Influence of cocation on catalytic activity of CuMOR catalysts for NO SCR by propene. Effect of water presence

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Catalytic activity of CuMOR catalysts for NO selective catalytic reduction by propene was investigated as a function of the cocation (H, Na, Cs, Mg and Ba) present in the zeolite. It was verified that the cocation plays an important role in the CuMOR activity, its effect being more pronounced at low temperatures. Moreover, the results suggest that we can prevent the catalyst deactivation by choosing the appropriate cocation.

Keywords: NO SCR, CuMOR catalysts, cocation effect, water tolerance, catalyst deactivation

1. Introduction

Copper-exchanged zeolites have been widely studied for both decomposition and selective catalytic reduction (SCR) of nitrogen oxides present in oxygen-rich exhaust gases [1–3]. However, there are only few investigations about the influence of the co-exchange cation (cocation) on catalytic activity for NO conversion into N_2.

Regarding the NO decomposition, Kagawa et al. [4] reported that the coexistence of metal cations, such as alkaline earth and transition metal cations with copper ions in ZSM-5 zeolites, promotes the catalytic activity of copper ions at temperatures above 450°C. This promotion effect depends on the ion exchange method [4] or is due to the stabilisation of the active copper sites [5].

Concerning the NO SCR, Teraoka et al. [6] concluded that the coexistence of alkaline earth and transitional metal cations with copper ions in ZSM-5 catalysts is effective in the promotion of the maximum activity and the expansion of the active temperature range for NO reduction with ethene in presence of excess oxygen.

Cu-mordenite has not been studied as extensively as Cu-ZSM-5 catalysts, though it has also been shown to be an efficient catalyst for NO reduction by hydrocarbons [3,7,8].

Water is generally present in real exhaust gases, thus its effect on catalytic activity for NO reduction and catalyst deactivation must be taken into account.

The aim of this work is to investigate the cocation effect on the catalytic performance of copper-exchanged mordenites for NO selective catalytic reduction by propene in an oxidising atmosphere. The change in the catalytic activity upon the addition of water is also examined.

2. Experimental

The starting material was NaMOR zeolite with Si/Al = 6, supplied by Norton Co. (Zeolon 900). The hydrogen form of mordenite (HMOR) was obtained by exchanging Na^+ with NH_4^+ in an aqueous solution of ammonium nitrate (10 M) at 100°C. The other forms of mordenite (CsMOR, MgMOR and BaMOR) were prepared by ion exchange of NaMOR with an aqueous solution of acetate of the corresponding cation, at 85°C. Afterwards, the catalysts were calcined under air flow (4 ℓ/h gcat.) from room temperature to 500°C (held 8 h), at 5°C/min. Then, the catalysts were ion exchanged with copper(II) acetate at room temperature, following the method described in ref. [9].

The metal contents were determined by flame emission and atomic absorption techniques. The copper exchange level was determined by 2×(moles of copper)/(moles of aluminium). In the text, the catalysts will be identified as: cocation-copper-zeolite structure-Si/Al ratio-copper exchange level, e.g., NaCuMOR-6-20. The main characteristics of the catalysts are given in table 1.

Catalytic activity was measured between 200 and 600°C in a fixed bed flow reactor at atmospheric pressure, using 0.5 g of catalyst pretreated at 550°C for 1 h under helium flow (15 ℓ/h). The reactant mixture flow (15 ℓ/h) was composed of NO (800 ppm), C_3H_6 (800 ppm), O_2 (4%) and H_2O (0–10%) diluted in He. The reactants and products were analysed by gas chromatography [9]. The catalytic activity was evaluated in terms of NO conversion into N_2 as $2\times[N_2]_{out}/[NO]_{in}$. The propene conversion into CO_2 was calculated in a similar way.

