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NO Decomposition over Cu–Sm–ZSM-5 Zeolites Containing Low-Exchanged Copper

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Catalysts were prepared by exchange and co-exchange techniques following Iwamoto's procedure. Copper-exchange degree in the zeolites varied between 21.2% and 128% while the Sm content varied in inverse order, between 27.2% and 18.8%. The catalysts were characterized by NO-DRIFT, O_2-TPD, and XPS. Catalytic tests were performed in a microreactor in the temperature range 673–873 K. It was found that the presence of Cu in close proximity of the Al framework, i.e., in the exchangeable positions, is increased in the presence of Sm. The presence of Sm stabilizes the Cu(I)–O–Cu(II) "redox buffer," increasing the activity of this catalyst. This behavior is mainly observable for low Sm concentration. © 2000 Academic Press

Key Words: **Cu–Sm–ZSM-5; NO decomposition; NO-DRIFTS; O_2-TPD; XPS.**

1. INTRODUCTION

In principle, NO decomposition is the most attractive way to reduce NO_x air pollution because this process does not involve the addition of reductants and therefore does not create a risk of another pollution. The literature indicates that Cu–ZSM-5 is the best catalyst for this reaction, provided that the quantity of Cu introduced is larger than the exchange capacity of the zeolite (1, 2). Unfortunately, "overexchanged" Cu–ZSM-5 is active only in a limited interval of temperature and in the absence of oxygen (3). In addition, other molecules like water or SO_2 act as inhibitors or cause rapid deactivation (4). One of the solutions to improve the catalytic performances of Cu–ZSM-5 was thought to be the addition of a second active species that would be able to improve the redox properties and to stabilize the exchanged copper.

A first attempt to improve the catalyst in a such a way was made by Iwamoto *et al.* (5) who investigated a series of Cu–Y zeolites using Ni, Co, Zn, Ag, Cu, Fe, Mn, or Ca, as promoters. They found that only Ni and Co had a positive influence. Following the same line, Kagawa *et al.* (6) tested a very large number of cations and found that, except for yttrium and silver, all other cations gave catalysts that were less active than pure overexchanged Cu zeolites. Zeolites described by these authors were prepared by successive or simultaneous ion exchange. Other studies concerning bicomponent zeolites were reported by Eranen *et al.* (7) who used Co, Ni, and Ga as promoters. Later, several studies stressed the positive influence of rare-earth elements. Zhang and Flytzani-Stephanopoulos (8, 9) reported a positive effect of cerium. Studies of Budi *et al.* (10) and Kucherov *et al.* (11) mentioned a noticeable influence of lanthanum and Pârvulescu *et al.* (12) that of samarium. In all these studies the promoter was introduced in a rather high amount.

Although the last papers presented evidence in favor of the positive influence of these promoters, no unequivocal explanation of the mechanism through which the rare-earth elements promote the copper activity has been give until now. Zhang and Flytzani-Stephanopoulos (13) suggested that the effect of cerium was to hinder the sintering of the catalytically active species rather than to influence the metastable zeolite support. Budi *et al.* (10) and Kucherov *et al.* (11) interpreted the effects in terms of a treatment-induced bonding change between the isolated Cu^{2+} cations and the framework oxygens of ZSM-5 which, in turn, are linked to the Al^{3+} ions.

The motivation of the present investigation was to clarify the beneficial role of samarium. We had shown that samarium promotes the activity of Cu–ZSM-5 in NO decomposition. Our former work using overexchanged samples (12) considered two possible effects, namely,

(i) either that samarium blocked exchange sites where copper would be trapped in a non-active form, thereby directing the implantation of copper to favorable sites,

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(ii) or that samarium, in close association with active copper, would adjust the oxido-reduction properties of active copper (possibly the Cu(I)-to-Cu(II) ratio), thus facilitating NO decomposition.

Although no unequivocal conclusion emerged from that study, the first interpretation seemed more probable. A reason was that the atomic ratio Sm/Cu was much lower than 1. This made the second explanation difficult, namely, how one single Sm atom could modify the oxido-reduction properties of several Cu atoms. However, doubt remained because no evaluation was possible (or is still possible) of the proportion of Cu atoms or pairs of atoms which are actually active in Cu–ZSM-5 catalysts. On the other hand, the benefit of overexchange suggested that copper atoms did not easily form active sites and that many were lost in inactive positions or as inactive species during catalyst preparation. Although we had no proof yet, it was tempting to suppose that Sm somehow favored the "implantation" of Cu at places where it could form active sites. Copper exchanged in amounts below the exchange capacity is much less active per Cu atom than additional Cu. We could therefore speculate that the effect of samarium to favor "implantation" at the right places should appear more clearly when working with Cu–ZSM-5 catalysts containing Cu in amounts smaller than that corresponding to the exchange capacity. In this work, data concerning Cu–Sm–ZSM-5 catalysts which contained low amounts of copper will be compared with those collected with pure Cu–ZSM-5 of similar Cu contents.

2. EXPERIMENTAL

A series of Cu–Sm–ZSM-5 zeolites was prepared starting from a ZSM-5 (Valfor PQ) with a Si/Al ratio of 25 using a one-step co-exchange procedure (12). Copper(II) acetate monohydrate (Aldrich, purity >98%) and samarium nitrate (Fluka, purity >98%) were used as precursors. According to this procedure, 15 g L^{-1} of the parent H–ZSM-5 was suspended in 300 ml of distilled water. The suspension was sonicated for 30 min and then 2×10^{-3} mol L^{-1} samarium nitrate and various amounts of copper acetate between 5.2×10^{-3} and 3.6×10^{-2} mol L^{-1} were added. After the solution was stirred for 24 h, the pH was raised to 7.5 with ammonia and the suspension stirred for 1.5 h, following the procedure adopted by Iwamoto *et al.* (15). The sample was then centrifuged and redispersed in distilled water until the conductivity of the washing water was lower than 7 mS cm^{-1}. The solid was then dried overnight under vacuum, at room temperature, prior to pretreatment. Cu–ZSM-5 zeolites with various extents of copper exchange were prepared following the same procedure. Cu–Sm–ZSM-5 was also prepared without pH modification; after being stirred for 24 h, the solutions were centrifuged and redispersed in distilled water until the conductivity of the washing water was lower than 7 mS cm^{-1}. The chemical composition and textural characteristics of the obtained samples are given in Table 1. Before the catalytic tests the zeolites were heated from room temperature to 823 K under helium at a rate of 1 K min^{-1} and maintained at this temperature for 6 h. For

