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Determining the Nature of the Active Sites of Cu-Beta Zeolites for the Selective Catalytic Reduction (SCR) of NO_x by Using a Coupled Reaction-XAES/XPS Study

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The present work reports a XPS and XAES study of Cu-Beta zeolites with different Cu loadings, coupled with an *in situ* type of catalytic experiments conducted in a high-pressure gas cell installed in the preparation chamber of the spectrometer. It has been found that the most active Cu-Beta zeolites for SCR of NO_x are those in which the conversion between Cu^{+2} and Cu^{+1} species is quickly produced under reaction conditions. This conversion between both oxidation states is easier in over-exchanged Cu-Beta samples. When exposed to the reaction conditions, the over-exchanged Cu-Beta zeolites show a high level of dispersed Cu^{+1} species, and a correlation between the ratio of Cu^{+1} to total Cu on the surface in the working catalyst and catalytic activity has been found. ⓒ 1997 Academic Press

1. INTRODUCTION

During the past few years special attention has been focused on the selective catalytic reduction (SCR) of NO_x by hydrocarbons, such as propane, propene, ethane, methane, and isobutene, in an excess of oxygen (1–14).

Although many types of catalysts have been studied for this purpose, only a few copper loaded zeolites have demonstrated to be adequate, and among them Cu-ZSM-5 zeolite (9, 10) and Cu-Beta zeolite (15) give good yields while they are stable under reaction conditions.

The activity of these catalysts was found to depend on the Cu content. Thus, only for over-exchanged Cu-ZSM-5 or Cu-Beta zeolites relevant activity has been measured. Thus, Iwamoto *et al.* (16) showed that the activity of Cu-ZSM-5 increased with the increment of the Cu exchange level, reaching maximum at the exchange level of 80–100%. These catalysts have been characterized by techniques such as infrared spectroscopy (17–19), luminescence (20), electronic spectroscopy (21, 22), EXAFS (22, 23), and EPR (24), but until now, the identification and structure of Cu species actives in SCR of NO_x and the detailed mechanism for this reaction have not been established.

The facile reduction from Cu^{+2} to Cu^{+1} suggested that a possible redox mechanism could be involved (20). On the other hand, Kucherov *et al.* (25) suggested that Cu^{+2} species is very stable in Cu-ZSM-5 zeolite and, in this way, the redox mechanism previously proposed by some reports would need to be raised again. A recent paper (18), suggesting that a redox mechanism could be involved in this reaction, states that the active Cu species have their origin in the $(Cu^{+2}–OH)^+$ cations, balanced by one framework aluminium, and the reason for the high activity of Cu-ZSM-5 is suggested to be the existence of isolated framework Al atoms. Shpiro *et al.* (21) suggested that copper in over-exchanged Cu-ZSM-5 zeolites exists as small clusters of Cu–O or as isolated ions whose oxidation state (Cu^{+2} or Cu^{+1}) depends on the atmosphere present.

It certainly would be of interest to determine the active species in SCR catalysts based on large pore bidirectional zeolites, such as Beta zeolites, which can be synthesized with high Si/Al ratios. It is best always to characterize the catalysts under reaction conditions and if it is not possible, one should at least look to the catalysts which have been working without exposing them to atmospheres other than those required for the reaction.

The present paper reports a XPS and XAES study of Cu-Beta zeolites with the aim to characterize the copper species involved in the selective catalytic reduction of NO_x. For this purpose we have selected three samples of Cu-Beta zeolite with different cation exchange levels whose catalytic activity has been studied in a previous paper (15).

2. EXPERIMENTAL

2.1. *Materials*

Three Cu-Beta zeolite samples A, B, and C with a nominal Cu exchange of 194, 106, and 55% respectively were prepared in the following way. The starting zeolite was a commercial PQ (CP811) sample with a Si/Al ratio of 11. Thus, 10g of zeolite Beta was slurried, for 24 h at room temperature, in 1000 ml of distilled water containing copper (II)

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TABLE 1

Chemical Analysis of the Catalysts Used in the Present Study

Catalyst	%SiO_2	%Al_2O_3	%Na_2O	%CuO	Si/Al	Cu/Al	Cu/Si	%Cu exchange
A	84.7	6.0	0.14	9.2	11.9	0.97	0.081	194
B	87.8	6.6	0.18	5.4	11.4	0.53	0.046	106
C	90.0	6.8	0.32	2.9	11.3	0.27	0.023	55

acetate with the adequate concentration to achieve the desired ion exchange. To prepare samples with more than 100% Cu ion exchange, an amount of NH_4OH was added and the pH was adjusted to 6.0. The Cu exchanged zeolite was collected by filtration and washed extensively with distilled water. The resulting material was dried and calcined for 4 h at 450°C. The Cu content of the final sample was measured by chemical analysis, and the results are given in Table 1.

