



On the researching of a new zeolite structure for the selective catalytic reduction of NO

The possibilities of Cu-exchanged IM5

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Abstract

A new zeolite (IM5) whose structure has not been resolved yet is tested for the selective catalytic reduction (SCR) of NO with C₃H₈ and characterized by in situ X-ray photoelectron spectroscopy. The catalytic behavior of copper exchanged IM5 zeolite is compared with that of copper exchanged ZSM5 zeolites. The influence of the partial pressure of oxygen, reaction temperature and exchange level of the metal in the catalyst is similar to that observed with copper exchanged ZSM5 zeolite, but Cu-IM5 is a more active and hydrothermally more stable catalyst than Cu-ZSM5. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nitric oxides are mainly formed by the combustion of nitrogen-containing compounds and by thermal fixation of atmospheric nitrogen. These pollutants, after emission into the atmosphere, take part in the formation of photochemical smog and are one of the main components of the acid rain. Therefore, limiting the NO_x emissions and the search for new

NO_x abatement processes has become a priority in many countries. Among the emission control technologies envisaged, the most widely applied methods are the selective catalytic reduction (SCR) by NH₃ for stationary sources, and the three-way catalysts for mobile sources. The former one needs the use of ammonia that makes the operation of the utility complicated [1–3]. The three-way catalysts give excellent results when the air to fuel ratio is near to the stoichiometric ratio; however, the efficiency diminishes quickly when there is an excess of oxygen [4,5]. Nowadays the trend is to use engines with better fuel efficiency, lean burn engines, which operates with an excess of oxygen over the stoichiometric ratio, and limit the use of the traditional three-way

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catalysts. For these reasons the discovery of an alternative is an imperative need. Other alternatives involve the catalytic decomposition of NO_x using metal-exchanged zeolites as catalysts, but the activity of these materials is strongly diminished by the presence of O_2 , water and SO_2 [6–9]. Another approach is the SCR of NO_x with hydrocarbons in presence of O_2 [10,11]. This alternative is attracting much interest and it is believed to be a promising way to eliminate nitrogen oxide.

Large and medium pore zeolite structures exchanged with different cations, i.e., Cu, Ga, Ce, Fe, Rh, Pt, Pd, Ag, Ni, Mn, etc., have shown activity for reducing NO_x with hydrocarbons such as propane, propylene, ethylene and other hydrocarbons [4,9,12–23]. The best results were initially achieved with ZSM5 and Beta zeolite structures when exchanged with copper, obtaining the maximum conversion at 623 K and 1–2% oxygen concentrations. Nevertheless, the activity is strongly diminished in presence of water vapor, SO_2 , or after a hydrothermal treatment of the original catalyst [24], probably due to changes in the copper active sites environment [25]. These zeolites when exchanged with cobalt are also able to remove NO and N_2O simultaneously [26,27] at temperatures in the 673–723 K range and in the presence or not of oxygen [28–32], showing a high hydrothermal stability. It is also interesting to point out that with this type of catalysts, methane (not considered traditionally as a selective reductor) can be used as reductor, even though, the conversion achieved is not very high and the system is very sensitive to the O_2 concentration [28]. Other zeolites such as faujasite, mordenite, ferrierite and MCM22 have been shown to be less active.

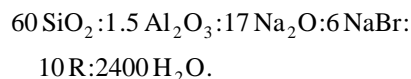
The reason why these zeolite structures are active for the NO removal when metal exchanged is still a matter of discussion and active research [33,34]. Recently, a new zeolite named IM5 has been discovered [35]. The structure of this zeolite is still unknown, but its pore volume ($0.13 \text{ cm}^3 \text{ g}^{-1}$), its catalytic behavior in test reactions and the hydrocarbon adsorption measurements [36] suggest that the pore topology may be formed by either 10 MR crossing pores or 10 MR pores with lobes, close to the structure of ZSM5. For this reason, this material could be active for the SCR of NO [37]. In this work, the IM5 zeolite with different Cu contents has been

tested for the SCR of NO with propane and it has been characterized by X-ray photoelectron spectroscopy. The catalysts were analyzed immediately after in situ SCR reaction by using a high-pressure reaction cell (HPRC) installed into the preparation chamber of the spectrometer. The variations of the $\text{Cu}2p_{3/2}$ transition, shake-up satellite associated to this transition and the Auger $\text{Cu}L_3\text{VV}$ peak, after treatment under different reaction conditions, were used to clarify the oxidation state of copper.

2. Experimental

2.1. Materials

IM5 was synthesized hydrothermally in static conditions at 175°C in PTFE-lined stainless steel autoclaves [36]. Chemical composition of the synthesis gel was the following:



The required amount of silica (Aerosil 200, Degussa) was added to a solution of the organic structure-directing agent (1,5-bis(methylpyrrolidinium) pentane in its bromide form, R) in water under stirring. Then a solution of sodium aluminate (56% Al_2O_3 , 37% Na_2O , Carlo Erba), sodium hydroxide (98% Prolabo) and sodium bromide (99% Scharlau) in water was added and the mixture was kept under stirring for 30 min. After 10 days of heating the autoclaves were quenched and the content was filtered and extensively washed with distilled water. The recovered solid was calcined in air at 580°C for 3 h and exchanged twice with an aqueous solution of NH_4Cl followed by calcination at 500°C to obtain the zeolite in its acid form.

The metal exchange was done in an aqueous solution containing $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with the adequate concentration to achieve the desired amount of metal on the zeolite, and with a solid/liquid ratio = 10 g l^{-1} . The exchange was carried out at room temperature under stirring for 24 h. To prepare samples with copper content above the exchange capacity, an amount of NH_4OH was added for adjusting the pH to 6. After that the zeolite was filtered

and washed, and then calcined at 550°C for 4 h. The composition of the samples was analyzed by atomic absorption, and the results are given in Table 1.

Along the text, zeolites are named starting with the name of the zeolite structure, followed by numbers indicating the Si/Al ratio and the level of metal exchange (100% atomic exchange is considered when the Cu/Al ratio is 0.50).

2.2. Catalyst characterization

The surface areas of catalysts were obtained in an ASAP 2000 apparatus, using the BET method from the nitrogen adsorption isotherms at 77 K.

X-ray diffraction patterns (XRD) were collected using a Philips X'Pert-PW3719 diffractometer provided with a graphite monochromator, operating at 40 kV and 20 mA and employing nickel-filtered CuK α radiation ($\lambda = 0.1542$ nm).

