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Activity and durability of Fe/ZSM-5 catalysts for lean burn NO_x reduction in the presence of water vapor

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Abstract

A novel method for the preparation of superior Fe/ZSM-5 catalysts is described. $FeCl_3$ is sublimed into the cavities of H/ZSM-5, where it reacts chemically with the acid sites of the zeolite. With this method, Fe/ZSM-5 with an iron loading as high as Fe/Al=1 can be easily achieved. This preparation method is less sensitive to the origin of the zeolite and its synthesis history than the conventional ion-exchange method. HRAEM, FTIR, H_2-TPR and CO-TPR results show that iron is located at the exchange sites of the zeolite. An oxygen bridged binuclear iron complex is a plausible prototype for the active iron species. The iron is reduced from +3 to +2 below 800°C. These catalysts are very active and selective in the catalytic reduction of NO_x with *iso*-butane; they have a high durability under conditions simulating vehicular emission. A conversion of NO to N_2 of about 76% was observed near 350°C. Remarkably and in contrast to most other M/ZSM-5 catalysts, the performance of the new catalysts was not impaired when 10% H_2O was added to the feed. H_2O actually enhances the NO_x conversion at low temperatures. CO and CO_2 are both true primary products of NO_x SCR over Fe/ZSM-5 catalysts. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: DeNO$_x$; SCR; Fe/ZSM-5; H_2O effect; Sublimation

1. Introduction

Much research has been done in recent years on the selective catalytic reduction (SCR) of nitrogen oxides (NO_x) by hydrocarbons in the emissions from lean burn engines. Active catalysts are materials that contain metal ions and oxoions in the cavities of zeolites such as MFI. The combinations Cu/ZSM-5, Co/ZSM-5, Co/Ferrierite, Ga/ZSM-5, In/ZSM-5 and Pd/ZSM-5 have been thoroughly studied [1–4]. An important shortcoming of these systems is, however, their sensitivity to water vapor, an ubiquitous and inevitable component of all internal combustion engine emissions. With Cu/ZSM-5 catalysts it was shown that water vapor has both a reversible and an irreversible effect [5–9]. Replacing a dry feed of NO, O_2 and hydrocarbons, by a wet feed, immediately reduces the NO_x reduction activity by a large factor; moreover the activity of the catalyst in long term tests decreases much faster in the presence of water vapor than in its absence, because dealumination and formation of Cu-aluminate destroy the zeolite matrix [9]. There is, therefore, no certainty that a zeolite-based catalyst will ever be found that meets anticipated legislation standards for emissions from lean burn Otto or diesel engines either in vehicular or stationary applications.

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Recently, however, reports have appeared in the literature that iron containing catalysts are remarkably insensitive to water vapor. Feng and Hall [10,11] prepared "overexchanged" Fe/ZSM-5 catalysts by exchanging $[FeOH]^+$ ions into Na/ZSM-5 from an aqueous solution containing oxalate ions. Upon testing this Fe/ZSM-5 at 500°C in a gas flow simulating vehicular emissions from lean burn engines, they found that it was highly active and durable even in the presence of 10% H_2O and 150 ppm SO_2. After 2500 h only minimal loss of activity was observed; ^{27}Al NMR revealed that all detectable Al was still tetrahedrally coordinated with oxygen. The authors assumed that absence of Brønsted sites is crucial for the high durability of their catalyst and that an important function of the oxalate ion is to act as proton getter. Lunin et al. [12] also reported a remarkable stability of montmorillonite supported Fe catalysts towards H_2O, they actually observed a slight increase in NO_x reduction activity in the presence of 1% H_2O.

While attempting to reproduce the results of Feng and Hall, we found that the performance of such catalysts is very sensitive to subtle differences in the history of the zeolite; even samples of virtually identical composition from different vendors showed large differences in catalytic performance and also in their TPR (temperature programmed reduction) profiles. We, therefore, decided to prepare Fe/ZSM-5 catalysts by a different method, avoiding ion exchange from aqueous solutions. In the present paper we report on catalytic tests of NO_x reduction with Fe/ZSM-5 catalysts with high Fe/Al ratios, that were prepared by subliming $FeCl_3$ vapor onto H/ZSM-5. The chemistry of this chloride sublimation method is similar to that described in our previous work on Ga/ZSM-5 [13,14] and Pd/HY [15].

2. Experimental

2.1. Catalysts preparation

2.1.1. Fe/ZSM-5 *prepared by ion exchange in an aqueous slurry*

Samples 1–3 were prepared by the conventional ion-exchange method [16] using different batches of ZSM-5 zeolite. Their origins and their elemental compositions as determined by ICP analysis are given in Table 1. A quantity of 2.0 g zeolite was added to 400 ml H_2O. In a nitrogen atmosphere, 1.0 g of crystalline $FeSO_4{\cdot}7H_2O$ (Baker) was slowly added to the slurry (within 6 h). The pH of the slurry was kept at 6.8–7.0. After 48 h, it was vacuum filtered, washed and air dried. Samples 4 and 5 were prepared in the same way, but using $FeC_2O_4{\cdot}2H_2O$ instead of $FeSO_4$. In view of its low solubility only 0.2 g $FeC_2O_4{\cdot}2H_2O$ (99%, Aldrich), corresponding to Fe/Al≈0.6, was added.

