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Iron Clusters Occluded in Zeolite ZSM5 Micropores

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Abstract

The effect of high temperature calcination and steaming on iron-containing zeolite was studied. Iron was introduced by sublimation of $FeCl_3$. FTIR measurements clearly show the disappearance of Broensted acid sites upon such treatments. This is attributed to a reaction between small occluded Fe oxide clusters obtained after initial low temperature calcination and the zeolite protons to give cationic Fe species compensating the negative zeolite charge. High temperature calcination and especially steaming considerably increase the catalyst activity in nitrous oxide decomposition. The two treated catalysts exhibit a higher apparent activation energy than the original sample. This high apparent activation energy is compensated by a high pre-exponential factor. In Fe/ZSM5 the activity mainly derives from small Fe oxide clusters, while upon treatment more active cationic species are generated. The kinetic parameters point to a stronger Fe–O bond for the latter case.

INTRODUCTION

Transition metals in zeolite host matrices provide unique catalytic properties [1]. A prime example is the ability of small occluded Fe oxide particles in pentasil zeolite to selectively hydroxylate benzene to phenol with nitrous oxide as oxidant [2–8]. Fe/ZSM5 also provides possibilities for selective reduction of NO_x [9–15] and the decomposition of N_2O [15–19].

Various preparation methods are available to introduce Fe in the zeolite micropores. Generally, ion exchange leads to bulky iron oxide agglomerates on the zeolite external surface. While the preferred preparation route for catalysts active in benzene hydroxylation appears to be steaming of isomorphously Fe-substituted zeolites [2–8, 20, 21], sublimation of $FeCl_3$ provides a controlled way to deposit a higher amount of Fe in the zeolite micropore space [11–17, 22, 23]. The amount of Fe can be tuned by the choice of the Si/Al ratio of the parent zeolite. These catalysts have shown a high activity in SCR of NO_x [19] and nitrous oxide decomposition [19, 22].

In the present contribution, we further study the effect of various high temperature pretreatments on catalysts prepared by the sublimation method. The catalysts are extensively characterized by FTIR and ^{27}Al NMR and tested in the decomposition of N_2O. Furthermore, their ability to produce phenol from benzene and nitrous oxide was evaluated.

EXPERIMENTAL

Catalyst preparation

NH_4ZSM5 (Akzo Nobel, Si/Al = 19.4) was calcined in pure oxygen at 823 K for 2 h to yield HZSM5. Anhydrous $FeCl_3$ (Aldrich, reagent grade 99.9 %) was sublimed onto HZSM5 (Akzo Nobel, Si/Al = 19.4) [11, 12]. The temperature of the iron precursor and zeolite were 573 K and 593 K, respectively. Subsequently, the sample was washed in 2500 ml deionized water twice by stirring for 1 h each time. After drying in an oven at 383 K overnight, 1 g of the resulting material (Fe/ZSM5) was calcined in 20 % vol. O_2 in He at a flow rate of

200 Nml/min for 2 h. Further treatment of the original catalyst was carried out: (a) 200 mg Fe/ZSM5 was calcined in 20 % vol. O_2 in He at a flow of 200 ml/min at 973 K for 3 h (Fe/ZSM5-HTC), (b) 200 mg Fe/ZSM5 was steamed in mixture of 20 % vol. O_2 and 10 % vol. water vapor at a flow rate of 200 ml/min at 973 K for 3 h (Fe/ZSM5-HTS).

Characterization

The samples contained approximately 3.6 % mass Fe (ICP-OCES), which corresponds to a Fe/Al ratio of 0.97. The Fe content of the three samples were found to be identical.

Infrared spectra of self-supporting 10 mg catalyst wafers were recorded at room temperature on a Bruker IFS113 Fourier Transform IR spectrometer with DTGS detector at a resolution of 4 cm^{-1}. Prior to IR measurement, the catalyst was pretreated *in situ* at 773 K for 1 h *in vacuo* (pressure $<10^{-6}$ mbar). Normalization of the overtones of the zeolite lattice vibrations (1870–1950 cm^{-1}) was applied to quantitatively determine the number of Broensted acid sites.

Solid-state ^{27}Al magic-angle spinning NMR spectra were obtained on a 11.7-T Bruker DMX500 spectrometer equipped with a 2.5-mm MAS probe head, and operating at a ^{27}Al NMR frequency of 130 MHz. The sample-rotation rate was 30 kHz. Rotor-synchronized echoes were recorded with a two-pulse sequence p_1-τ-p_2-τ-acquisition with $p_2 = 2p_1 = 2.4$ μs, and $\tau = 31.5$ μs. The interscan delay, 1 s, was long enough to avoid ^{27}Al-saturation effects. Chemical shifts were referenced to a saturated $Al(NO_3)_3$ solution.