XPS and XAES measurements were carried out using a Vacuum Generators Escalab-210 system, in the conventional mode, by using the Mg K α (1253.6 eV) radiation of a twin anode in the constant analyzer energy mode with a pass energy of 40 eV. The vacuum during spectra acquisition was better than 5×10^{-9} mbar. To avoid the reduction of copper ions during the X-ray exposure, samples were cooled at 173 K during the acquisition and the X-ray power was limited to 100 W (10 mA–10 kV). The spectral acquisition time was also reduced to prevent the damage of the sample. In order to remove charging

shifts and deal with Fermi edge coupling problems, binding energies were scaled against the peak of the C–(C,H) component coming from carbon contamination (set to 284.6 eV). The content of copper on the surface was calculated using the surface area under Cu2p $_{(3/2)}$ peak, the effective ionization cross-section [38], the electron escape depth [39] and transmission analyzer factors. The relative amount of Cu $^{+2}$ /Cu $^{+1}$ species has been obtained from the core-level satellite intensity relative to that of the Cu2p $_{(3/2)}$ transition, with an accuracy of ca. 20% [40].

In situ type experiments were conducted in a HPRC mounted directly to the preparation chamber of the spectrometer. The analysis were obtained on self-supporting wafers of 9 mm diameter and ca. 5 mg weight that were fixed on a circular sample holder, specially designed for the reaction cell, in such a way that all the reactant flow pass through the catalyst. The reactant gases were introduced into the reaction cell through mass flow controllers (gas flow rate of 150 ml/min). Catalyst pretreatment was carried out in situ in flowing N $_2$ at 150 ml/min during 2 h at 623 K, followed by cooling in vacuum to room temperature. Next the catalyst was exposed, at different reaction temperatures, to one or more of the following reactant gases: NO (600 ppm), O $_2$, C $_3$ H $_8$ (380 ppm), balanced with N $_2$.

2.3. Catalytic measurements

The NO $_x$ reduction experiments were carried out in a fixed bed, quartz tubular reactor of 2.2 cm of

Table 1
Chemical analysis of the zeolites

Catalyst	wt.% SiO $_2$	wt.% Al $_2$ O $_3$	wt.% Na $_2$ O	wt.% CuO	Si/Al	metal/ Al	% exchanged
ZSM5–Cu- 16-120	91.0	4.7	0.02	4.4	16.4	0.6	120
ZSM5–Cu- 16-47	93.4	4.76	0.1	1.73	15.7	0.24	47
ZSM5–Cu- 17-195	88.6	4.98	0.07	6.8	16.8	0.97	195
IM5–Cu- 15-183	87.7	5.2	0.03	7.2	15	0.91	183
IM5–Cu- 19-117	92.2	4.1	0.08	3.7	19.2	0.6	117
IM5–Cu- 15-64	92.2	5.2	0.05	2.6	15.2	0.32	64

diameter and 53 cm of length. In a typical experiment, 1 g of a zeolite catalyst, as particles of 0.25–0.42 mm size, were introduced in the reactor and were heated up to 623 K under nitrogen flow. At this temperature the flow was maintained for 6 h. After that, the desired reaction temperature was set and the reaction feed admitted. This consists of 650 ml min^{-1} of a mixture composed by 600 ppm of NO, 380 ppm of C_3H_8 , variable quantities of oxygen and balanced with nitrogen. The NO_x present in the outlet gases from the reactor was continuously analyzed by means of a chemiluminescence detector model Rosemount 951 A. The presence of N_2O was detected by gas chromatography with a 5A Molecular Sieve column used to separate oxygen, nitrogen and carbon monoxide and a Poraplot Q column for the separation of carbon dioxide and hydrocarbons.

3. Results and discussion

The chemical composition of the catalysts is shown in Table 1. The catalysts tested have areas higher than 300 m^2/g , without a significant decrease in the area after the metal exchange.

Fig. 1 shows the XRD patterns of the IM5 zeolite in its acid form (a) and after copper exchange (b). The ion-exchanged samples have crystallinities between 94% and 100% with respect to the crystallinity of the parent zeolite, indicating that the catalyst lattice was practically undisturbed after ex-

change with copper and that although copper is overexchanged, CuO crystals were not detected.

3.1. Electron spectroscopy

To study the influence of the catalyst treatments on the copper species, we have monitored the $\text{Cu}2\text{p}_{(3/2)}$ electronic transition and the CuL_3VV Auger transition, in addition to Si2p, Al2p and O1s transitions of the zeolite framework. Since the $\text{Cu}2\text{p}_{(3/2)}$ transition does not allow to distinguish the oxidation states of copper by itself, these have been assigned using $\text{Cu}2\text{p}_{(3/2)}$ binding energies, the associated shake-up satellites, the kinetic energies of the CuL_3VV Auger transitions and the modified Auger parameter (α'). The shake-up satellite peaks are final state effects that arise after a substantial reorganization of the valence electrons that may involve excitation of one of them to a higher unfilled level (shake-up). As a result the photoelectron losses energy and appears at a higher binding energy in the XP spectrum. This effect is clearly observed for certain transition metals and rare earth with unpaired electrons in 3d or 4f shells, respectively. In the case of copper, these final state effects are only observed in Cu(II) species showing a shake-up satellite at ca. 10 eV higher than the $\text{Cu}2\text{p}_{(3/2)}$ transition, being this characteristic 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.

3.1.1. As prepared catalysts and activated in nitrogen

The spectral parameters corresponding to the Cu–IM5 catalysts are summarized in Tables 2 and 3. Figs. 2 and 3 illustrate the $\text{Cu}2\text{p}$ and CuL_3VV spectra, respectively, obtained for the catalyst IM5–Cu-15-183. As can be seen there, the as-prepared catalyst (Fig. 2a) shows the shake-up satellite at ca. 944 eV indicating the presence of Cu(II) species (Cu^{+2} ca. 100%). The main transition is characterized by two components at ca. 933.4 and 935.6 eV. No other peaks, either from copper or the zeolite framework, were split or broadened indicating the absence of differential charge effects. The component at 933.4 eV is similar to that observed for

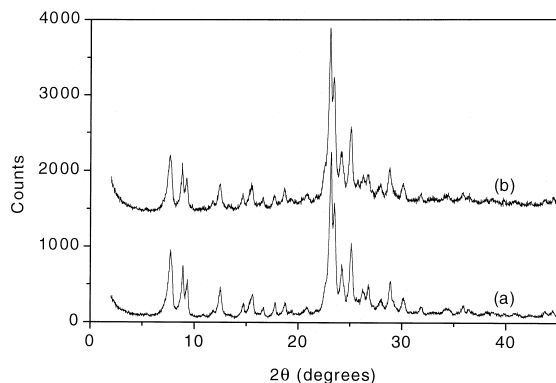


Fig. 1. XRD patterns of IM5 zeolite in its acid form (a) and after Cu ion exchange (b).