2.1.2. Fe/ZSM-5 *prepared by the sublimation method*

Samples 6–8 were prepared by chemical vapor deposition, i.e. subliming $FeCl_3$ into the cavities of H/ZSM-5. This acid zeolite was prepared from Na/ZSM-5 via ion exchange with a dilute $NH_4{\cdot}NO_3$ solution and calcination in an O_2 flow at 500°C for

Table 1
Summary of Fe/ZSM-5 prepared by ion exchange in an aqueous slurry

Sample	Parent zeolite	Fe^{2+} source	Fe/ZSM-5			H_2/Fe[d]
			Si/Al	Na/Al	Fe/Al	
1	UOP (13923-60, Si/Al=14.2, Na/Al=0.67)[a]	$FeSO_4{\cdot}7H_2O$	14.2	0.49	0.29	0.45
2	Uetikon (PZ-3/30, Si/Al=14.6, Na/Al=1.0)[b]		14.6	0.84	0.11	1.1
3	ALSI-5 (SN55, Si/Al=23.0, Na/Al=1.42)[c]		23.0	0.72	0.21	0.9
4	UOP (13923-60, Si/Al =14.2, Na/Al=0.67)[a]	$FeC_2O_4{\cdot}2H_2O$	14.2	0.42	0.52	0.85
5	Uetikon (PZ-3/30, Si/Al=14.6, Na/Al=1.0)[b]		14.6	0.87	0.50	1.35

[a] Template preparation. Before being used for ion exchange, it was first calcined and back exchange with $NaNO_3$ solution for three times. The Na/Al ratio of the obtained sample is 0.91.
[b] Template-free preparation.
[c] Template-free preparation. Before being used for ion exchange, it was washed thoroughly to remove residual sodium from the extra lattice.
[d] Mole ratio of H_2 consumption during H_2-TPR (Fig. 1) to iron content.

Table 2
Summary of Fe/ZSM-5 catalysts prepared by sublimation method

Sample	Parent zeolite	Fe/ZSM-5		C_{max}[d] (%)		T_{max}[e] (°C)		$C_{300°C}$[f] (%)		TON ($\times 10^{-4}$ s^{-1})[g]	
		Si/Al	Fe/Al	0% H_2O	10% H_2O	0% H_2O	10% H_2O	0% H_2O	10% H_2O	0% H_2O	10% H_2O
6	ALSI-5(SN27)[a]	10.7	1	64.8	65.9	325	325	41.7	53.1	7.0	8.9
7	UOP(13923-60)[b]	14.2	1	75.9	76.6	350	350	33.8	49.7	7.2	10.6
8	ALSI-5(SN55)[c]	23.0	1	76.8	79.6	350	350	22.9	34.6	7.6	11.5

[a] Template-free preparation, Si/Al=10.7, Na/Al=0.89.
[b] Template preparation, Si/Al=14.2, Na/Al=0.67.
[c] Template-free preparation, Si/Al=23.0, Na/Al=1.42.
[d] The maximum conversion of NO to N_2.
[e] Temperature corresponding to the maximum conversion of NO to N_2 (reactant feed: GHSV 42 000 h^{-1}, *iso*-C_4H_{10} 0.2%, NO 0.2%, O_2 3%, H_2O 0% or 10%).
[f] The conversion of NO to N_2 at 300°C.
[g] Molecules of NO to N_2 at 300°C per iron per second.

4 h. Three zeolites with different Si/Al ratios and different preparation methods were used; details are given in Table 2. In a glove bag under N_2 (UHP, Linde) flow, 5.0 g of the calcined H/ZSM-5 was loaded into one side of a U-shaped reactor, and 1.0 g $FeCl_3$ (99.99+%, Aldrich) was loaded into the other side of the same reactor. A porous frit kept the zeolite separated from the $FeCl_3$. Chemical vapor deposition was carried out in an Ar (UHP, Linde) flow (100 ml/min) while the temperature of the reactor was kept at 320°C. 100 ml of 1 M NaOH solution was used to absorb HCl from the outlet gas. After a certain time, the color of the zeolite bed became uniformly yellow. The sample was then removed and washed with doubly deionized H_2O. After drying in air, it was calcined for 2 h in flowing O_2 at 600°C.

2.2. *Reaction studies*

Selective catalytic reduction of NO was studied in a continuous flow reactor as described previously [17]. Test conditions were chosen similar to those used by Feng and Hall [11]. A typical inlet gas composition was 0.2% NO, 0.2% *iso*-C_4H_{10}, 3% O_2 and when desired, 10% H_2O. Helium was used as a diluent. 0.200 g catalyst was used and a total flow rate of 280 ml/min. Based on a bulk density of 0.5 g/ml for the zeolite sample, the calculated gas hourly space velocity (GHSV) is 42 000 h^{-1}. The composition of the effluent was analyzed by GC at constant temperature of the catalyst, after preconditioning it for 30 min at each temperature. The conversion of NO was determined from the formation of N_2. The conversion of *iso*-C_4H_{10} was determined from the amounts of CO_2 and CO in the effluent. The effectiveness factor (EF) is defined as the ratio of the numbers of consumed NO and *iso*-C_4H_{10} molecules, EF=$[NO/iso\text{-}C_4H_{10}]_{consumed}$.

2.3. *Catalysts characterization*

The HCl which was released during the sublimation process was absorbed in a NaOH solution and determined quantitatively by titration with $AgNO_3$. FTIR, XRD, high-resolution analytical electron microscopy (HRAEM), H_2-TPR and CO-TPR were used to characterize the iron species in the zeolite. Details of these methods have been described in our previous work [14,18]. For FTIR spectroscopy, samples were preheated up to 400°C. Before TPR runs, the samples were calcined in flowing O_2 at 500°C for 2 h.

3. Results

3.1. Fe/ZSM-5 *catalysts prepared by ion exchange in an aqueous slurry*

Three different ZSM-5 zeolites were used to prepare Fe/ZSM-5 catalysts by conventional ion exchange, using $FeSO_4$ as the precursor. The data are compiled in Table 1. Samples 1 and 2 have nearly the same Si/Al ratio; however, the iron loading is higher in sample 1 than in sample 2. Accordingly, the Na/Al ratio is lower for sample 1.