TABLE 1

Chemical Composition and Surface Area of the Investigated Zeolites

Zeolite	Cu content (wt%)	Cu exchange (%)	Sm content (wt%)	Sm exchange (%)	Langmuir surface area (m^2 g^{-1})
Cu–Z-13.1	0.20	13.1	—	—	412
Cu–Z-20.5	0.32	20.5	—	—	410
Cu–Z-28.3	0.43	28.3	—	—	411
Cu–Z-44.4	0.69	44.4	—	—	414
Cu–Z-61.2	0.94	61.2	—	—	409
Cu–Z-91.8	1.41	91.8	—	—	408
Cu–Sm–Z-21.2-27.2	0.35	21.2	0.71	27.2	412
Cu–Sm–Z-29.8-25.3	0.49	29.8	0.66	25.3	408
Cu–Sm–Z-36.3-24.2	0.60	36.3	0.63	24.2	406
Cu–Sm–Z-44.0-23.0	0.73	44.0	0.60	23.0	410
Cu–Sm–Z-54.3-21.1	0.90	54.3	0.55	21.1	409
Cu–Sm–Z-58.6-21.1	0.97	58.6	0.55	21.1	407
Cu–Sm–Z-73.0-20.3	1.21	73.0	0.53	20.3	411
Cu–Sm–Z-96.0-19.2	1.59	96.0	0.50	19.2	408
Cu–Sm–Z-128.0-18.8	2.11	128.0	0.49	18.8	409
Cu–Sm–Z-32.3-22.7[a]	0.51	32.3	0.59	22.7	410
Cu–Sm–Z-41.2-20.7[a]	0.64	41.2	0.53	20.7	411
Cu–Sm–Z-54.5-19.6[a]	0.90	54.5	0.51	19.6	408
Cu–Sm–Z-69.8-19.5[a]	1.08	69.8	0.51	19.5	409

[a] Prepared without modification of pH.

pretreatments 0.5 g of catalyst was subjected to a helium flow of 30 ml min^{-1} for each sample.

Samples were characterized by elemental analysis, adsorption of N_2 at 77 K, temperature-programmed desorption of O_2 (O_2-TPD), diffuse reflectance infrared fourier transform spectroscopy (DRIFTS), and XPS.

Elemental analysis of Si, Al, Sm, and Cu was performed by atomic emission spectroscopy with inductively coupled plasma atomization (ICP-AES) after the samples were dried overnight at 373 K (Table 1). Adsorption and desorption curves of N_2 at 77 K were obtained with a Micromeritics ASAP 2000 apparatus after the samples were degassed at 423 K for 12 h under vacuum. This permitted the determination of the surface area and the pore volume of the samples. Micropore measurements performed using the same device were carried out at low N_2 pressures using the Dubinin–Raduskevitch and Horvath–Kawazoe formalisms.

The TPD measurements with O_2 were carried out in the same fixed bed quartz microreactor as that used for the catalytic testing. A sample (400 mg) was heated from room temperature to 773 K at a rate of 1 K min^{-1} in a diluted flow of O_2 (40% O_2 in He at 27 ml min^{-1}) and kept at 773 K for 8 h. After the sample was cooled to room temperature under an O_2 flow, it was purged with He (15 ml min^{-1}) for 3 h. The temperature was then increased at a rate of 5 K min^{-1} up to 773 K under the same He flow. The O_2 desorbed was analyzed by a Balzers Quadrupole QMG 311 mass spectrometer.

Diffuse reflectance DRIFTS spectra were recorded using a Brucker IFS88 instrument, equipped with KBr optics and a DTGS detector. Samples were placed inside a commercial environment-controlled DRIFTS chamber (Spectra-Tech 0030-103) equipped with ZnSe windows without packing or dilution. Before NO adsorption the samples were activated for 1 h at 773 K under 30 ml min^{-1} of He flow. They were subsequently cooled to room temperature in He and the flow was switched to a 30 ml min^{-1} 5% NO–He flow. The temperature was then increased, and a spectrum was recorded each 100 K after 30 min of stabilization. The spectra corresponded to the accumulation of 200 scans at a 4-cm^{-1} resolution. These were plotted by taking the Beer–Lambert absorbance. It was already reported that the Kubelka–Munk function depresses all weakly absorbing bands, resulting in the possibility of important details being lost (14).

The XPS spectra were recorded using a SSI X probe FISONS spectrometer (SSX-100/206) with monochromated Al$K\alpha$ radiation. The spectrometer energy scale was calibrated using the Au $4f_{7/2}$ peak (binding energy, 84.0 eV). The samples were moderately heated by a quartz lamp in the introduction chamber of the spectrometer to promote degassing, thus improving the vacuum in the analysis chamber. For the calculation of the binding energies, the C1*s* peak of the C–(C,H) component at 284.8 was used as an internal standard. The composite peaks were decomposed by a fitting routine included in the ESCA 8,3 D software. The superficial composition of the investigated samples was determined using the same software. It used the bands assigned to Cu $2p_3$, Cu $2p_1$, Sm $3d_{5/2}$, Al 2*s*, O 1*s*, and Si 2*p*, respectively.

All samples were tested for the decomposition of NO to N_2 and O_2. The tests were carried out in a continuous flow system with a fixed bed quartz microreactor containing 0.5 g of catalyst. The reactant gas feed contained 4400 ppm of NO with He as the carrier gas. The total flow was 30 ml min^{-1} ($W/F = 2$ g s ml^{-1}). Each catalyst was tested between 623 and 873 K and the products of the reaction were analyzed with an on-line Balzers Quadrupole QMG 311 spectrometer scanning the masses from 28 to 46. The activity of the catalysts was expressed in terms of NO total conversion and NO conversion to N_2. The O_2/N_2 ratio is also reported. The formation of nitrogen oxides shows that this ratio is lower than unity.

3. RESULTS

3.1. *Implantation of Copper*

The amount of copper retained in the zeolites, conventionally expressed as the percentage of the zeolite-exchange capacity, varied between 21.2% and 128.0%, while the Sm content varied in inverse order, between 0.71 and 0.49 wt% which means a Sm exchange between 27.2% and 18.8% (Table 1). Figure 1 shows the relation between the concentration of copper in the exchange solution and the exchange degree in conditions where the concentration of samarium was kept constant, namely, 2×10^{-3} mol L^{-1} samarium nitrate. These data show that there is a competition between the two species during the exchange process, the presence of copper diminishing the fixation of samarium. However, the presence of samarium favors the implantation of copper as shown by the fact that the Cuexchange is higher than that in

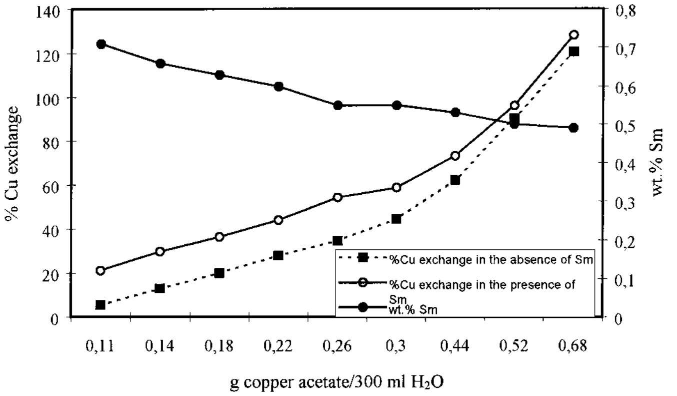

FIG. 1. Modification of the chemical composition of the zeolites as a function of the chemical composition of the exchange solution (samarium nitrate content, 2×10^{-3} mol L^{-1}).

