Deactivation of CuMFI catalysts under NO selective catalytic reduction by propene: influence of zeolite form, Si/Al ratio and copper content

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Deactivation of CuMFI catalysts under NO selective catalytic reduction (SCR) by propene in both the absence and the presence of water was investigated as a function of zeolite form, Si/Al ratio and copper content. It was verified that the CuMFI deactivation extent is higher on H-form zeolite compared to Na-form and decreases when the copper exchange level increases, which can be achieved either by increasing the zeolite Si/Al ratio or the copper content. Furthermore, the results indicated that the catalyst deactivation is mainly due to a change in copper species rather than in MFI structure.

Keywords: NO SCR, CuMFI catalysts, water tolerance, catalyst deactivation

1. Introduction

Copper-exchanged MFI zeolites have been pointed out as effective catalysts for NO selective catalytic reduction (SCR) by hydrocarbons in oxidising gas streams [1,2]. However, their catalytic activity is strongly affected by the coexistence of water [3], which is a serious concern for the development of these materials for practical purposes. Generally, the water effects can be classified into reaction inhibition [4–6] and catalyst deactivation [2,7–10].

The catalyst deactivation may be attributed to either degradation of the support or deactivation of copper, or even both. Petunchi et al. [7] reported that dealumination accompanied NO selective reduction, particularly above 350°C, which was probably caused by steaming of the catalyst by the water produced in the reaction. Yan et al. [11] suggested that the presence of steam induces dealumination of the zeolite, and that the copper states are irreversibly changed due to copper interacting with the alumina formed in the dealumination process. On the other hand, Kharas et al. [8] concluded that CuZSM-5 deactivation was not due to zeolite dealumination, but caused by the sintering of active copper into inactive phases, such as CuO, and disruption of zeolitic crystallinity and porosity. A similar conclusion was obtained by Tabata et al. [9], who did observe neither dealumination, carbon deposition nor loss of micropore in a deactivated CuZSM-5 sample. These authors attributed the catalyst deactivation to the CuO cluster formation and resultant loss of copper surface area. However, Matsumo et al. [2] postulated that the hydrothermal treatment causes the Cu^{2+} species to migrate to another location in ZSM-5 (without aggregation), where they are stabilised and become less active. This hypothesis is further supported by the work of Tanabe et al. [10], who suggested that the deactivation of CuZSM-5 occurred through the migration of copper ions to sites where gas molecules like nitrogen oxide and propene cannot reach them.

Hence, the aim of this work is to investigate the influence of zeolite form (H vs. Na), Si/Al ratio and copper content on CuMFI catalyst deactivation under NO SCR by propene in oxidising conditions. For the deactivation studies, catalytic experiments were performed in the absence and presence of water (2%) in a wide temperature range.

2. Experimental

HMFI zeolites with different Si/Al ratios, supplied by French Petroleum Institute, were used as starting material. The sodium-form MFI zeolite (NaMFI) was obtained by exchanging H^+ with Na^+ in an aqueous solution of sodium nitrate (1 M) at room temperature.

The copper-exchanged MFI catalysts (table 1) were prepared by ion exchange of the H- and Na-forms of the

Table 1
Main characteristics of copper-exchanged MFI catalysts

Catalyst	Si/Al	Cu content (wt%)	Cu/Al	Cu exchange level (%)
NaCuMFI-11-40[a]	11	1.7	0.2	40
HCuMFI-11-40	11	1.4	0.2	40
HCuMFI-11-80	11	3.4	0.4	80
HCuMFI-11-140	11	5.6	0.7	140
HCuMFI-27-80	27	1.4	0.4	80

[a] Na content = 0.9 wt%.

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zeolites with an aqueous solution of copper(II) acetate, of an appropriate concentration, at room temperature for 24 h. During the ion exchange process an aqueous ammonia solution (3 M) was gradually added to the ion exchange solution until its pH increased to approximately 7.5. After filtration and washing with water, the catalysts were dried at 110°C for 24 h. Afterwards, the catalysts were calcined under air flow (4ℓ/h gcat.) from room temperature to 500°C (held 8 h), at 5°C/min.

