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Selective catalytic reduction of NO over Cu-Al-MCM-41

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Abstract

Al-MCM-41 and Cu-Al-MCM-41 were prepared by a modified hydrothermal method. The characterization using XRD, NMR, and N_2 adsorption isotherms revealed that the structure of Al-MCM-41 remained unchanged after the complete exchange of protons for copper ions. Cu-Al-MCM-41 catalysts were studied for the selective catalytic reduction (SCR) of NO by C_3H_6 in the presence of excess oxygen. Particular attention was paid to the influence of both copper content and Si/Al ratio on the nature of the active copper sites and, therefore, on the performance of the catalysts. It was observed that the most active catalyst have ~100% of copper exchange. For the underexchanged catalyst of the same copper content, it was found that the NO reduction activity decreased with decreasing Si/Al ratio. H_2-TPR and NO-TPD experiments showed that copper is mainly in the form of isolated Cu^{2+} ions in Cu-Al-MCM-41 catalysts with copper exchange $\leqslant$ 100%, whereas at higher copper loadings CuO species are also present. Moreover, when the catalyst Si/Al ratio increases copper is more easily reduced. These results are in agreement with the view accepted in the field of Cu-zeolite catalysts that the isolated Cu^{2+} ions are involved in the SCR of NO by propylene.

Keywords: Cu-Al-MCM-41 catalyst; Nitric oxide; Selective catalytic reduction; Copper content; Si/Al ratio

1. Introduction

Lean-burn gasoline and diesel engines are of high fuel efficiency and the application of this technology can therefore reduce the amount of CO_2 emission. However, due to the engine operation at a high air to fuel (A/F) ratio, excess oxygen exists in the exhaust gas and thus, the removal of NO_x becomes difficult [1]. The selective catalytic reduction of NO_x by hydrocarbons (HC-SCR) in the presence of excess oxygen has been recognized as a most challenging technology. Ever since Iwamoto et al. [2] reported that transition-metal ion-exchanged zeolites, in particular Cu-ZSM-5, showed high HC-SCR activity, the copper-containing zeolite catalysts have been comprehensively investigated [3–7]. Copper-exchanged ZSM-5, mordenite and ferrite were found active, whereas zeolites X and Y were shown to be poor supports [2,3]. This indicated that the zeolite framework composition played an important role for the copper ion-exchanged zeolites in the SCR reaction. Considering the similarities between MCM-41 and zeolites [8,9], it is worth exploring its properties as a support for Cu-based deNO_x catalysts. Intensive studies have however not yet been reported [4].

The catalytic activity of Cu-exchanged zeolites for NO conversion to N_2 is known to depend on the amount of copper as well as on the aluminum content of the host zeolite [5–7]. For the different zeolite framework, the copper content and Si/Al ratio have different effects on the catalytic activity. On Cu-MOR catalysts, the catalytic activity increases with the increment of the exchange level, while it is almost independent of copper content in Cu-FAU [6,7]. Additionally, the nature and role of copper have been widely discussed [10,11]. Under reaction conditions it has been shown

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that copper exhibits dynamic interconversion between +1 and +2 oxidation states [12,13] and that copper is present as isolated ions or small oxide clusters [7,13]. Therefore, the effects of Si/Al ratio and copper loading on the performance of Cu-Al-MCM-41 catalysts deserve attention. Moreover, the nature of copper in Cu-Al-MCM-41 requires further specification.

The present contribution reports a study of NO SCR with propylene under lean-burn conditions over Cu-exchanged Al-MCM-41 catalysts and of the nature of the copper species present in these catalysts. Particular attention is paid to the influence of both copper-exchange level and Si/Al ratio on the nature of the active copper sites and, therefore, on the performance of the catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

The Al-MCM-41 samples were synthesized according to the procedure given in the literature [14]. An aqueous solution of tetramethylammonium hydroxide (TMAOH, 25%, Shanghai Chemical Reagent Co. (SHCR)) was well mixed with tetraethyl orthosilicate (TEOS, 98%, SHCR) to form mixture A. Sodium aluminate ($NaAlO_2$, 41 wt% Na_2O, 54 wt% Al_2O_3, SHCR) was added to a clear aqueous solution composed of *n*-tetradecyltrimethylammonium bromide (CTMABr, 99%, SHCR), *n*-tetradecyltrimethylammonium hydroxide (CTMAOH), and NaOH (98%, SHCR) under stirring to form mixture B. CTMAOH was obtained by the ion exchange of CTMABr in a column packed with anion-exchange resin. Mixture B was added to mixture A under stirring. After 30 min, a certain amount of deionized water was added and stirring was continued for 10 min further until the pH value of the reaction mixture remained constant. A gel of the following molar composition was obtained,

$$1SiO_2 : xAl_2O_3 : 0.23CTMA^+ : 0.15Na_2O \\ : 0.089TMAOH : 125H_2O,$$

where x could be regulated by controlling the ratio of TEOS to $NaAlO_2$. The gel was thereafter transferred into an autoclave with a polytetrafluoroethylene (PTFE) lining and subjected to hydrothermal treatment under autogenous pressure at 110 °C, for a period of 72 h. After the solution was filtered, the solid was washed, dried, and calcined at 540 °C for 10 h in a flow of air. The obtained samples exhibited an ordered structure of pore arrays. All Al atoms were incorporated tetrahedrally in the MCM-41 structure after calcination. Moreover, the samples showed a higher thermal and hydrothermal stability. A high order of mesoporous structure was kept after aging at 700 °C in dry air whereas a fair mesoporous structure was maintained after treatment in wet air (10% H_2O) at the same temperature.

The copper-containing catalysts were prepared by ion exchange of Al-MCM-41 with an aqueous solution of copper (II) acetate, of appropriate concentration, at room temperature under continuous stirring. The above process was repeated several times, each time being carried out for 24 h. After the exchange, the catalysts were filtered, washed thoroughly with deionized water, dried at 120 °C, and heated at 540 °C for 4 h. The catalysts were analyzed using atomic absorption spectroscopy, the whole rock fusion, and inductively coupled plasma (ICP) methods to determine the copper content and Si/Al ratio. The extent of copper-exchange level was calculated assuming that one divalent copper ion can be exchanged for two protons or sodium ions. The specifications of the catalysts calculated using the results of the analysis are given in Table 1. For example, Cu-Al-MCM-41-10-93 stands for a Cu ion-exchanged Al-MCM-41 catalyst with an initial Si/Al ratio of 10 and Cu ion-exchanged level of 93%.