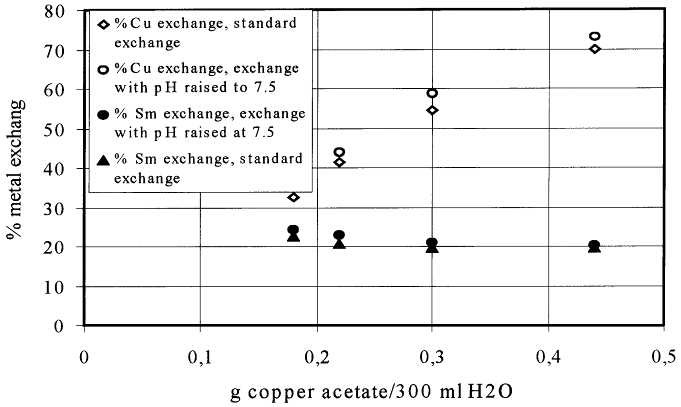

FIG. 2. Modification of the exchange degree of Cu and Sm when the pH is raised to 7.5 for different compositions of the exchange solution (samarium nitrate content, 2×10^{-3} mol L^{-1}).

the absence of Sm (Fig. 1). The difference, however, tends to decrease with the increase of the copper concentration in the solution.

Another factor which has a direct influence upon copper implantation is the pH. Actually, Iwamoto *et al.*'s preparation procedure (15) supposes two successive mechanisms: first, ionic exchange, and second, as a consequence of the increase in pH, precipitation. Our hope in distinguishing the two steps was the incentive to prepare samples starting from impregnation solutions of the same composition, but where the pH was raised to 7.5. The corresponding samples contained substantially more copper, but the samarium content was less influenced (Fig. 2).

3.2. O_2-TPD

Figure 3 shows the O_2-TPD profiles, with a first prominent maximum centered at about 647 K and a second one centered around 818 K, both at the same position for all Cu–Sm–ZSM-5 samples. The area of the peaks is in direct dependence with the copper content. The peak located at 647 K corresponds to a collective property of copper and zeolite and results from the formation of species containing extra-lattice oxygen (ELO) (16, 17). The additional release centered around 818 K corresponds to isolated Cu species (17). The evolution of the peak areas does not indicate any direct influence of the samarium content. In particular, it does not reflect the decrease of Sm when the Cu content increases or the formation of any Cu–Sm association. The oxygen release occurs only from Cu.

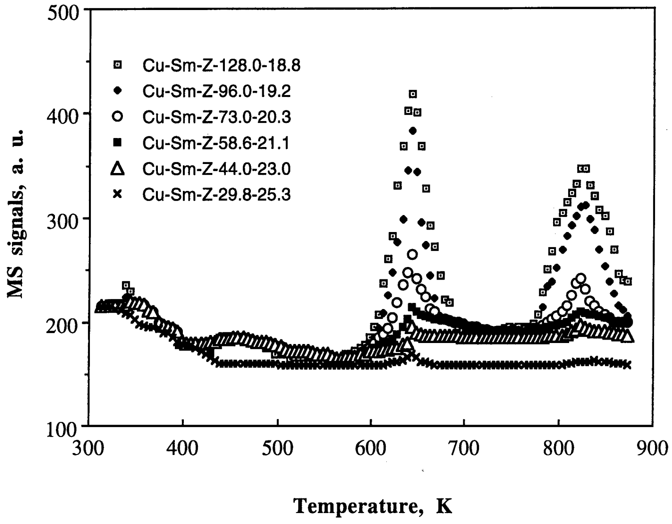

FIG. 3. O_2-TPD profiles of the investigated Cu–Sm–ZSM-5 zeolites.

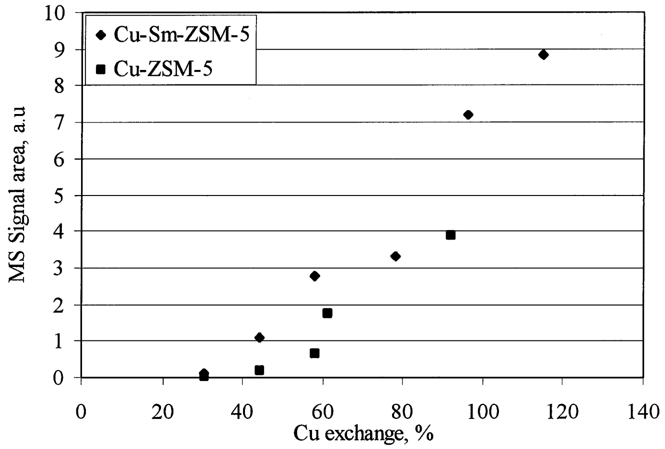

FIG. 4. Comparative MS signal areas of the O_2-TPD peak located at 647 K for Cu–ZSM-5 and Cu–Sm–ZSM-5 zeolites.

It is worth noting that the peak corresponding to ELO species appears faintly for Cu–Sm–Z-29.8-25.3, indicating that even for such a small concentration of copper dimer Cu–O–Cu species are formed. Figure 4 indicates the comparative areas of the peak corresponding to ELO species on Cu–Sm–ZSM-5 and Cu–ZSM-5. This behavior could be an indication that the presence of Sm orients the deposition of copper so that dimmer species are formed for smaller Cu concentrations (∼30% exchange compared to ∼45% exchange in the case where no Sm is present).

3.3. DRIFTS

Figure 5 shows the DRIFTS spectra of zeolite Cu–Sm–Z-58.6-21.1 compared with those of a monocomponent of similar composition (Cu–Z-61.2) in the region of ELO species recorded during several steps after various treatments, namely, activation and NO adsorption at various temperatures. The spectra contain bands due to the zeolite aluminosilicate lattice (1030–1070 cm^{-1}) and to Cu^{+} in ELO (960–970 cm^{-1}) (18). It is important to note that the presence of the ELO species is evidenced in zeolites with copper contents smaller than those corresponding to 100% exchange. This is a proof that even for these small concentrations, a part of copper can generate diatomic Cu–O–Cu clusters and not only monoatomic dispersed species.

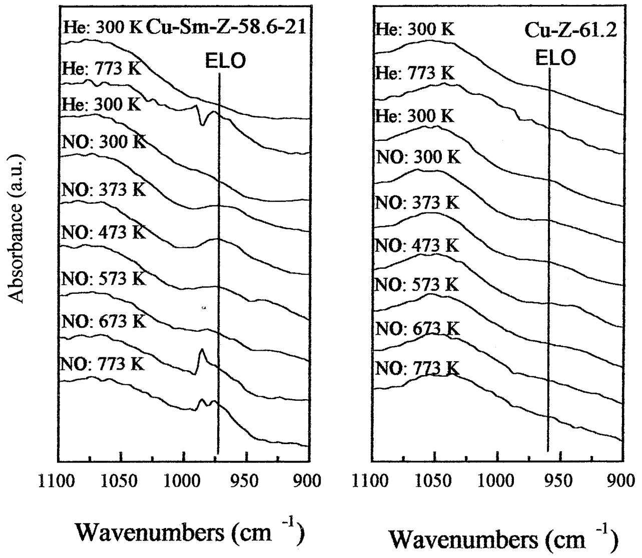

FIG. 5. DRIFTS spectra of Cu–Sm–58.6-21 and Cu–Z-61.2 zeolites in the ELO region.