The Si/Al ratio was determined by XRF and the copper content by atomic absorption spectroscopy. The extent of copper exchange level was calculated assuming that one Cu^{2+} is exchanged with two H^+ or Na^+ ions. Hereinafter, the catalysts will be designated as cocation-copper-zeolite structure-Si/Al ratio-copper exchange level, e.g., HCuMFI-11-40.

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 typically consisted of NO (800 ppm), C_3H_6 (800 ppm), O_2 (4%) and H_2O (0–2%) diluted in He at a flow rate of 15ℓ/h. The reactants and products were analysed by gas chromatography [12]. The catalytic activity was evaluated in terms of NO conversion into N_2 as $2\times[N_2]_{out}/[NO]_{in}$ after about 3 h on stream, since at this time the reaction practically reached the steady state. 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 diffractometer employing Cu Kα radiation filtered by Ni. For IR measurements, the catalytic samples were pelleted into KBr supporting discs (1 wt%, 1000 atm) and placed in a cell. Spectra were recorded at room temperature at a resolution of 4 cm^{-1} (about 100 scans) 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

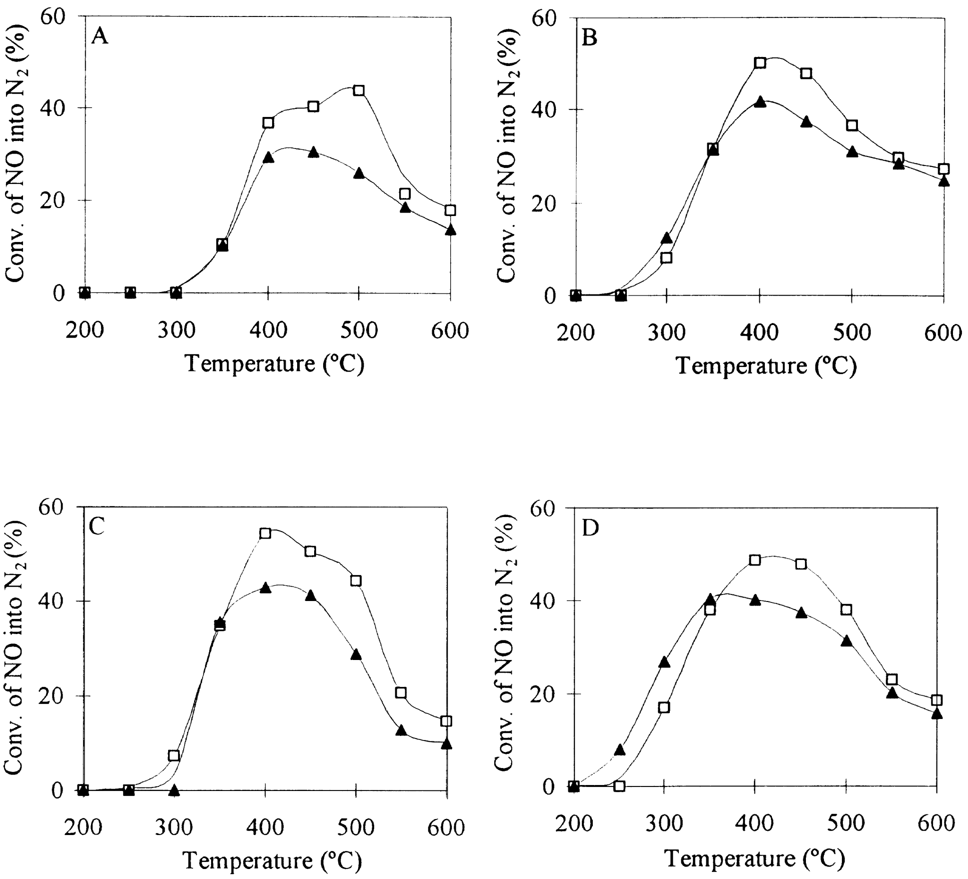

Fig. 1. Effect of water presence on catalytic activity of several copper-ion-exchanged MFI catalysts for NO reduction into N_2. (□) $[H_2O]$ = 0%, (▲) $[H_2O]$ = 2%. (A) HCuMFI-11-40, (B) NaCuMFI-11-40, (C) HCuMFI-27-80, (D) HCuMFI-11-80.