2.2. *XPS Measurements*

The XP spectra have been obtained with a VG-Escalab-210 electron spectrometer, by using the Mg $K\alpha$ (1253.6 eV) radiation of a twin anode in the constant analyser energy mode with a pass energy of 50 eV. To avoid the X-ray induced reduction of Cu^{+2} to Cu^{+1}, samples were maintained at 173 K during the acquisition and the X-ray power was limited to 200 W (20 mA–10 kV). The spectral acquisition time was also reduced to the maximum to prevent the damage of the sample and the possible reduction of Cu^{+2}. The pressure of the analysis chamber was maintained at 5×10^{-10} mB. The binding energy and the Auger kinetic energy scale were regulated by setting the C 1*s* transition at 284.6 eV. The accuracy of BE and KE values was ±0.2 and ±0.3 eV, respectively. Depending on the energy scale used, the spectral resolution ranged from 0.10 to 0.15 eV. The BE and KE values were obtained by using the Peakfit Program implemented in the control software of the spectrometer.

Ratios of the atomic concentrations in outer surface layers of the samples were estimated from the corresponding XPS peak area ratios by using the relation

$$\left[\frac{X}{Y}\right]_S = \frac{A_{(X)}}{A_{(Y)}}\frac{\sigma_{(Y)}}{\sigma_{(X)}}\frac{\lambda_{(Y)}}{\lambda_{(X)}}\sqrt{\frac{E_{K(X)}}{E_{K(Y)}}},$$

where A, σ, λ, and E_K are the integral of each peak after S-shaped background substraction, the effective ionization cross section, the escape depth, and the photoelectron kinetic energy, respectively. Cross section values were taken from Scofield (26) and the escape depth were calculated from the formulas given by Vulli and Starke (27).

2.3. *Catalytic Experiments*

The NO_x reduction experiments were carried out in a fixed bed quartz tubular reactor of 2.2 cm diameter and 53 cm length. In a typical experiment, 3 g of exchanged catalyst, as particles of 0.25–0.42 mm size, were introduced in the reactor and heated in a flow of nitrogen up to 723 K (15). At this temperature the flow was maintained for 6 h. Then the desired reaction temperature was set and the reaction feed admitted. This consists of 2.83×10^{-5} m^3 s^{-1} of a mixture of 850 ppm of NO, 470 ppm of C_3H_8, 2.5% of oxygen, and balanced with nitrogen. The NO_x present in the outlet gasses from the reactor was continuously analyzed by means of a chemiluminescence detector. The catalytic activity of the Cu-Beta zeolites is clearly dependent on the reaction temperature (15) (Fig. 1). Thus, in samples A and B, with high Cu loading, the catalytic activity is similar showing a maximum at ca. 623 K. On the other hand, sample C with low Cu exchange level shows similar catalytic activity at higher temperatures. Table 2 shows the activity measurements in the selective catalytic reduction of NO_x of the samples used in the present study.

In situ type experiments were conducted in a high-pressure gas cell (HPGC) installed in the preparation chamber of the spectrometer, so the catalysts could be moved to the analysis chamber of the spectrometer without exposure to air. To facilitate the analysis of the catalysts we obtained self-supporting wafers of 9 mm diameter and ca. 9 mg weight that were fixed on a circular sample holder, specially designed for the HPGC. The major advantage of this sample holder is that the gas flow passes through the wafer and, in this way, the reactions are not only produced on the surface. The different treatments were carried out into this cell at

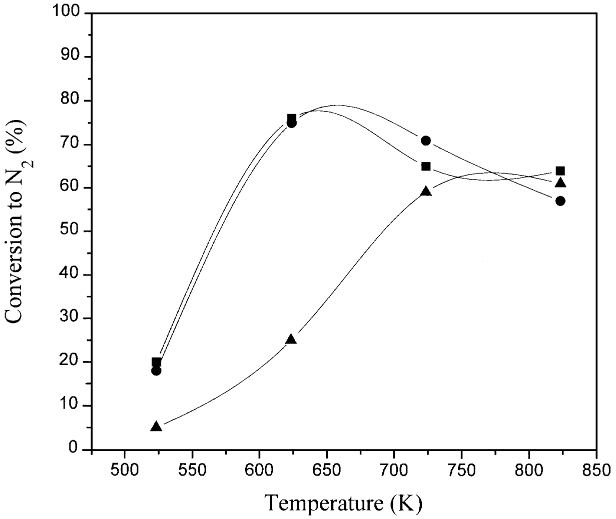

FIG. 1. Influence of temperature on the SCR of NO with propane ($W/F = 1.06 \times 10^5$ s g/m^3, 850 ppm of NO, 470 ppm of C_3H_8, 2.5% of O_2). Catalyst A (■), catalyst B (●), catalyst C (▲).

TABLE 2

Activity (A) (mol of NO_x converted per g of catalyst per second) in the Selective Catalytic Reduction of NO_x by Propane (2.5% of Oxygen, 850 ppm of NO, 470 ppm of C_3H_8, 3 g of Catalyst, 1700 ml min^{-1}) at 623 and 723 K

Catalyst	A at 623 K	A at 723 K
A	0.272	0.233
B	0.269	0.254
C	0.090	—

atmospheric pressure with a gas flow rate of 100 ml/min. Catalyst pretreatments were carried out *in situ* in flowing N_2 at 100 ml/min for 2 h at 623 K, followed by cooling in vacuum to room temperature. The catalysts were then exposed, at different reaction temperatures, to one or more of the following gas components: NO (850 ppm), O_2 (2.5%), C_3H_8 (470 ppm), balanced with N_2.

