence of NO at increasing higher temperatures up to 723 K does not further modify the chemical state of copper. This behavior is relevant because, as it will be shown below, NO is able to oxidize Cu^+ to Cu^{2+} in the absence of graphite. This effect and the noticeable decrease in the intensity of the copper
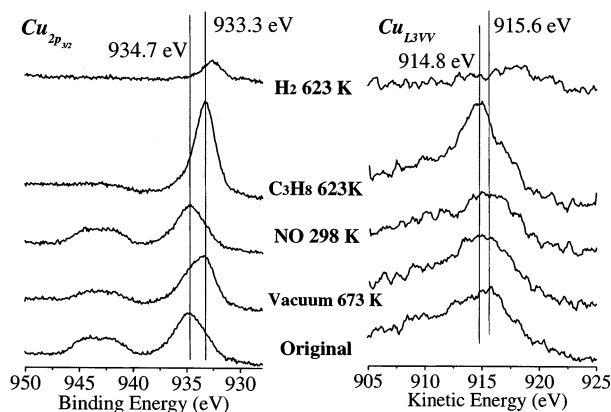
Figure 4. Cu2p photoelectron (left) and CuL$_3$VV Auger (right) spectra for the Cu/ZrO$_2$ catalyst subjected to the following treatments: (a) original sample, (b) heated in a vacuum at 673 K for 30 mm, (c) exposed to NO (10^{-1} Torr) at 298 K, (d) heated under 1 Torr C$_3$H$_8$ at 623 K for 30 min, and (e) heated under 1 Torr H$_2$ at 623 K.

signals after these heating treatments (cf. Table 1) suggests a certain agglomeration of the Cu$_2$O particles and/or their decoration or coating by a carbon layer.

Another interesting result from this experiment refers to the evolution of the intensity O 1s signal. Table 1 shows that after exposure of the sample to NO, the intensity of this signal increases systematically with the temperature of treatment to reach a maximum intensity at 723 K. The amount of oxygen in the sample at each temperature was always higher than that of nitrogen. Because no other source of oxygen apart NO exists under the conditions of the experiment, this result suggests that NO is dissociatively reduced by the graphite. After dissociation, while part of the nitrogen is released from the surface in the form of N$_2$, most oxygen remains on the graphite surface. Although the shape of the O 1s signal was in all cases very broad, the BE of its maximum, ranging between 532 and 531.3 eV, suggests that it may correspond to oxygen bonded to C (i.e., C=O, −COO−, −C−O−, etc.).[24] A slight increase in the asymmetry of the C1s peak at higher BE confirms that such type of species are formed on the surface of graphite during the NO treatments.[24]

XPS Characterization of Copper. The redox behavior of copper in the Cu/ZrO$_2$ catalyst has been investigated after different thermal treatments to determine the shape of the spectra of Cu^0, Cu$^+$, or Cu^{2+} states of copper and the stability of these states under different redox treatments. Figure 4 shows a series of Cu 2p photoemission and Cu L$_3$VV Auger spectra of the original Cu/ZrO$_2$ catalysts after being subjected to the indicated treatments. BEs, Auger parameter values, and satellite to main peak ratios of the Cu 2p$_{3/2}$ peaks for these spectra are summarized in Table 2 where values from well characterized copper species taken from the literature are included for comparison. From the inspection of the shape of the spectra and the values of the Cu 2p BEs and Auger parameters summarized in Table 2, it can be deduced that in the original catalyst there is Cu^{2+} species.[23] They are characterized by a Cu2p$_{5/2}$ BE of ∼934.8 eV, an Auger parameter value of ∼1850.6 eV, and a very intense and broad satellite peak at ∼943 eV. Outgassing in a vacuum at 450 °C yields a mixture of Cu^{2+} + Cu$^+$ species, as indicated by the relative decrease of the intensity of the satellite, the shift in the BE position of the maximum of the main photoelectron peak to 933.4 eV, and the change in the value of the Auger parameter to 1848.3 eV.[23] From this spectrum, the presence of some amount of Cu^{2+} species can be inferred from the still large intensity of the satellite peak and