Reactivity studies

Activity measurements were carried out in an atmospheric gas-phase single-pass fixed-bed reactor system (quartz reactor, i. d. 4 mm). Gas-phase reactants were fed by thermal mass flow controllers (Brooks). The reactant composition for nitrous oxide decomposition was 3500 ppm N_2O in He, which was fed to the reactor at a GHSV of 24 000 h^{-1}. Effluent products (N_2O, N_2 and O_2) were detected by an online quadrupole mass spectrometer. An amount of 40 mg catalyst (sieve fraction 125–425 μm) was diluted with carborundum to fulfill plug flow conditions. Prior to reaction, catalysts were pretreated in a 100 Nml/min He flow at 723 K for 1 h after heating at a rate of 2 K/min.

The catalysts were qualitatively tested for the production of phenol at 648 K. To this end, benzene was vaporized by a syringe in the nitrous oxide stream before the catalyst bed. The effluent products were condensed after the reactor and analyzed by GC-MS.

RESULTS

Characterization

Figure 1 displays infrared spectra for the various catalysts including the parent HZSM5. The band at 3613 cm^{-1} is the stretching vibration of the Broensted hydroxyl groups, while the band at 3745 cm^{-1} relates to the vibration

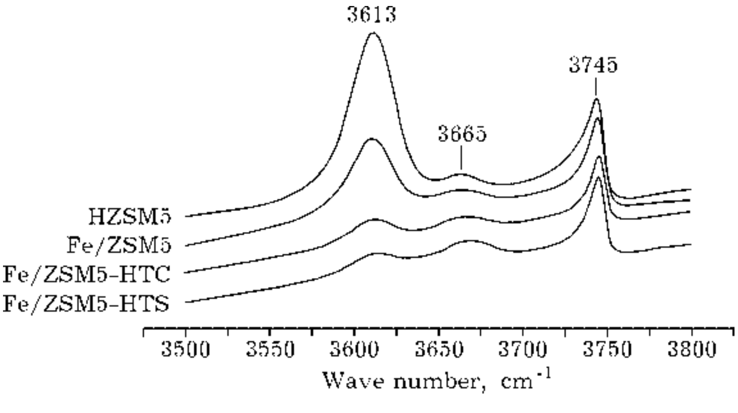

Fig. 1. Infrared spectra of the parent zeolite, Fe/ZSM5, Fe/ZSM5-HTC and Fe/ZSM5-HTS at room temperature after drying.

of terminal Si–OH groups (26, 27). Generally, the weak band at 3665 cm^{-1} is assigned to the hydroxyl groups connected to extra-lattice aluminium [24]. By calibration with the overtone of lattice vibrations, a quantitative comparison of the number of Broensted hydroxyl groups was possible. While Chen and Sachtler [11] described the disappearance of bridging hydroxyl groups after $FeCl_3$ sublimation, our IR data indicate that approximately 45 % of these groups are regenerated after washing and calcination at 723 K. The remaining charge-compensation derives from the coordination of cationic Fe-species to the zeolite framework. After calcination at 973 K, the band at 3613 cm^{-1} has further decreased in intensity and we calculate that approximately 8 % of the original Broensted acid sites persist. A similar effect is found for Fe/ZSM5-HTS. In this case, a small increase in the band at 3665 cm^{-1} points to partial dealumination of the zeolite structure. XRD spectra of the various samples showed that the MFI structure remains intact, while the steaming treatment results in a small increase of amorphous phases in Fe/ZSM5-HTS.

The magic-angle spinning (MAS) ^{27}Al NMR spectra of the various samples are collected in Fig. 2. The signal at 57 ppm is assigned to tetrahedrally coordinated aluminium in the zeolite lattice. The signal at 0 ppm in the spectra of Fe/ZSM5-HTC and Fe/ZSM5-HTS belongs to a fraction of octahedrally coordinated extra-lattice Al, which is particularly significant for the steamed zeolite. This is consistent with the findings of a signal of hydroxyl groups associated with extra-lattice aluminium at 3665 cm^{-1}. For Fe/ZSM5-HTS spectral intensity is also detected between the 57-ppm and the 6-ppm signal. Typically, a broad peak in this shift-range is attributed to non-lattice tetrahedrally or pentacoordinated aluminum [25]. Such Al species may exist in the zeolite micropores as small Al_2O_3 particles without associated hydroxyl groups. This explains why we cannot detect the increase of the 3665 cm^{-1} band in Fe/ZSM5-HTS. A quantitative comparison with the parent ZSM5 indicates that only ~10 % of the Al species is detectable in the echo spectra. This is probably a result of the line broadening caused by paramagnetic Fe and indicates that Fe is located close to the Broensted sites in the zeolites, although a decrease of the symmetry around Al nuclei can also play a role.