3. RESULTS AND DISCUSSION

To study the influence of the catalyst treatments on the state of Cu species, we have monitored the Cu($2p_{3/2}$) electronic transition and the CuL_3VV Auger transition (by excitation with Bremsstrahlung radiation), in addition to Si 2*p*, Al 2*p*, and O 1*s* transitions of the framework. Since the Cu($2p_{3/2}$) transition does not allow us to distinguish the oxidation states of copper, these have been characterized using both Cu($2p_{3/2}$) and CuL_3VV transitions, the modified Auger parameter (α'), and the shake-up satellite associated to the Cu($2p_{3/2}$) transition. Cu^{+2} species shows a shake-up satellite at ca. 10 eV higher than the Cu($2p_{3/2}$) transition that is not shown by Cu^{+1} or Cu^0 species; this characteristic is normally used to distinguish between Cu^{+2} and Cu^{+1} or Cu^0. The determination of reduced copper (Cu^{+1} or Cu^0) requires a careful analysis.

The relative amount of Cu^{+2} species has been obtained from the shake-up satellite intensity relative to that of the Cu($2p_{3/2}$) peak, with an accuracy of about ±20% (22). Thus, as reference for Cu^{+2} and Cu^{+1} species we have used samples oxidized in air at 623 K and reduced in flowing N_2 at 623 K, respectively.

3.1. *Treatment of Catalysts in Vacuum and in Oxidation Atmospheres*

Figure 2 shows that the shake-up satellite is present in the catalyst A, after heating in vacuum of 10^{-7}mB and 523 K, even though the intensity is very low. When this sample is heated in vacuum of 10^{-7} mB and 723 K for 2 h, the intensity of the shake-up is substantially reduced (Fig. 2b) and practically vanishes. On the other hand, the nonsymmetrical shape of the CuL_3VV transition in the sample heated at 523 K and vacuum is modified and the shoulder peaking at 916.5 eV (KE) is clearly transformed in a new peak, showing the maximum at 917 eV (KE) after heating.

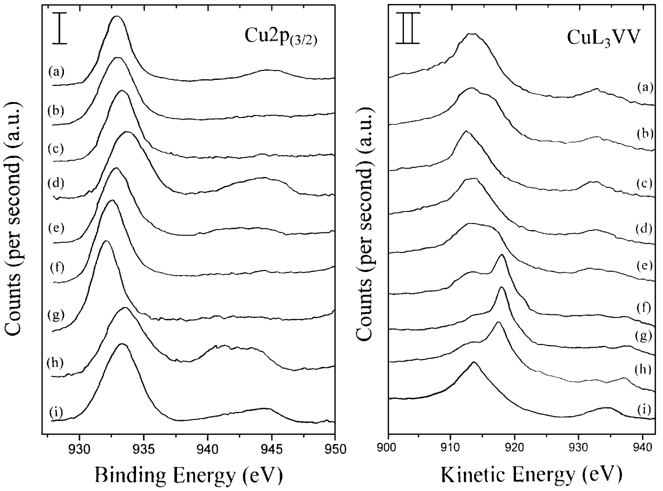

FIG. 2. (I) Cu $2p_{3/2}$ photoelectron spectra and (II) CuL_3VV Auger spectra of Cu-Beta zeolite (with 194% Cu ion exchange): (a) Cu-Beta zeolite heated *in situ* at 523 K and vacuum, (b) calcined *in situ* at 723 K and vacuum, (c) calcined *in situ* in flowing N_2 at 623 K for 2 h, (d) calcined *in situ* in flowing air at 623 K for 2 h, (e) calcined *in situ* in flowing H_2 (10% in N_2) at 473 K for 2 h, (f) calcined *in situ* in flowing H_2 (10% in N_2) at 573 K for 2 h, (g) calcined *in situ* in flowing H_2 (10% in N_2) at 673 K for 2 h, (h) previously reduced in H_2 at 773 K for 2 h and reoxidized in air at 523 K for 2 h, (i) exposed to the full reaction mixture at 623 K for 2 h.