Table 1
Textural characteristics of Al-MCM-41 and Cu-Al-MCM-41 catalysts

Catalyst	Si/Al	S_{BET} (m^2/g)	Pore size (nm)	Mesopore volume (ml/g)
Al-MCM-41-100	100	1080	3.7	0.92
Al-MCM-41-30	30	1050	3.6	0.92
Al-MCM-41-10	10	984	3.4	0.81
Al-MCM-41-3	3	873	3.2	0.76
Cu-Al-MCM-41-10-31	10	962	3.3	0.79
Cu-Al-MCM-41-10-61	10	846	3.1	0.69
Cu-Al-MCM-41-10-93	10	842	3.1	0.67
Cu-Al-MCM-41-10-120	10	728	2.9	0.61

The catalysts used in this study were characterized using X-ray powder diffraction, N_2 adsorption isotherm measurements, and ^{27}Al MAS NMR techniques. The X-ray powder diffraction pattern was carried out on a Rigaku D/Max-RB diffractometer with Cu$K\alpha$ radiation. The samples were loaded on a sample holder with a depth of 1 mm. N_2 adsorption isotherm was measured at −196 °C using a ST-03A analyzer. The catalysts were outgassed at 300 °C overnight before measurement. The catalyst pore size distribution was calculated using the Dollimore-Heal formula. The specific surface area (S_{BET}) of samples was determined from the linear part of BET plot ($p/p_0 = 0.05$–0.25). ^{27}Al MAS NMR spectra were recorded at 104.26 MHz using a Brucker AMX-400 spectrometer. The catalysts were equilibrated under the saturated water vapor of an NH_4Cl solution before packing into NMR-MAS rotors. Chemical shifts were referred to external $Al(H_2O)_6^{3+}$ in $AlCl_3$ aqueous solution.

2.2. Temperature-programmed reduction and desorption

The catalyst reducibility was characterized by temperature-programmed reduction (TPR) analysis. A U-shaped quartz cell of 6 mm o.d., 4 mm i.d. was used as the sample chamber. The temperature-programmed reduction experiments were performed with H_2 as the reducing agent. Prior to TPR experiment, the catalyst was heated in situ under flowing He (50 ml/min) at 500 °C for 2 h. Reduction of the catalyst was carried out from room temperature to 700 °C in

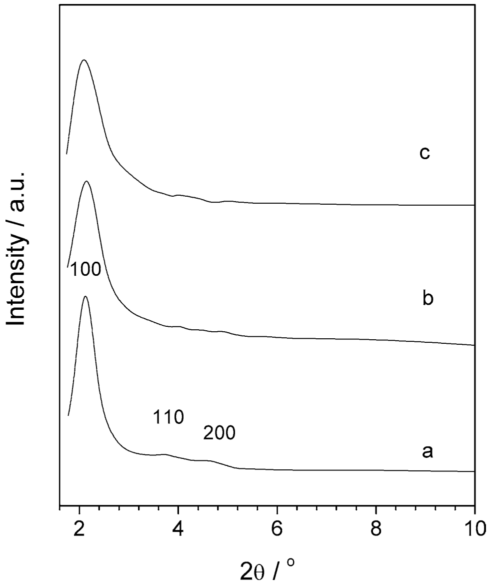

Fig. 1. X-ray diffraction pattern of Al-MCM-41 and Cu-Al-MCM-41 catalysts: (a) Al-MCM-41-10, (b) Cu-Al-MCM-41-10-31, and (c) Cu-Al-MCM-41-10-93.

a flow of 5% H_2/N_2 (30 ml/min) at 10 °C/min. The consumption of H_2 was monitored continuously using a thermal conductivity detector. The water produced during the reduction was trapped in a 5 A molecular sieve column.

Prior to the TPD measurements, the catalysts (about 500 mg) were pretreated in a way similar to that described for TPR experiments. The adsorption of NO was performed at room temperature by flowing 50 ml/min of NO (0.8 vol%)/He for 2 h. The catalyst was then flushed with helium (50 ml/min) at room temperature to remove all the physically adsorbed species. The TPD experiments were then carried out from room temperature to 700 °C, at 10 °C/min, under He flow. The gases desorbing from the catalysts were analyzed using a chemiluminescence gas analyzer (ML9841AS, Monitor Labs, Inc.).

2.3. Evaluation of catalytic activity

The reduction reaction was carried out in a fixed-bed flow reactor (a 10-mm diameter by 270-mm-long quartz tube). The reactor was heated externally in an electrical furnace and the temperature of the catalyst bed was controlled to within 1 °C. For each measurement 0.1 g of catalyst with 60–80 mesh was used. The feed gas containing 0.1 vol% NO, 0.1 vol% C_3H_6, 2 vol% O_2, and balanced with highly pure helium was fed into the reactor at a total flow of 500 ml/min. The GHSV was 100,000 h^{-1}. The concentrations of NO and NO_x in the feed and effluent were monitored continuously using the chemiluminescence gas analyzer. Two parallel-arranged gas chromatographs (one with a FID detector and a GDX-403 column and one with a TCD detector and a 5 A molecular sieve column) were used to analyze the concentrations of C_3H_6, CO, CO_2, O_2, and N_2 in the reaction gas stream.

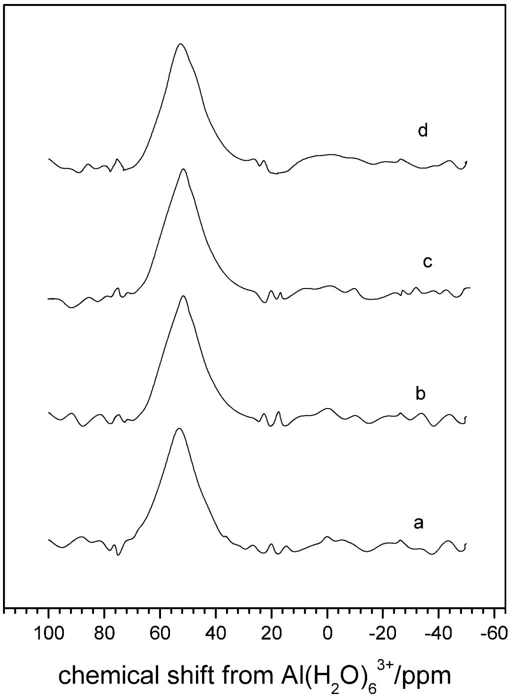

Fig. 2. NMR spectra of Al-MCM-41 and Cu-Al-MCM-41 catalysts: (a) Al-MCM-41-10, (b) Cu-Al-MCM-41-10-31, (c) Cu-Al-MCM-41-10-63, and (d) Cu-Al-MCM-41-10-93.

3. Results

3.1. Catalyst characterization

The XRD patterns of Al-MCM-41-10 and copper-exchanged Al-MCM-41 samples (Cu-Al-MCM-41-10-31 and Cu-Al-MCM-41-10-93) are depicted in Fig. 1. They are similar to those reported in the literature for MCM-41 [15]. Table 1 lists the BET surface area, pore size, and mesopore volume for Al-MCM-41 and Cu-Al-MCM-41-10 catalysts. The specific surface area and pore diameter of the catalysts were higher are 700 m^2/g and about 3.0 nm, respectively. Solid-state ^{27}Al MAS-NMR investigation (Fig. 2) shows further that the Al atoms were in tetrahedral coordination [16]. The results indicated that the uniformly arranged mesoporous framework of MCM-41 could still remain even after it has gone through the process of ion exchange, drying, and high-temperature calcination.

