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The role of Brønsted acidity in the selective catalytic reduction of NO with ammonia over Fe-ZSM-5

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ABSTRACT

The selective catalytic reduction of NO with NH_3 has been studied over Fe-ZSM-5 samples with equal exchange degrees and active sites but different Brønsted acidities. Additionally, the activity of fresh and aged samples in NH_3–SCR with NO (standard SCR) has been compared with that in NH_3–SCR with NO/NO_2 (fast SCR), where oxidation activity is not essential.

Using NH_3–TPD–FTIR experiments and DRIFTS measurements, it was shown that the concentration of Brønsted acid sites decreases with an increase in Fe loading, suggesting that, up to Fe/Al = 0.39, about one Brønsted acid site is substituted by one Fe site and that most of the iron is present as a dispersion of cations. A maximum of about 55% of all Brønsted acid sites can be exchanged in aqueous Fe^{2+} solution.

These experiments revealed that the acidity of the catalyst is not a crucial factor for high activity and that Brønsted acidity may not be required for adsorbing or activating the ammonia, but it is necessary to bind and disperse the metal ions. On the other hand, the oxidation activity of Fe-ZSM-5 was found to be the main factor that controls the high activity. The altered oxidation activity is largely responsible for the decreased SCR activity after hydrothermal aging.

1. Introduction

Despite several studies on the structure–activity relationship of Fe-ZSM-5 catalysts for the selective catalytic reduction of nitrogen oxides (NO_x, $x = 1, 2$) with ammonia (SCR), the debate over the nature of active sites in this catalyst is ongoing. This applies to the nature of the iron center, which we have investigated in another study [1]) as well as to the role of the Brønsted acid sites in the SCR mechanism. It is well known that for the SCR of NO (standard SCR) over Fe-ZSM-5, part of the NO first has to be oxidized to adsorbed NO_2 species, which is the rate-determining step of the mechanism. This takes place at iron centers with unknown nuclearity [2–7]. However, it is also generally assumed that Brønsted acidity is required for binding and activating the ammonia, thereby forming ammonium ions which react further with the surface NO_x species to form N_2 and H_2O [3,6,8–10].

$$2Z - NH_4^+ + NO + NO_2 \rightarrow 2N_2 + 3H_2O + 2Z - H^+ \quad (\text{with } Z = \text{zeolite}) \qquad (1)$$

It has been proposed that once NH_3 has been activated, NO_2 reacts with two adjacent NH_4^+ ions to form an active complex, $[(NH_4)_xNO_2]$ (with $x = 1, 2$) [7,11,12], which is the same key compound proposed by Sun et al. [13] and Yeom at al. ($x = 1$) [14]. Li et al. [15] showed that the SCR reaction is very efficiently catalyzed by zeolites due to the protonation of the intermediate $[NH_4NO_2]$ complex in the SCR cycle by the Brønsted acid sites, leading to an intermediate product that decomposes even at room temperature. On the other hand, very recently Schwidder et al. [16] showed that even with Fe-ZSM-5 catalysts without Brønsted acidity, a quite large reaction rate could be achieved for standard SCR between about 250 and 650 °C. These results support the existence of a promoting effect of Brønsted acid sites, but also indicate that the Brønsted acidity may not be indispensable.

Other studies of the SCR mechanism on a broad variety of materials point in the same direction. Results from Peña et al. [17] showed that Brønsted acidity is not necessary for the SCR of NO over different metal oxides on TiO_2 at low temperature, but that Lewis acidity is required. Amores et al. [18] investigated TiO_2 catalysts supported with different metal oxides, and concluded from their results that NH_4^+ ions are not involved in standard SCR. This is in line with a study of this reaction by Liang et al. [19] demonstrating the importance of Lewis acidity for high activity over Mn/Al-SBA-15 molecular sieves as well as the minor impact of Brønsted acidity. Liu et al. [20] compared the reactivity of iron impregnated Al_2O_3, TiO_2, and BEA zeolite and found the order of

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SCR performance to be Fe/BEA ≫ $Fe/TiO_2 > Fe/Al_2O_3$, which is in the same order as ammonia adsorption capacity. Remarkably, no evidence that the presence of either Brønsted or Lewis acidity is a key factor for the activation of ammonia was found. The authors suggested that the form in which ammonia is held by the support is not crucial and assumed that the support acts mainly as a reservoir for ammonia, which can then migrate to the active site for reaction with NO_x.