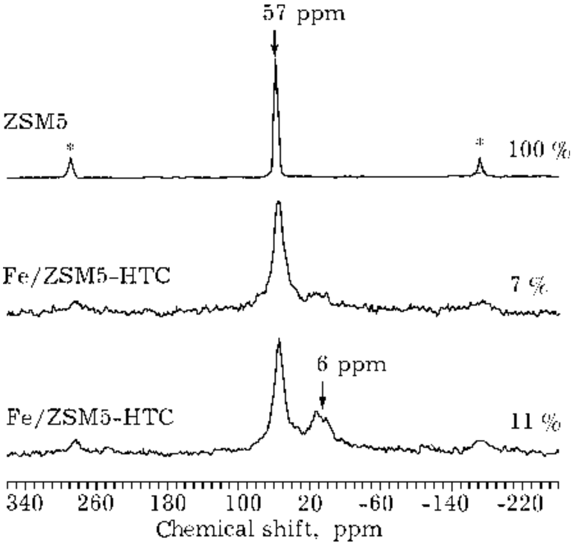

Fig. 2. ^{27}Al NMR MAS spectra of parent HZSM5(15), Fe/ZSM5-HTC and Fe/ZSM5-HTS. MAS sidebands are indicated with an asterix.

Reactivity

Figure 3 shows the nitrous oxide conversion as a function of the reaction temperature for the catalysts under study. The activity of Fe/ZSM5 can be efficiently increased by high temperature treatments (Fe/ZSM5-HTC and Fe/ZSM5-HTS). While Fe/ZSM5-HTC decreases the temperature needed for 50 % conversion by 30 K, steaming allows a further reduction of 10 K. The apparent activation energies and pre-exponential factors for the various catalysts are condensed in Table 1.

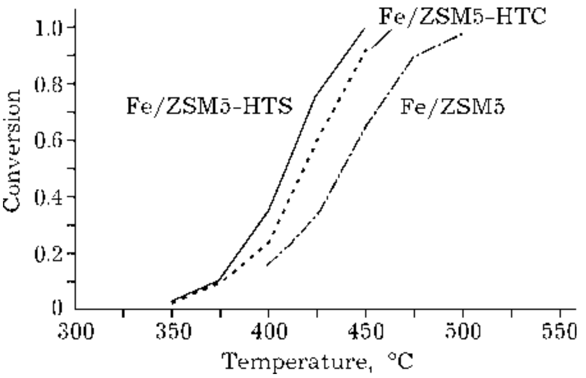

Fig. 3. Nitrous oxide conversion as a function of temperature for Fe/ZSM5, Fe/ZSM5-HTC and Fe/ZSM5-HTS (GHSV = 24 000 h^{-1}).

TABLE 1

Kinetic parameters for Fe/ZSM5 catalyst in nitrous oxide decomposition (activation energies: ± 8 kJ/mol; pre-exponential factors: ± 10 %)

Catalyst	Apparent activation energy, kJ/mol	Pre-exponential factor, 1/s
Fe/ZSM5	136	$4\ 10^{10}$
Fe/ZSM5-HTC	186	$5\ 10^{14}$
Fe/ZSM5-HTS	195	$4\ 10^{15}$

The benzene hydroxylation tests showed that phenol was not formed on the Fe/ZSM5 catalysts. Both Fe/ZSM5-HTC and Fe/ZSM5-HTS showed phenol production with the latter one producing considerably more phenol.