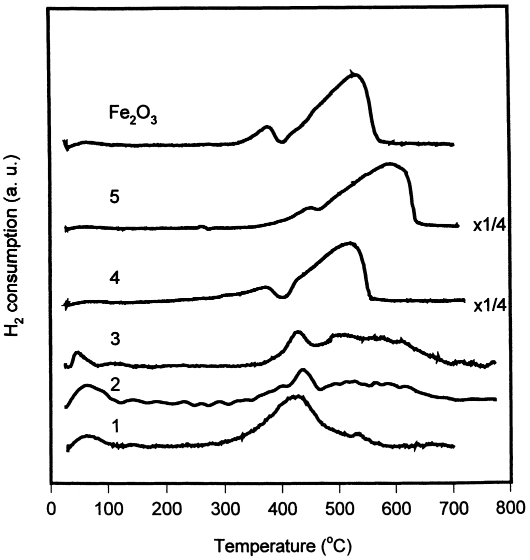

Fig. 1. H_2-TPR profiles of calcined Fe/ZSM-5 and Fe_2O_3: (1)–(5) sample 1 to sample 5

The H_2-TPR profiles of these samples are shown in Fig. 1. A small peak between 30°C and 100°C is an artifact, which is due to desorption of residual Ar. Sample 1 shows one main reduction peak at 430°C, the H_2 consumption expressed as the ratio H_2/Fe for this peak is 0.45. This could indicate that the majority of the Fe is reduced from 3+ to 2+. At the high temperature side, a small shoulder at about 530°C can also be seen. This could indicate that a small amount of iron oxide is reduced to metallic iron. Samples 2 and 3 also show a reduction peak at 430°C, but its relative intensity is much lower; instead a broad H_2 consumption peak appears at high temperature. The total H_2/Fe ratio is higher than 0.5, as shown in Table 1. This indicates that some Fe is reduced to a lower valency than 2+.

Catalytic test results of the SCR of NO with *iso*-butane are shown in Fig. 2, where the conversions of NO to N_2 and of *iso*-C_4H_{10} to CO and CO_2 are plotted against the temperatures. Sample 1 shows a maximum SCR of NO of about 55% at 350°C. The corresponding value for samples 2 and 3 are lower, and they are obtained at a higher temperature of 400°C. Also, the combustion activities are much lower over these two samples.

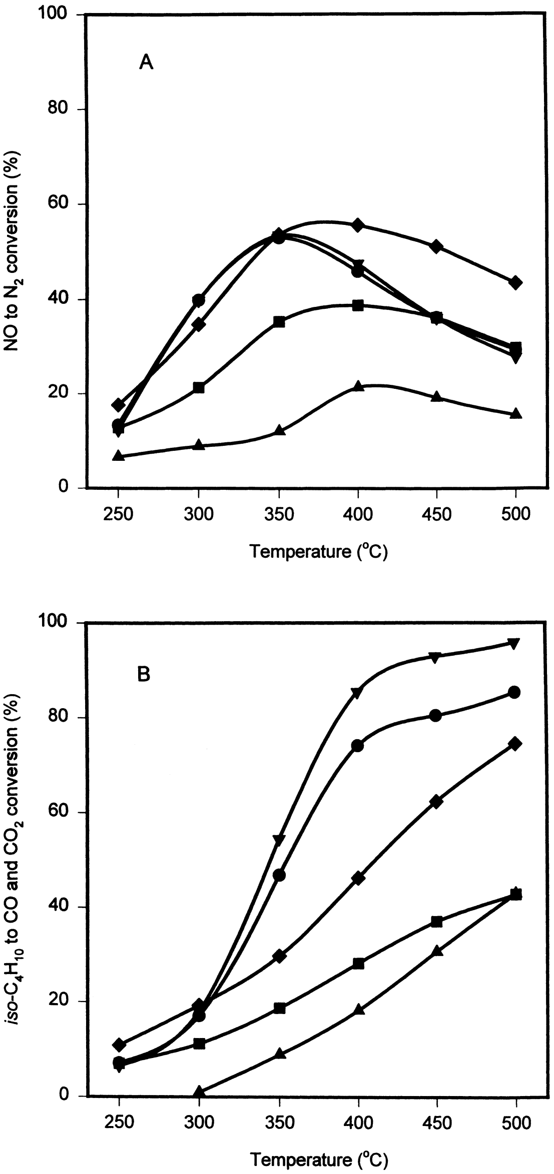

Fig. 2. The effect of temperature on the *iso*-C_4H_{10}+NO+O_2 reaction over Fe/ZSM-5. Reactant feed: GHSV 42 000 h^{-1}, *iso*-C_4H_{10} 0.2%, NO 0.2%, O_2 3%. (A) Conversion of NO to N_2; (B) conversion of *iso*-C_4H_{10} to CO and CO_2 ((●) sample 1, (■) sample 2, (▲) sample 3, (▼) sample 4, and (◆) sample 5).