TABLE 2

NO Adsorption Bands Detected on Cu–Sm–Z and Their Assignments

Assignment	Band (cm^{-1})
$\nu_{(NO)}\delta+$	1911, 1897
$\nu_{(N2O3)}\delta-$	1858, 1868
$\nu_{(NO)}\delta-$	1813
$\nu_{(NO2)2}$	1787, 1742, 1680
$\nu_{(NO2)2}\delta-$	1705
$\nu_{(NO2)}$	1625, 1616
$\nu_{(NO2-)}$, $\nu_{(NO3-)}$	1599
$\nu_{(N2O3)}$	1550

The comparative analysis of these spectra also gives indications concerning the influence of samarium. The peak corresponding to ELO species is much smaller, or even nonexistent, in the monocomponent zeolite. It can be stressed that the copper exchange in the two zeolites corresponds to comparable values. As there is no evidence of the formation of Cu–O–Sm bonds, it is possible to suppose that this larger amount of ELO species in the Cu–Sm–ZSM-5 sample is due to the fact that samarium has oriented the implantation of copper so that the formation of ELO species is possible. The O_2-TPD and DRIFTS measurements agree in this respect.

Figure 6 shows the DRIFTS spectra collected on the Cu–Sm–Z-58.6-21.1 zeolite in the presence of NO and indicates the wavenumbers of the various bands or shoulders. Table 2 presents a list of the bands due to NO adsorbed species detected on the investigated zeolites and their assignments (5, 19–21). The spectra show that, under a flow of 30 ml min^{-1} 5% NO–He, no *gem*-dinitrosyl bands (1827, 1735 cm^{-1}) (21) can be detected, even at room temperature. Instead, the bands assigned to $\nu_{(N2O3)}\delta-$ (1858, 1868 cm^{-1}) are present in all the spectra. Figure 6 might suggest a shift of the $\nu_{(N2O3)}\delta-$ band to higher wavenumbers. There is, however, some doubt concerning the reality of this effect. A figure to be presented later (Fig. 7), obtained by subtraction of the spectrum obtained at a given temperature from that obtained at a higher temperature, shows that a band at 1813 cm^{-1} ($\nu_{NO}\delta-$, corresponding to Cu^+ species) disappears almost completely upon heating, and no clear shift of the small residues at 1858 or 1868 cm^{-1} is visible. Heating at 373 K leads to a loss of the intensity for all the bands. One might argue that the apparent shift of the band at 1858 cm^{-1} is simply due to the desorption of NO and disappearance of the corresponding band at 1813 cm^{-1}. Consequently, we shall not discuss further a possible shift of the $\nu_{(N2O3)}\delta-$ bands. Upon heating, the bands assigned to $\nu_{(NO2)2}$ vibrations (1787, 1742, and 1680 cm^{-1}) disappear.

An attempt to deconvolute the 1858- to 1868-cm^{-1} band for temperatures higher than 473 K fails to give more than

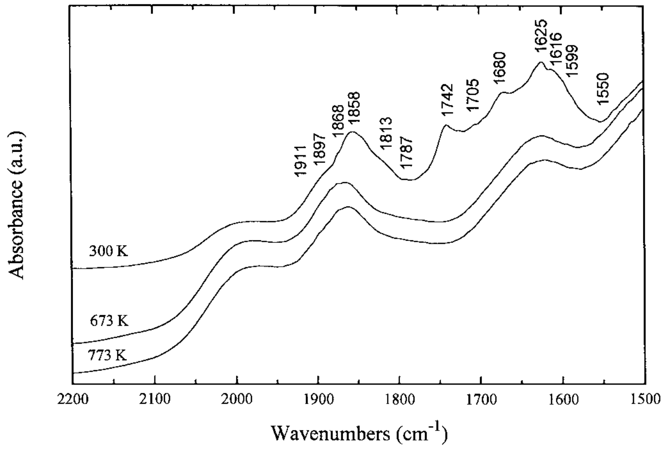

FIG. 6. DRIFTS spectra collected on Cu–Sm–Z-58.6-21.1 in the presence of NO.

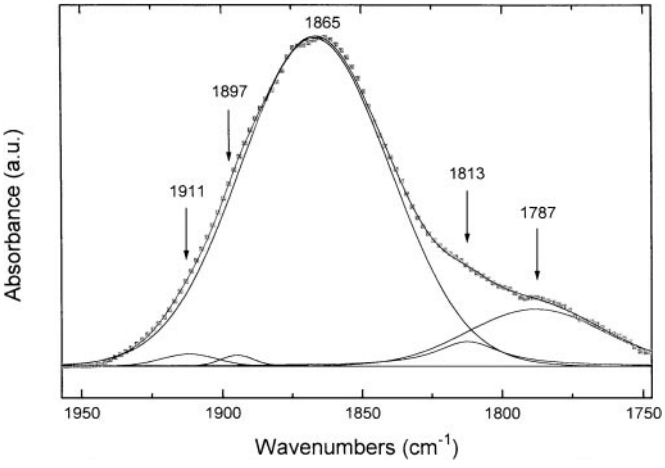

FIG. 7. Subtraction of the spectra collected on Cu–Sm–Z-58.6-21.1.

faint and dubious traces of $\nu_{(NO)}\delta-$ (remnant of the previously discussed band at 1813 cm^{-1}) and still weaker possible signals of $\nu_{(NO)}\delta+$ (1911, 1897 cm^{-1}). The bands at 1897 and 1911 cm^{-1} are assigned, respectively, to Cu^{2+} implanted in a position adjacent to single-framework Al and to non-active square pyramidal Cu^{2+} (22). For the band located at 1911 cm^{-1}, Lei *et al.* (18) also suggested the possibility that it could be attributed to the existence of $Cu^{(2-\delta)+}$ species resulting from the decomposition of the Cu^{2+}–O–Cu^{2+} dimers.

To achieve a better identification of the different NO species adsorbed on the catalyst surface at various temperatures and under different pretreatment conditions, we subtracted from a spectrum obtained at a given temperature that obtained at the desorption temperature corresponding to the previous measurement. Figure 7 presents the spectra collected on Cu–Sm–Z-58.6-21.1. The subtraction of the spectrum recorded in the presence of NO at room temperature from that recorded at 373 K indicates the disappearance of the bands located at 1742, 1813, and 1858 cm^{-1}, corresponding respectively to $(NO_2)_2$, $(NO)^{\delta-}$, and $(N_2O_3)^{\delta-}$. Another band assigned to the N_2O_3 species, namely, that located at 1550 cm^{-1}, also disappears at 773 K. This may correspond to the desorption of NO (and perhaps other species) or to the reaction of NO_2 or N_2O_3 (and perhaps NO). There is evidence in the literature that the reaction of NO on Cu–ZSM-5 catalysts can occur even at room temperature (23, 24), thus leaving open the debate concerning the fate of the various species mentioned previously. A further increase of the temperature leads to the additional disappearance of the bands assigned to NO bonded on Cu^{2+} implanted in a position adjacent to single-framework Al. This decrease starts from 573 K which is a typical temperature at which the conversion of NO on Cu–ZSM-5 reaches higher rates (25). At the same temperature, namely, 573 K, the subtraction spectrum also indicates the disappearance of the band centered at 1680 cm^{-1} which is assigned to a vibration corresponding to the $\nu_{(NO2)2}$ species. One should note that a previous subtraction at 473 K indicated an accumulation of these species on the catalyst surface. The next subtraction made at 673 K showed a further disappearance of this species.

Summarizing the information obtained from the subtraction of the spectra recorded at various temperatures in the presence of an initial high concentration of NO (flow of 30 ml min^{-1}), two species seem to be involved in the catalytic process: NO and N_2O_3 species bonded on Cu^{2+} implanted in an adjacent position to single-framework Al, NO species bonded on Cu^{+} and $(NO_2)_2$ species.