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 [13].

3. Results and discussion

The effect of water presence on NO reduction by propene was analysed on catalysts prepared from different forms of zeolite (H vs. Na), with different Si/Al ratios (11 and 27) and different copper contents ($1.4 \leqslant Cu \leqslant 5.6$ wt%). Fig. 1 shows the effect of water on NO reduction into N_2 over some of these catalysts. The shape of the curves and the most active temperature were practically unchanged by the presence of water. Though, the addition of 2% of water to the reactant mixture leads to an appreciable decrease in NO conversion over all samples, indicating that these materials are very sensitive to water. Nevertheless, the activity of these catalysts in the presence of 2% water is still significant. Moreover, at low temperatures ($T \leqslant 350$°C), the catalytic activity for NO conversion was not suppressed by the water presence, and it was even higher over HCuMFI-11-80. Hence, the effect of water is more pronounced at high temperatures.

The decrease of the catalytic activity by water was not reversible, i.e., the activity was not recovered when water was removed from the reactant mixture. This indicates that the decrease in NO conversion was not due to the reaction inhibition, but due to the catalyst deactivation. Although, the extent of catalyst deactivation depends on the zeolite form, Si/Al ratio and copper content, as will be discussed later.

Concerning the total oxidation of propene (fig. 2), it was not affected by the water presence, i.e., the conversion of C_3H_6 into CO_2 was nearly the same over all catalysts in the absence and the presence of water. This fact may be related with the water ability to oxidise hydrocarbons via the steam reforming reaction [14].

The effect of zeolite form, Si/Al ratio and copper content was further investigated on the stability of CuMFI catalysts after catalytic experiments carried out in the absence and the presence of water. Thus, several runs (1–3) 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 cat-