In the present study, we tried to obtain a more detailed picture of the role of Brønsted acidity in the SCR of NO by ammonia in Fe-ZSM-5 catalysts. For this purpose, catalysts with different Brønsted acidities, but with identical structure and active site concentration were studied. In contrast to previous investigations, a silanization agent was used instead of simple alkali or earth alkaline metals to specifically reduce the Brønsted acidity without hampering the iron sites of the catalyst significantly. Additionally, hydrothermally aged Fe-ZSM-5 samples were used as comparison materials with both reduced Brønsted acidity and lowered oxidation activity.

We used liquid ion exchange for the preparation of the Fe-ZSM-5 samples, whereby special attention was paid to controlling the iron concentration during the exchange process and to keeping the exchange times constant. Our preparation differs from the standard liquid ion exchange methods by the use of ammonium chloride to control the exchange degree, which yields in particularly homogenously exchanged Fe-ZSM-5 samples.

2. Experimental

2.1. Preparation of the samples

Fe-ZSM-5 samples (Table 1) were prepared by liquid ion exchange of NH_4–ZSM-5 (Süd-Chemie AG, Si/Al atomic ratio = 13.5). Within this work, the samples are labeled as Fe-ZSM-5 (*n*), where n is the exchange degree Fe/Al. For the ion exchange, 5–15 g/L of $FeCl_2{\cdot}4H_2O$ and 2–20 g of ammonium chloride, depending on the desired exchange degree, were added to a suspension of NH_4–ZSM-5 in water. After it was stirred overnight under nitrogen at 80 °C, the resulting Fe-ZSM-5 material was filtered, washed with 200 ml/g of deionized water, dried overnight in air at 80 °C, and calcined at 500 °C for 3 h under nitrogen. The addition of ammonium chloride to the reaction mixture shifted the equilibrium of the exchange reaction toward free solvated metal salts. Thus, micropore diffusion was retained and the dispersion of the metal improved [21], resulting in a more homogeneous distribution of the exchange metal. In our opinion, very low concentration exchange solutions or short exchange times, as is often described in the literature in order to obtain low-loaded zeolites, inevitably lead to a non-homogeneous metal distribution inside the zeolite. This may be because iron ions will be quantitatively and strongly fixed on the periphery of the grains [22] in these types of exchange conditions.

The catalyst with a reduced Brønsted acidity, denoted as Fe-ZSM-5 (0.04)*, was prepared by exchanging a hydrothermally pre-treated NH_4–ZSM-5 as a starting material (650 °C, 10% H_2O for 1.5 h).

Fe-ZSM-5 (0.3) was aged under hydrothermal conditions (10% H_2O in air) for 8 h at 650 °C and 800 °C, respectively, in order to prepare samples with reduced Brønsted acidity as well as lowered redox activity.

A silanized Fe-ZSM-5 catalyst was prepared using triisopropylchlorosilane (TIPCS) as the silanization reagent. A superstoichiometric amount of the organosilane was added to a zeolite/toluene suspension under nitrogen in a glove box. This mixture was stirred under reflux overnight under nitrogen, then filtered and washed with toluene.

The highly exchanged sample CDV–Fe/ZSM-5 (0.74) was prepared via the chemical vapor ion exchange (CVD) method described by Chen and Sachtler [23], since it is not possible to prepare Fe-ZSM-5 samples with an exchange degree higher than Fe/Al ≈ 0.5 by liquid ion exchange. NH_4–ZSM-5 was converted into the acidic form by calcination in air at 450 °C for 2.5 h. A U-shaped quartz reactor was used for the CVD exchange. The reactor was built with a porous frit in each of the legs, allowing the separation of the H-ZSM-5 support and the $FeCl_3$ precursor. In order to remove adsorbed moisture, 15 g of the H-ZSM-5 was loaded onto one frit and flushed with nitrogen (100 mL/min) for 1 h at 380 °C. Afterwards, an appropriate amount of anhydrous $FeCl_3$ (98%, Fluka) was loaded on the second frit and the reactor was heated to 350 °C for 30 min under N_2 (35 mL/min). The resulting Fe-ZSM-5 material was washed with 200 mL/g deionized water, dried overnight in air at 80 °C, and calcined at 500 °C for 3 h under nitrogen.