Table 2
Spectral parameters obtained for the catalyst IM5–Cu-15-183 by XPS and XAES

Identification	Si/O ^a	Treatment	Cu2p _{3/2} (eV)	CuL ₃ VV (eV)	α ^b	Cu/Si ^a	(Cu ⁺¹ , %)
Res01	0.49	vacuum	933.4 935.6	913.7	1847.1 1849.3	0.029	0
Res02	0.48	N ₂ , 623 K	933.5 936.5	913	1846.5 1849.5	0.030	100
Res03	0.53	N ₂ , O ₂ , 623 K	933.5 936.3	913.2	1846.7 1849.5	0.027	0
Res04	0.50	N ₂ , NO, 723 K	933.6 936.3	913.3	1846.9 1849.6	0.021	0
Res05	0.50	N ₂ , O ₂ , NO, C ₃ H ₈ , 623 K	933.4 936.3	913.3	1846.7 1849.6	0.025	33
Res06	0.51	N ₂ , O ₂ , NO, C ₃ H ₈ , 723 K	933.0 913.5 935.9		1846.5 1849.4	0.024	0
Res07	0.50	N ₂ , H ₂ , 623 K	931.9	919.5	1851.4	0.012	0
Res08	0.50	Res07 + reoxidation in air at 623 K	933.4 936.3	913.5 918.0	1846.9 1849.8	0.014	–
Res09	0.49	N ₂ , NO, C ₃ H ₈ , 723 K	933.4 936.2	913.4	1846.8 1849.6	0.024	50
Res010	0.49	N ₂ , NO, C ₃ H ₈ , 623 K	933.4 936.3	913.5	1846.9 1849.8	0.022	45
Res011	0.49	N ₂ , NO, C ₃ H ₈ , 723 K O ₂ (14%)	933.4 936.3	913.5	1846.9 1849.8	0.022	0
Cu (metal)			932.4	918.6	1851.0		
Cu ₂ O			932.3	916.6	1848.9		
CuO			933.8	917.6 ^c	1851.4		

^aOn surface.

^bModified Auger parameter = BE(Cu2p_{3/2}) + KE(Cu L₃VV).

^cAnomalous KE value.

Cu(II) [41–43]. The component at higher binding energy has been described previously for Cu–ZSM5

zeolites being ascribed to the presence of copper coordinated with extralattice-oxygen [44]. Moreover,

Table 3
Spectral parameters obtained for the catalyst IM5–Cu-15-64 by XPS and XAES

Identification	Si/O ^a	Treatment	Cu2p _{3/2} (eV)	CuL ₃ VV (eV)	α ^b	Cu/Si ^a	(Cu ⁺¹ , %)
Res01	0.44	vacuum	933.5	913.9	1847.4	0.011	0
Res02	0.45	N ₂ , 623 K	933.4	913.1	1846.5	0.012	100
Res03	0.50	N ₂ , O ₂ , 623 K	933.5	913.3	1846.8	0.010	0
Res04	0.47	N ₂ , NO, 723 K	933.8	913.3	1847.1	0.008	0
Res05	0.48	N ₂ , O ₂ , NO, C ₃ H ₈ , 623 K	933.1	913.1	1846.2	0.013	20
Res06	0.50	N ₂ , O ₂ , NO, C ₃ H ₈ , 723 K	933.0	913.1	1846.3	0.012	0
Res07	0.48	N ₂ , H ₂ , 623 K	931.9	919.8	1851.7	0.006	0
Res08	0.49	Res07 + reoxidation in air at 623 K	933.5	918.1	1851.6	0.007	–
Res09	0.49	N ₂ , NO, C ₃ H ₈ , 723 K	933.5	913.3	1846.8	0.010	35
Res010	0.49	N ₂ , NO, C ₃ H ₈ , 623 K	933.4	913.2	1846.6	0.011	15
Res011	0.49	N ₂ , NO, C ₃ H ₈ , 723 K O ₂ (14%)	933.8	913.3	1847.1	0.011	0

^aOn surface.

^bModified Auger parameter = BE(Cu2p_{3/2}) + KE(Cu L₃VV).

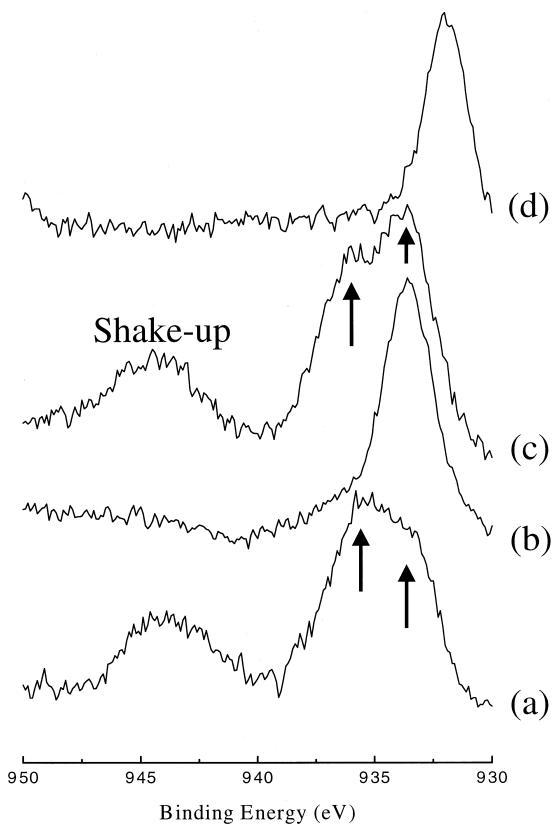


Fig. 2. XPS Cu $2P_{3/2}$ core level spectra of the catalyst IM5–Cu–15–183: (a) as-synthesized, (b) after activation in nitrogen at 623 K, (c) after activation in nitrogen at 623 K followed by the reaction with NO at 723 K, and (d) after reduction in H₂ at 623 K.

the authors establish a clear correlation between the stability of these species and the SCR catalytic activity. It is worth noting that the kinetic energy of the CuL₃VV Auger peak (Fig. 3a) is ca. 4 eV lower in energy with respect to that observed for the standard CuO, this observation being indicative of the high dispersion of copper ions into the zeolite. The results obtained with IM5–Cu–15–64 are similar to those previously described for the over-exchanged catalyst showing a shake-up satellite indicating the presence of Cu(II) species (see Table 3). Nevertheless, the Cu $2p_{(3/2)}$ transition in the as-prepared catalyst shows only a component at ca. 933.5 eV. As occurs in the over-exchanged sample, the low kinetic energy of the Auger CuL₃VV peak is consistent with the high dispersion of copper ions into the zeolite matrix.

When the catalysts are activated in flowing nitrogen at 623 K, the shake-up satellite vanishes, indicating the reduction to Cu(I) species (see Tables 2 and 3). It is noticeable to point out that after heating in nitrogen at 623 K the component observed at high binding energy in catalyst IM5–Cu–15–183 is now importantly reduced (see Fig. 2b), showing (after curve fitting) a small component at ca. 936.5 eV. Nevertheless, the Auger peaks are practically unchanged, indicating that the aggregation state of copper is not modified.