While trying to follow the procedure of Feng and Hall [11] for the preparation of Fe/ZSM-5 catalysts from $FeC_2O_4{\cdot}2H_2O$, we failed to achieve substantially higher iron loadings than with the $FeSO_4$ precursor. For instance, upon exchanging an Uetikon ZSM-5(PZ-3/30) with iron oxalate for 48 h in an apparatus similar to the one described by Feng et al., we obtained only an iron loading of Fe/Al=0.1, as in sample 2. The TPR profile and SCR activity of the oxalate derived catalyst are similar to those of the sulfate derived sample 2. In order to verify whether slow diffusion of iron ions through the frit was responsible for the low iron loading, a sample was prepared by adding a certain amount of $FeC_2O_4{\cdot}2H_2O$ directly to the zeolite slurry. In this case, the possible limitation of diffusion is avoided, but a mixture of two phases will be obtained if not all the iron oxalate can be solved and exchanged into the zeolite. Samples 4 and 5 were prepared in this way. The nominal Fe/Al ratios for these two samples in Table 1 include all the iron present. If more Fe was exchanged against Na in these samples, one would expect a lower Na/Al ratio which was, however, not observed. It follows that in these two samples a substantial fraction of the iron remains outside the zeolite. This was confirmed by H_2-TPR, as shown in Fig. 1. The profile of sample 4 can be deconvoluted into two parts: reduction from +3 to +2 of the iron at the exchange sites and reduction of Fe_2O_3 to metallic iron. (For comparison, the H_2-TPR of Fe_2O_3 is also included in Fig. 1; it gives a ratio $H_2/Fe=1.5$, corresponding to the reduction of Fe^{3+} to Fe^0.) From the ratio of $H_2/Fe=0.85$ one can calculate that the amount of iron that is actually exchanged into the zeolite is $Fe/Al=0.34$, i.e. the same exchange level as in sample 1. Indeed, samples 1 and 4 show the same Na/Al ratio, which further suggests that the ion-exchange level is the same. The TPR profile of sample 5 is however different from all other samples, and it gives a higher H_2/Fe ratio. The SCR activity shown in Fig. 2 demonstrates that the extra zeolite Fe in these samples gives additional combustion of *iso*-butane but no substantially higher SCR of NO_x.

3.2. Fe/ZSM-5 *prepared by the sublimation method*

ZSM-5 samples with three different Si/Al ratios were used to prepare Fe/ZSM-5 catalysts by sublimation of $FeCl_3$. Their elemental compositions are listed in Table 2. An iron loading as high as $Fe/Al=1$ is obtained in all three cases.

The infrared spectra in the hydroxyl stretching region of ZSM-5 (UOP) before and after sublimation of $FeCl_3$ are shown in Fig. 3. With H/ZSM-5 a peak at $3750\,cm^{-1}$ and a strong peak at $3610\,cm^{-1}$ are observed, they have been assigned to isolated and terminal silanol groups and acidic bridging hydroxy groups, respectively [19]. After sublimation of $FeCl_3$ these peaks disappear. After washing the sample with H_2O to remove the remaining chloride, followed by calcination, the peak at $3750\,cm^{-1}$ re-appears. Although the peak at $3610\,cm^{-1}$ can also be seen, its intensity is greatly reduced. XRD results (not shown) demonstrate that sublimation does not cause any damage to the zeolite structure or dealumination. No $FeCl_3$ or iron oxides phases are detected by XRD.

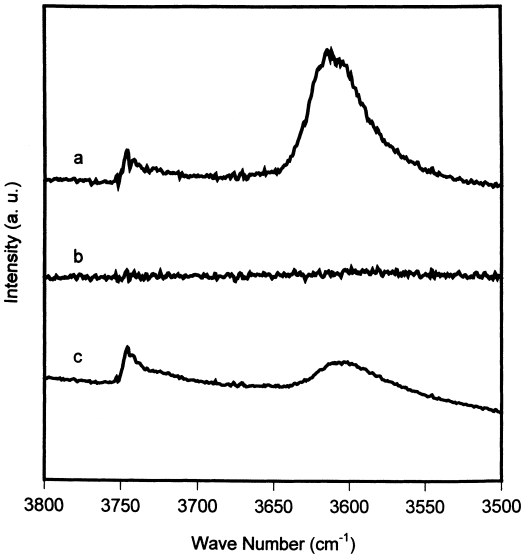

Fig. 3. FTIR spectra in the OH stretching region of (a) pure H/ZSM-5 (UOP), (b) after sublimation, and (c) after calcination (sample 7).

Electron micrographs taken under high-resolution conditions of the samples after sublimation and after calcination are shown in Fig. 4. The samples after sublimation clearly show interference fringes of the ZSM-5 crystal structure. This suggests that all the $FeCl_3$ is located inside the cavities of ZSM-5 and disperses uniformly over the zeolite. After calcination the HRAEM micrograph still shows perfect fringes, but a few dark particles can also be found. They were identified by EDX to be iron oxides.

H_2-TPR profiles of the calcined Fe/ZSM-5 catalysts are shown in Fig. 5. All samples show one main reduction peak at about 410°C, and the area of this peak decreases with decreasing iron content of the zeolite. For these samples, the molar ratio of the H_2 consumption under the main reduction peak to iron content is about 0.5. This indicates that almost all the