3.2. Catalytic performance

3.2.1. Effect of copper content

The reduction of NO by C_3H_6 in the presence of oxygen was first conducted over the nonexchanged Al-MCM-41 sample with a Si/Al ratio of 10. Despite a C_3H_6 oxidation conversion of about 80%, the concentration of NO does not change over the temperature range up to 550 °C, indicating that Al-MCM-41 itself is inactive for SCR of NO. However, with copper-exchanged Al-MCM-41, a significant NO conversion is reached.

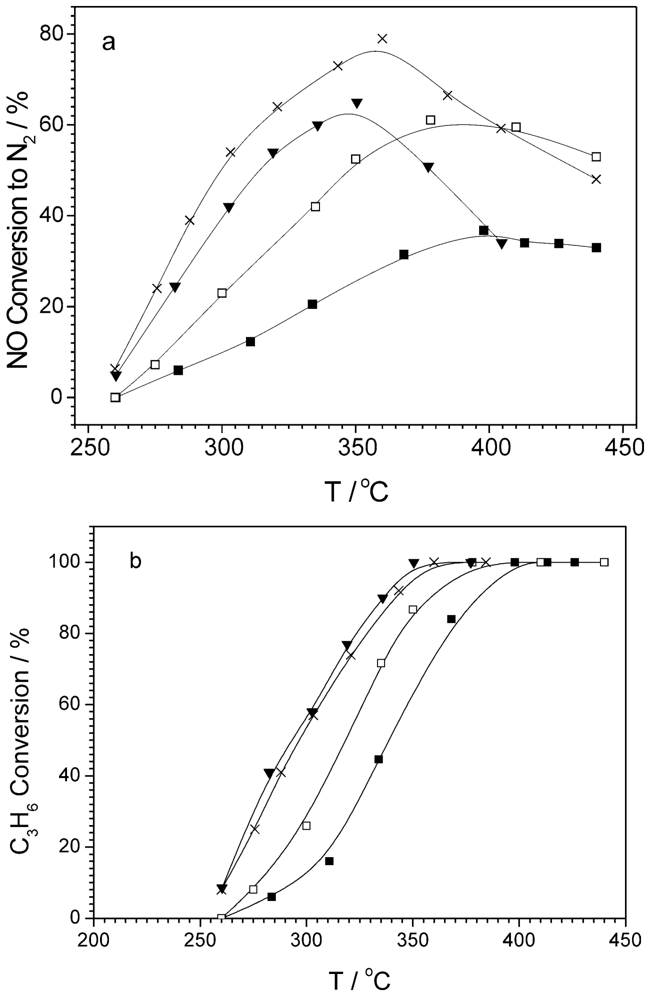

Fig. 3. Catalytic performance of Cu-MCM-41 catalysts with Si/Al = 10 and different copper contents for C_3H_6-SCR reaction: (■) Cu-Al-MCM-41-10-31, (□) Cu-Al-MCM-41-10-61, (×) Cu-Al-MCM-41-10-93, and (▼) Cu-Al-MCM-41-10-120 (reaction conditions: GHSV = 100,000 h^{-1}, 0.1 vol% NO, 0.1 vol% C_3H_6, 2 vol% O_2).

Fig. 3a shows the variation of NO conversion for four Cu-Al-MCM-41 catalysts with a Si/Al ratio of 10 but different copper loadings ($0.85 \leqslant Cu \leqslant 3.2$ wt%). As the copper loading in the catalyst increased from 0.85 to 2.45 wt%, the maximum conversion in NO increased remarkably from 36 to 79%, and the corresponding temperature decreased from 395 to 360 °C. Nevertheless, further introduction of copper decreased the NO reduction. N_2 is the only product at temperatures below the maximum conversion. Some NO_2 (yield no more than 2%) was also observed at higher temperatures. A different behavior is observed in the conversion of C_3H_6. Fig. 3b indeed shows that the reaction temperature required for a given conversion of C_3H_6 steadily decreases with an increase in copper loading.

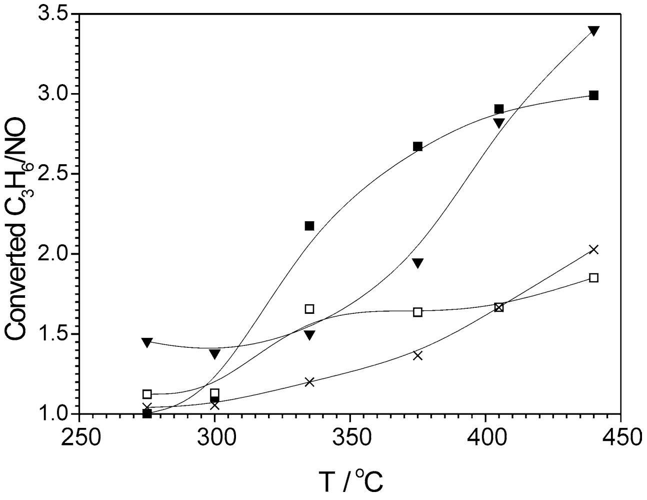

Fig. 4. The ratio of converted C_3H_6/converted NO as a function of temperature: (■) Cu-Al-MCM-41-10-31, (□) Cu-Al-MCM-41-10-61, (×) Cu-Al-MCM-41-10-93, and (▼) Cu-Al-MCM-41-10-120 (reaction conditions: GHSV = 100,000 h^{-1}, 0.1 vol% NO, 0.1 vol% C_3H_6, 2 vol% O_2).

Fig. 4 shows the curves of converted C_3H_6/converted NO as a function of temperature. For the catalysts with copper exchange lower than 100%, the ratio of the conversions for the two reactants is close to 1 at lower temperatures. This ratio increases at higher temperatures. At lower temperatures, N_2 is the only product of NO reduction, but as noted above some NO_2 was observed at higher temperatures. This behavior indicates that there are three reaction stages during the C_3H_6-SCR. At lower temperatures, the 1/1 stoichiometric ratio indicates that NO reduction and C_3H_6 oxidation are successive reactions of the same intermediate adsorbed species over Cu-exchanged catalyst. Some parallel C_3H_6 oxidation occurs under these conditions when overexchanged oxidic copper is also present. As temperature is increased competing propylene oxidation occurs, parallel to NO reduction. At still higher temperature propylene deep oxidation predominates and NO reduction is inhibited due to the corresponding depletion of the reducing agent. This reduced NO conversion rate leads to the observed maximum in NO conversion (Fig. 3a) and seems to be associated with the appearance of NO_2.