3.4. *XPS Spectra*

We already reported the XPS spectra obtained with Cu–Sm-containing zeolites (12). No shifts in the binding energies of the analyzed elements were detected when the chemical composition of zeolites changed. But we observed a modification of the surface atomic composition as a function of the exchange degree of the two species and of the conditions in which zeolites were treated. Figures 8 and 9 summarize the composition of these zeolites (using Si as the reference) as determined by XPS (surface composition) and ICP-AES (overall composition). Freshly prepared samples exhibit a higher superficial concentration of Cu compared with the results obtained from chemical analysis (Fig. 8). Exposing the samples for 6 h to NO at 823 K leads to a strong decrease of the XPS signal, a phenomenon which is generally interpreted as being due to a migration of Cu inside the zeolite channels. The result is that the Cu/Si ratio becomes slightly lower than that determined from chemical analysis. The analysis of Sm in the same catalysts (Fig. 9) indicates a complementary behavior. Both chemical analysis and XPS measurements show a very slight increase in the Sm/Si ratio

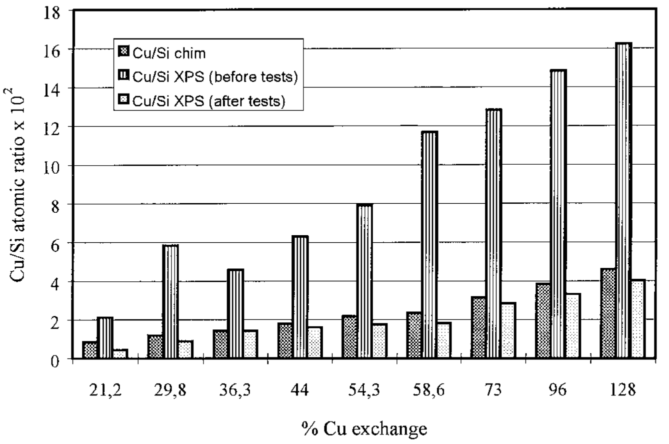

FIG. 8. Variation of the XPS Cu/Si atomic ratio compared to that determined analytically.

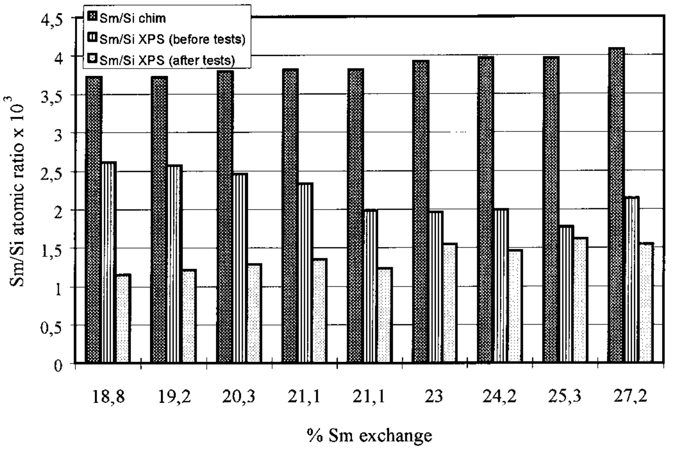

FIG. 9. Variation of the XPS Sm/Si atomic ratio compared to that determined analytically.

with the increase of the Sm content. However, contrarily to copper, the XPS Sm/Si ratios, both before and after the catalytic test, are lower than the overall ratios, as determined by ICP-AES, suggesting, among other possibilities, an enrichment in Sm inside the zeolite channels. Due to the low Sm content of the sample, we have no evidence that some clustering or agglomeration of the species containing Sm occurs. Nevertheless, the XPS data collected from the fresh catalysts indicate that the XPS Sm/Si ratio decreases when the overall content (percentage "exchange") increases. This is typical behavior when sintering or agglomeration occurs. If this is the case, the formation of large particles of material containing Sm at the surface, to the detriment of atomically dispersed Sm, could alternatively explain that the Sm/Si ratio is lower than the overall value.

If we take the first explanation, namely, penetration in the pores, the data would confirm the existence of competition between the two species. Less copper implanted in zeolite allows a deeper penetration of Sm inside the zeolite channels.

Another piece of information obtained from the XPS analysis concerns the Cu(I)-to-Cu(II) ratio (12). For the fresh catalysts this ratio increases with the extent of Cu exchange, indicating that more reducible species are present at the higher copper contents (Fig. 10). After the catalytic tests the Cu(I)-to-Cu(II) ratio is almost the same for all the catalysts. The consequence is that the decrease is more accentuated for the catalysts containing more cooper, while no change between the fresh and the tested catalyst occurs for a Cu-exchanged degree equal to or lower than 29.8%. Most of the Cu remains in an oxidized state of (II) after the test, which is in perfect concordance with DRIFTS data.

Figure 11 shows the modification of the XPS Cu(I)-to-Cu(II) ratio as a consequence of the modification of the pH after 1 day during the ionic exchange. The decrease of this ratio suggests that copper implanted under these conditions is less reducible.

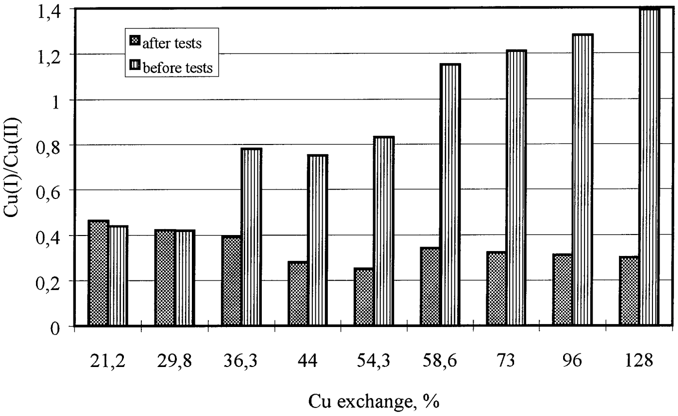

FIG. 10. Variation of the XPS Cu(I)/Cu(II) ratio as a function of the copper-exchange degree and catalysts treatment.

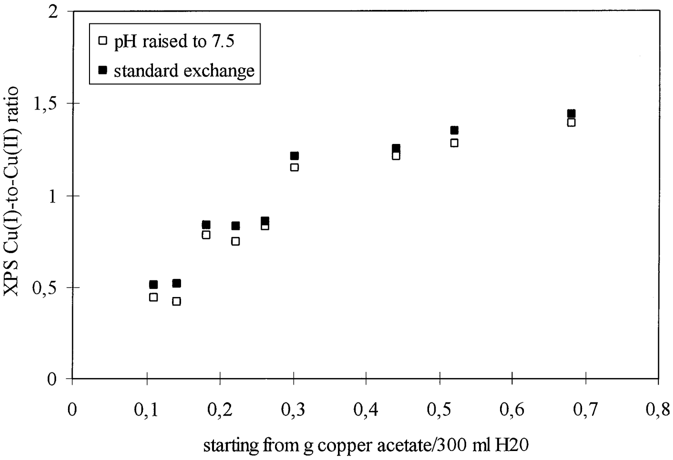

FIG. 11. Influence of pH modification (raised to 7.5) on the XPS Cu(I)/Cu(II) ratio.