3.1.2. Exposure to NO

The result of exposing the catalysts previously activated in nitrogen to NO at 723 K resulted in the full oxidation to Cu(II) species, as deduced from the presence of the core level satellite (see Fig. 2c and Tables 2 and 3). The Cu $2p_{(3/2)}$ transition is slightly

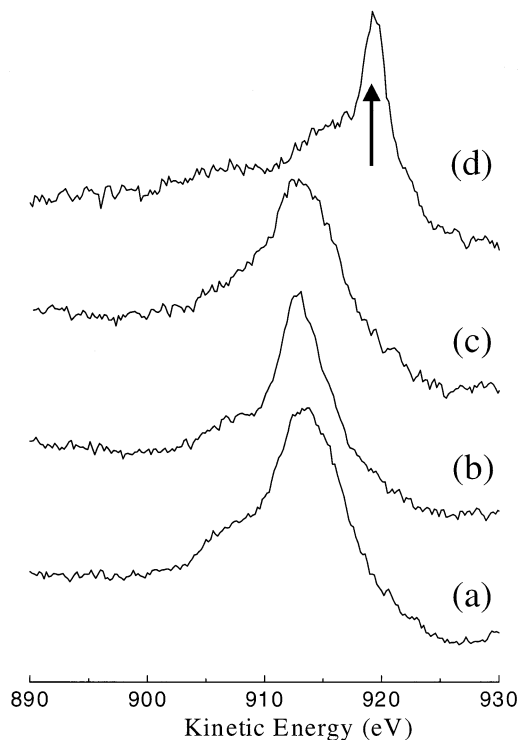


Fig. 3. XAES CuL₃ VV spectra of the catalyst IM5–Cu–15–183: (a) as-synthesized, (b) after activation in nitrogen at 623 K, (c) after activation in nitrogen at 623 K followed by the reaction with NO at 723 K, and (d) after reduction in H₂ at 623 K.

shifted to higher energy and additionally, in the case of the over-exchanged catalyst (IM5–Cu-15-183), the component of higher binding energy (by ca. 936 eV) appeared again after reaction. As can be derived from the Auger peaks, the aggregation state of copper after exposure to NO is practically constant even though a slight decrease in the Cu/Si atomic ratio on the surface is observed. The decrease of the copper level could be justified as due to a possible migration of copper into the bulk zeolite matrix.

3.1.3. Exposure to H_2

Figs. 2d and 3d show the results obtained with the catalyst IM5–Cu-15-183 when subjected to a reduction in hydrogen using the conditions indicated in Tables 2 and 3. As can be seen in Tables 2 and 3, reduction of the catalysts at 623 K gives spectral parameters typical of the bulk metal. After exposing the samples to a reducing atmosphere, the $Cu2p_{(3/2)}$ transition is characterized by a sharp peak at ca. 932 eV. In sample IM5–Cu-15-183, the split observed in the $Cu2p_{(3/2)}$ transition and the shake-up satellite disappear. The kinetic energy of the $CuL3VV$ Auger transition is shifted to higher values (by ca. 6.5 eV) ($\alpha' = 1851.4$ eV) indicating the formation of large particles of metallic copper on the surface [33]. It is worth noting that the Cu/Si atomic ratio is clearly reduced, indicating that the level of copper on the surface is decreased possibly due to the aggregation effects and also to the migration of copper into the bulk zeolite matrix.

As can be derived from Tables 2 and 3, the exposure of catalysts previously reduced in flowing hydrogen to oxygen at 623 K results in $Cu2p_{(3/2)}$ transitions similar to those observed with the as-prepared catalysts or after treatment in air at 623 K. However, the CuL_3VV Auger transition is clearly different, showing peaks at high kinetic energies indicating that although copper has been oxidized to Cu(II), the aggregation state is partially maintained. This reoxidation reaction does not modify substantially the Cu/Si atomic ratio, this result being in agreement with the non-reversibility of the process. In this way, the large particles of metallic copper obtained after treatment in hydrogen can be reoxidized to Cu(II) but not redispersed into the zeolite matrix, as derived from the Auger kinetic energies.

3.1.4. Exposure to the reaction mixture

The result of exposing the catalysts, previously activated in nitrogen, to the reaction mixture at 623 K in absence of oxygen has been studied (Tables 2 and 3, Figs. 4 and 5). The appearance of the shake-up satellite indicates some oxidation to Cu(II). Exposure of catalysts to the reaction mixture at higher temperature (723 K) caused a slight decrease of the satellite, indicating a partial reduction to Cu(I). Addition of oxygen to this atmosphere (2.5%) still gave a mixture of Cu(II) and Cu(I) at 623 K but in this case with majority of Cu(II) species (see Tables 2 and 3). At higher temperatures (723 K) the copper was fully oxidized to Cu(II). In these conditions, the $Cu2p_{(3/2)}$ transition corresponding to the catalyst IM5–Cu-15-183 was shifted to lower binding energy (by ca. 0.4 eV) remaining practically unchanged the other parameters.

In order to estimate the effect of high concentration of oxygen on the catalytic reaction, samples were exposed to the full reaction mixture at 723 K using 14% O_2 . After reaction, the $Cu2p_{(3/2)}$ transitions were shifted to higher binding energy showing similar values to that observed for the standard CuO [41–43]. The relative amount of Cu(II) and Cu(I)

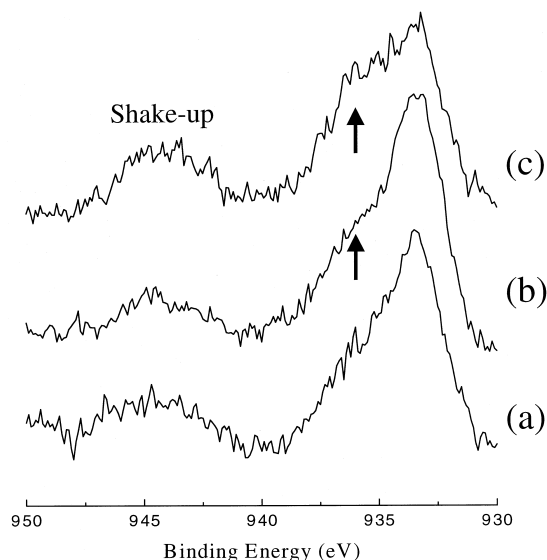


Fig. 4. XPS $Cu2P_{3/2}$ core level spectra of the catalyst IM5–Cu-15-183 after the SCR reaction: (a) at 623 K without oxygen, (b) at 623 K with oxygen, and (c) at 723 K with 14% oxygen.