In order to investigate whether the effect of the copper content on NO SCR is dependent on the Al-MCM-41 Si/Al ratio, catalytic tests were carried out on another series of catalysts with Si/Al = 30 and different copper contents ($0.22 \leqslant Cu \leqslant 1.1$ wt%). Fig. 5 shows the catalytic results as a function of temperature. The same dependence on the copper content existed in the conversion of C_3H_6 as for the catalysts with Si/Al = 10. The increase in copper content resulted in a steady increase in C_3H_6 conversion at constant reaction temperature. Moreover, the catalyst with copper content close to the exchange capacity was the most active for NO reduction. There still exist three steps in NO conversion. Table 2 lists the maximal NO conversion and corresponding temperature over Cu-Al-MCM-41. The maximal NO conversion appeared at different copper loadings, i.e., 2.45 wt% vs 0.85 wt%, corresponding to 100% exchanged level. This was in contrast to the results shown for Cu-ZSM-5 by Kharas et al. [17], who reported that the most active catalyst for reduction of NO using propene had ion-exchange levels between 150 and 200. However, this result was obtained on the

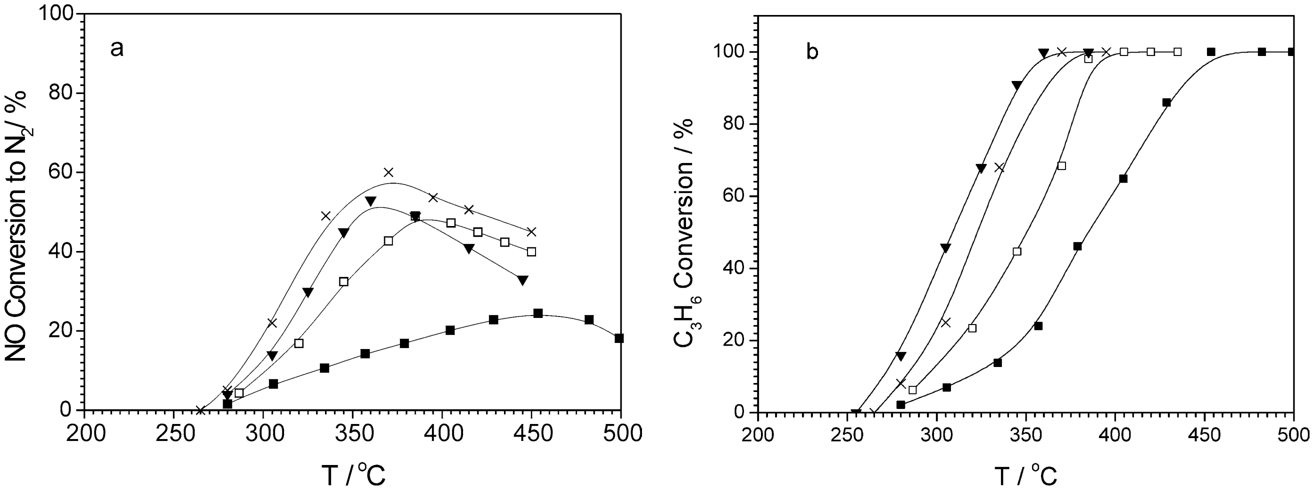

Fig. 5. Catalytic performance of Cu-MCM-41 with different copper contents for C_3H_6-SCR reaction with Si/Al = 30: (■) Cu-Al-MCM-41-30-25, (□) Cu-Al-MCM-41-30-60, (×) Cu-Al-MCM-41-30-97, and (▼) Cu-Al-MCM-41-30-12 (reaction conditions: GHSV = 100,000 h^{-1}, 0.1 vol% NO, 0.1 vol% C_3H_6, 2 vol% O_2).

Table 2
Effect of exchange of copper on C_3H_6-SCR reaction over Cu-Al-MCM-41

Catalyst	Si/Al	Cu content (wt%)	Cu exchanged level[a] (%)	NO conversion[b]	
				X_{max} (%)	T_{max} (°C)
Cu-Al-MCM-41-10-31	10	0.85	31	36	395
Cu-Al-MCM-41-10-61	10	1.6	61	61	380
Cu-Al-MCM-41-10-93	10	2.45	93	79	360
Cu-Al-MCM-41-10-120	10	3.2	120	65	350
Cu-Al-MCM-41-30-25	30	0.22	25	24	455
Cu-Al-MCM-41-30-60	30	0.52	60	49	385
Cu-Al-MCM-41-30-97	30	0.85	97	60	370
Cu-Al-MCM-41-30-127	30	1.1	127	53	360
Cu-Al-MCM-41-100-322	100	0.85	322	28	356
Cu-Al-MCM-41-3-9	3	0.85	9	26	480

[a] The % of exchange is calculated as 2(n(Cu)/n(Al)) × 100 %.
[b] Reaction conditions: GHSV = 100,000 h^{-1}, 0.1 vol% NO, 0.1 vol% C_3H_6, 2 vol% O_2.

basis of only five catalysts with a comparatively wide range of 60 to 500%. In addition, it was reported that the most active Cu-MFI catalysts for selective reduction of NO_x were with exchange levels between 80 and 100%, which coincides with the present results [6,18].

Both Cu-Al-MCM-41-10-120 and Cu-Al-MCM-41-30-127 catalysts showed a lower NO conversion but a higher C_3H_6 conversion at low temperatures than Cu-Al-MCM-41-10-93 and Cu-Al-MCM-41-30-97, respectively, suggesting again the participation of non-ionic copper species in propylene oxidation.

3.2.2. *Effect of Si/Al ratio*

To analyze the effect of Si/Al ratio in Al-MCM-41 on NO SCR, four catalysts with approximately the same copper content of 0.85 wt% and different Si/Al ratios ($3 \leqslant$ Si/Al $\leqslant 100$) were prepared. The catalytic behavior of these samples as a function of temperature is illustrated in Fig. 6. Comparing the underexchanged catalysts with Si/Al ratio from 3 to 30 shows the Si/Al ratio of 30 yielded the highest NO conversion, this effect being more pronounced at 370 °C. However, when the Si/Al ratio increased to 100, the catalyst exhibited a higher NO conversion at low temperatures but a lower conversion at high temperatures than the catalyst with Si/Al = 30. Cu-Al-MCM-41-100-322 was clearly overexchanged and the complete oxidation of propylene over this catalyst above 360 °C inhibited the reduction of nitric oxide. These results show a trend similar to that reported by Torre-Abreu et al. over Cu-ZSM-5 [6]. These authors reported that a catalyst with a Si/Al ratio of 27 was the most active among catalysts having the same copper loading and Si/Al ratios of 11, 27, 50, and 100.

3.2.3. *Preliminary study of the effect of water vapor*

Since water was shown to be a poison for Cu-ZSM-5, it is especially important to examine the effect of water vapor on the activity of Cu-Al-MCM-41 in NO SCR. A full study is currently undertaken in our laboratory and only some preliminary results are reported here as Figs. 7 and 8.