In samples A and B (Figs. 2 and 3) when the activation is carried out by heating in N_2 at 623 K for 2 h a vanishing of the shake-up satellite occurs, and this reflects the reduction of Cu^{+2} to Cu^{+1} or Cu^0. In contrast, in sample

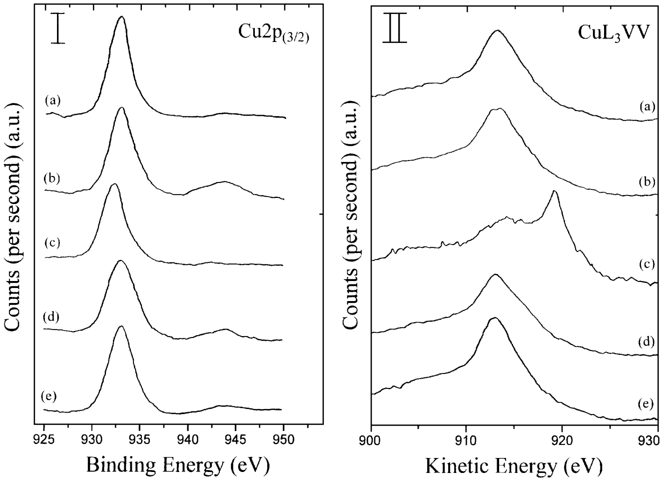

FIG. 3. (I) Cu $2p_{3/2}$ photoelectron spectra and (II) CuL_3VV Auger spectra of Cu-Beta zeolite (with 106% Cu ion exchange): (a) calcined *in situ* in flowing N_2 at 623 K for 2 h, (b) oxidized *in situ* in air at 623 K for 2 h, (c) reduced *in situ* in flowing H_2 (10% in N_2) at 623 K for 2 h, (d) exposed to the full reaction mixture at 473 K for 2 h, (e) exposed to the full reaction mixture at 623 K for 2 h.

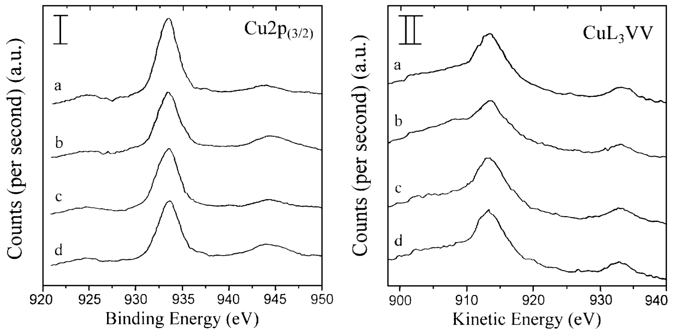

FIG. 4. (I) Cu $2p_{3/2}$ photoelectron spectra and (II) CuL_3VV Auger spectra of Cu-Beta zeolite (with 55% Cu ion exchange): (a) calcined *in situ* in flowing N_2 at 623 K for 2 h, (b) oxidized *in situ* in air at 623 K for 2 h, (c) calcined *in situ* in flowing H_2 (10% in N_2) at 573 K for 2 h, (d) exposed to the full reaction mixture at 723 K for 2 h.

C (Fig. 4), this treatment does not fully reduce the Cu^{+2} species and ca. 35% of Cu^{2+} is still observed. To distinguish the species that were originated from this activation we have analyzed the Auger CuL_3VV transition on the zeolitic samples and also three appropriate reference compounds: Cu, Cu_2O, and CuO. In the results given in Table 3 it can be seen that the CuL_3VV peak appears at 918.6 eV (KE) (28, 29) ($\alpha = 1851$ eV) for the metal, while the peak positions for Cu_2O and CuO oxides are located at 916.6 eV (KE) (28, 29) ($\alpha = 1848.9$ eV) and 917.6 eV (KE)(28, 29) ($\alpha = 1851.4$ eV), respectively. In samples A and B (Tables 3 and 4) the CuL_3VV transitions peak at 912.8 eV, showing a small shoulder at ca. 916 eV, indicating that Cu^{+1} species are present. In sample C (Table 5) the results are similar even though not all of the Cu^{+2} has been reduced to Cu^{+1}. On the other hand, it is interesting to notice that the Auger kinetic energies are lower than those observed for the bulk (in some cases up to 3 eV) that, as will be discussed later, can be connected with the dispersion degree of copper ions.

In contrast to Cu-ZSM-5 zeolite (22), the surface Cu/Si atomic ratio in the three Cu-Beta zeolite samples is lower than the bulk value, indicating that copper is highly dispersed in the zeolite matrix.

TABLE 3

Spectral Parameters Obtained for the Catalyst A (194% of Cu Exchange) by XPS and XAES