For activity measurements, the catalytic materials were washcoated on 40.5 mm × 17.6 mm × 12.8 mm cordierite monoliths with a cell density of 400 cpsi. The respective slurries were composed of a liquid phase of 1.5 mL Ludox AS-40 in 40 mL deionized water and a solid phase of approximately 10 g of Fe-ZSM-5. The monoliths were coated with the zeolites by immersing the monoliths in the slurries, blowing out the excess slurry, and drying them in an air flow at 110 °C for 1 min. This procedure was repeated until the monoliths were coated with 0.8–1.0 g zeolite, corresponding to approximately 100 $g_{cat.}$/L. Finally, the coated monoliths were calcined at 550 °C in air for 3 h.

Table 1
Sample characteristics of the parent H-ZSM-5 material and the prepared Fe-ZSM-5 catalysts.

Sample (exchange degree[a])	Brønsted acidity (NH_3 desorp. during TPD at ≈490 °C) (mol/kg)	Exchange ratio H^+/Fe[b]	Brønsted acidity relative to H-ZSM-5 (DRIFTS)	Total NH_3 adsorption capacity (total NH_3 desorp. during TPD) (mol/kg)	Fe (wt.%)[a]
H-ZSM-5	0.95	–	1	3.1	–
Fe-ZSM-5 (0.04)	n/a	n/a	0.89	n/a	0.27
Fe-ZSM-5 (0.04)[d]	0.49	n/a	0.22	1.8	0.27
Fe-ZSM-5 (0.08)	0.85	1.0	0.83	3	0.57
Fe-ZSM-5 (0.16)	0.74	1.1	0.71	2.9	1.1
Fe-ZSM-5 (0.25)	0.67	0.9	0.6	2.7	1.7
Fe-ZSM-5 (0.3)	0.56	1.1	0.52	2.8	2
Fe-ZSM-5 (0.39)	0.56	0.8	0.38	2.6	2.6
Fe-ZSM-5 (0.74)	0.48	0.4	0.43	2.0	5
Fe-ZSM-5 (0.3)–TIPCS	n/a	–	0.04	2.2	2
Fe-ZSM-5 (0.3), 650 °C, 8 h	0.21	–	0.007	1.2	2
Fe-ZSM-5 (0.3), 800 °C, 8 h	0.07[c]	–	0.006	0.6	2

[a] Iron content measured by ICP–AES.

[b] Calculated by dividing the molar amount of consumed Brønsted acidity (measured by TPD) by the molar amount of exchanged iron (measured by ICP–AES).

[c] Inaccurate value due to very small peak.

[d] Prepared by exchanging hydrothermally pretreated H-ZSM-5 with reduced Brønsted-acidity.

2.2. Catalyst characterization and activity measurements

Inductively coupled plasma–atomic emission spectroscopy (ICP–AES) was employed in the quantitative analysis of the elemental composition of all samples. The results of this analysis are shown in Table 1.

The Brønsted acidity was measured by FTIR spectroscopy and temperature-programed desorption (TPD) of ammonia (Table 1). Infrared spectra of the zeolite surface were recorded with a Nicolet Magna IR 560 spectrometer equipped with an in situ DRIFT gas cell. The samples were dried in the cell under 20% oxygen at 550 °C for 10 min, under flowing nitrogen for another 10 min and then the spectra were recorded at 150 °C. The concentration of Brønsted acid sites was determined from the area of the band at about 3610 cm^{-1}. By feeding NH_3 over the zeolite, all Brønsted acid sites were saturated, thereby creating a background sample without acidity but with the same particle size distribution, particle shape, and packing densities. Very accurate measurements could be performed with this procedure since the background was made of the sample, which prevented changes in the scattering of light.