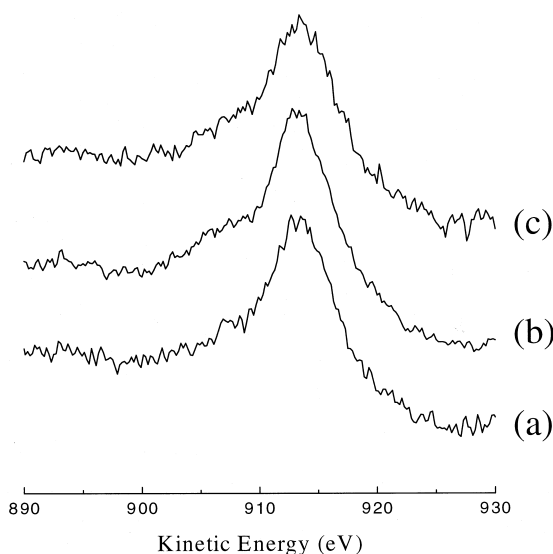


Fig. 5. XAES CuL_3 VV spectra of the catalyst IM5-Cu-15-183 after the SCR reaction: (a) at 623 K without oxygen, (b) at 623 K with oxygen, and (c) at 723 K with 14% oxygen.

was again estimated from the shake-up satellite intensity, indicating the full oxidation to Cu(II) (Tables 2 and 3).

It is interesting to note that after different reaction conditions the kinetic energy of the CuL_3 VV Auger

peaks undergo few changes and its behavior approaches to that expected for a uniform distribution of the copper ions across the bulk zeolite matrix, showing the same, or at least similar, aggregation states.

The results obtained with Cu-IM5 catalysts are comparable to those obtained with Cu-ZSM5 and with other Cu-exchanged zeolites (Cu- β). Also with those zeolites, by electron spectroscopy, it has been detected that different types of copper ions whose interconversion is clearly dependent on the atmosphere present and temperature used in the reaction.

3.2. Catalytic test

Before use in the SCR reaction, catalysts were activated by heating in flowing nitrogen at 623 K, resulting in the full reduction of Cu(II) to Cu(I), as was determined by XPS, and subsequently were exposed to the different reaction conditions.

In a preliminary experiment the stability of the catalysts was studied by carrying out the NO_x reduction at 623 K within the presence of 2.5% oxygen. No significant changes in activity were observed at least during the 2-h duration of the experiment (Fig. 6) and this allowed us to perform several experi-

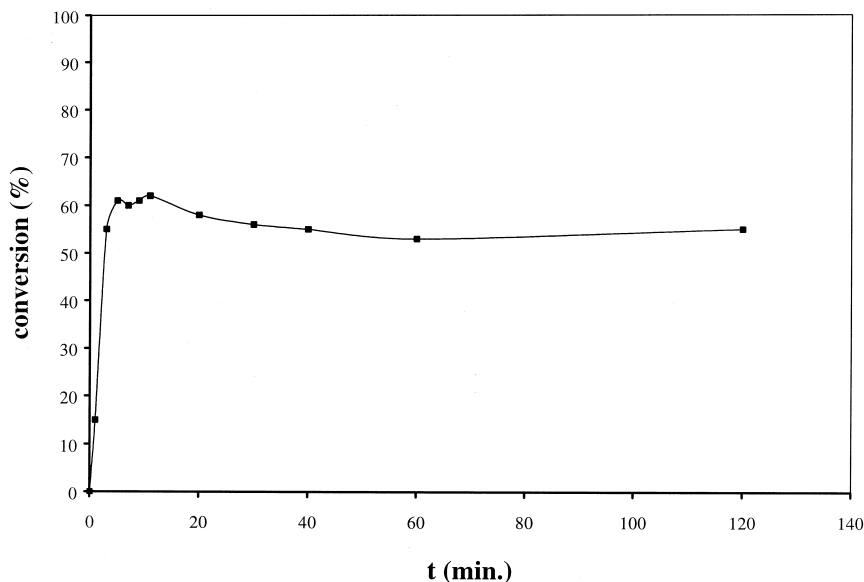
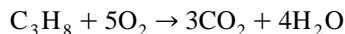
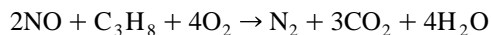


Fig. 6. Stability of IM5-Cu-15-183 in the course of the reaction, $T = 623$ K, 2.5% O_2 , 600 ppm NO , 380 ppm C_3H_8 , N_2 as effluent.

ments with the same catalyst sample. The formation of N_2O in these reaction conditions is very low, then the consideration that all the NO_x is converted into N_2 is assumed. The stability of the catalyst was checked by repeating at the end of the last run the experiment under the experimental conditions that gives a maximum in conversion.

The impact of the reaction conditions on the catalytic activity was studied for the IM5 exchanged with copper and compared with that of Cu–ZSM5. In Fig. 7, the influence of the reaction temperature on the activity of Cu–IM5 for the reduction of NO with propane is presented and compared with a sample of ZSM5 zeolite with similar Si/Al ratio and exchanged with copper at a similar level. The maximum activity for both catalysts is achieved at 623 K, observing a strong increase in the conversion when the temperature goes from 523 to 623 K. At higher temperatures than the above, the conversion decreases as a consequence of the higher activation energy of the competing reaction, i.e., the oxidation of propane, which produces a depletion of reductor

with the corresponding decrease in the efficiency of NO_x reduction:



It should be pointed out that an increase in the reaction temperature does not cause a permanent loss in catalyst activity, since when the reaction temperature was restored to 623 K the maximum conversion was again observed. These results can be connected with those previously obtained from the catalyst characterization. As derived from the XPS results, the interconversion between the different copper species is clearly dependent on the temperature and the reaction atmosphere used, constituting a dynamic equilibrium that can be reversible whenever metallic copper is not obtained. If compared to the activity of the copper-exchanged IM5 with that of Cu–ZSM5, a similar trend with temperature is observed, but Cu–IM5 has higher activity at any of the temperatures tested.