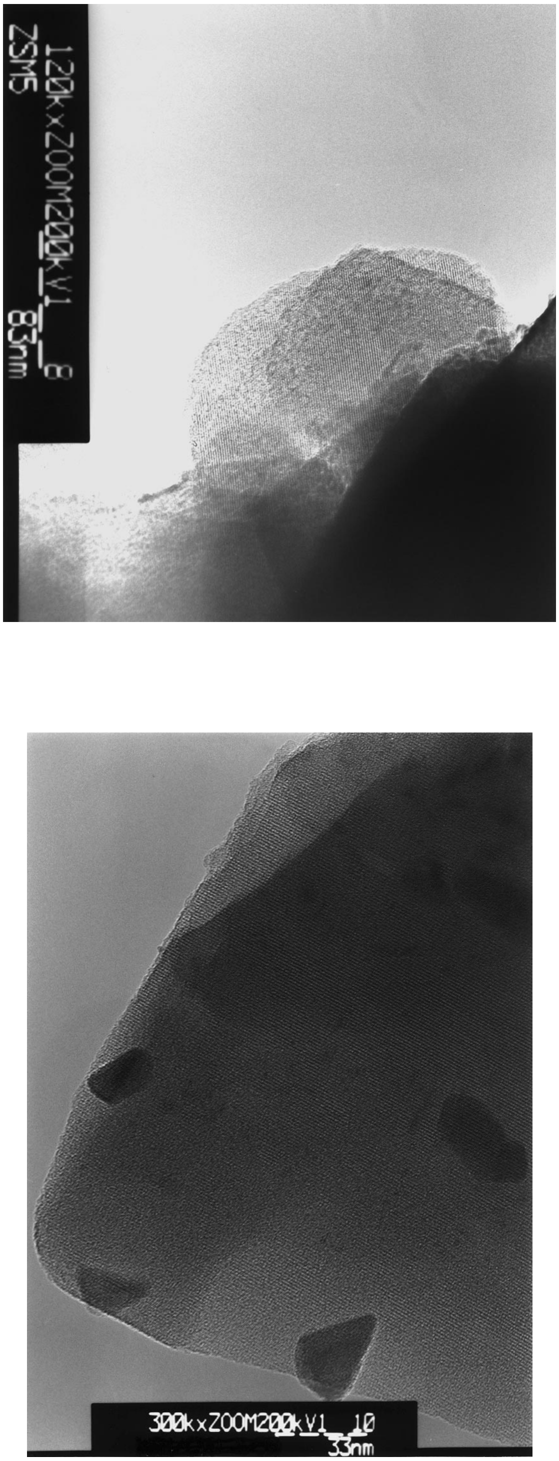

Fig. 4. High-resolution electron micrograph of zeolite (UOP) after: (A) sublimation and (B) calcination (sample 7).

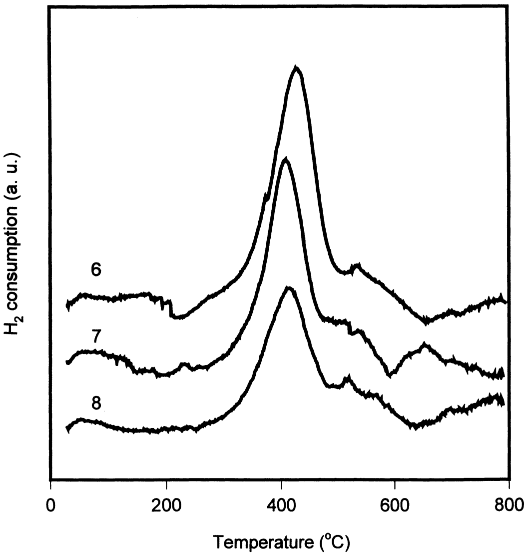

Fig. 5. H_2-TPR profiles of calcined Fe/ZSM-5 prepared by sublimation method: (6)–(8) sample 6 to sample 8.

iron is located at exchange sites where it can only be reduced from +3 to +2. However, there are also some small reduction peaks at high temperature. These peaks suggest that some iron oxide particles are present which are reduced to metallic iron.

Fig. 6 shows the CO-TPR of sample 7. There is one CO_2 evolution peak at 385°C; it corresponds to the main reduction peak in the H_2-TPR profile and is assigned to the reduction of iron at the exchange sites from +3 to +2. There is a shoulder at high temperature. The total amount of CO_2 measured by MS gives a ratio of $CO_2/Fe=0.8$. When the sample was exposed to CO at 800°C, there were no more reduction peaks in the subsequent H_2-TPR run.

Fig. 7(A) shows the SCR of NO in the absence of H_2O over sample 7 at various temperatures. The reaction starts at about 250°C, with the NO to N_2 conversion increasing as the reaction temperature increases, then passes through a maximum at about 350°C, then decreases. The maximum conversion of NO to N_2 is near 76%, which is much higher than for the ion exchanged samples tested under identical conditions. The shape of the SCR activity vs. temperature pattern is similar to those reported for the SCR of NO over Cu/ZSM-5 [20] and Fe/ZSM-5 [11,21]. Unlike Cu/ZSM-5, which produces mainly CO_2 under these conditions, the Fe/ZSM-5 catalyst

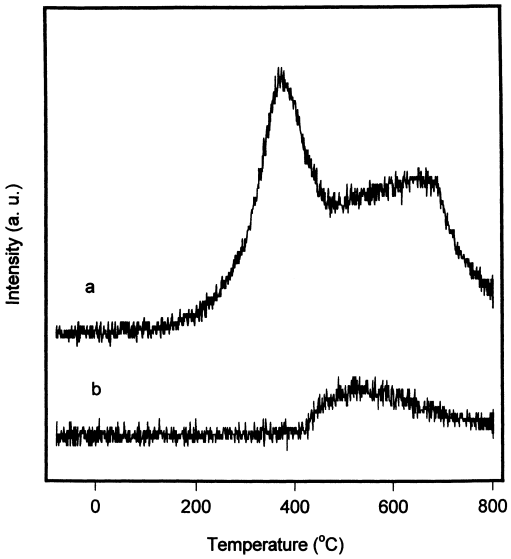

Fig. 6. CO-TPR profile of Fe/ZSM-5 (sample 7): (a) CO_2 (M/e =44); (b) H_2O (M/e=18).

produces a considerable amount of CO. The CO and N_2 yields display a similar dependence on the temperature. At 350°C the CO/CO_2 ratio is about 1. The conversion of *iso*-C_4H_{10} to CO_2 increases with temperature in the whole temperature range investigated. The slope is steep at low temperatures. Once all hydrocarbon is consumed, further increase of CO_2 formation is due to secondary oxidization of CO. Both CO and CO_2 are true primary oxidation products. Fig. 7 also shows the effectiveness factor which decreases with temperature.

When 10% H_2O was added to the reactant feed, the catalytic activity of Fe/ZSM-5, as shown in Fig. 7(B), was not suppressed by the presence of H_2O. Actually, at low temperatures, the N_2 yield is even higher than in the absence of H_2O. At high temperatures, the conversion of NO to N_2 is identical in the absence and the presence of water; however, the secondary oxidation of CO to CO_2 is suppressed by the presence of H_2O. Clearly, the yield of CO is higher and that of CO_2 is lower when H_2O was added.