TABLE 2: Electronic Parameters of Copper for Cu/ZrO$_2$ Catalyst Subjected to the Indicated Treatments. Data from Literature Are Included for Comparison

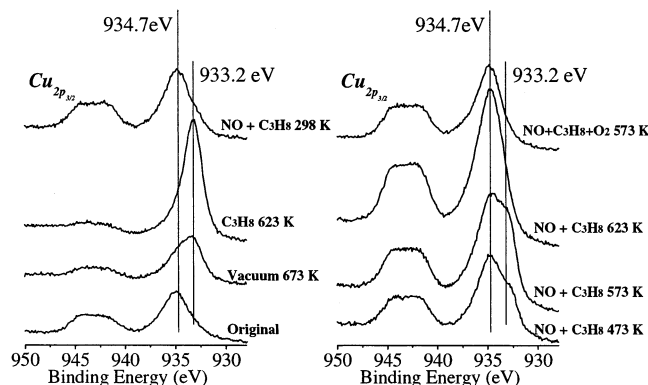| chemical states of copper or treatment of Cu/ZrO$_2$ catalyst	Cu2p$_{3/2}$ BE (eV) at the position of the maximum	α' (eV)	satellite/ main peak ratio	ref
Cu^0	932.4	1850.8	<0.01	(8, 19)
Cu$^+$	932.5	1849.3	0.09	(8, 19)
Cu^{2+}	933.8	1851.6	0.60	(8, 19)
Cu/ZrO$_2$				
original	934.8	1850.6	0.46	
NO 473 K	934.6	1850.3	0.50.	
vacuum 673 K	933.4	1848.2	0.24	this work
C$_3$H$_8$ 673 K	933.3	1848.0	0.07	
H$_2$ at 573 K	932.6	1850.5	0.01	

Figure 5. Cu2p photoelectron spectra of Cu/ZrO$_2$ catalysts subjected to the following thermal treatments: (a) original sample, (b) heated in a vacuum at 673 K, (c) heated with C$_3$H$_8$ (1 Torr) at 623 K, (d) dosed with NO + C$_3$H$_8$ at 298 K, (e) heated with NO + C$_3$H$_8$ at 473 K, (f) heated with NO + C$_3$H$_8$ at 573 K, (g) heated with NO + C$_3$H$_8$ at 623 K, and (h) heated with NO + C$_3$H$_8$ + O$_2$ at 573 K.

the presence of a shoulder at the right side of the main photoemission peak. Meanwhile, heating the original sample under 10^{-1} Torr C$_3$H$_8$ at 623 K yields a spectrum typical of the Cu$^+$ state as proved by the almost full removal of the satellite intensity and the new value of the Auger parameter (i.e., 1848.3 eV). Total reduction to Cu° occurs by heating in H$_2$ at 500 °C; this state is characterized by an Auger parameter of 1850.5 eV and a very small satellite peak. Figure 4 also shows that reoxidation to Cu^{2+} takes place by exposure of the catalyst with Cu$^+$ species to NO at 298 K.

XPS Analysis of Copper under SCR Conditions. The oxidation state of copper was also investigated after heating the Cu/ZrO$_2$ samples under the mixture of NO + C$_3$H$_8$ chosen to reproduce the reaction conditions during the catalytic test (see the Experimental Section). Figures 5 and 6 show Cu 2p photoelectron spectra for the Cu/ZrO$_2$ catalyst heated under the NO + C$_3$H$_8$ mixture at increasing higher temperatures up to 623 K. The sample was subjected to two different pretreatments prior to heating with the gas mixture. In Figure 5, the sample, after outgassing at 673 K, was first heated with C$_3$H$_8$ at 623 K. As indicated in Figure 4, this treatment leads to the formation of Cu$^+$ species. Then, the Cu$^+$ species are reoxidized to Cu^{2+} by exposure to NO at 298 K. In the experiment in Figure 6, the pretreatment consisted of exposing the sample to 10^{-1} Torr of NO at 298 K after outgassing at 673 K, whereby a full oxidation of copper to Cu^{2+} was obtained. In this second case, heating under the NO + C$_3$H$_8$ mixture from 298 K up to 623 K or higher temperatures always yields Cu^{2+} even if after outgassing Cu$^+$ species are formed (cf. Figure 6). This is not the situation for the sample previously heated with C$_3$H$_8$ (cf. Figure 5). Here, heating in the 473−573 K interval with NO + C$_3$H$_8$ produced