Identification	Si/O[a]	Treatment	Cu $2p_{3/2}$ (eV)	CuL_3VV (eV)	α'[b]	Cu/Si[a]	(Cu^{+1}, %)
Res04	0.46	Vacuum, 523 K	932.9	913.3	1846.2	0.063	61
				916.5	1849.4		
Res05	0.51	Vacuum, 723 K	932.9	913	1845.9	0.064	96
				917	1849.9		
Res02	0.51	N_2, 623 K	933	912.8	1845.8	0.049	100
				915.9	1848.9		
Res08	0.48	N_2, O_2, 373 K	933	913	1846.0	0.046	67
				916.1	1849.1		
Res017	0.50	N_2, O_2, 623 K	933.3	913.6	1846.9	0.080	0
Res09	0.49	N_2, O_2, NO, 623 K	933.1	913.2	1846.3	0.081	51
				917	1850.1		
Res010	0.50	N_2, NO, 623 K	933	913.2	1846.2	0.036	48
				917.3	1850.3		
Res012	0.50	N_2, H_2, 473 K	932.8	913.4	1846.2	0.064	60
				917.4	1850.2		
Res013	0.53	N_2, H_2, 573 K	932.3	914.7	1847.0	0.056	—
				918.7	1851.0		
Res014	0.53	N_2, H_2, 673 K	931.9	915	1846.9	0.034	0
				918.9	1850.8		
Res015	0.54	N_2, H_2, 773 K	931.9	915.4	1847.3	0.033	0
				919.2	1851.1		
Res016	0.52	Res015 + reoxid. in air at 523 K	933.4	913	1846.4	0.036	—
				917.7	1851.1		
Res018r	0.51	N_2, O_2, NO, C_3H_8, 473 K	933.3	913.6	1847.0	0.031	33
Res019r	0.50	N_2, O_2, NO, C_3H_8, 623 K	933.3	912.9	1846.2	0.030	60
				916.3	1849.6		
Res020r	0.50	N_2, O_2, NO, C_3H_8, 723 K	933.3	912.9	1846.2	0.051	86
				916.8	1850.1		
Cu (metal)		—	932.4	918.6	1851.0		
Cu_2O		—	932.3	916.6	1848.9		
CuO		—	933.8	917.6[c]	1851.4		

[a] On surface.

[b] Modified Auger parameter = BE(Cu $2p_{3/2}$) + KE(CuL_3VV).

[c] Anomalous KE value.

TABLE 4

Spectral Parameters Obtained for Catalyst B (106% of Cu exchange) by XPS and XAES

Identification	Si/O[a]	Treatment	Cu $2p_{3/2}$ (eV)	CuL$_3$VV (eV)	α'^{b}	Cu/Si[a]	(Cu^{+1}, %)
Res01	0.54	N_2, 623 K	933.2	912.8	1846	0.021	100
				916	1849.2		
Res02	0.54	N_2, O_2, 623 K	933.2	912.8	1846	0.021	5
				916.2	1849.4		
Res03	0.54	N_2, O_2, NO, 623 K	933.2	912.9	1846.1	0.019	40
				916.4	1849.6		
Res04	0.56	N_2, H_2, 623 K	932.4	914	1846.4	0.008	—
				918.8	1851.2		
Res05	0.55	N_2, O_2, NO, C_3H_8, 473 K	933.1	913	1846.1	0.017	36
				916.4	1849.5		
Res06	0.55	N_2, O_2, NO, C_3H_8, 623 K	933.3	912.9	1846.2	0.021	62
				916.5	1849.8		
Res07	0.55	N_2, O_2, NO, C_3H_8, 723 K	933.3	912.8	1846.1	0.021	78
				916.7	1850		

[a] On surface.
[b] Modified Auger parameter = BE(Cu $2p_{3/2}$) + KE(CuL$_3$VV).

Table 3 shows that the reduction to Cu^{+1} in sample A is parallel to the decrease in the Cu/Si atomic ratio (going from 0.061 in the sample treated at 523 K and vacuum to 0.049 in the reduced sample), indicating that migration of copper ions from the surface to the zeolite bulk has occurred. By heating catalyst A at 373 K in flowing air for 2 h, the level of Cu^{+2} is practically unchanged and only when the temperature is raised to 623 K is the copper fully oxidized. This oxidation produces not only an increase in the modified Auger parameter (α') of ca. 0.9 eV but also an increase in the Cu/Si atomic ratio on the surface. When the zeolite catalyst was contacted with air and NO mixture (NO, 850 ppm; O_2, 2.5%) at 623 K, the oxidation was not so effective. Under these conditions, the Cu/Si ratio is not modified and the Cu^{+2} content after reaction was around 50%.

The results obtained on samples B and C under oxidation in air or the air and NO mixture are similar to those observed on sample A, even though the effectivity of this reaction was slightly reduced (see Tables 4 and 5).

3.2. *Treatment of Catalysts in a Reducing Atmosphere*

Figures 2e–2g show the results obtained with sample A when subjected to a reduction in flowing H_2 (10% in N_2) at different temperatures. It can be seen there that the reduction of copper at low temperature is not observed and the result is similar to that shown in the starting sample, treated at 523 K and vacuum (see Fig. 2e). In contrast, when temperature is increased to 573 K the shake-up satellite associated to the Cu $2p_{3/2}$ transition vanishes, indicating the reduction of Cu^{+2} species (Fig. 2f). At this temperature, a new peak in the Auger transition appears at around 919 eV (KE) ($\alpha = 1851$ eV) in addition to an important reduction of the Cu/Si atomic ratio on the surface. No other peaks were split or broadened, from either copper or the zeolite components, indicating the absence of differential charging on the sample. In this way, the emergence of this new peak at ca. 919 eV (KE) in the Auger transition indicates that a new copper species is formed by reduction. The modified Auger