The catalysts were characterised by XRD, IR, ^{27}Al NMR, NO temperature-programmed desorption (NO-TPD) and H_2 temperature-programmed reduction (H_2-TPR). XRD patterns were recorded using a Rigaku dif-

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Table 1
Main characteristics of copper-exchanged MOR catalysts

Sample	Si/Al	Cocation content (wt%)	Cu content (wt%)	Cu/Al	Cu exchange level (%)
HCuMOR-6-20	6	–	1.0	0.1	20
NaCuMOR-6-20	6	3.6	1.0	0.1	20
CsCuMOR-6-20	6	n.a.[a]	1.0	0.1	20
MgCuMOR-6-20	6	1.2	0.8	0.1	20
BaCuMOR-6-20	6	10.2	1.0	0.1	20

[a] n.a. – not available.

fractometer employing Cu Kα radiation filtered by Ni. IR spectra were recorded on a PE 1600 FTIR equipped with a DTGS detector. ^{27}Al NMR spectra were obtained using a Brucker MSL 400 (9,4T) multinuclear spectrometer at 12 kHz. NO-TPD experiments were carried out on catalysts pretreated under He flow (50 ml/min) at 550°C for 1 h. NO adsorption was then performed at room temperature by flowing 50 ml/min of NO (1 vol%)/He (99 vol%) for 30 min. Thereafter, TPD experiments were carried out by heating the sample from room temperature to 500°C at 10°C/min under He flow. The TPR measurements were performed after pretreatment of the catalysts in a similar way to that described for TPD experiments. The reduction of the catalysts was carried out by flowing 20 ml/min of H_2 (3 vol%)/Ar (97 vol%) and raising the catalyst temperature from room temperature to 900°C at 10°C/min. Further details of the apparatus used for NO-TPD and H_2-TPR are described elsewhere [10].

3. Results and discussion

In order to analyse the effect of cocations on NO reduction by propene, experiments on several CuMOR catalysts with different cocations (H, Na, Cs, Mg and Ba), but with the same Si/Al ratio (6) and copper content (about 1 wt%) were performed. The catalytic performance of these samples is displayed in fig. 1 as a function of temperature. The results show that the activity of CuMOR catalysts depends on the cocation exchanged into the zeolite. Both the maximum catalytic activity for NO reduction and the most active temperature are influenced by the cocation. The H- and MgCuMOR-6-20 are the samples with the narrowest active temperature window, which is exhibited at higher temperatures. These two catalysts present the maximum catalytic activity for NO conversion at a restricted temperature (400°C for HCuMOR-6-20 and 450°C for MgCuMOR-6-20), whereas the other samples with Na, Cs and Ba, present the maximum catalytic activity in a range of temperature exhibiting, therefore, a wider active temperature window. The catalyst NaCuMOR-6-20 is the most active for NO reduction in almost the whole range of temperature, presenting the unique catalytic activity at quite low temperatures (200 and 250°C). Satsuma et al. [11] studied the catalytic behaviour of alkaline-exchanged mordenites in the reduction of NO by propene and attributed the catalytic activity of the NaMOR catalyst at low temperatures to the high concentration of moderately stabilised NO_3^- and/or NO_2 species in zeolite channels.

Regarding the total oxidation of propene, it tends to forming a plateau in all catalysts with almost the same value of propene conversion into CO_2. Though, the achievement of the plateau occurs at higher temperatures for the catalysts Mg- and HCuMOR-6-20.

Another interesting feature that can be observed in fig. 1 is that the cocation effect on CuMOR activity is more pronounced at low temperatures ($T < 400$°C).

Concerning the origin of the cocation effect, Tavernier et al. [12] postulated that the occupancy by copper of the different cationic sites existing in mordenite catalysts depends on the cocation. Sass et al. [13]

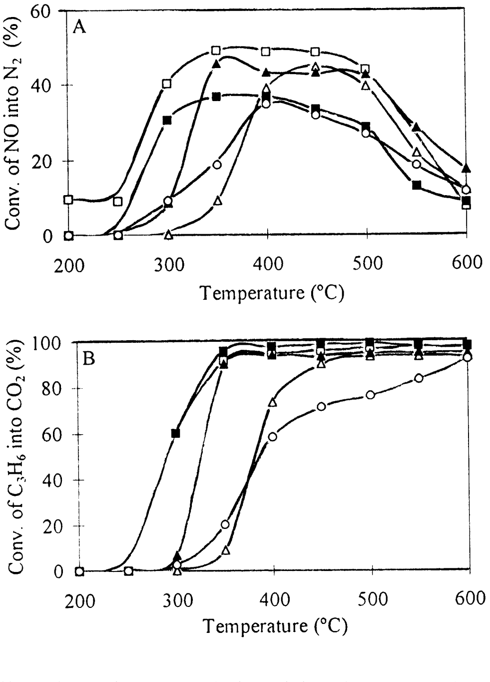

Fig. 1. Effect of cocation on catalytic activity of copper-exchanged mordenite for NO SCR by propene; [NO] = [C_3H_6] = 800 ppm, [O_2] = 4%. (○) HCuMOR-6-20, (□) NaCuMOR-6-20, (■) CsCuMOR-6-20, (△) MgCuMOR-6-20, (▲) BaCuMOR-6-20.