For TPD measurements, 100 mg of the sample was heated at 550 °C for 10 min in a flow of 20% O_2 and then cooled to RT under He. NH_3 was adsorbed for 1 h at RT from a gas stream containing 1% NH_3 in nitrogen, followed by the actual desorption experiment at a heating rate of 10 °C/min from 30 °C to 800 °C in a He flow. The concentration of desorbed NH_3 in the gas phase was analyzed with a Nicolet Magna IR 560 spectrometer equipped with a heated gas measuring cell and a liquid nitrogen cooled MCT detector. The overlapping peaks were deconvoluted into Gaussian functions and the absolute number of Brønsted acid sites was quantified by multiplying the area of the peak at about 490 °C with the feed gas flow rate.

The measurements of the SCR activities as well as of the NO and CO oxidation activities were carried out in a heated quartz reactor. The concentrations of the gaseous reaction products were determined by FTIR spectroscopy. Details of the setup of the test apparatus and the gas analysis method have been reported previously [24]. For SCR measurements, the composition of diesel exhaust gas was approximated by a model feed gas containing 10% O_2, 5% H_2O, 1000 ppm NH_3 and 1000 ppm NO (standard SCR), or 500 ppm NO and 500 ppm NO_2 (fast-SCR) and N_2 balance. NO oxidation was investigated using a feed gas consisting of 10% O_2, 5% H_2O, 1000 ppm NO, and N_2 as the balance. For CO oxidation activity measurements, the gas feed consists of 2000 ppm CO and 15% O_2 with the remaining balance made up by N_2. The gas hourly space velocity (GHSV) was 52,000 h^{-1} for feeds containing NO (standard SCR) up to 450 °C and experiments with CO. At 500 °C, standard SCR was carried out with a GHSV of 200,000 h^{-1}. The GHSV was 280,000 h^{-1} for all fast SCR measurements.

3. Results

The NH_3 desorption profiles during TPD from H-ZSM-5 and Fe-ZSM-5 SCR catalysts with different exchange degrees were compared (Fig. 1a and b). All catalysts were prepared by liquid ion exchange, except for the sample with Fe/Al = 0.74, which was prepared by CVD. The measured amounts of desorbed NH_3 are given in Table 1. NH_3 desorbed in three main peaks at about 140 °C, 230 °C and 490 °C. The peaks observed at 140 °C and 230 °C are caused by weakly adsorbed NH_3 on Lewis acid sites, while the peak at about 490 °C is related to NH_3 adsorbed on Brønsted acid sites [25–28]. The cause of the relatively small peak at about 650 °C is unclear, but it might be due to strong Lewis acid sites [29,30]. Alternatively this peak could account for especially strong Brønsted acid sites, which are formed from the interaction of Brønsted acid sites with extra-framework aluminum species [31].