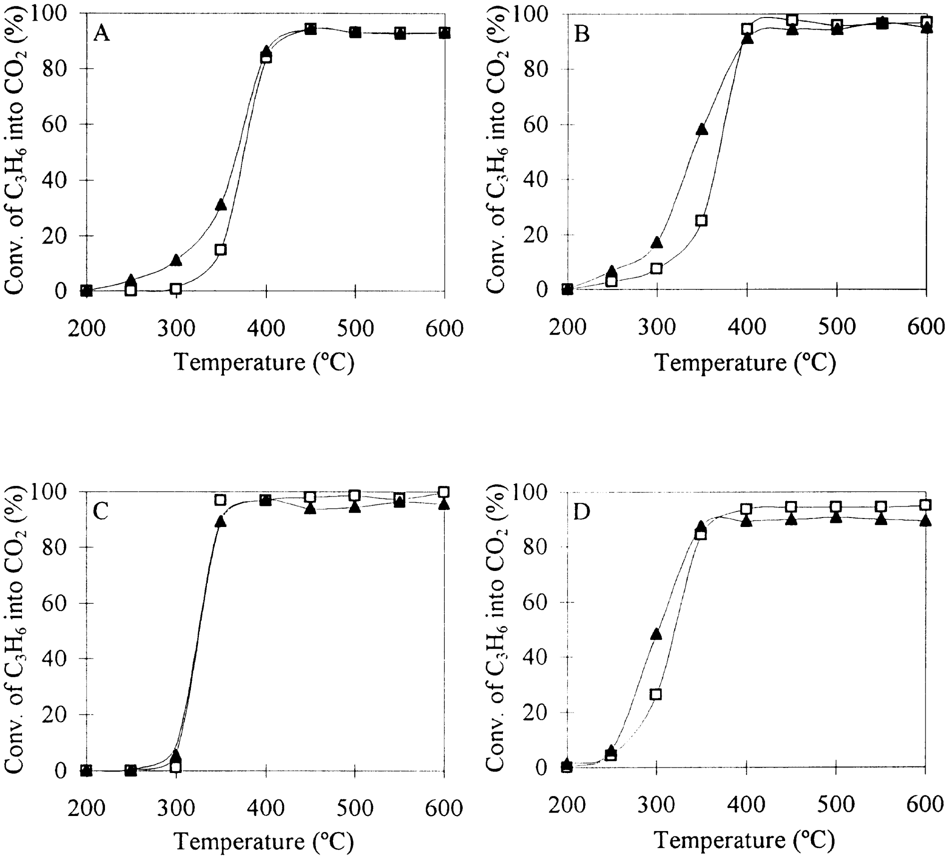

Fig. 2. Effect of water presence on catalytic activity of several copper-ion-exchanged MFI catalysts for propene total oxidation. (□) $[H_2O] = 0\%$, (▲) $[H_2O] = 2\%$. (A) HCuMFI-11-40, (B) NaCuMFI-11-40, (C) HCuMFI-27-80, (D) HCuMFI-11-80.

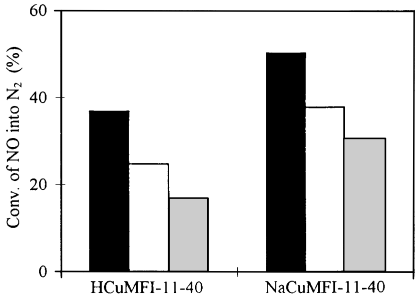

Fig. 3. Effect of zeolite form on stability of copper-exchanged MFI catalysts; $[NO] = [C_3H_6] = 800$ ppm, $[O_2] = 4\%$ and $T = 400°C$. (■) Run 1, (□) run ▨2, ( ) run 3.

alytic 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.

Fig. 3 compares the catalytic stability of two catalysts with the same Si/Al ratio (11) and copper content (about 1.4 wt%), but prepared from different forms of zeolite: H-form (HCuMFI-11-40) and Na-form (NaCuMFI-11-40). The catalyst in sodium form is more active for NO conversion into N_2 than the acid form, regardless of the kind of experiments performed on the catalysts. Furthermore, NaCuMFI-11-40 is more stable than HCuMFI-11-40. In fact, the catalyst prepared from the acid form suffered 33% of deactivation after the set of catalytic experiments performed without water and 54% after the set of catalytic experiments performed without and with water, whereas the sodium form catalyst was deactivated 25 and 40%, respectively.

To investigate the effect of zeolite Si/Al ratio on HCuMFI stability, two catalysts with the same copper content (1.4 wt%) and different Si/Al ratios (11 and 27) were tested, the results being illustrated in fig. 4. Whatever the set of experiments carried out on the catalysts, HCuMFI-27-80 is more active than HCuMFI-11-40. Moreover, the catalyst with higher Si/Al ratio is the most stable. In other words, in run 2 the catalyst HCuMFI-27-80 recovered 94% of its original activity, while HCuMFI-11-40 only recovered 67% and in run 3 the first sample recovered 61% while the latter only recovered 46%. This behaviour seems to indicate that the HCuMFI catalyst stability increases with zeolite Si/Al ratio.

In order to analyse the effect of copper content on HCuMFI stability, three samples of MFI zeolite with the same Si/Al ratio (11) and different copper contents ($1.4 \leqslant Cu \leqslant 5.6$ wt%) were tested. The results are depicted in fig. 5. The catalyst with medium copper content, HCuMFI-11-80, suffered 13% of deactivation after the set of catalytic experiments performed without water and 33% after the set of catalytic experiments performed without and with water. Comparing these values with the deactivation values reported above for HCuMFI-11-40 we can conclude that the catalyst with lower copper content is more deactivated by the set of catalytic experiments performed either without or with water. By contrast, the sample with the highest copper content, HCuMFI-11-140, does not suffer any deactivation when submitted to the set of experiments without water. Though, after experiments carried out in the presence of water, its catalytic activity slightly decreases compared to run 2, but it is still higher than the original activity (run 1). This seems to indicate that the effect of water on NO conversion is relatively unimportant on overexchanged catalysts. Hence, from the results present in fig. 5 we conclude that the catalytic stability increases with copper content.