DISCUSSION

The sublimation procedure effectively replaces all Broensted acid sites with iron chlorine complexes [11]. The IR results show that approximately 45 % of these Broensted acid sites are regenerated after washing, drying and calcination at 773 K. This results in various Fe species including bulky iron oxide agglomerates on the external zeolite surface, and positively charged Fe^{3+} species and neutral nanoclusters in the zeolite micropores. For such intracrystalline species, diiron species have been advanced by several authors [5, 11] in analogy with the active center in methane monooxygenase enzyme [26]. High temperature calcination (Fe/ZSM5-HTC) or steaming (Fe/ZSM5-HTS) results in the disappearance of nearly 90 % of the bridging hydroxyl groups. This dramatic decrease is explained by the reaction of neutral iron oxide nanoclusters with the Broensted acid sites at elevated temperatures [22]. Dehydroxylation can only play a minor role since high temperature calcination of the parent zeolite only resulted in a small decrease of Broensted acidity. Furthermore, Broensted acid sites in Fe/ZSM5-HTC can be regenerated by exposure to water vapor at 773 K [23]. This shows that cationic Fe species generated in Fe/ZSM5-HTC can be rehydrolysed. Neutral species include Fe oxide particles at the external zeolite surface and Fe oxide nanoclusters occluded in the zeolite micropores. We propose that such nanoclusters which is in close proximity to the Broensted acid sites reacts with the zeolitic protons. Bulky Fe oxide clusters, prepared by impregnation of $Fe(NO_3)_3$ on a silica support, are not active in N_2O decomposition below 773 K, while Fe oxide agglomerates formed on the external zeolite surface after steaming iron-substituted ZSM5 cannot activate nitrous oxide as oxidant for aromatics [21]. This indicates that the active species in Fe/ZSM5 are Fe oxide nanoclusters and cationic Fe species. High temperature calcination results in an increase of the number of cationic Fe species. The almost complete disappearance of Broensted acidity may indicate that such further treatment leads to a catalyst with almost exclusively cationic Fe species present in the micropore space. It appears that these cationic species display a much higher nitrous oxide decomposition activity than small Fe oxide species. Alternatively, the high temperature treatment may lead to migration of Fe species from the zeolite pores to the external surface, thus opening up the micropores. However, preliminary TEM measurements show that the amount of external Fe oxide clusters does not increase to a large extent upon high temperature treatments. Moreover, the reaction of Fe oxide species and zeolite protons appears to be reversible upon exposure to water vapor at 773 K [23]. Large crystals on the external surface will not redistribute again under such conditions.

The large change in apparent activation energy between original Fe/ZSM5 and further treated Fe/ZSM5 as determined over a wide temperature range indicates that indeed the catalytic nature of Fe oxide and cationic Fe species are very different. This is taken as further evidence that the neutral nanoclusters are also able to catalyze N_2O decomposition although at a much lower rate. The much higher apparent activation energy for the more active species is compensated by a high pre-exponential factor. The difference is 4–5 orders of magnitude. Thus, we draw the main conclusion that in Fe/ZSM5 various iron species are responsible for nitrous oxide decomposition.

While the reaction between Fe oxide nanoclusters upon high temperature calcination is partly reversible, steaming essentially leads to partial dealumination as derived from the presence of pentacoordinated Al species. However, the fact that part of the aluminium is not detected by NMR due to the presence of the paramagnetic iron nuclei makes this interpretation inconclusive.

The rate limiting step for nitrous oxide decomposition over Fe/ZSM5 is proposed to be the removal of adsorbed oxygen, generated by the reaction of N_2O with an iron center, by N_2O [27]. The large change in kinetic parameters can thus be explained by the nature of the adsorbed oxygen atom (O*). From its higher apparent activation energy, we conclude that the Fe−O* bond energy is higher for the more active catalyst. Such a strong Fe−O* bond leads to a large gain in entropy in the rate limiting step, thus providing a tentative explanation for the increase of the pre-exponential factor. The difference in the nature of the Fe species can partly be proven by their oxidation ability towards hydrocarbons. We have done some preliminary tests of the conversion of benzene to phenol using N_2O as the oxidant on various Fe/ZSM5 samples. In our initial qualitative analysis, the original Fe/ZSM5 has a very low activity whereas the high temperature calcined and especially steamed Fe/ZSM5 show good catalytic performance.

CONCLUSION

High temperature treatments of Fe/ZSM5 prepared by the sublimation of $FeCl_3$ on HZSM5 is found to strongly increase the rate of nitrous oxide decomposition. The activity strongly depends on the nature of Fe species inside the zeolite micropores. In Fe/ZSM5 the catalytic activity mainly derives from Fe oxide nanoclusters. Calcination or steam treatments at 973 K induces a reaction between these nanoclusters and zeolite protons, resulting in cationic Fe species. Such species have an appreciably higher activity, while kinetic parameters point to a stronger Fe−O bond for this case.

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