TABLE 5

Spectral Parameters Obtained for Catalyst C (55% of Cu exchange) by XPS and XAES

Identification	Si/O[a]	Treatment	Cu $2p_{3/2}$ (eV)	CuL$_3$VV (eV)	α'^{b}	Cu/Si[a]	(Cu^{+1}, %)
Res01	0.53	N_2, 623 K	933.3	913.1	1846.4	0.012	65
				916.3	1849.6		
Res02	0.56	N_2, O_2, 623 K	933.3	913.1	1846.4	0.010	10
				916.3	1849.6		
Res03	0.54	N_2, H_2, 573 K	933.3	913	1846.3	0.013	38
Res04	0.53	N_2, O_2, NO, C_3H_8, 623 K	933.4	913	1846.4	0.012	14
				916.2	1849.6		

[a] On surface.
[b] Modified Auger parameter = BE(Cu $2p_{3/2}$) + KE(CuL$_3$VV).

parameter corresponding to this new peak is similar to that measured for Cu metal (Cu^0 bulk) and for this reason this peak could be ascribed to the formation of large particles of copper located on the surface of the catalyst, this being in agreement with results previously reported for Cu-ZSM-5 zeolites (22). Nevertheless, when the reduction temperature increases to 673 K the Cu($2p_{3/2}$) transition is slightly shifted to 931.9 eV and, parallelly, the Auger peak is clearly modified showing a small shoulder at around 915 eV and a main peak at ca. 919 eV. These observations could indicate that under reduction in H_2 at 573 K the copper ions are mainly as Cu^0 and at least a small amount of Cu^{+1}, and only when temperature increases to 673 K is all Cu^{+1} reduced to Cu^0.

In the catalysts with lower Cu ion exchange (samples B and C), the reduction by flowing H_2 (10% in N_2) has been carried out at 623 and 573 K, respectively. In catalyst B, a shoulder at ca. 918.8 eV (KE) in the CuL_3VV transition appears which also could be related to the formation of large particles of Cu^0 on the surface, which goes together with the decrease in the Cu/Si ratio. As occurs in catalyst A, at this temperature it is not possible to affirm if all copper is fully reduced to Cu^0 or if the Cu^{+1} species is still present. The results obtained with catalyst C are quite different and, in this case, after exposure to H_2 at 573 K the shake-up satellite is still present even though the intensity has been substantially reduced (Fig. 4c). On the other hand, the CuL_3VV transition is not modified and the Cu/Si ratio is maintained constant after reaction. These results indicate that Cu^{+2} and Cu^{+1} species are not reduced to Cu^0 under these treatment conditions.

Exposure of catalyst A (previously reduced in H_2 at 773 K for 2 h) to oxygen at 523 K results in a Cu $2p_{3/2}$ transition similar to that observed for this catalyst when it was previously activated and oxidized (Fig. 2h), showing the shake-up satellite and thus indicating the oxidation to Cu^{+2}. However, the Auger CuL_3VV transition is quite different to that originated from the catalyst directly oxidized, showing a peak at 917.7 eV (KE) as in the reduced samples in flowing H_2. On the other hand, this reoxidation reaction does not modify the Cu/Si ratio on the surface (see Table 1), as occurs during an oxidation reaction. These observations can be justified if we consider that the aggregation state of copper is practically unchanged during the reoxidation process. By reduction, the copper species migrate from the surface to the zeolite bulk and the copper remaining on the surface is partially aggregated forming relatively large particles of metal copper. By exposing this sample to oxygen these copper particles on the surface are quickly oxidized, remaining in a similar aggregation state. This result would indicate that, at least under these treatment conditions, the reduction to Cu^0 is a nonreversible process because the aggregation state is not modified and the copper particles cannot be redispersed.

3.3. *"In situ" Catalytic Reaction*

The results obtained when heating the catalyst in a flow of the reaction mixture (O_2, 2.5%; NO, 850 ppm; C_3H_8, 470 ppm; and N_2) for 2 h at different temperatures are shown in Tables 3–5. The intensity of the satellite, and therefore the level of Cu^{+2}, depends on the temperature used and also on the Cu content of the sample. In this way, in samples A and B the intensity of the shake-up is higher at low temperature (473 K), the percentage of Cu^{+2} being 67 and 64, respectively. When temperature is increased to 623 K the intensity of the shake-up and the relative amount of Cu^{+2} are reduced. Exposure to higher temperatures (723 K) caused an important reduction of Cu^{+2}, and very low amounts of this species remain present.

By comparing the results with those obtained for some standards (Cu metal, Cu_2O, and CuO) we can find some interesting features. The binding energies corresponding to the Cu($2p_{3/2}$) transition for the Cu^{+1} species in the catalysts are higher than that observed in Cu_2O (BE, 932.3 eV). This observation could be a consequence of the formation of more highly ionic Cu–oxygen bonds and also to the increase in the Madelung potential or to relaxation processes. On the other hand, in oxidized samples where copper is Cu^{+2}, the binding energy of the Cu $2p_{3/2}$ transition is lower than that measured for CuO.