The results reported in Fig. 7 were obtained for NO and C_3H_6 conversions over Cu-Al-MCM-41-10-61 both with a dry feed and in the presence of 10% of H_2O in the feed

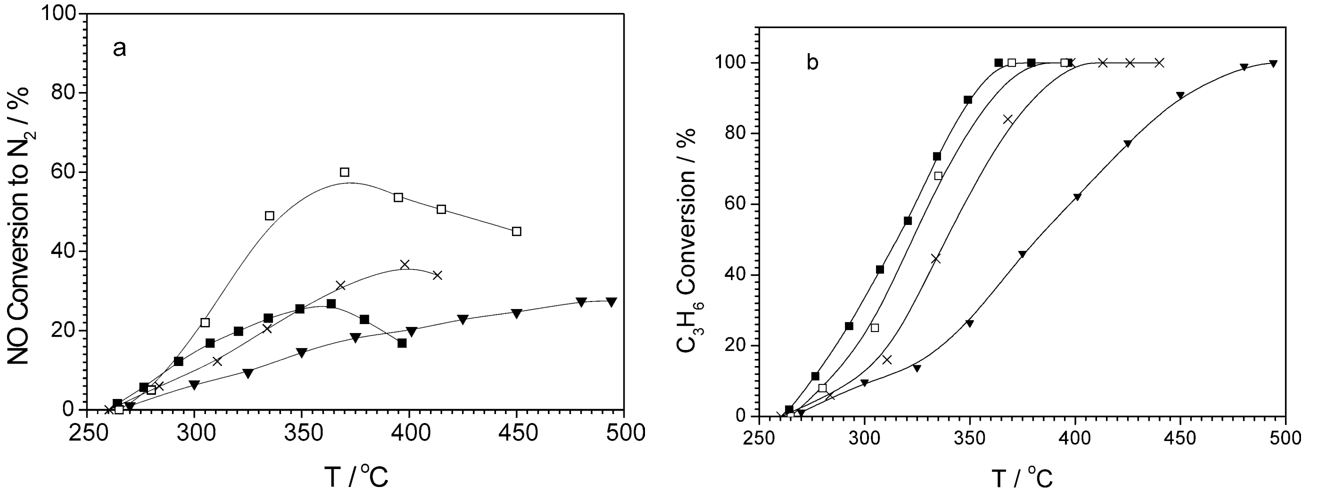

Fig. 6. Catalytic performance of Cu-MCM-41 catalysts with different Si/Al ratios for C_3H_6-SCR reaction: (■) Cu-Al-MCM-41-100-322, (□) Cu-Al-MCM-41-30-97, (×) Cu-Al-MCM-41-10-31, and (▼) Cu-Al-MCM-41-3-9 (reaction conditions: GHSV = 100,000 h^{-1}, 0.1 vol% NO, 0.1 vol% C_3H_6, 2 vol% O_2).

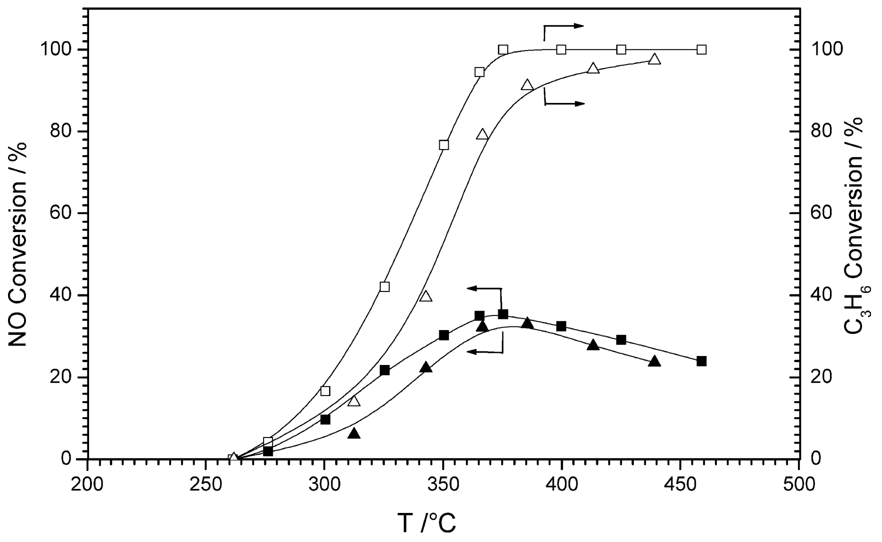

Fig. 7. Effect of 10% H_2O on the selective reduction of NO over Cu-Al-MCM-41-10-61 (■□, NO and C_3H_6 conversion under dry condition; ▲△, NO and C_3H_6 conversion under wet condition; ■▲, NO conversion; □△, C_3H_6 conversion) (reaction conditions: GHSV = 200,000 h^{-1}, 0.1 vol% NO, 0.1 vol% C_3H_6, 2 vol% O_2).

gas. Only a minor decrease in catalytic activity is observed upon introduction of water vapor. The maximum NO conversion reached 37% at 370 °C with the dry feed. Introducing 10% H_2O in the feed gas decreased the maximum conversion to 34% and the corresponding peak temperature was about 380 °C.

Fig. 8 shows the dynamic effect of introducing 10% H_2O in the feed, on catalytic activity at 400 °C. The decrease in NO conversion was sensible but still not very high and by sequential suppression of the water gas feed the effect was found to be reversible.

3.3. Temperature-programmed reduction

The TPR profiles of Cu-Al-MCM-41 catalysts with the same Si/Al ratio of 10, but different copper contents ($0.85 \leqslant Cu \leqslant 3.2$ wt%) are illustrated in Fig. 9. For the underexchanged catalysts, the profiles were similar, whereas that of the overexchanged sample was different. The former showed two reduction peaks: the first one at 170–215 °C, and the second one in the range 480–570 °C, which suggests a two-step reduction process of isolated Cu^{2+} species [19]. The low-temperature peak was assigned to the reduction of isolated Cu^{2+} to Cu^{+} ions. The peak at a higher temperature was attributed to the reduction of Cu^{+} ion to Cu^{0}, as was done for Cu-ZSM-5 [19]. Since the CuO aggregates would be reduced to Cu^{0} by H_2 in one step at about 350 °C [19], the peak at 348 °C in Cu-Al-MCM-41-10-120 indicated the presence of CuO in this sample. It is suggested that copper in underexchanged catalysts was mainly in the form of isolated copper ions, while in overexchanged catalyst, there was a proportion of CuO species. Delahay et al. [20] also reported

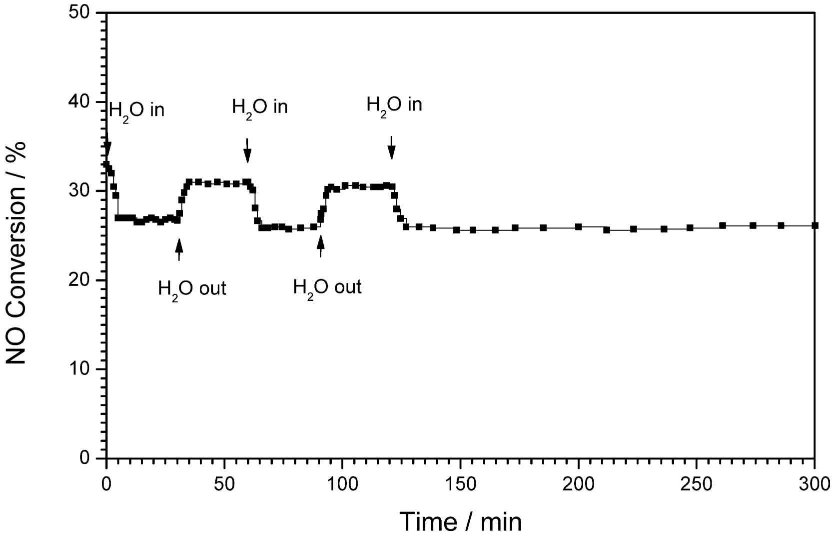

Fig. 8. Effect of water vapor on NO conversion over Cu-Al-MCM-41 at 400 °C.