From the analysis of figs. 3–5 we can conclude that the CuMFI deactivation extent is higher on H-form zeolite compared to Na-form and decreases when copper exchange level increases, which can be achieved by increasing either the zeolite Si/Al ratio or copper content. This means that CuMFI catalysts become more stable as the Brønsted acidity of the catalyst decreases. This observation is consistent with the work of Petunchi et al. [7], where it is reported 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. Tanabe et al. [10] also reported that

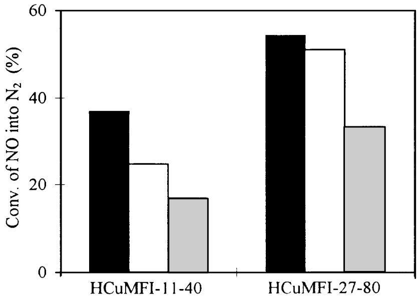

Fig. 4. Effect of zeolite Si/Al ratio on stability of copper-exchanged MFI catalysts. Both catalysts contain 1.4 wt% of copper. $[NO] = [C_3H_6] = 800$ ppm, $[O_2] = 4\%$ and $T = 400°C$. (■) Run 1, (□) run 2, (▨) run 3.

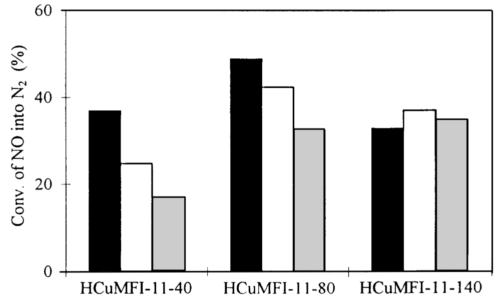

Fig. 5. Effect of copper content on stability of copper-exchanged MFI catalysts. All catalysts contain Si/Al = 11. $[NO] = [C_3H_6] = 800$ ppm, $[O_2] = 4\%$ and $T = 400°C$. (■) Run 1, (□) run 2, (▨) run 3.

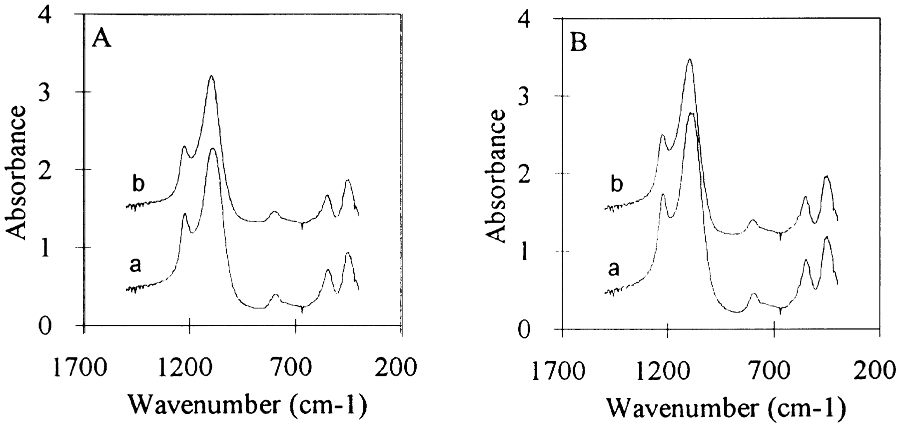

Fig. 6. IR spectra of (A) HCuMFI-11-40 and (B) NaCuMFI-11-40 catalysts. (a) Fresh, (b) after catalytic experiments performed without and with water – run 3.

the presence of H^+ causes deactivation of CuZSM-5.

Several techniques were applied to check the causes of catalyst deactivation. XRD was used to verify if there was any alteration in MFI structure, IR and ^{27}Al NMR were applied in order to see if there was dealumination of the catalysts and NO-TPD and H_2-TPR measurements were performed to analyse if the copper nature was changed after the set of catalytic experiments carried out in the absence and the presence of water. These techniques were performed on several CuMFI catalysts in order to obtain an overview of the causes of catalyst deactivation.