Similar SCR activities were observed over samples 6 and 8. However, the maximum NO conversion over sample 6 is shifted to lower temperature. The maximum conversion of NO to N_2 and the corresponding temperature are listed in Table 2. In addition, the conversion of NO to N_2 at 300°C is also given in the same table.

To further investigate the effect of H_2O on the Fe/ZSM-5 catalyst, a long duration test was carried out over a catalyst similar to sample 7. (Because of the

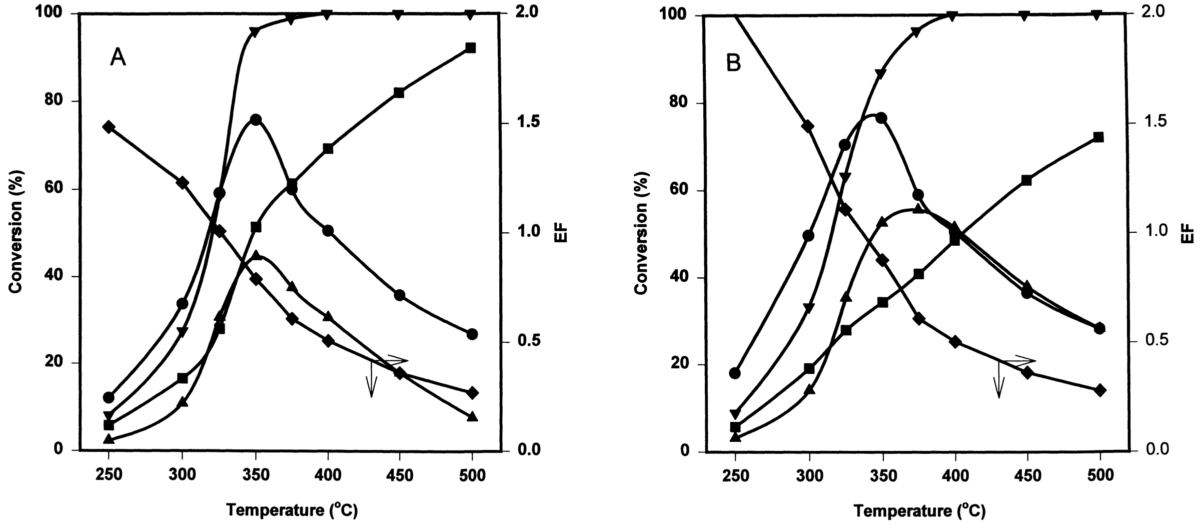

Fig. 7. The effect of temperature on the *iso*-C_4H_{10}+NO+O_2 reaction over Fe/ZSM-5 (sample 7). Reactant feed: GHSV 42 000 h^{-1}, *iso*-C_4H_{10} 0.2%, NO 0.2%, O_2 3%. (A) 0% H_2O; (B) 10% H_2O (conversion of (●) NO to N_2, (■) *iso*-C_4H_{10} to CO_2, (▲) *iso*-C_4H_{10} to CO, (▼) *iso*-C_4H_{10} to CO_2 and CO, and (◆) effectiveness factor).

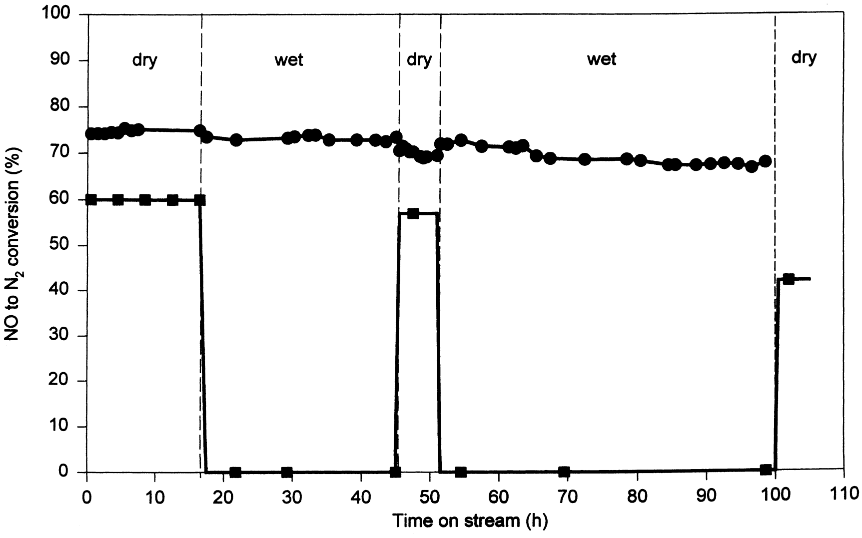

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Fig. 8. Effect of the introduction of H_2O on the conversion of NO to N_2 over: (●) Fe/ZSM-5 (temperature=375°C, GHSV 42 000 h^{-1}, *iso*-C_4H_{10} 0.2%, NO 0.2%, O_2 3%, H_2O: 0% for dry; 10% for wet); (■) Cu/ZSM-5 (temperature=400°C, GHSV 120 000 h^{-1}, C_3H_8 0.1%, NO 0.1%, O_2 2%, H_2O: 0% for dry; 10% for wet).

different calcination procedure, the temperature of maximum NO conversion is shifted to 375°C.) The conversion of NO to N_2 is plotted in Fig. 8 as a function of time on stream. Clearly, the presence of 10% H_2O has almost no effect on this Fe/ZSM-5; the same result was reported by Feng and Hall [11].