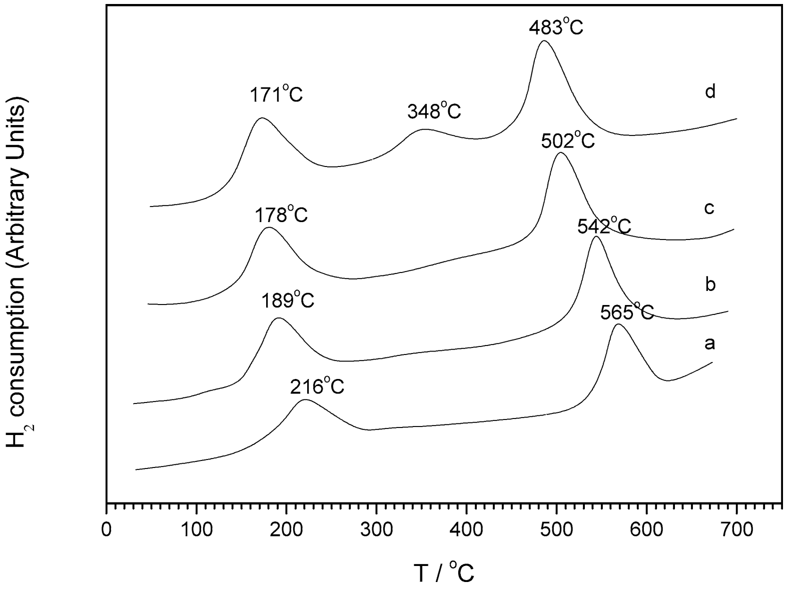

Fig. 9. H_2-TPR profiles of Cu-Al-MCM-41 samples with Si/Al = 10: (a) Cu-Al-MCM-41-10-31, (b) Cu-Al-MCM-41-10-61, (c) Cu-Al-MCM-41-10-93, and (d) Cu-Al-MCM-41-10-120.

that copper was mainly present as isolated Cu^{2+} species in underexchanged Cu-Beta and Cu-MFI zeolites.

A similar dependence was found in catalysts with different copper contents ($0.22 \leqslant Cu \leqslant 1.1$ wt%) of Si/Al = 30 (see Fig. 10). Isolated copper ions were the main species in catalysts of a copper-exchanged level lower than 100%, while CuO occurred in the catalyst with 127% copper exchange.

Fig. 11 shows the TPR profiles of Cu-Al-MCM-41 catalysts with the same copper contents of 0.85 wt% but different Si/Al ratio from 3 to 100; the respective temperatures and H_2/Cu ratios are given in Table 3. It was also observed that there existed CuO species in the overexchanged catalyst Cu-Al-MCM-41-100-322, while only copper ions were detected in the underexchanged catalysts. Comparing the H_2/Cu ratios of the two reduction peaks, we observed that in catalyst Cu-Al-MCM-41-3-9, copper was mainly present as Cu^{2+} ion, since the areas of the two peaks were very close. Increasing the Si/Al ratio led to a decrease of the H_2/Cu ratio for the first peak and an increase for the second. This phenomenon could be accounted for as the result of partial reduction of Cu^{2+} to Cu^{+} during the course of catalyst preparation (calcinations at 540 °C) or pretreatment at 500 °C in a flow of He [4]. It is indicated that lowering the Si/Al ratio enhanced the reduction of isolated Cu^{2+} ions.

The peaks maxima in Figs. 9–11 appeared at a lower temperature as the catalyst copper-exchanged level and Si/Al ratio increased. It is suggested that the Cu^{2+} and Cu^{+} ions were more easily reduced, which is likely due to a decrease of the electrostatic interaction between copper ions and zeo-

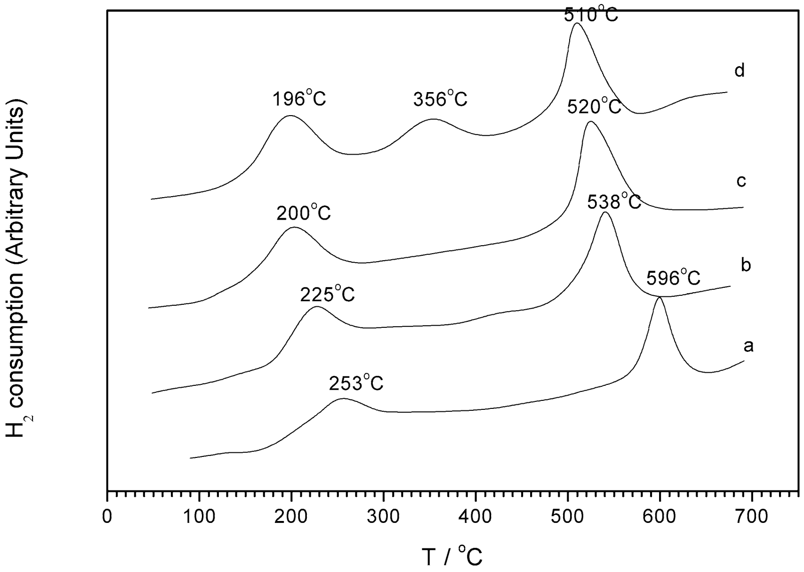

Fig. 10. H_2-TPR profiles of the catalyst samples with Si/Al = 30: (a) Cu-Al-MCM-41-30-25, (b) Cu-Al-MCM-41-30-60, (c) Cu-Al-MCM-41-30-97, and (d) Cu-Al-MCM-41-30-127.

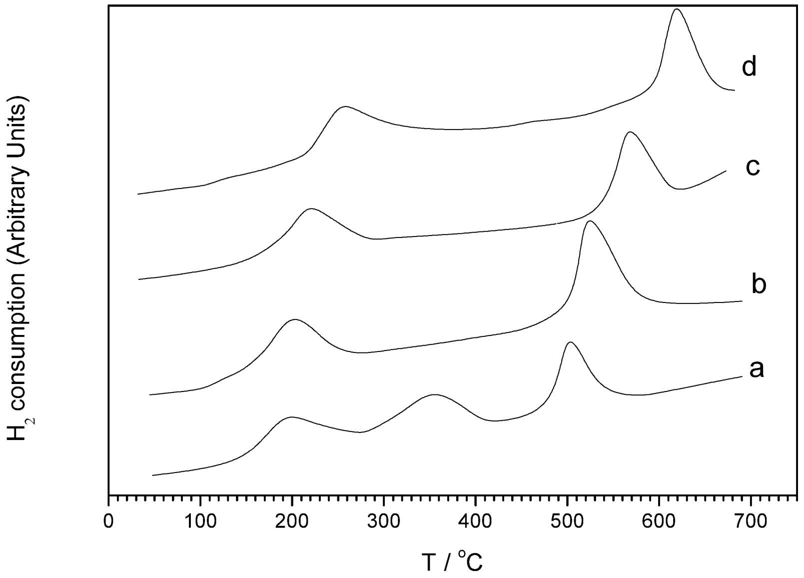

Fig. 11. H_2-TPR profiles of Cu-Al-MCM-41 with 0.85 wt% Cu and various Si/Al ratios: (a) Cu-Al-MCM-41-100-322, (b) Cu-Al-MCM-41-30-97, (c) Cu-Al-MCM-41-10-31, and (d) Cu-Al-MCM-41-3-9.