also proposed that the cocation influences the exchange location of Cu^{2+} in ZSM-5. Furthermore, it was suggested that on direct decomposition of NO the cocation effect results not from the direct participation of cocations in NO decomposition catalysis, but from the modification of the state, location and/or properties of copper ions, because catalysts without copper did not show any NO decomposition activity [4]. Recently, it was reported that alkaline-exchanged mordenites (catalysts free of copper) exhibit significant catalytic activity for the selective reduction of NO by propene in the presence of oxygen [11]. However, under our reaction conditions, NaMOR showed no significant activity for NO conversion (about 10% at 350°C) [10]. But, we detected by NO-TPD and H_2-TPR studies that the cocation (H, Na and Ba) mainly affects the copper location, the copper catalysts in sodium form being more easily reduced than those in acid form [10]. Hence, the effect of the cocation on CuMOR activity for NO SCR can result from the direct participation of the cocation in the catalysis or from the modification of the copper nature, or even from both.

Fig. 2 shows the NO reduction activities of H-, Na- and BaCuMOR-6-20 catalysts in the presence of water (2%). The shape of the curves was not changed by the water presence and the order of activities continues to be: Na- > Ba- > HCuMOR-6-20.

Comparing figs. 1 and 2, one can verify that the addition of 2% of water to the reactant mixture leads to an appreciable decrease in NO conversion over all samples investigated, indicating that these catalysts are very sensitive to water.

The effect of water concentration on NO SCR was studied on NaCuMOR-6-20; the results are depicted in fig. 3. Although the NO reduction is sharply decreased with addition of 2% of water, the conversion into N_2 was still around 20% in the presence of 10% of water, in the range 300–450°C. On the other hand, the propene total oxidation was not affected by water, i.e., the conversion of C_3H_6 into CO_2 remains nearly constant over all catalysts after introduction of water, regardless of the water concentration.

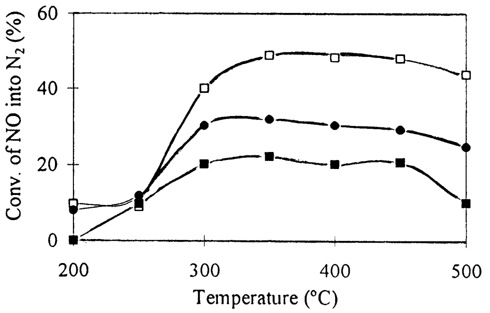

Fig. 3. Effect of water concentration on catalytic activity of NaCuMOR-6-20 for NO SCR by propene; [NO] = $[C_3H_6]$ = 800 ppm, $[O_2]$ = 4%. (□) $[H_2O]$ = 0%, (●) $[H_2O]$ = 2%, (■) $[H_2O]$ = 10%.

The cocation effect (H, Na and Ba) was further examined on the stability of CuMOR catalysts after catalytic experiments carried out in the absence and the presence of water (fig. 4). Thus, several runs (1–4) were performed at 400°C using a gas stream containing: [NO] = $[C_3H_6]$ = 800 ppm and $[O_2]$ = 4% diluted in He. Run 1 was performed on fresh catalysts; run 2 was carried out after the catalysts had been submitted to catalytic experiments without water ([NO] = $[C_3H_6]$ = 800 ppm and $[O_2]$ = 4% diluted in He), in the temperature range between 200 and 600°C, and run 3 was performed after run 2 and catalytic experiments carried out in the presence of 2% of water ([NO] = $[C_3H_6]$ = 800 ppm, $[O_2]$ = 4% and $[H_2O]$ = 2% diluted in He), in the temperature range between 200 and 600°C. From the data illustrated in fig. 4 it is possible to observe that HCuMOR-6-20 is the less stable catalyst, losing 9% of activity after a complete set of catalytic experiments performed without water (see run 2) and 21% after the set of catalytic experiments performed without and with water (see run 3). By contrast, Na- and BaCuMOR-6-20 do not suffer any deactivation when submitted to the set of experiments without water. Moreover, after the set of catalytic experiments carried out with 2% of water and upon elimination of water from the system they practically recover their original activity (run 3), exhibiting 95% of initial NO conversion. Therefore, the coexistence of 2% of water causes an irreversible deactivation on