3.5. *Catalytic Activity*

The catalytic data were recorded after 3 h of reaction, namely, when the reaction reached steady state activity. The results are summarized in Figs. 12 and 13. Products other than O_2 and N_2 are N_2O (mainly during the first 80 min) and NO_2. The variations presented in these figures eliminate possible further decomposition of NO_x into the mass spectrometer chamber. A continuous increase of both the conversion to N_2 and the total conversion with the increase of the copper-exchange degree is observed. But the general behavior is identical, irrespective of the temperature at which the catalysts were investigated (Fig. 12).

Generally, a total conversion of about 60% for flow gases containing NO concentrations in the range reported in this paper is achieved for a copper exchange higher than 100% (25, 26). For our Cu–Sm zeolites this occurs for a copper-exchange degree as low as about 73% and an increase of the exchange degree over 100% has little influence. Such behavior is also evidenced by Fig. 14. The total conversion of NO is almost 20% higher on zeolites containing Sm.

We note that low copper-exchange degrees such as 40% or smaller correspond to catalysts with low catalytic activity, and very low selectivity to N_2. The sites catalytically active for NO decomposition begin to develop for an exchange degree of about 30%–36%. The fact that exchanged Sm decreases when the exchange degree of Cu increases implies that the increase in the total conversion of NO occurs for a decrease in the Sm exchange.

Very low total conversion of NO corresponds to very low conversion to N_2 (also indicated by very low O_2-to-N_2 ratios). This behavior has already been noticed in the literature (27). The very low O_2-to-N_2 ratios correspond to an important release of NO_2 which actually contains the absent oxygen. There is no relation between the catalytic reaction and this secondary reaction, $\frac{1}{2}O_2 + NO = NO_2$, which actually occurs in homogeneous conditions after the catalytic

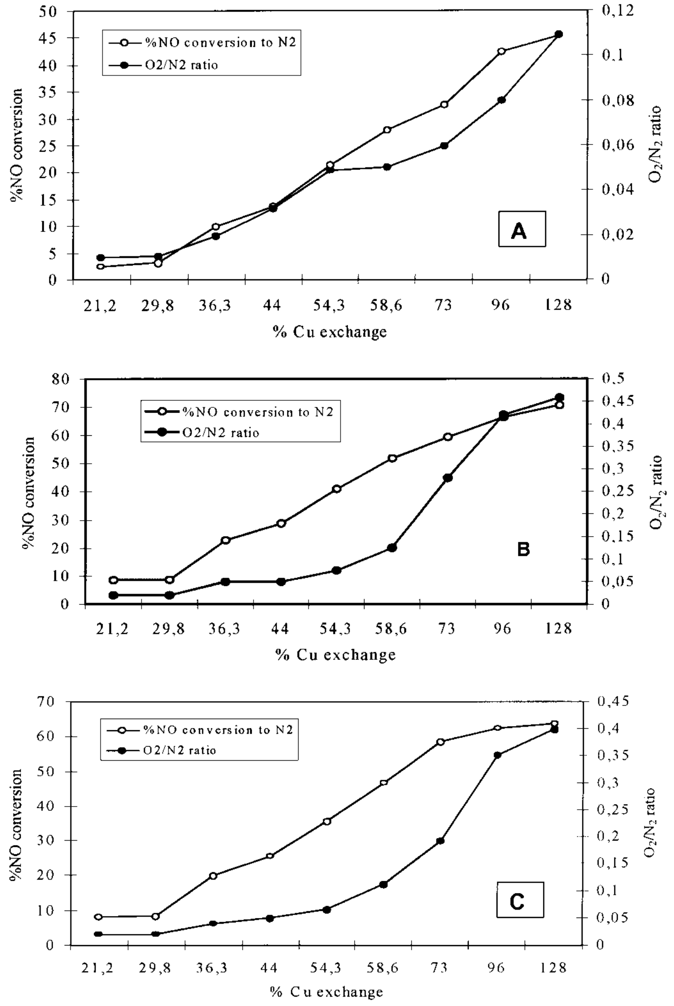

FIG. 12. NO conversion to N_2 and O_2/N_2 ratio for the investigated catalysts (total flow, 30 ml min^{-1}; W/F = 2 g s ml^{-1}; A, 673 K; B, 773 K; C, 823 K).

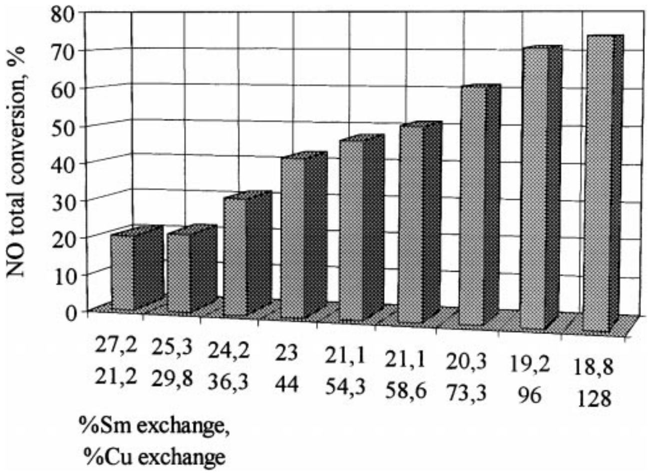

FIG. 13. NO total conversion for the investigated catalysts (total flow, 30 ml min^{-1}; W/F = 2 g s ml^{-1}; temperature, 773 K).

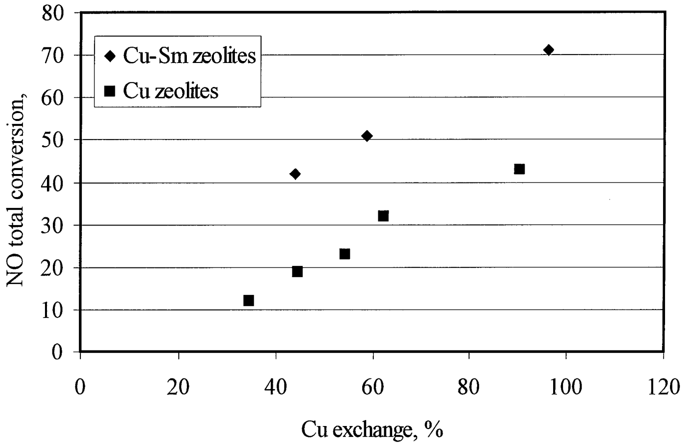

FIG. 14. Comparative NO total conversion over Cu– and Cu–Sm–ZSM-5 zeolites (total flow, 30 ml min^{-1}; W/F = 2 g s ml^{-1}; temperature, 773 K).

bed. We should mention that the connection between the reactor and mass spectrometer was heated at 300°C, but even under such conditions K_p is about 55.

Concerning the effect of the temperature, the behavior we observed is typical for the Cu zeolite catalysts, except that as we previously reported (12), the maximum of conversion for Cu–Sm zeolites is reached at 723 K with a plateau up to 773 K and then a decrease which is accentuated after 873 K.

4. DISCUSSION

Let us recall that the main ojective of this work was to try and clarify the role of Sm in promoting the NO-decomposition activity of Cu–ZSM-5 catalysts. For that we focused on catalysts with Cu loadings below the exchange capacity of the zeolite. The reason was that we suspected them to be particularly sensitive to the presence of Sm. Sm might inhibit the fixation ("implantation") of Cu at places where it would form inactive species. But the data reported above suggest that other types of information may also be obtained.