XRD patterns of fresh and used CuMFI catalysts were recorded and the data revealed almost no loss of crystallinity. For instance, the most deactivated catalyst, HCuMFI-11-40, presents 95% of crystallinity in relation to the fresh sample after catalytic experiments carried out in the absence and the presence of water (run 3).

Fig. 6 shows the IR spectra of the fresh and used H- and NaCuMFI-11-40 in the region of the vibration modes of the TO_4 tetrahedra (T = Si or Al). Comparing the intensity, width and position of the bands of the fresh and used samples, we verify that they are quite similar, which indicates that there was no dealumination caused by the set of catalytic experiments performed without and with water. This observation is valid both for H- and NaCuMFI-11-40.

In fig. 7 are depicted the ^{27}Al NMR spectra of the fresh and used HCuMFI-27-80. The presence of only one peak (at around 50 ppm) is noticed, which is assigned to the tetrahedral aluminium. The peak related with the octahedral aluminium is not observed in any spectrum, i.e., neither after the set of catalytic experiments performed without water (run 2) nor with water (run 3). This feature points out that the NO SCR experiments performed either in the absence or the presence of 2% of water do not cause zeolite dealumination, as it was observed before by IR for other zeolite samples.

Fig. 8 compares the NO-TPD profiles of the fresh and used HCuMFI-27-80. The TPD profiles and the NO adsorption capacity of both samples are quite different. The used catalyst presents a much smaller peak at low temperature and does not exhibit the high-temperature

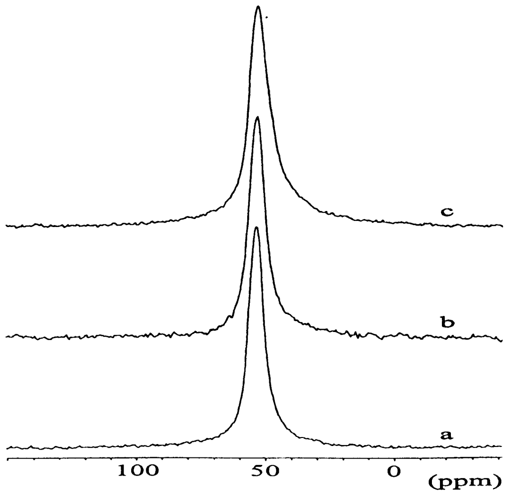

Fig. 7. ^{27}Al NMR spectra of HCuMFI-27-80 catalyst. (a) Fresh, (b) after catalytic experiments performed without water – run 2, (c) after catalytic experiments performed without and with water – run 3.

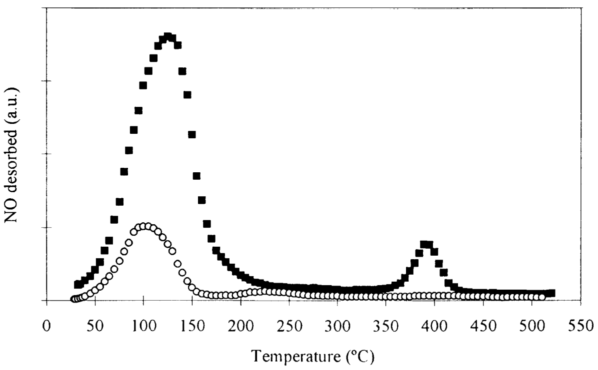

Fig. 8. NO temperature-programmed desorption profiles of HCuMFI-27-80 catalyst. (■) Fresh, (○) after catalytic experiments performed without and with water – run 3.

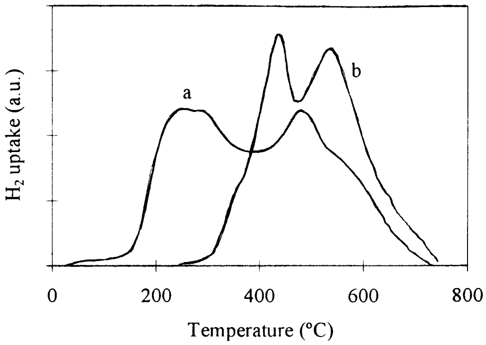

Fig. 9. Temperature-programmed reduction profiles of HCuMFI-11-40 catalyst. (a) Fresh, (b) after catalytic experiments performed without and with water – run 3.