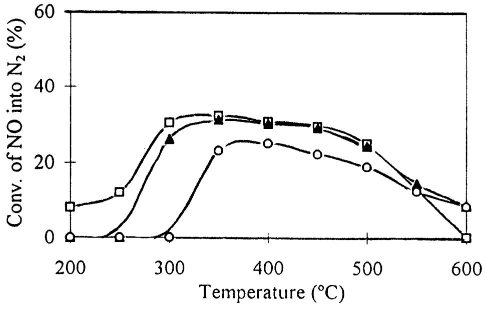

Fig. 2. Effect of cocation on catalytic activity of copper-exchanged mordenite for NO SCR by propene in presence of water; [NO] = $[C_3H_6]$ = 800 ppm, $[O_2]$ = 4%, $[H_2O]$ = 2%. (○) HCuMOR-6-20, (□) NaCuMOR-6-20, (▲) BaCuMOR-6-20.

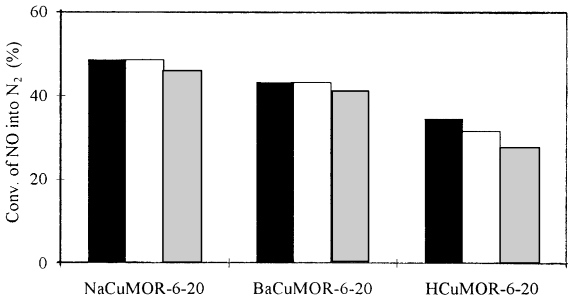

Fig. 4. Effect of cocation on stability of copper-exchanged mordenite; [NO] = $[C_3H_6]$ = 800 ppm, $[O_2]$ = 4% and T = 400°C. (■) Run 1, (□) run 2, (▨) run 3.

HCuMOR, while Na- and BaCuMOR were essentially inhibited, exhibiting reversible deactivation.

These results suggest that the catalyst deactivation can be prevented by choosing the appropriate cocation. In fact, Petunchi et al. [14] reported earlier that the deactivation of the catalyst may be prevented by designing the catalyst and choosing conditions so that formation of Brønsted acid sites is minimised. They further reported that Na-zeolites are more resistant to hydrothermal rearrangements to fairly high temperatures than H-zeolites and that CuZSM-5 catalysts tend to fall between these extremes. Our recent study about deactivation of CuMFI catalysts also revealed that these catalysts become more stable as the Brønsted acidity of the catalyst decreases [15].

For the catalyst NaCuMOR-6-20, we further performed run 4, which was carried out after run 3 and catalytic experiments performed with coexistence of 10% of water ($[NO] = [C_3H_6] = 800$ ppm, $[O_2] = 4\%$ and $[H_2O] = 10\%$ diluted in He) in the temperature range between 200 and 600°C. In run 4 only 85% of initial NO conversion was reached, which means that the NaCuMOR-6-20 suffered 15% of irreversible deactivation due to the presence of 10% of water. Nevertheless, this value is still lower than the deactivation value (21%) caused by the presence of 2% of water on HCuMOR-6-20.

Several deactivation modes have been suggested: zeolite dealumination [14]; loss of copper surface area due to sintering of active copper into inactive phases, such as CuO [16,17]; and migration of copper ions (without aggregation) to sites where gas molecules like nitrogen oxide and propene cannot reach them [18,19].

A variety of techniques were applied to check the causes of catalyst deactivation, including XRD, IR, ^{27}Al NMR, NO-TPD and H_2-TPR.