A first important result is the possible hypotheses concerning the role of additives in Cu–ZSM-5, and Sm in particular. As mentioned in the introduction, the second possible interpretation of the favorable role of Sm was that it could modify the oxido-reduction properties of Cu (isolated atoms or Cu(I)-O-Cu(II) pairs). Figure 10 involves data in cases where the Sm content does not change much, but the Cu content varies from atomic amounts similar to those of Sm to more than 6 times that amount. This figure shows little change in the Cu(I)/Cu(II) ratio. The only substantial effect occurs at low Cu-exchange degrees, namely, a range where the catalysts are very poorly active (Figs. 12 and 13). We can therefore conclude that there is absolutely no indication that, in catalysts prepared according to our method, Sm could modify the oxido-reduction properties of the active Cu atoms, and this conclusion very likely extends to overexchanged samples where an interaction would suppose that one single Sm atom could influence many Cu atoms. The higher Cu(I)/Cu(II) ratio for low Cu contents may constitute a clue for identifying the places where Cu is trapped as inactive species (Fig. 13).

Catalytic activity. It is striking that, when containing Sm, catalysts with amounts of Cu lower than those corresponding to a 100% theoretical exchange possess activity similar to "overexchanged" ZSM-5 zeolites.

Role of preparation in the formation of active sites. Figure 1 shows that the presence of Sm leads to an increase of the amount of copper "implanted" in the zeolite during the "exchange" procedure. The decrease of the Sm content when the amount of Cu increases suggests some sort of competition between both species. This competition favors the formation of active Cu species for Cu loadings lower than those with conventional catalysts. These may be diatomic Cu clusters, and the competition may favor the formation of these clusters, perhaps already in the exchange solution in the pores. But it seems impossible, at this stage of the investigation, to further analyze this mechanism.

Data presented in Fig. 2 possibly support these speculations. They show that the modification of the pH following the procedure by Iwamoto *et al.* leads to an increase of the implanted copper. Taking into account the very numerous papers which reported the necessity to have overexchanged zeolites, one can suppose that this step supplies the part of copper which makes the active clusters, namely, those with copper present in exchangeable sites. Although other explanations are possible, the slight increase of "implanted" Sm with the increase of the pH could be an indication of a stronger competition to Sm with Cu.

Another contribution of samarium can be deduced from the comparative DRIFTS analysis of zeolites with and without samarium but with a comparable amount of copper (Fig. 5). The spectra show that the presence of samarium leads to an increased population of ELO species. Let us note, incidentally, that the DRIFTS spectra give no evidence of the formation of a Cu–O–Sm bond. Therefore, one can speculate that the contribution of samarium is not only to increase the amount of implanted copper but, quite specifically, to orient the implantation of copper.

Nature of the active site. Another very important result of the present study comes from a comparison of the shapes of the O_2-TPD curve and the activity curve. There is a strong parallelism. Inactive Cu, present in catalysts with Cu contents below 30% exchange capacity, have very weak O_2-TPD signals. That copper is almost completely inaccessible to O_2 or not able to fix oxygen.

Many studies stressed the necessity for Cu to be in close proximity to the Al atoms in the zeolite framework, i.e., in the exchangeable positions (21, 23). There are also many studies which discuss the necessary presence of the so-called ELO species. These ELO species result from the presence of two copper atoms in close proximity (22, 28, 29). One Cu(II) would clearly be one possible structural unit on an isolated Cu ion which is ELO. But at higher temperatures $2Cu(OH)^+$ can lead to water elimination and the formation of Cu–O–Cu dimer. NO can also interact with $Cu(OH)^+$, leading to the same dimer, and N_2O (30). We should note that at the beginning of the reaction we always observe N_2O. Such a behavior is also sustained by the superficial migration of copper which was observed by XPS. It is true that during this process a part of copper migrates in totally inactive positions. But the implantation of copper at the Al exchangeable sites is not a simple process and after deposition of an amount of copper corresponding to 100% exchange it was found that there are still unoccupied exchangeable sites (31, 32). This means that the formation of the diatomic clusters containing ELO species starts, even for an exchange degree lower than 100% (and this explains a certain level of activity of these catalysts). The high activity of the overexchanged ZSM-5 zeolites suggests that a quasi-complete formation of these diatomic species can be achieved only after overexchange occurs.

In attempting to discuss the effects of Sm and, more particularly, the active sites which might be modified by Sm, the previous remarks must be remembered. More generally, diffusion limitations and selective chromatographic effects during the penetration of the exchangeable ions Sm and Cu in the zeolite pores show that composition is certainly not homogeneous in the catalysts. In particular, composition gradients are certainly important between the outer parts of the zeolite and the interior. The XPS data demonstrate the existence of such effects. The changes after the test also prove that. The occurrence of some migration phenomena implies the existence of concentration gradients.

The consequence is that the identification of sites in Cu–Sm–ZSM-5 is extremely difficult. Many possible species are present including, very likely, a tiny accumulation of oxides (of Sm and/or Cu) without active roles, possibly highly disperse but unstable phases (perhaps part of the copper responsible for the high XPS signal in fresh catalysts) which could either diffuse to other parts or sinter to relatively large aggregates corresponding to very weak XPS signals, etc. The following discussion, therefore, will necessarily involve a large degree of uncertainty. Correlations, because they are made between quantities reflecting the properties of parts of catalysts of different structures, could not be expected to be quantitative.

In particular, it is very difficult to determine the fraction of copper which is favorably influenced by the presence of samarium. This can be either the reducible copper located in close proximity to aluminum or the less reducible one which, together with the first, creates a diatomic cluster, or pair, believed to be the active site in NO decomposition. In the fresh catalysts, the Cu(I)-to-Cu(II) ratios determined by XPS for the series of Cu–Sm–ZSM-5 studied in the present investigation vary parallel to the increase of the degree of copper exchange. But these Cu(I)-to-Cu(II) ratios are nearly the same in the really active catalysts, namely, in the state they are in after 3 h of reaction. These very close values could also be a suggestion that the support is a contribution to this process, only certain positions being able to accommodate stable Cu(I) species. The presence of samarium orientates this process. The dependence presented in Fig. 10 for only exchanged ZSM-5 can account for the same process.

These data show the same tendencies as those we have previously reported concerning Cu–Sm–ZSM-5 samples in which the amount of copper corresponded to that overexchanged (33). We had suggested that the active sites were not symmetric Cu(II)–O–Cu(II) but asymmetric Cu(I)–O–Cu(II) diatomic clusters. These clusters could easily play a redox role and our XPS data also showed that Cu(I) predominated in the presence of Sm, and both Cu(I) and Cu(II) still existed after the catalytic tests. The association Cu(I)–O–Cu(II) could create a redox buffer. The formation of this kind of species was confirmed by the calculations made by Sayle *et al.* (34).

The increase of the amount of implanted copper in zeolites leads to a logical increase in the population of ELO species and O_2-TPD results are a confirmation in this sense.