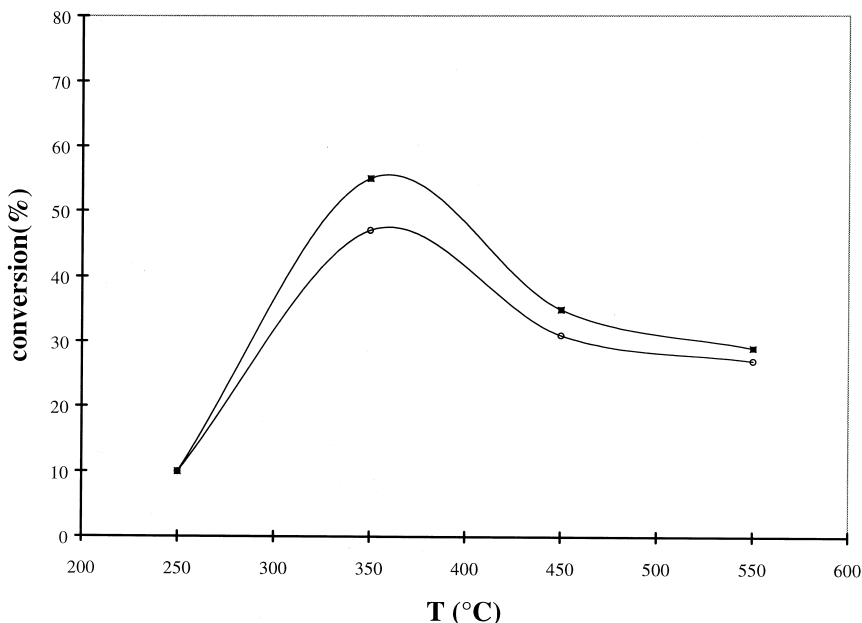


Fig. 7. Influence of the temperature in the SCR of NO. (○) ZSM5–Cu-17-195, (■) IM5–Cu-15-183, 2.5% O_2 , 600 ppm NO, 380 ppm C_3H_8 , N_2 as effluent.

In Fig. 8, the influence of the oxygen concentration on the SCR of NO with propane at 623 K is shown, and in all cases the conversion is very low when oxygen is not present in the reaction mixture. However, activity increases rapidly after adding small quantities of O₂ and a maximum in conversion is obtained with oxygen contents of about 0.3–1%. A further increase in the oxygen concentration results in a decrease of the activity, reaching a stable conversion when 5–6% oxygen is present. These results are qualitatively similar for Cu–IM5 and Cu–ZSM5 catalysts but, except in the absence of oxygen, better conversion is obtained with the copper-exchanged IM5 zeolite. In all cases the decrease in conversion when increasing the oxygen content does not lead to a permanent loss of the catalyst activity and the activity is restored to its original value when the initial concentration of oxygen is restored.

These results can be correlated with the changes produced on the oxidation state of copper ions during the SCR reaction. After exposing the over-exchanged Cu–IM5 zeolite to the reaction mixture at 623 K in the absence of O₂, the level of Cu(II)

species was ca. 55% and by adding O₂ to the reaction mixture the amount of Cu(II) ions increased to ca. 66%. This result would indicate that the increase of the Cu(II) level is, at least partially, responsible for the increased activity at these reaction conditions. Similar results were obtained with Cu–ZSM5 zeolites [45,46], indicating that Cu(II) was the major species present after SCR reaction conditions and this oxidation state has been directly ascribed as responsible for the catalytic reduction of NO.

It is known that in SCR of NO on metal containing zeolites the metal content plays a very important role on activity. Indeed, for Cu–ZSM5, as well as for Cu-beta zeolite catalysts, the optimum activity at 623 K is obtained for Cu contents slightly above the exchange capacity of the zeolite [10,17,47]. This is also the case for the IM5 (Fig. 9), which shows the best results with samples containing enough metal to exchange all the hydroxyl sites, probably with an excess over the stoichiometric exchange ratio (0.5 atom atom⁻¹). An excess over the exchange capacity does not modify the activity of the samples studied.

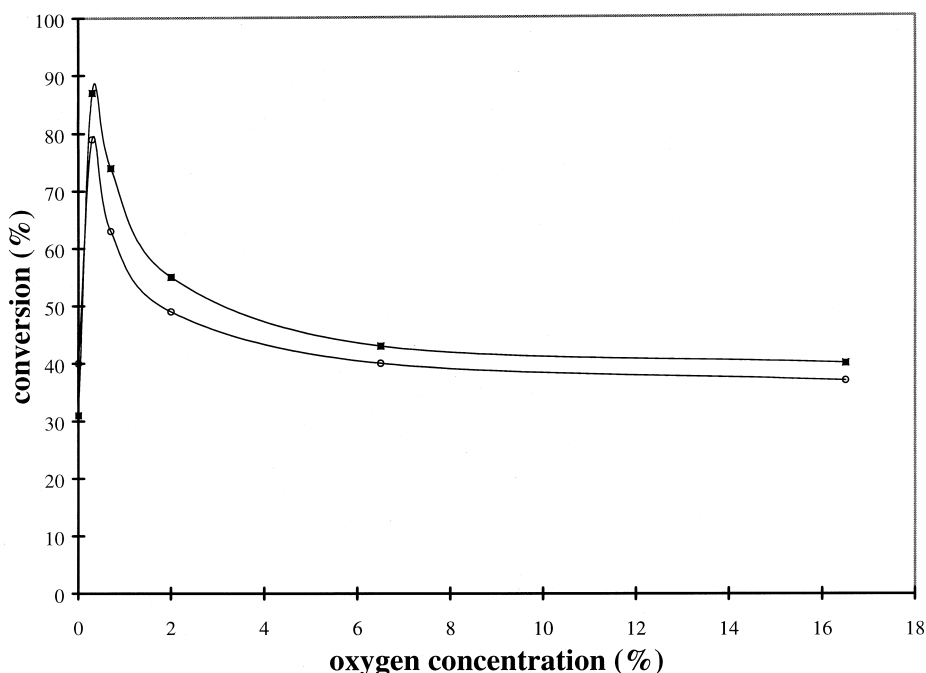


Fig. 8. Influence of the oxygen concentration in the SCR of NO with propane. (○) ZSM5–Cu-17-195, (■) IM5–Cu-15-183, 600 ppm NO, 380 ppm C₃H₈, N₂ as effluent, T = 623 K.

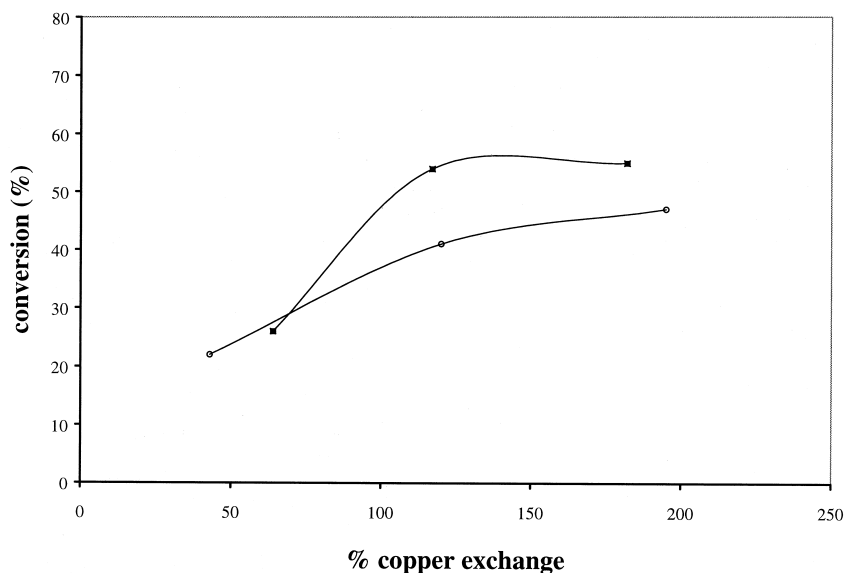


Fig. 9. Influence of catalyst composition in the SCR of NO with propane. (○) ZSM5–Cu–15, (■) IM5–Cu–15, 600 ppm NO, 380 ppm C_3H_8 , N_2 as effluent, 2.5% oxygen, $T = 623$ K.