XRD patterns of CuMOR catalysts coexchanged with H, Na and Ba were recorded on fresh samples and after catalytic experiments performed with water. No loss of crystallinity of the mordenite phase was observed. Therefore, the catalytic experiments performed at temperatures $\leqslant$600°C and water concentration $\leqslant$10% do not destruct the mordenite structure.

To investigate the possibility of zeolite dealumination during NO selective reduction IR and ^{27}Al NMR spectra were recorded from catalysts before and after reaction in the absence and presence of water. The data revealed that the NO SCR experiments performed either in absence or presence of water do not cause zeolite dealumination.

Fig. 5 shows the NO-TPD profiles of the fresh and used NaCuMOR-6-20. The TPD profiles and the uptake capacity for NO of both samples are quite different. The used catalyst presents a much smaller peak at low temperature and does not exhibit the high-temperature NO desorption peak. Since the low-temperature peak was ascribed to the desorption of NO from isolated Cu^{2+} ions [10,20], the results indicate that the used sample contains a lower quantity of this copper species accessible to NO than the fresh sample. This feature seems to indicate that the catalyst deactivation was due to a modification in copper species. In fact, Yan et al. [21] concluded from their EPR results that the deactivation of the catalyst induced migration of some Cu^{2+} ions to sites with different coordination environments.

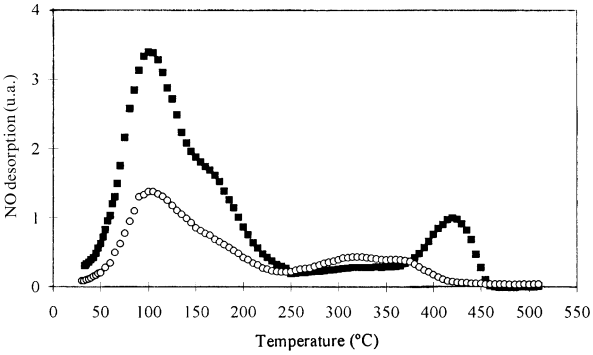

Fig. 5. NO temperature-programmed desorption profiles of NaCuMOR-6-20. (■) Fresh, (○) after catalytic experiments performed in absence and presence of 2 and 10% of water – run 4.

Fig. 6 compares the H_2-TPR profiles of the fresh and used NaCuMOR-6-20. Both samples exhibit two distinct peaks with similar surface area, indicating that the copper is mainly in the form of isolated Cu^{2+} ions [10,22]. Nevertheless, the difference of peak maxima temperature observed in these samples suggests that, in spite of the copper being mainly present as isolated Cu^{2+} ions in both samples, the reducibility of the copper species is different. This indicates that there was an alteration in copper species caused by the catalytic experiments performed with 10% of water, which may be due to a modification of the copper environment and different copper location or distribution.

Comparing figs. 5 and 6 it is possible to observe that NO-TPD results indicate that the number of copper ions accessible to NO became much lower after catalytic experiments, while both H_2-TPR spectra present almost the same quantity of Cu ions reduced by H_2. This dis-

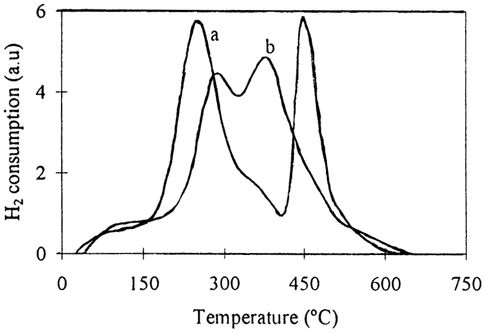

Fig. 6. Temperature-programmed reduction profiles of NaCuMOR-6-20. (a) Fresh, (b) after catalytic experiments performed in absence and presence of 2 and 10% of water – run 4.

agreement can be explained considering that deactivation causes the migration of copper ions to sites inaccessible to NO but accessible to H_2.

Therefore, our results indicate that the catalyst deactivation occurred due to a change of the active component, i.e., of the copper ions, rather than zeolite dealumination. A similar conclusion was also obtained for CuMFI catalysts [15]. This is in agreement with results obtained by Matsumo et al. [19], who reported that the hydrothermal treatment causes the Cu^{2+} species to migrate to another location in ZSM-5 where they are stabilised and become less active.

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