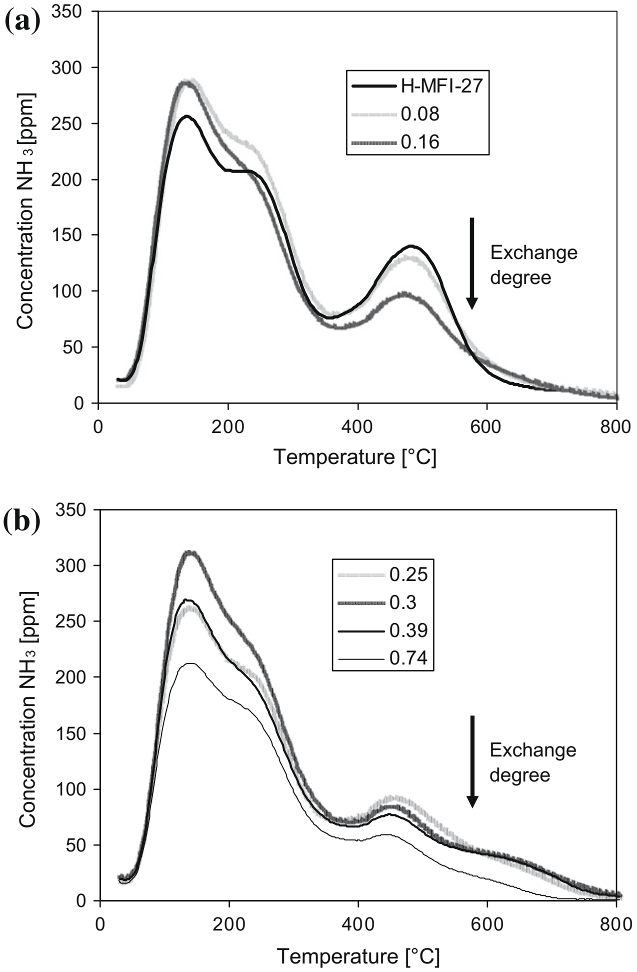


Fig. 1. Measured NH_3 concentration during TPD for (a) H-ZSM-5 and Fe-ZSM-5 (0.08, 0.16) and (b) Fe-ZSM-5 (0.25, 0.3, 0.39, and 0.74).

Fig. 1a and b show that the ion exchange results in a reduction of Brønsted acidity. At the same time the peaks in the temperature range below 300 °C tend to become larger with increasing iron content, which might be explained by the creation of new Lewis acid sites [32]. This interpretation is hampered by an experimental error which is significant for weakly adsorbed NH_3 species below 300 °C. The height of these peaks was affected by the experimental conditions, which were slightly different from run to run in the used TPD instrument. Interestingly, the maximum of the peak at about 490 °C shifts to lower temperature with increasing iron content. This effect may be explained by decreasing heats of adsorption [26] with increasing iron content and decreasing Brønsted acidity. The change of heat of adsorption, however, is not related to the NH_3 surface coverage, because Hunger et al. [25] measured slightly increasing heats of desorption for decreasing surface coverages on H-ZSM-5. The peak shifting is rather explained by different types of Brønsted sites with slightly different acidities and affinities to bind iron. An alternative explanation would be the creation of new Lewis acid sites during ion exchange, desorbing NH_3 at about 450 °C. Regardless of the reason for the peak shift, the overlapping peaks were deconvoluted into Gaussian functions and the absolute number of Brønsted acid sites was quantified by multiplying the area of the peak at about 490 °C with the feed gas flow rate (Table 1). For H-ZSM-5, a Brønsted acid site concentration of 0.95 mol/kg was calculated, which is about 21% lower than expected based on the Si/Al ratio of 13.5 in this material. This result is in line with those obtained from conductometric titration [33] and another NH_3–TPD study [34]. This might be explained by some dealumination that occurred during the previous calcination of the zeolite, resulting in a loss of Brønsted acidity [28,33].

The exchange ratio H^+/Fe in Table 1, with H^+ being the molar amount of consumed Brønsted acidity, shows that about one Brønsted acid proton is replaced by one Fe atom up to an exchange degree of Fe/Al = 0.39, which is in line with the literature values [35]. In contrast, the highest loaded sample (Fe/Al = 0.74) showed a smaller H^+/Fe ratio, suggesting that above Fe/Al ≈ 0.4, a part of the iron formed Fe_xO_y particles or clusters instead of replacing H^+.

The concentration of Brønsted acid sites was also measured by FTIR spectroscopy in order to confirm the TPD results (Fig. 2). The band at 3610 cm^{-1} was assigned to the OH stretch of Brønsted acid sites [36], while the band at 3660 cm^{-1} arose from OH groups associated with extra-framework Al [36,37]. The relative concentration of Brønsted acid sites, expressed as H/Al, was calculated by normalizing the peak area of the band at 3610 cm^{-1} for the Fe-ZSM-5 samples to the peak area observed for H-ZSM-5 (Fig. 3). In Fig. 3, the exchange degree (Fe/Al_{av}) was calculated based on the concentration of Brønsted acid sites that are available for ion exchange (Al_{av}) rather than the concentration of Al determined by ICP. The measured concentration of the available Brønsted acid sites in H-ZSM-5 is 0.95 mol/kg, as determined by TPD (data shown in Table 1). The regression line of the data shown in Fig. 3 has a slope of −1.1, proving the conclusion from Fig. 1a and b that approximately one Brønsted proton is exchanged for one Fe atom. However, the Fe-ZSM-5 (0.74) sample with Fe/Al_{av} = 0.94 shows a higher remaining Brønsted acidity (H/Al ≈ 0.45) than expected on basis of the exchange degree, revealing that a maximum of about 55% of all Brønsted acid sites can be exchanged in aqueous Fe^{2+} solution. This finding is consistent with the literature reports [35,38]. Note that Fe-ZSM-5 (0.74) was exchanged by chemical vapor deposition of $FeCl_3$, but that it was washed and calcined afterwards. In accordance with the literature [38], the FTIR signal of the Brønsted acid sites disappeared completely after H-ZSM-5 had been loaded with $FeCl_3$ (data not shown) but restored after washing and calcination.