XPS and IR study of Cu−Zirconia

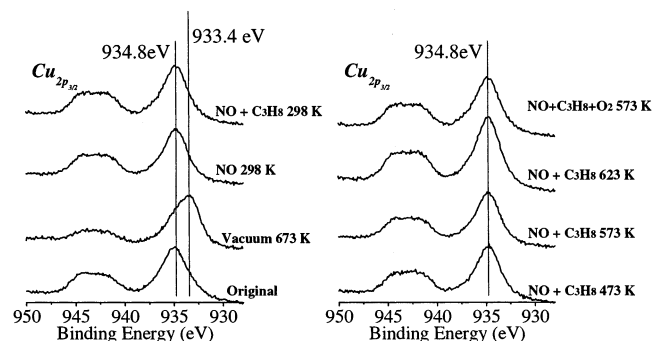*J. Phys. Chem. B, Vol. 106, No. 39, 2002* **10189**

Figure 6. Cu2p photoelectron spectra of Cu/ZrO$_2$ catalyst subjected to the following thermal treatments: (a) original sample, (b) heated in a vacuum at 623 K for 30 min, (c) dosed with 10^{-1} Torr NO at 298 K, (d) dosed with NO + C$_3$H$_8$ at 298 K, (e) heated with NO + C$_3$H$_8$ at 473 K, and (f) heated with NO + C$_3$H$_8$ at 633 K.

a mixture of Cu^{2+} + Cu$^+$ species as deduced from the shape of spectra and the relative intensity ratio of satellite to main peak (cf. Table 2). The relative amount of Cu$^+$ species reaches a maximum at 573 K and then decreases up to 623 K when full oxidation to Cu^{2+} species is achieved. The addition of O$_2$ to the reaction mixture yields Cu^{2+} species already at 573 K, when the maximum amount of Cu$^+$ species was detected with the NO + C$_3$H$_8$ gas mixture. A point that should be stressed from the results in Figure 5 is that Cu$^+$ species are formed by heating with NO + C$_3$H$_8$ in a temperature interval where very little or no conversion of NO is found with our catalyst (cf. Figure 1), suggesting that Cu^{2+} is the sole state active in the NO reduction reaction. In any case, as during the XPS measurements, there is no direct contact with the gas phase, it cannot be discarded the presence of some Cu$^+$ species in real reaction conditions.

Another interesting feature in the previous experiments refers to the evolution of the intensity of the C1s signal. It increases after heating the catalysts in C$_3$H$_8$ but always decreases under conditions where Cu^{2+} species are formed at $T \geq 623$ K, either by heating with NO or with the NO + C$_3$H$_8$ mixture. It is likely that under these conditions the carbon residues, present on the surface by contamination of the sample and/or by partial cracking of C$_3$H$_8$, are effectively removed by oxidation with NO in a similar way as we have found with graphite.