Table 3
Peak temperature and area in the TPR profiles underexchanged Cu-Al-MCM-41 with 0.85 wt% Cu

Sample	Si/Al	Temperature of peak maximum (°C)		H_2/Cu(TPR) (mol/mol)	
		First	Second	First	Second
Cu-Al-MCM-41-3-9	3	260	630	0.47	0.51
Cu-Al-MCM-41-10-31	10	220	570	0.42	0.53
Cu-Al-MCM-41-30-97	30	195	517	0.38	0.56

lite framework as the content of copper ions increased and Al content decreased. A similar behavior with however less significant temperature changes was observed for Cu-MFI catalysts [21]. The decrease in reduction temperature of Cu^{2+} and Cu^{+} upon increasing the Cu-exchange loading is likely associated with a distribution of the strength of electrostatic interactions, the stronger sites attracting first the Cu ions at lower Cu loading. A broader distribution is certainly to be expected in Al-MCM-41 than in zeolites. The similar effect of an increased Al content on reduction temperatures is in line with the well-documented increase in lattice basicity for zeolites with lower Si/Al ratios. It was also verified that the CuO concentration depends on the zeolite Si/Al ratio and copper content; however, its reduction temperature is almost independent of these parameters. This may be due to CuO species not strongly interacting with the zeolite framework.

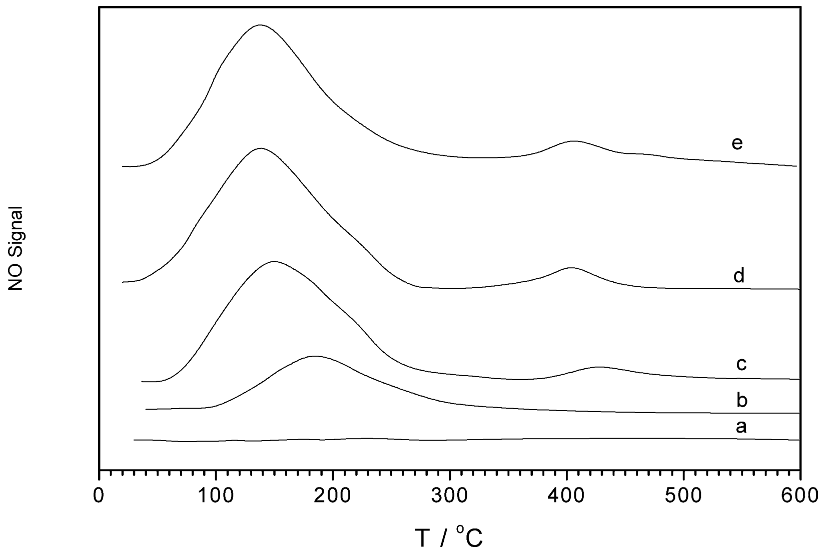

Fig. 12. TPD profiles of NO adsorbed on Al-MCM-41 and Cu-Al-MCM-41: (a) Al-MCM-41-10, (b) Cu-Al-MCM-41-10-31, (c) Cu-Al-MCM-41-10-61, (d) Cu-Al-MCM-41-10-93, and (e) Cu-Al-MCM-41-10-120.

Table 4
Characteristics of NO-TPD of Cu-Al-MCM-41 with Si/Al ratio of 10

Sample	NO desorption[a] (μmol g^{-1})	NO desorption[a] (μmol μmol Cu^{-1})	$A_L/A_L + A_H$[b]
Cu-Al-MCM-41-10-31	14.2	0.106	1
Cu-Al-MCM-41-10-61	34.8	0.138	0.95
Cu-Al-MCM-41-10-93	40.6	0.108	0.9
Cu-Al-MCM-41-10-120	41.8	0.083	0.9

[a] Based on the peak area at low temperature.
[b] A_L: peak area at low temperature; A_H: peak area at high temperature.

3.4. NO temperature-programmed desorption (TPD)

The TPD profiles of Cu-Al-MCM-41 catalysts with Si/Al = 10 but different copper contents ($0 \leqslant \text{Cu} \leqslant 3.2$ wt%) are depicted in Fig. 12. The corresponding desorption data are shown in Table 4. The copper-free sample, Al-MCM-41-10, desorbed trace amounts of NO in comparison with the copper-containing samples. This suggests that copper was the adsorption center for nitric oxide. With the exception of the sample having 31% exchange, the NO desorption curves had the same shape. Two NO adsorption peaks were detected at about 150 and 410 °C. In agreement with the literature [7], the low-temperature peak was ascribed to the desorption of NO from Cu^{2+} ions, while the second peak was associated with the decomposition of nitrate (NO_3^-), nitrite (NO_2^-), or NO_2^+ adsorbed species. At low exchange levels, the amount of desorbed species at high temperature may be too small to detect.

Assuming that the sensitivity factor is the same for the peaks at low and high temperatures, their areas could be used to estimate a normalized desorption of NO and the effect of copper content and Si/Al ratio on NO desorption. As listed in Table 4, the ratio of the amount of desorbed NO at low temperature to the total amount was close to 1. Combined with the TPR results, this feature indicates that copper mainly exists as isolated Cu^{2+} in these catalysts.

The total amount of NO desorbed increased with the copper-exchanged level up to 100% and then tended to a plateau. This fact may be related to the concentration of copper sites for NO adsorption no more increasing after the exchange saturation. Nevertheless, Coq et al. [7] reported a sharp decrease of the accessibility of copper sites to NO upon formation of copper oxide in Cu-MOR catalysts due to the blocking of the mordenite channels by CuO species. Since the pore channel of Al-MCM-41 is much larger than in mordenite, we believe that the small amount of CuO aggregates would not clog the mesopore and, therefore, had little effect on NO adsorption.

Fig. 13 shows the NO TPD profiles of Cu-Al-MCM-41 catalysts with 0.85 wt% of copper content but different Si/Al ratios ($3 \leqslant \text{Si/Al} \leqslant 100$); the respective desorption data are presented in Table 5. Only one NO desorption peak is observed at around 190 °C for samples with low Si/Al ratios. On the contrary, the other samples with a higher Si/Al ratio present two peaks: a principal peak at low temperatures (about 140 °C) and a second NO desorption peak at higher temperatures (440 °C), which are related to the desorption of Cu^{2+}–NO, and NO_3^-, NO_2^- or NO_2^+ species, respectively. It is clear that increasing the Si/Al ratio in the underexchanged