It is interesting to note that the data shown in Table 1 show slightly different profiles for the decrease in the amount of Brønsted acid sites measured by FTIR spectroscopy and NH_3–TPD. NH_3–TPD resulted in a slightly lower decrease of the Brønsted acidity with rising iron content compared to FTIR spectroscopy. Although the difference is only small, it might be explained by the experimental error or, alternatively, by the creation of new

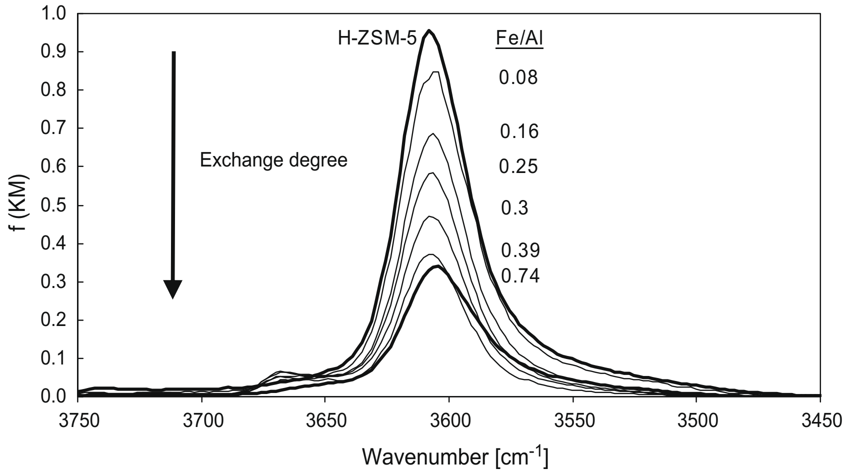


Fig. 2. FTIR spectra of the hydroxyl stretching region for Fe-ZSM-5 samples with various exchange degrees.

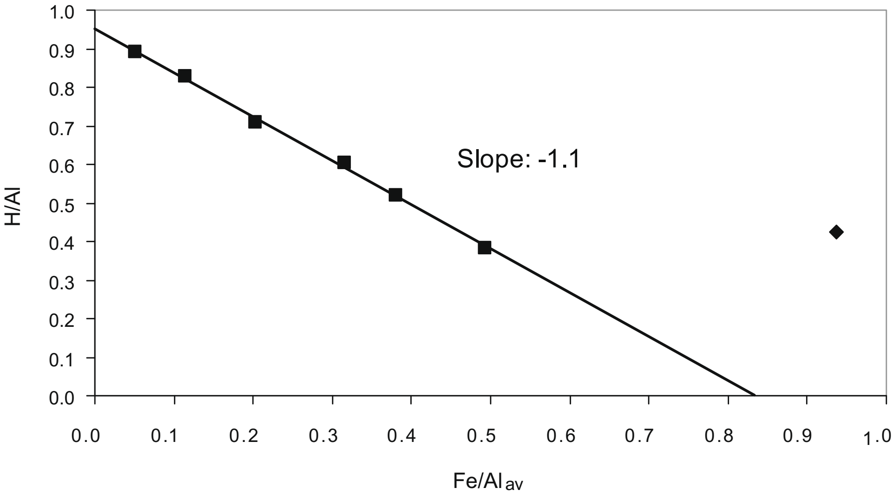


Fig. 3. Change of H/Al ratio with Fe/Al_{va} ratio for Fe-ZSM-5 samples with various exchange degrees, with Al_{va} corresponding to the concentration of available Brønsted acid sites determined in Table 1.

Lewis acid sites in the metal exchange process, which desorb NH_3 in the temperature region used for the quantification of Brønsted acid sites.