It has to be pointed out that again Cu–IM5 shows a superior activity than Cu–ZSM5. However, at temperatures higher than 623 K, the maximum conver-

sion is obtained for the zeolite with less copper exchanged (Fig. 10). These results suggest that analogously to what has been suggested for Cu–ZSM5

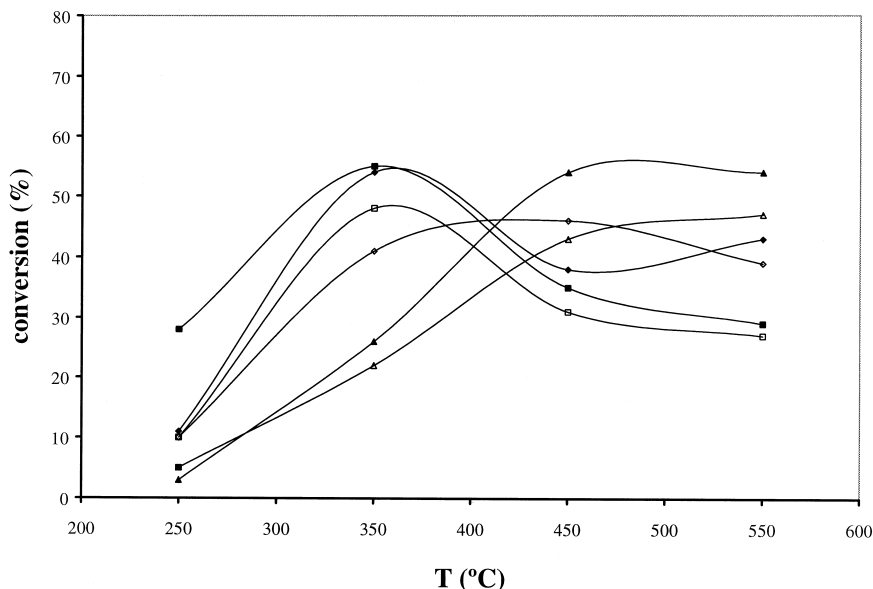


Fig. 10. Influence of catalyst composition in the SCR of NO with propane at different temperatures. (▲) IM5–Cu–15–64, (◆) IM5–Cu–19–117, (■) IM5–Cu–15–183, (△) ZSM5–Cu–15–47, (◇) ZSM5–Cu–16–120, (□) ZSM5–Cu–17–195, 600 ppm NO, 380 ppm C_3H_8 , N_2 as effluent, 2.5% oxygen, $T = 623$ K.

[47], also in Cu–IM5 different copper active sites exist with different activity at different temperatures. As can be seen in Tables 2 and 3, after the SCR reaction at 723 K, copper is fully oxidized to Cu(II) in both catalysts and, however, the activity is clearly different. These results can only be justified if different copper active sites exist. Recently, Cu(II) species with different coordination to lattice-oxygen have been identified in Cu–ZSM5 zeolites after different reaction conditions [46]. Thus, from results obtained with adsorption of CO, authors conclude that the activity of Cu–ZSM5 for NO reduction could be associated to Cu(II) ions coordinated to two-lattice-oxygen species. On the basis of the results obtained, it is reasonable to think that, as it occurs with Cu–ZSM5, different copper active sites are also present in Cu–IM5 depending on the experimental conditions. One type appears when the zeolite is underexchanged and it is active at ca. 723 K and another type appears when the zeolite is overexchanged being active at 623 K, both in the presence of oxygen.

The hydrothermal stability of Cu–IM5 has also been investigated and compared with that of Cu–ZSM5. To do this, the catalyst was steamed at 600°C (1 bar steam) and the resultant sample was tested in the presence of different oxygen concentration (Fig. 11). A decrease of the catalytic activity was observed at 623 K. This decrease depends on the oxygen concentration, being quite important for an oxygen concentration of 0.33% (where the maximum activity is obtained), but is not so important for a higher oxygen concentration. It is interesting to note that if the catalyst is tested at 723 K, the conversion is higher than the steamed catalyst, probably due to a redispersion of the copper active sites. If compared with a hydrothermally treated Cu–ZSM5 (Fig. 12), it becomes clear that IM5 shows a higher hydrothermal stability, since Cu–ZSM5 gives almost no activity at 623 K, and the activity at 723 K is lower than for Cu–IM5. The different behavior of the aged catalysts at 623 and 723 K indicates again the presence of two different centers in these zeolites. These centers that are active at 723 K also appeared in the

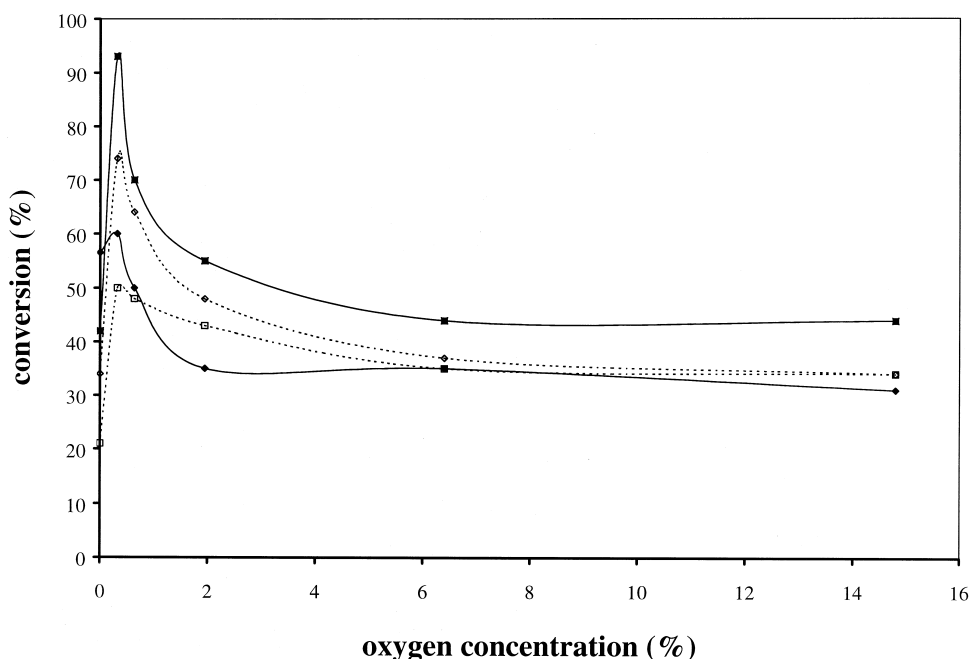


Fig. 11. Effect of steam treatment of the IM5-Cu catalyst on NO conversion (□) aged catalyst, reaction temperature = 623 K, (◇) aged catalyst, reaction temperature = 723 K, (■) fresh catalyst, reaction temperature = 623 K, and (◆) fresh catalyst, reaction temperature = 723 K.