After 100 h TOS the NO_x conversion had decreased by 5%. Remarkably, however, this decrease is not caused by hydrothermal degeneration of the zeolite, but by some carbonaceous deposit. Upon removing it by oxidation, the original activity of the catalyst is fully restored. In order to illustrate the totally different response to water of the Fe/ZSM-5 and Cu/ZSM-5 catalysts, we have included in Fig. 8 our previous result with Cu/ZSM-5 [9]. In this comparison a GHSV of 120 000 h^{-1} was used for Cu/ZSM-5. Upon adding 10% H_2O to the feed gas, the NO conversion over Cu/ZSM-5 was totally suppressed. Part of this effect is reversible; with dry feed gas the catalyst regains some activity, without, however, reaching its original level.

4. Discussion

It is well known that monovalent cations can be exchanged more easily into a zeolite than di- or trivalent cations because the positive charge of multivalent cations has to be balanced by spatially separated negative charges of the zeolite matrix. This situation strongly favors hydrolysis of multivalent ions, such as Cu^{2+} or Fe^{2+}, to protons and monopositive oxoions or hydroxoions, such as $Cu(OH)^+$ [22,23] or $Fe(OH)^+$ [11]. An exchange of the Na^+ ions in Na/ZSM-5 with $Fe(OH)^+$ should lead to a limiting exchange level of Fe/Al=1. However, as it is known that $Fe(OH)^+$ ions can exist only in a very narrow pH region [24], where it will be in equilibrium with Fe^{2+} and/or $Fe(OH)_2$. Accurate control of the pH is, however, problematic inside the pores of a zeolite. This may be one cause for the difficulty to obtain reproducible results by ion exchange of Fe^{2+} ions in aqueous slurries with ZSM-5 samples of different origin. Some commercial ZSM-5 catalysts are made by means of a template, others from caustic alkaline solutions.

Although in our catalyst preparations from aqueous slurries of the solution we controlled the pH to be 6.8–7.0, we have no certainty about the local pH inside the channels. This could explain that for the UOP zeolite, which is a template preparation, the Na/Al ratio remained <1, although we tried to back-exchange the proton with sodium. The remaining protons are likely to shift the equilibrium between Fe^{2+} and the corresponding oxo- or hydroxo- ions in favor of Fe^{2+}. For the Uetikon and ALSI-5 zeolites, which are template-free preparations, the high pH in the pore of zeolite may introduce precipitation of $Fe(OH)_2$.

An advantage of the sublimation method for the preparation of Fe/zeolite catalysts is that it is much less sensitive to the origin of the zeolite and its history. Another obvious advantage is the ease to reach high Fe/Al ratios up to Fe/Al=1. The history of zeolite-based De-NO_x catalysts is one of "excessively exchanged" metal ions [5,25] or high metal loadings. A probable cause for this preference is that in De-NO_x catalysts oxo-, hydroxo- and oxygen bridged ions are crucial, and their relative concentration is known to increase with metal loading [18,23,26].

$FeCl_3$ has a low sublimation temperature of 316°C. In the gas phase, dimeric Fe_2Cl_6 prevails. Its dimensions enable it to enter the cavities of ZSM-5, as was argued previously for the $GaCl_3$+ZSM-5 system [13,14]. During sublimation, the gas flow carries the Fe_2Cl_6 vapor into the cavities of the zeolite, where the chemical reaction with the acid sites inside the zeolites takes place:

$$Fe_2Cl_6 + 2H^+ = [Fe_2Cl_4]^{2+} + 2HCl \qquad (1)$$

The $[Fe_2Cl_4]^{2+}$ ions stay inside the zeolite cavities. Once all the acid sites are consumed, Fe_2Cl_6 molecules will simply pass through the zeolite bed. After sublimation, the ratio of Fe to Al in the zeolite and to the HCl absorbed by NaOH is found to be Fe/Al/Cl=1/1/1, in agreement with the assumption that reaction (1) is the driving force for the introduction of iron into the zeolite.

FTIR spectroscopy of the sample after sublimation shows that both peaks at 3750 and 3610 cm^{-1} disappear, in conformity with reaction (1). Reaction (1) needs two protons located within a suitable distance. A recent paper by Feng and Hall [27] shows that the probability for such proton sites is very high for ZSM-5 with a Si/Al ratio of 10–20. Therefore, uniformly dispersed iron and a high iron loading up to Fe/Al=1 are easily obtained.

Fe^{3+} salts in aqueous solution are known for their high tendency to hydrolyze; a binuclear complex $[Fe–O–Fe]^{4+}$ has been described in the literature [28]. It is reasonable to assume that an oxygen bridged binuclear iron complex $[(HO)Fe–O–Fe(OH)]^{2+}$ would be formed on the zeolite upon exposing the sample to water. An oxygen bridged binuclear iron complex was first proposed by Garten et al. [16] for Fe/Y . They found this to act as an oxygen carrier, which can be reduced with H_2 and oxidized with O_2. Those results were confirmed by Hall et al. [29,30] over Fe/Y and Fe/M zeolites. They found that NO and N_2O could also be used as oxidizing agents, while CO, which is unable to reduce naked Fe^{3+} ions, worked equally well as a reducing agent. In the present work the H_2-TPR profile in Fig. 1 shows that there is only one reduction peak. The ratio of H_2/Fe=0.5 justifies its assignment to the removal of the bridging oxygen.

That CO-TPR gives a higher CO/Fe=0.8 ratio is in agreement with previous results reported by Petunchi and Hall [30] over Fe/M . The additional CO consumption (>CO/Fe=0.5) is caused by reaction of CO with structural hydroxyls i.e. basically a water–gas shift reaction [31]. Indeed, we observed desorption of H_2O in the temperature region where the CO-TPR shoulder appeared (Fig. 6). Over Fe/Y, unlike Fe/ZSM-5, the CO reduction ion leads only to a ratio of CO/Fe=0.5. This suggests that the hydroxyls that are consumed during water–gas shift over Fe/ZSM-5 were originally ligated to iron. Such ligancy is, however, not possible for the Fe^{2+} ions in a Y zeolite where they are known to be preferentially located inside the hexagonal prisms.