Fig. 4 shows the NO reduction efficiencies of the Fe-ZSM-5 catalysts with various exchange degrees (Fe/Al). In the high-temperature range above 500 °C, the conversion level decreases with rising iron content (with the exception of the zeolite with Fe/Al = 0.74), whereas in the low temperature range below 350 °C the NO conversion increases with rising iron content (with the exception of the zeolite with Fe/Al = 0.74) but decreasing Brønsted acidity. Since the SCR reaction is independent of the concentrations of ammonia and oxygen and first-order with respect to NO [6,39–42] under the testing conditions applied in this study, the SCR activity may be expressed quantitatively by an apparent first-order rate constant. This can then be used to visualize the dependence of the activity on exchange degree and remaining Brønsted acidity. When assuming plug-flow reactor conditions and the absence of diffusion limitation, which hold for low and intermediate temperatures, the apparent first-order rate constant may be calculated from the NO conversion (X) by:

$$k = \frac{\dot{V}}{m} \ln(1 - X) \tag{1}$$

where $\dot{V}$ is the gas flow rate at the reaction temperature and m is the catalyst mass.

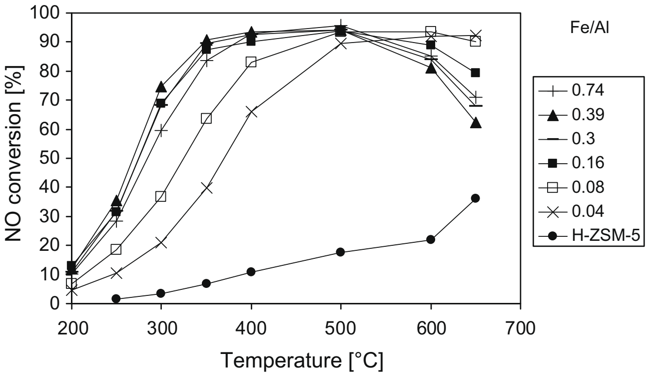


Fig. 4. NO reduction as a function of temperature over Fe-ZSM-5 catalysts with various exchange degrees (Fe/Al). Reaction conditions: 1000 ppm NO, 1000 ppm, NH_3, 10% O_2, 5% H_2O, remaining gas feed consists of N_2. GHSV = 52,000 h^{-1}.

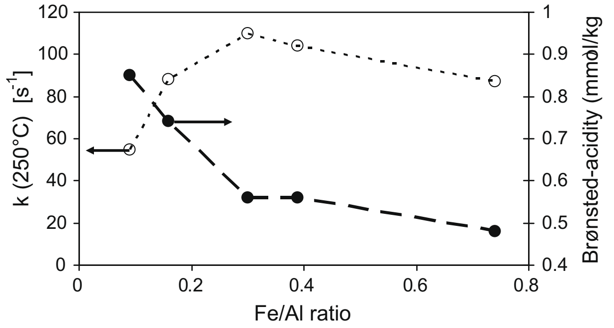
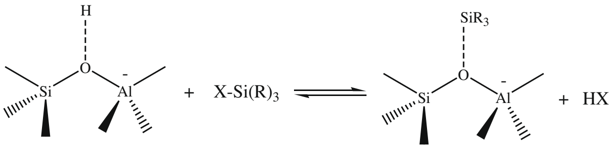


Fig. 5. First-order rate constants for the SCR reaction and Brønsted acidity as a function of the exchange degree.

Fig. 5 illustrates that at 250 °C, the activity of the catalysts increases with rising iron content about fivefold between Fe/Al = 0.04 and 0.39, whereas the number of Brønsted acid sites decreases significantly.

Fig. 6 compares the SCR activity of two catalysts, both with an exchange degree of Fe/Al = 0.04, but with different Brønsted acidities. The Brønsted acidity of the Fe-ZSM-5 samples was previously determined by DRIFTS to be 89% for sample Fe-ZSM-5 (0.04) and 22% for sample Fe-ZSM-5 (0.04)*, which was related to the acidity of the parent H-ZSM-5. Both catalysts exhibit equal SCR activity, indicating that Brønsted acidity might be not decisive for a high NO conversion. It should be noted that from NH_3–TPD (Fig. 7) the sample Fe-ZSM-5 (0.04)* had an apparent higher remaining Brønsted acidity of about 50% relative to the parent H-ZSM-5 (Table 1), which might be explained by the creation of new Lewis acid sites due to the hydrothermal aging.