IR Study of the NO−Carbon Species Interaction. The previous results by XPS suggest that stabilization of Cu$^+$ species by exposure of the catalyst to the NO + C$_3$H$_8$ mixture requires the previous formation of some carbonaceous species on the surface of the catalyst support. In our experiment, this occurs by heating the catalyst with the hydrocarbon. The experiment with the Cu−graphite model system also indicates that Cu$^+$ species become stabilized on graphite even when it is in contact with NO at high temperatures. To analyze the possible chemical characteristics and the possible formation of some carbon species by reaction of C$_3$H$_8$ with the surface of the zirconia catalyst, we have carried out an experiment by IR spectroscopy. Figure 7 shows IR spectra of the Cu/ZrO$_2$ catalyst heated with C$_3$H$_8$ at 773 K and then exposed to NO at increasing temperatures up to 773 K. The band structure appearing in the interval 1600−1300 cm^{-1} after heating the zirconia catalyst with C$_3$H$_8$ can be attributed to surface carboxyl species[25] and, more specifically, to formate species.[22] However, bands at similar positions have been also related with the formation of carbonaceous coke species over the support.[21] Together with these bands, a little one at 2135 cm^{-1} is detected after treatment with NO at 623 K and higher, which can be adscribed to the formation of −CN species,[22] similar to those previously detected by XPS in the
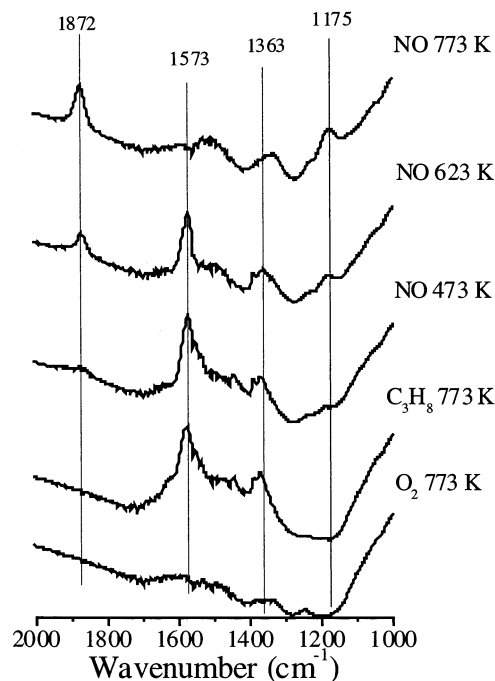

Figure 7. FTIR spectra of the Cu/ZrO$_2$ catalyst subjected sequentially to the indicated treatments.

graphite system. This structure starts to decrease in intensity at $T \approx 623$ K when the sample is put in contact with NO. It is around this temperature where the NO catalytic conversion starts over the Cu/ZrO$_2$ catalyst (cf. Figure 1). After contact with NO at 773 K, practically no traces of these carbonaceous species can be detected in the spectrum suggesting their full oxidation with the NO of the gas phase. This experiment shows that all carbonaceous deposits have been eliminated by reaction with NO. The new bands at 1872, 1520, 1336, 1224, and 1175 cm^{-1} appearing in the spectrum can be attributed to Cu^{2+}−NO (1872 cm^{-1}) and adsorbed NO$_x$− species over the ZrO$_2$ surface[25,26] and are similar to those obtained directly by contact of NO with a pristine catalyst at 773 K.

Discussion

The infrared and XPS studies of C$_3$H$_8$ adsorption on the Cu/ZrO$_2$ system have shown that carbonaceous species are formed on the surface of the catalyst when heated to 773 K. They were stable in the presence of NO only at temperatures below 623 K. In this temperature range, Cu$^+$ species can be stabilized. However, because in this interval of temperatures no significant conversion of NO is found (cf. Figure 1), it cannot be concluded that Cu$^+$ species are involved in the reduction reaction of NO with the hydrocarbon. At higher temperatures, the physico-chemical state of the catalyst is completely modified: the copper is oxidized to Cu^{2+} species, the carbonaceous species adsorbed on the ZrO$_2$ surface are labilized and eliminated by the NO in the gas phase or by NOx species previously adsorbed on the support through the Cu^{2+} ions. Accordingly, the reduction of NO with C$_3$H$_8$ becomes remarkable. In principle, a reasonable hypothesis would be that Cu^{2+} species, able to adsorb NO molecules from the gas phase, might be involved in the activation of this molecule, thus allowing its reaction with the carbonaceous deposit on the ZrO$_2$ surface.