NO desorption peak. Since the low-temperature peak was ascribed to the desorption of NO from isolated Cu^{2+} ions [13,15], the results indicate that the used sample contains a lower quantity of isolated Cu^{2+} ions accessible to NO than the fresh sample.

Fig. 9 shows the H_2-TPR profiles of the fresh and used HCuMFI-11-40. Both samples exhibit two distinct peaks with similar surface area, indicating that the copper is mainly in the form of isolated Cu^{2+} ions [13,16]. Although, the temperature of peak maxima is different for both samples, occurring at higher temperatures for the used catalyst. This 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, the copper present in the used catalyst being more difficult to reduce.

Hence, the NO-TPD and H_2-TPR data indicate that the fresh and used CuMFI catalysts should have a different copper distribution, which suggests that the deactivation of CuMFI catalysts is probably related with the migration of copper species (without formation of CuO) to another location, where they are inaccessible to NO and less active. A similar conclusion was also obtained by Matsumo et al. [2] and Tanabe et al. [10]. Moreover, Yan et al. [11] concluded from EPR results that the deactivation of the catalyst induced migration of some Cu^{2+} ions to sites with different coordination environments.

Therefore, from our results we conclude that the cause of catalyst deactivation is mainly due to a change in copper species rather than in MFI structure. A similar remark was also obtained for CuMOR catalysts [17].

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References

[1] M. Iwamoto and H. Yahiro, Catal. Today 22 (1994) 5.
[2] S. Matsumoto, K. Yokota, H. Doi, M. Kimura, K. Sekizawa and S. Kasahara, Catal. Today 22 (1994) 127.
[3] R. Gopalakrishnan, P.R. Stafford, J.E. Davidson, W.C. Hecker and C.H. Bartholomew, Appl. Catal. B 2 (1993) 165.
[4] M. Shelef, C.N. Montreuil and H.W. Jen, Catal. Lett. 26 (1994) 277.
[5] E. Kikuchi and K. Yogo, Catal. Today 22 (1994) 73.
[6] H. Hamada, Catal. Today 22 (1994) 21.
[7] J.O. Petunchi and W.K. Hall, Appl. Catal. B 3 (1994) 239.
[8] K.C.C. Kharas, H.J. Robota and D.J. Liu, Appl. Catal. B 2 (1993) 225.
[9] T. Tabata, M. Kokitsu, O. Okada, T. Nakayama, T. Yasumatsu and H. Sakane, in: *Catalyst Deactivation*, Stud. Surf. Sci. Catal., Vol. 88, eds. B. Delmon and G.F. Froment (Elsevier, Amsterdam, 1994) p. 409.
[10] T. Tanabe, T. Lijima, A. Koiwai, J. Mizuno, K. Yokota and A. Isogai, Appl. Catal. B 6 (1995) 145.
[11] J.Y. Yan, G.-D. Lei, W.M.H. Sachtler and H.H. Kung, J. Catal. 161 (1996) 43.
[12] C. Torre-Abreu, M.F. Ribeiro, C. Henriques and F.R. Ribeiro, Appl. Catal. B, in press.
[13] C. Torre-Abreu, M.F. Ribeiro, C. Henriques and G. Delahay, Appl. Catal. B, in press.
[14] J. Barbier Jr. and D. Duprez, Appl. Catal. B 3 (1993) 61.
[15] W. Zhang, H. Yahiro, N. Mizuno, J. Izumi and M. Iwamoto, Langmuir 9 (1993) 2337.
[16] J. Sárkány, J.L. d'Itri and W.M.H. Sachtler, Catal. Lett. 16 (1992) 241.
[17] C. Torre-Abreu, M.F. Ribeiro, C. Henriques and F.R. Ribeiro, Catal. Lett. 43 (1997) 25.