As can be derived from Tables 3–5, under different reaction conditions both the CuL_3VV transition and the modified Auger parameter show important changes. These changes can be correlated with the Cu/Si atomic ratio on the surface and with the aggregation state of copper ions (22). It is worth noting that the kinetic energy of the Auger CuL_3VV transitions are generally lower (up to ca. 3 eV) than the Auger kinetic energies reported for bulk compounds (see Table 3). This observation can be connected with the high dispersion of copper ions.

In catalyst A, the reduction from Cu^{+2} to Cu^{+1} is conducted together with a decrease in the Cu/Si ratio on the surface, due to the migration of copper ions into the zeolite channels and, in this way, the dispersion degree of copper is also increased. On the other hand, the oxidation to Cu^{+2} is produced together with an increase in the Cu/Si atomic ratio on the surface, justifying the possible formation of small clusters of copper oxide on the surface and, in this way, the smallest dispersion degree of Cu^{+2}. Under reduction in flowing H_2, the Cu/Si atomic ratio is dramatically reduced depending on the temperature used. Under these conditions, aggregation of copper particles is produced generating Cu^0 clusters with different sizes as can be seen in Fig. 5. In the other samples (catalysts B and C) the results are not so clear, possibly because the Cu ion exchanged is lower and, in this case, the dispersion degree is most homogeneous. Nevertheless, by reduction to Cu^0 (in sample B) a dramatic decrease in the Cu/Si atomic ratio on the surface

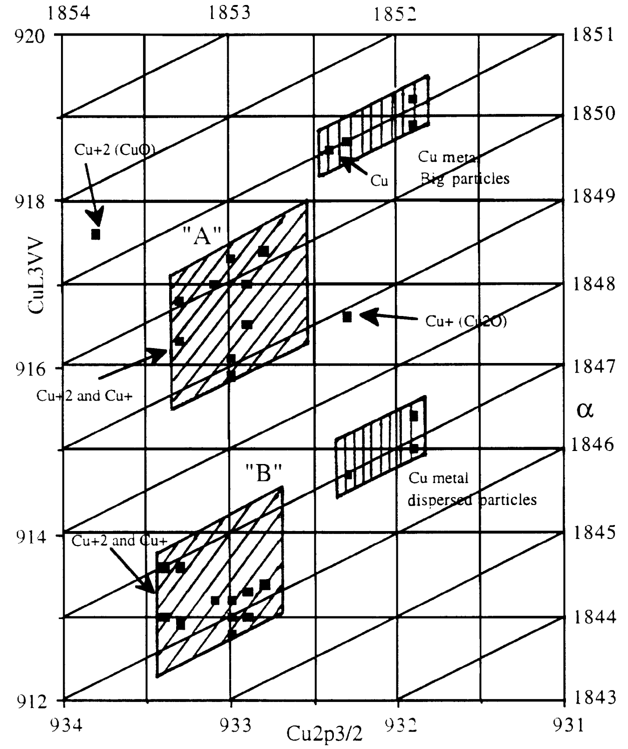

FIG. 5. Chemical state plot of Cu-Beta zeolites derived from results obtained by electron spectroscopy. "A" and "B" indicate Cu^{+2} and Cu^{+1} species on the surface and into the zeolite, respectively.

is also observed, due to the migration of copper into the bulk zeolite matrix.

Figure 5 shows the chemical state plot derived from the results obtained by electron spectroscopy. In this plot several zones assigned by using different standards and results previously reported on other systems can be distinguished (22, 29b.) At low binding energy, copper is in the metal form. Earlier in the CuL_3VV transitions, we noticed that the reduction to Cu^0 is produced together with the appearance of a new Auger peak at higher kinetic energy (assigned to large particles of copper metal). On the other hand, at lower kinetic energy the zone possibly due to dispersed particles of copper metal or forming small clusters within the zeolite channels is shown. The rest of this plot is not so clear, showing a relatively large scatter, but two zones can be distinguished identified on the plot as "A" and "B", ascribed to different locations of copper in the zeolite. Thus, zone "A" has been assigned to Cu^{+1} and Cu^{+2} on the surface and zone "B" to the same species into the zeolite channels.

When characterization results obtained by electron spectroscopy are compared with the catalytic activity of these samples (Fig. 6), some interesting results can be derived. Thus, in catalysts A and B (with similar catalytic activity), the amount of Cu^{+1} species measured after heating at 623 K in the full reaction mixture is similar and higher than that measured in catalyst C (characterized by its low activity). Nevertheless, when the temperature is increased to 723 K, the catalytic activity is modified. At this temperature, the level of Cu^{+1} species measured for catalysts A and B is slightly higher than that measured at 623 K even though the catalytic activity for catalyst A is slightly lower. The variation observed in the Cu/Si atomic ratio is different depending on the level of Cu loading. In the case of sample A, the Cu/Si ratio resulting from the reactions at 473 and 623 K is similar in both cases and half of that shown by the same catalyst after activation under vacuum or vacuum and 723 K. When temperature is raised to 723 K, this atomic ratio is slightly increased. Regarding to the behavior of sample B, when temperature increases to 723 K the Cu/Si atomic ratio is practically unchanged. In samples A and B, the variations observed in the catalytic activity due to the temperature effect could be related with both the level of Cu^{+1} species and the Cu/Si atomic ratio. Thus, in sample A when the temperature increases to 723 K, the catalytic activity is relatively reduced, possibly due to the aggregation of copper (Cu^{+1}) on the surface. With regard to sample B the increase in temperature does not modify the catalytic activity, probably because the aggregation state of the copper ions is unchanged.