A large number of studies have appeared in the literature concerning the chemical state of copper (i.e., Cu$^+$ or Cu^{2+}) active for SCR processes and the way these species participate in the reaction.[1,4] These studies include a large variety of results

by XPS,[6,14] ESR,[7,14] IR,[10,14] or DTP[2] on Cu/zeolite catalysts trying to determine the role of copper in SCR reactions. These studies were aimed at the characterization of the active sites of copper on the catalyst surface and that of the intermediate species in the reaction mechanism. A widely accepted interpretation in the literature is that an active center is a $[Cu-O-Cu]^{2+}$ dimmer species and that a reductive adsorption of NO on Cu^{2+} results in the formation of a high temperature ($\sim$550 K) Cu^+-NO^+ adsorption state. A dissociative thermal desorption at 550 K will regenerate the $[Cu-O-Cu]^{2+}$ complex.[8] It is also concluded that under reaction conditions some copper remains as Cu^+ and that this state will act as reductive adsorption site for NO.

Our results suggest a relatively more complex situation for the Cu/ZrO_2 catalysts. According to them, copper would favor the partial oxidation reaction of the hydrocarbon and the formation of adsorbed carbonaceous species. This partial oxidation reaction may take place with NO, adsorbed species of oxygen on the surface of the support, or oxygen ions from the ZrO_2 substrates (ZrO_2 is an ionic conductor with a high mobility and exchange capacity of $O^=$ ions[27]).

Stabilization of the Cu^+ state of copper even in the presence of the NO + C_3H_8 mixture is highly dependent on the concentration of carbonaceous species on the surface of the catalyst and on the temperature of the system. Our experiment with the model system shows that Cu^+ can be stabilized on graphite even when it is heated with NO at high temperatures. In the same way, the experiments with the Cu/ZrO_2 catalyst treated "in situ" with the NO + C_3H_8 mixture show that Cu^+ species can be formed when abundant carbonaceous species preexist on the surface and the temperature is below 623 K. Above this temperature, only Cu^{2+} species are formed. As a consequence, we think that for a proper interpretation of the results reported in the literature about the stabilization of Cu^+ species[3] it should be considered the eventual deposition of carbon in the vicinity of copper centers and the temperature of the system. In fact, our results show that Cu^+ is stabilized in a temperature interval where practically no NO conversion in found, thus suggesting that stabilization of Cu^+ species is not critical for de-NO_x reaction over Cu/ZrO_2 catalysts.

On the other hand, our FTIR results suggest that a likely reduction route of NO over Cu/ZrO_2 catalysts is its reaction at $T > 623$ K with intermediate, partially oxidized, hydrocarbon species formed on the surface of the oxide support. It seems that Cu^{2+} centers favor the adsorption of NO over the catalyst system, but whether Cu^+ is an active center for activating the NO molecule under reaction conditions cannot be either demonstrated or discarded definitively by our experiments. In fact, these experimental results cannot discard that under reaction conditions at $T > 623$ K, dynamically adsorbed carbonaceous species could locally reduce some copper centers to Cu^+ state, able to act as active intermediate center for the SCR reaction. As a conclusion, it can be stated that at $T < 623$ K the reaction processes between NO, copper, and carbonaceous species can

be well characterized by the methodology proposed here combining XPS and FTIR analysis, on the understanding that our results are just valid for the Cu/ZrO_2 system. However, whether, some of the proposed processes for the formation of Cu^+ or carbonaceous species could be eventually involved in the SCR reaction at $T > 623$ K has still to be proved and further experiments are being carried out in our laboratory along this line. Other studies according to a methodology similar to that developed here, would be also of interest to determine the reaction pathways and the stability of intermediate species with other catalyst and de-NO_x reaction processes.

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