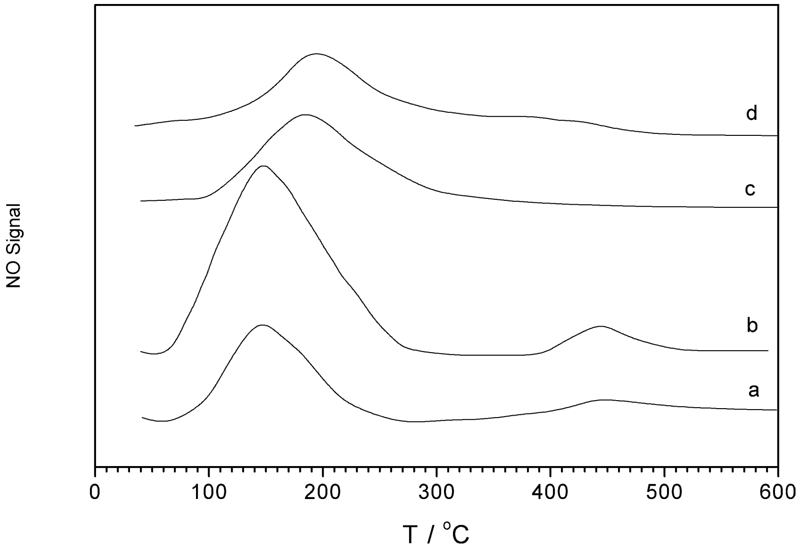

Fig. 13. TPD profiles of NO adsorbed on Cu-Al-MCM-41 with similar copper contents but different Si/Al ratios: (a) Cu-Al-MCM-41-100-322, (b) Cu-Al-MCM-41-30-97, (c) Cu-Al-MCM-41-10-31, and (d) Cu-Al-MCM-41-3-9.

Table 5
Amount of NO desorbed from Cu-Al-MCM-41 with different Si/Al ratio

Sample	Cu exchanged (%)	NO desorption[a] (μmol g^{-1})	$A_L/A_L + A_H$[b]
Cu-Al-MCM-41-100-322	322	14.6	0.98
Cu-Al-MCM-41-30-97	97	33.2	0.9
Cu-Al-MCM-41-10-31	31	14.2	1
Cu-Al-MCM-41-3-9	9	8.4	1

[a] Based on the peak area at low temperatures.

[b] A_L: peak area at low temperature; A_H: peak area at high temperature.

catalysts enhanced the NO adsorption, which indicated further that the interaction of copper ions and Al atoms in the framework was affected by the Si/Al ratio. The oxidic phase may also cover part of the cationic sites in the overexchanged catalysts.

Since the SCR of NO is going on at temperatures exceeding 250 °C it is likely that the low-temperature adsorbed NO will not be stable under reaction conditions. This would mean that one of the NO_x species that contribute to the high-temperature desorption peak is involved in the SCR surface process. Thus a very small fraction of the Cu ions would constitute the SCR active sites most of the other Cu atoms being spectator species.

4. Discussion

The characterization using XRD, NMR, and N_2 isothermal adsorption revealed that the structure of Al-MCM-41 remained unchanged after the exchange of copper ion. Since Al-MCM-41 was proved to be inactive for the reduction of NO and low active for the oxidation of propylene, the copper ions exchanged to Al-MCM-41 should provide the active centers for both the SCR of NO and the oxidation of propylene.

In the present study, we investigated the effect of copper content and Si/Al ratio on the catalytic activity of Cu-Al-MCM-41 catalysts for NO SCR by propylene. The results demonstrated that not all copper sites present in Al-MCM-41 catalysts were equal in activity for NO SCR, since the catalysts with the same Si/Al ratio but different copper contents or the same copper content but different Si/Al ratio exhibited different catalytic activities for NO and propylene conversions. The catalyst with the highest amount of copper was not the most active. Furthermore, our results indicated that the activity for NO conversion into N_2 was related to the ability of the catalyst for propylene oxidation to carbon dioxide. Kintaichi et al. [22] also observed that the NO selective reduction is closely related to the extent of hydrocarbon oxidation.

TPR and NO TPD experiments showed that the nature of copper and the relative quantity of the different copper species exchanged into Al-MCM-41 depended on the copper-exchanged level and Si/Al ratio of the catalysts.

The results revealed that copper was mainly in the form of isolated copper ions in Cu-Al-MCM-41 catalysts at a copper-exchanged level $\leqslant$ 100%, while at higher copper contents CuO species were also present. It can be concluded that the isolated copper ions are more effective for adsorption and reduction of NO than CuO species, since indeed the maximal NO conversion and adsorption amounts were obtained at the copper-exchange level of about 100%. In underexchanged catalysts, the activity of NO reduction and the amount of NO adsorption increased as the copper contents (i.e., isolated copper ions) increased. On the other hand, the CuO species in overexchanged catalysts promoted the oxidation of propylene at low temperatures and therefore, inhibited the reduction of NO. Moreover, in addition to the variation in average distance between surface Al ions, the Si/Al ratio had an effect on the electrostatic interaction between copper ions and Al-MCM-41 framework and, thus, on the activity for NO reduction.

All these results suggest that the copper ions in Cu-Al-MCM-41 behave as NO-SCR catalysts in a manner quite similar to isolated copper ions in Cu-ZSM-5. This is somewhat surprising as the Brønsted acid sites in H-ZSM-5 are much stronger acids than the ones in Al-MCM-41. The latter are indeed low acid strength amorphous materials. The Cu ions are therefore expected to be lower strength Lewis acids. Thus the Lewis acidity of the copper ions does not seem to be the dominant factor that determines the SCR active sites.

It seems also that the oxidic copper (CuO) forms only once the lattice acid sites are fully copper exchanged. This is indeed associated with the large specific surface area and large pore diameter of MCM-41 which allow an easy access of the copper ions during ion exchange.

The low and reversible deactivation by water vapor during NO-SCR is also significant for potential commercial application of these new catalysts. The results shown in Figs. 7 and 8 are indeed preliminary and more work should be performed before a valuable discussion of these effects could be made. It is however already clear that the surface chemistry of the support, its hydrophilicity, will require investigations before any definitive conclusion can be made.

5. Conclusions

The main conclusions obtained from XRD, N_2 adsorption isotherm, NMR, TPR, NO TPD, and the analysis of reactivity results can be summarized as follows:

1. The uniformly arranged mesoporous framework of Al-MCM-41 could still be well maintained after copper exchange.
2. Cu-Al-MCM-41 are active catalysts for NO selective catalytic reduction by propylene in an oxidizing atmosphere. Their activity depends on the copper-exchanged level and Si/Al ratio. At constant Si/Al ratio, this activity, as indicated by NO conversion to N_2, increases with increasing Cu ion-exchange level up to about 100% and then decreases. At constant copper content, the maximal NO conversion decreases with decreasing Si/Al ratio in the underexchanged catalysts.
3. Copper is mainly in the form of isolated Cu^{2+} ions in Cu-Al-MCM-41 catalysts with copper-exchange level $\leqslant$ 100%, whereas at higher copper-exchange CuO species are also present.
4. When the catalyst Si/Al ratio increases copper is more easily reduced.
5. The isolated copper ions play an important role in the SCR of NO by propylene in the presence of an excess of oxygen, although only a minor fraction of these ions constitutes the active SCR sites.
6. Preliminary results suggest that Cu-Al-MCM-41 catalysts of NO-SCR are only slightly deactivated by water vapor and this deactivation is reversible.

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