The totality of the TPR data, in particular the CO-TPR data, thus suggests that in our Fe/ZSM-5 samples the majority of the Fe^{3+} will be present as an oxygen bridged binuclear iron complex such as $[(HO)Fe–O–Fe(OH)]^{2+}$.

FTIR results of the washed and calcined samples show that the band at 3610 cm^{-1} is very weak. This suggests that most of the iron remains at exchange sites. The FTIR data also show that not only Brønsted acid sites, but also isolated and terminal silanols are consumed during sublimation. The interaction of $FeCl_3$ with silanol groups is, however, weaker than with Brønsted acid sites. During hydrolysis, iron migrates away from the weaker sites, by consequence the peak at 3750 cm^{-1} re-appears in the washed and calcined sample and some iron oxide is detected by HRAEM.

Samples 1 and 4 have similar iron contents at the exchange sites and they show nearly the same SCR activities. This indicates that iron at the exchange sites is the active species for the SCR reaction. For the sample prepared by sublimation, there are more of these Fe species present in the catalyst, hence its activity is higher.

The SCR of NO with a hydrocarbon in the presence of excess O_2 can be schematized as a competition of two reactions, as the hydrocarbon reacts with both NO_x and O_2. Initially, both reaction rates will increase with temperature, but when most of the hydrocarbon is consumed, the rates will decrease. The maximum conversion of NO_x is a result of this competition; it does not reflect an absolute rate. The latter can be estimated from the reaction at low conversion. In Table 2 the NO conversion at 300°C is given; at this temperature, less than 40% of the hydrocarbon is converted over all catalyst samples. The data show that catalyst activity increases with Fe loading. In the last column of this table, the NO turn-over numbers (TON) at 300°C are given. All three catalysts show the same conversion per mole of iron; these data suggest that all samples make use of the same active sites.

An oxygen bridged binuclear iron complex is considered a plausible prototype for the active sites. It can be reduced by removing the bridging oxygen. H_2-TPR and CO-TPR show that this reduction requires a higher temperature (about 400°C) than removal of the bridging oxygen from the corresponding $[Cu–O–Cu]^{2+}$ complex in Cu/ZSM-5 which takes place near 15°C [9]. It is therefore clear that the oxidation activity of Fe/ZSM-5 is much lower than that of Cu/ZSM-5. If CO is formed in the oxidation of the hydrocarbon, its further oxidation to CO_2 will therefore be much faster with Cu/ZSM-5 than with Fe/ZSM-5, which explains that CO is only detected with the latter catalyst.

The effect of H_2O is quite different for Fe/ZSM-5 and Cu/ZSM-5. The presence of 10% H_2O does not lower the SCR of NO_x over Fe/ZSM-5. This is in strong contrast to Cu/ZSM-5 where both a reversible and an irreversible deleterious effect of H_2O are observed. The irreversible deactivation of Cu/ZSM-5 has been attributed to dealumination, sintering of copper forming agglomerated copper oxide and formation of Cu-aluminate [6–9]. The reversible effect is usually considered as being caused by competitive adsorption of H_2O on the transition metal cation site [2,32].

With Fe/ZSM-5 catalysts, the presence of H_2O merely suppresses the combustion activity, especially for the secondary oxidation of CO to CO_2, but H_2O does not affect the SCR of NO_x. This finding is in line with previous results of Lunin et al. [12] with montmorillonite supported Fe catalysts and results of Feng and Hall [11] with Fe/ZSM-5. The reason for this insensitivity is not clear at this moment. Our previous results suggest that in SCR of NO_x with alkanes over ZSM-5 supported metals an adsorbed complex, NO_y, is crucial. It is formed from NO and O_2 and it is the active site for the interaction with the hydrocarbon [33]. With some metals, NO_y has been identified as a nitro group, and with others as a nitrito ligand or a mono- or bidentate nitrate ion. If the same chemistry holds for the Fe/ZSM-5 catalyst, one could assume that the NO_y ligand is held more strongly by the Fe ions than by Cu or Co ions, so that displacement of NO_y from Fe by H_2O ligands does not occur. It is too early to say, however, whether this mechanism applies to SCR over Fe/ZSM-5. The present study shows that at low reaction temperatures, the presence of H_2O even slightly enhances the NO conversion. This could indicate that H_2O impedes the formation of carbonaceous deposits. As shown above, the combustion activity of Fe/ZSM-5 is not very high, so that the carbonaceous deposits can form on the catalyst at low temperature.

Reduction of naked ions (such as Fe^{3+}) with H_2 results in the formation of protons; however, in the reduction of oxoions the product is H_2O. As protons are instrumental in the dealumination of zeolites, it is conceivable that the high resistance of Fe/ZSM-5 against destruction of the zeolite matrix is a consequence of the fact that only oxoions are operating. A related phenomenon is the resistance against dealumination. It was shown by Bolt [34] that the formation of metal aluminates depends on the nature of the metal. Copper eagerly forms an aluminate, but iron hardly diffuses into alumina both in the absence and in the presence of steam.

5. Conclusion

1. Fe/ZSM-5 with iron loading as high as Fe/Al=1 can be easily achieved by subliming $FeCl_3$ into H/ZSM-5. This preparation method is less sensitive to the origin of zeolite and its history than the conventional ion-exchange method.

2. Fe/ZSM-5 shows high SCR activity and durability both in the absence of H_2O and in its presence.
3. At low temperatures, the presence of H_2O even enhances the NO conversion.
4. Over Fe/ZSM-5, CO and CO_2 are both primary products of the SCR of NO_x with *iso*-butane.
5. An oxygen bridged binuclear iron complex $[(HO)Fe–O–Fe(OH)]^{2+}$ is a plausible prototype for the active iron species.

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