Along with the results on the SCR activity reported previously (15), the quantitative determination and the characterization of the different species of copper by electron spectroscopy would indicate that SCR activity of Cu-Beta catalysts is related to the ratio of Cu^{+1} to total Cu on the surface. This is reflected in Fig. 6 where the catalytic activity

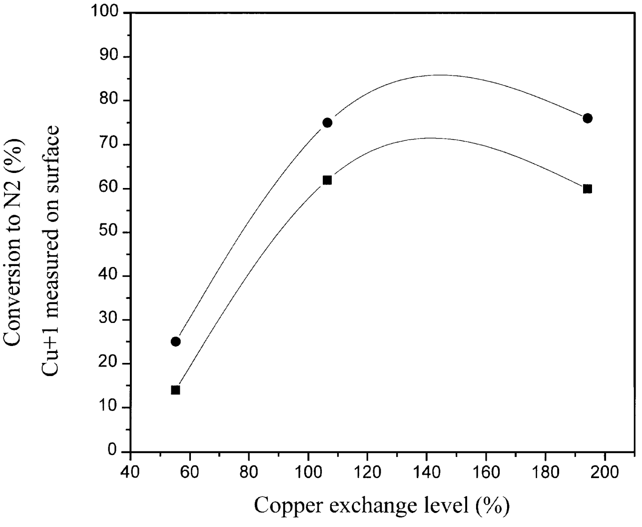

FIG. 6. Correlation between the catalytic activity measured at 623 K in samples A (194 % Cu ion exchange), B (106% Cu ion exchange), and C (55% Cu ion exchange) and the level of Cu^{+1} species measured on surface after reaction at 623 K for 2 h in the full reaction mixture (O_2, 2.5%; NO, 850 ppm; C_3H_8, 470 ppm). (●) Activity at 623 K, (■) Cu^{+1} amount (%) measured on surface at 623 K.

and the level of Cu^{+1} have been ploted vs the Cu ion exchange level of the catalysts used. As can be seen, in catalysts with low Cu amount the level of Cu^{+1} species is low (as measured after SCR reaction), and the catalytic activity is also low. In catalysts with a higher Cu amount the level of Cu^{+1} species is significantly increased in parallel to the catalytic activity.

4. CONCLUSIONS

The results obtained in the present work with Cu-Beta zeolites are comparable to those previously reported for Cu-ZSM-5 zeolites. For this reason one could speculate that the active copper species and the mechanisms involved in the reduction of NO_x are similar in both cases.

By electron spectroscopy different types of copper ions in Cu-Beta zeolite have been detected, depending on the atmosphere present and temperature used in the reaction. Thus, as occurs in over-exchanged Cu-ZSM-5 zeolite, Cu^{+2} species are quickly reduced to Cu^{+1} in flowing N_2 (g) at 623 K or even only in vacuum at 723 K. The oxidation under exposition to oxygen is also quickly conducted. However, the effectivity of these reduction–oxidation reactions depends on the Cu loading of the zeolite. In this way, when the Cu content is relatively high (over-exchanged Cu-Beta zeolites) the interconversion between Cu^{+2} and Cu^{+1} species is easier than in samples with a lower Cu ion exchange level. This result together with the activity of these samples in the SCR reaction can be the evidence that a redox mechanism is involved in the lean NO_x reaction.

The copper species in the Cu-Beta zeolite show important changes in their distribution and aggregation state. Thus, oxidation to Cu^{+2} results in an increase in the Cu/Si atomic ratio on the surface, and the opposite is when copper is reduced to Cu^{+1}. The migration of copper through the zeolite channels is a dynamical and reversible process. However, when copper is reduced to Cu^0, the large particles of copper metal originated on the surface cannot be redispersed under oxidative conditions.

The reduction to Cu^0 is only achieved by heating in flowing H_2. This suggests that the initial hypothesis (30) suggesting that oxygen is also necessary to prevent the reduction from Cu^{+1} to Cu^0 needs to be raised again.

In summary, the most active Cu-Beta zeolites in the SCR reaction of NO_x are those in which the conversion between Cu^{+2} and Cu^{+1} species is quickly produced under standard reaction conditions. Our results indicate that this conversion between both oxidation states is easier at higher Cu exchange levels. When exposed to the reaction mixture, the over-exchanged Cu-Beta zeolites show a high level of dispersed Cu^{+1} species (as occurs on activation at vacuum or in flowing N_2) by migration from the surface. Thus, by considering the results obtained for the analyzed samples in the reaction mixture, it seems reasonable to think that the activity in the SCR reaction on Cu-Beta zeolite is related to the ratio of Cu^{+1} to total Cu present in the sample.

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