The activity data of the present catalysts are the logical consequence of the characteristics already discussed. The NO total conversion increases with the increase of the copper-exchange degree. The same parallelism, actually still more accentuated, is observed for the conversion to N_2. It is worth noting that when the 128%-exchanged Cu zeolite containing Sm was used, the conversion was similar to that measured using the 220%-exchanged Cu zeolite in monocomponent zeolites (25). The role of Sm must therefore be interpreted as enhancing the proportion of copper-building active sites in Cu–ZSM-5 zeolites.

The DRIFTS spectra recorded under a flow of 30 ml min^{-1} 5% NO–He indicate species which could be involved in this reaction. Concerning copper, the spectra recorded at room temperature show the existence of copper with different coordinations with, according to the previous cases, different oxidation states. Concerning nitrogen compounds, except the *gem*-dinitrosyl bands, all other bands already identified in FTIR for low NO pressures were detected (19–21, 33). The spectra recorded at different temperatures and particularly the data obtained by successive subtraction of the successive spectra in temperature regions where the catalytic reaction occurs suggest that mainly NO and N_2O_3 species are bonded on Cu^{2+} implanted in a position adjacent to single-framework Al, NO species bonded on Cu^{+} and $(NO_2)_2$ species may be involved in various reactions of NO. These conclusions are in agreement with those of our previous NO-FTIR investigation using Cu–Sm–ZSM-5 catalysts (33). Again, no particular interaction of Sm with NO species was identified, but its presence increased the population of the above species as a consequence of a better positioning of copper.

5. CONCLUSIONS

The investigation of Cu–Sm–ZSM-5 with low copper but also samarium exchange indicated that the main contribution of the rare-earth element occurs during the ionic exchange when copper is directed to the better positions. None of the characterizations we have made, O_2-TPD, DRIFTS, and XPS, gave any evidence on direct interaction Cu–Sm or direct contribution of Sm in NO decomposition.

Because of this better positioning of copper, we have shown that it is possible to reach high conversion of NO, even for low-exchanged Cu–ZSM-5 zeolites.

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REFERENCES

1. Iwamoto, M., Furukawa, H., and Kagawa, S., *in* “Proceedings, 10th International Congress on Catalysis, Budapest 1992” (L. Guczi, F. Solymosi, and P. Tetenyi, Eds.), p. 1285. Akadémiai Kiadó, Budapest, 1993.
2. Iwamoto, M., Furukawa, H., and Kagawa, S., *in* “New Developments in Zeolite Science and Technology” (Y. Murakami, A. Iijima, and J. W. Ward, Eds.), Studies in Surface Science and Catalysis, Vol. 28, p. 943. Elsevier Science, Amsterdam, 1986.
3. Pârvulescu, V. I., Grange, P., and Delmon, B., *Catal. Today* **46**, 233 (1998).
4. Kikuchi, E., Yogo, K., Tanaka, S., and Abe, M., *Chem. Lett.* 1069 (1991).
5. Iwamoto, M., Yokoo, S., Sakai, K., and Kagawa, S., *J. Chem. Soc. Faraday Trans. 1* **77**, 1629 (1981).
6. Kagawa, S., Ogawa, H., Furukawa, H., and Teraoka, Y., *Chem. Lett.* 407 (1991).
7. Eranen, K., Kumar, N., and Lindfors, L. E., *Appl. Catal. B: Environ.* **4**, 213 (1994).
8. Zhang, Y., and Flytzani-Stephanopoulos, M., *in* “Environmental Catalysis” (J. N. Armor, Ed.), p. 7. American Chemical Society, Washington, DC, 1994.
9. Zhang, Y., Sun, T., Sarofim, A. F., and Flytzani-Stephanopoulos, M., *in* “Reduction of Nitrogen Oxide Emissions” (U. S. Ozkan, Ed.), p. 133. American Chemical Society, Washington, DC, 1995.
10. Budi, P., Curryhyde, E., and Howe, R. F., *Catal. Lett.* **41**, 47 (1996).
11. Kucherov, A. V., Hubbard, C. P., Kucherova, T. N., and Shelef, M., *in* “Progress in Zeolite and Microporous Materials” (H. Chon, S. K. Ihm, and Y. S. Uh, Eds.), Studies in Surface Science and Catalysis, Vol. 105, p. 1469. Elsevier Science, Amsterdam, 1997.

12. Pârvulescu, V. I., Oelker, P., Grange, P., and Delmon, B., *Appl. Catal. B: Environ.* **16**, 1 (1998).
13. Zhang, Y., and Flytzani-Stephanopoulos, M., *J. Catal.* **164**, 131 (1996).
14. Horr, T. J., Ralston, J., and Smart, R. St. C., *Colloids Surf.* **64**, 67 (1992).
15. Iwamoto, M., Yahiro, H., Mina, Y., and Kagawa, S., *Chem. Lett.* 213 (1989).
16. Li, Y., and Armor, J. N., *Appl. Catal.* **76**, L1 (1991).
17. Rebrov, E. V., Simakov, A. V., Sazonova, N. N., Rogov, V. A., and Barannik, G. B., *Catal. Lett.* **51**, 27 (1998).
18. Lei, G. D., Adelman, B. J., Sarkany, J., and Sachtler, W. M. H., *Appl. Catal. B: Environ.* **5**, 245 (1995).
19. Valyon, J., and Hall, W. K., *J. Phys. Chem.* **97**, 1204 (1993).
20. Aylor, A. W., Larsen, S. C., Reimer, J. A., and Bell, A. T., *J. Catal.* **157**, 592 (1995).
21. Hadjiivanov, K., Klissurski, D., Ramis, G., and Busca, G., *Appl. Catal. B: Environ.* **7**, 251 (1996).
22. Wichterlova, B., Dedecek, J., and Vondrova, A., *J. Phys. Chem.* **99**, 1065 (1995).
23. Iwamoto, M., Yahiro, H., Mizuno, N., Zhang, W.-X., Mine, Y., Furukawa, H., and Kagawa, S., *J. Phys. Chem.* **96**, 9360 (1992).
24. Giamello, E., Murphy, D., Magnacca, G., Morterra, C., Shioya, Y., Nomura, T., and Anpo, M., *J. Catal.* **136**, 510 (1992).
25. Curtin, T., Grange, P., and Delmon, B., *Catal. Today* **35**, 121 (1997).
26. Curtin, T., Grange, P., and Delmon, B., *Catal. Today* **36**, 57 (1997).
27. Li, Y., and Hall, W. K., *J. Phys. Chem.* **94**, 85 (1990).
28. Sarkany, J., and Sachtler, W. M. H., *Zeolites* **14**, 7 (1994).
29. Valyon, J., and Hall, W. K., *J. Phys. Chem.* **97**, 7054 (1993).
30. Pirone, R., Garufi, E., Ciambelli, P., Moretti, G., and Russo, G., *Catal. Lett.* **43**, 255 (1997).
31. Parrillo, D. J., Dolenec, D., Gorte, R. J., and McCabe, R. W., *J. Catal.* **142**, 708 (1993).
32. Parrillo, D. J., Fortney, J. P., and Gorte, R. J., *J. Catal.* **153**, 190 (1995).
33. Pârvulescu, V. I., Grange, P., and Delmon, B., *J. Phys. Chem. B* **101**, 6933 (1997).
34. Sayle, D. C., Catlow, C. R. A., Perrin, M. A., and Nortier, P., *J. Mater. Chem.* **7**, 1917 (1997).