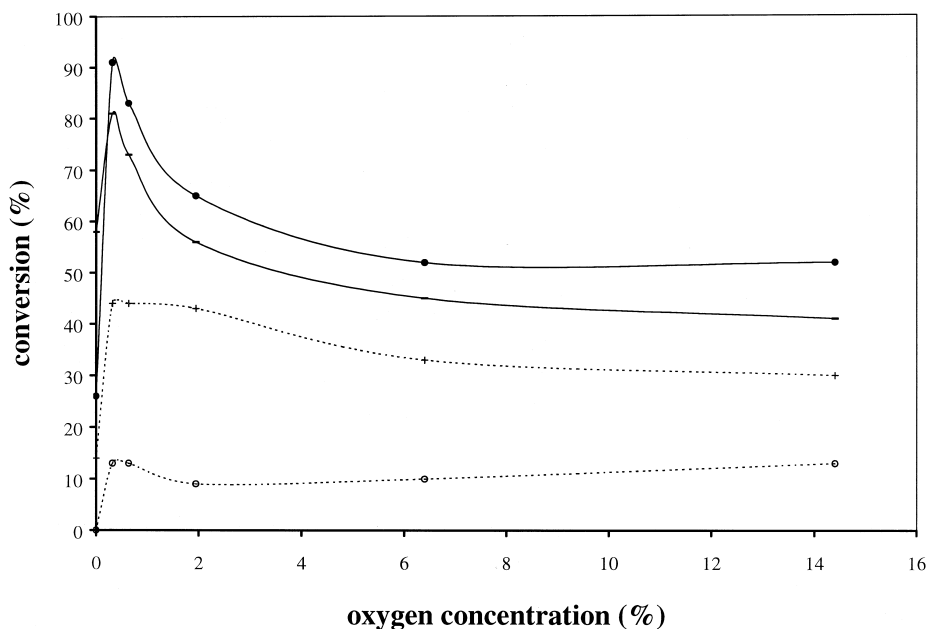


Fig. 12. Effect of steam treatment of the ZSM5-Cu catalyst on NO (○) aged catalyst, reaction temperature = 623 K, (+) aged catalyst, reaction temperature = 723 K, (●) fresh catalyst, reaction temperature = 623 K, and (-) fresh catalyst, reaction temperature = 723 K.

zeolites underexchanged and seems to be more stable than the others that were active at 623 K and that are present in the overexchanged samples.

From a practical point of view, it is necessary to study the influence of potential catalyst poisons such as water and SO_2 . As it can be seen in Fig. 13, the

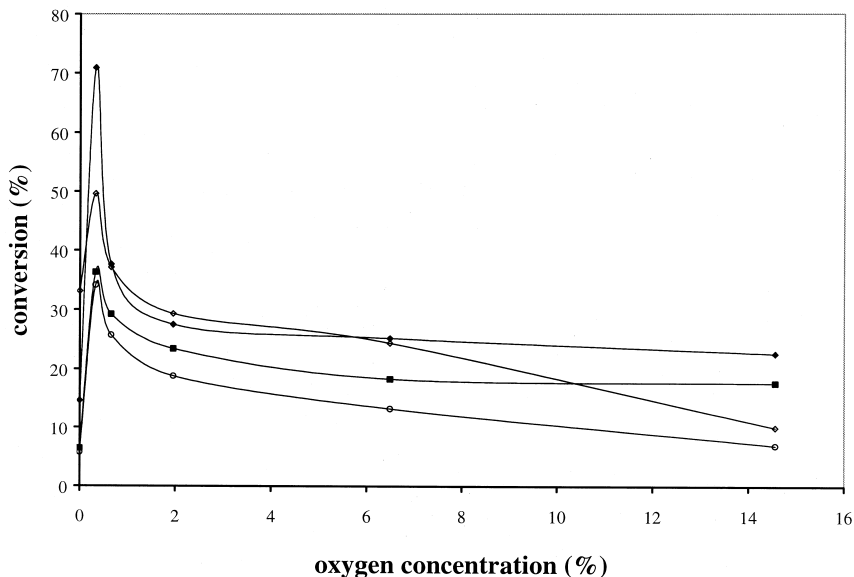


Fig. 13. Influence of water in the SCR of NO with propane at different temperatures. (○) ZSM5-Cu-17-195, $T = 623$ K; (◆) IM5-Cu-15-183, $T = 723$ K; (◇) ZSM5-Cu-17-195, $T = 723$ K; (■) IM5-Cu-15-183, $T = 623$ K; 600 ppm NO, 380 ppm C_3H_8 , N_2 as effluent, 2.5% oxygen, 2.5% water.

presence of 2.5% water vapor leads to an important decrease of the activity at 623 K, but much less at 723 K. This behavior is similar to that showed by ZSM5, although the activity of the Cu–IM5 is again higher than that of Cu–ZSM5. In these conditions the deactivation is reversible, and after regeneration of the catalyst the original activity was recovered. The influence of different concentrations of SO₂ was also studied, observing that the presence of 20 ppm of SO₂ does not affect the activity, but a negative effect appears at SO₂ concentration higher than 60 ppm, decreasing the activity of the catalyst by about 20% of the original conversion.

From the results presented it is clear that Cu-exchanged IM5 zeolites are active for the NO selective reduction with propane. The behavior of this zeolite is qualitatively similar to that observed for ZSM5, but the activity achieved with the former is higher at all the conditions tested. This would indicate that while the same active sites are present in Cu–ZSM5 and Cu–IM5, these centers are more stabilized in IM5 than in ZSM5, as it can be concluded from the results obtained with the steamed catalysts. The reason for this cannot be further discussed until the structure of this new material will be resolved. The results also suggest that two types of active centers exist. One of them appears on zeolites underexchanged and are the most active at 723 K and in the presence of water or after a steam treatment of the catalyst. The other type of sites appear when the zeolite is overexchanged, and they give the maximum activity at 623 K. These centers are less stable and are not active after steam treatment or in the presence of water and SO₂. XPS results suggest that these centers are related with Cu (II) and Cu (I) with different coordination; nevertheless, further work is in progress to characterize the different species responsible of the activity of Cu–IM5 zeolites for the NO SCR reaction.

Acknowledgements

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