In order to further elucidate the influence of Brønsted acidity on SCR activity, we compared the SCR activity of a fresh Fe-ZSM-5 (0.3) sample with the activity of different Fe-ZSM-5 samples with equal exchange degree, but reduced Brønsted acidity. We reduced the Brønsted acidity in two different ways: by aging the Fe-ZSM-5 (0.3) sample at either 650 °C or 800 °C under hydrothermal conditions (10% H_2O), and by poisoning the Brønsted acid sites by silanization according to Eq. (2).



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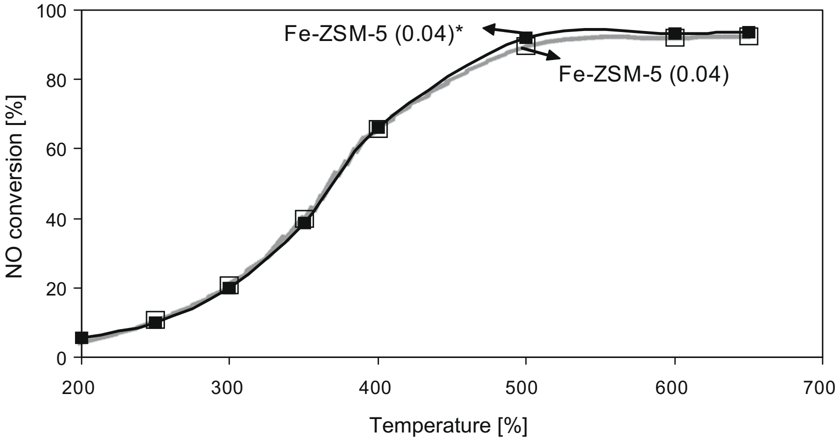

Fig. 6. NO reduction as a function of temperature over two Fe-ZSM-5 samples with equal exchange degree (Fe/Al = 0.04), but with different Brønsted acidities: Fe-ZSM-5 (0.04) 89% and Fe-ZSM-5 (0.04)* 22% relative to the acidity of the parent H-ZSM-5. Reaction conditions: 1000 ppm NO, 1000 ppm, NH_3, 10% O_2, 5% H_2O, remaining gas feed consists of N_2. GHSV = 52,000 h^{-1}.

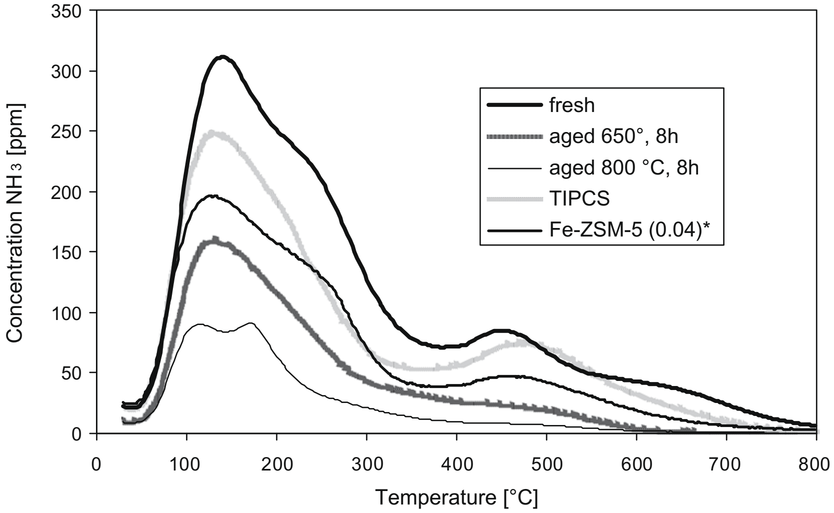

Fig. 7. Measured NH_3 concentration during TPD of Fe-ZSM-5 (0.04)* and Fe-ZSM-5 (0.3) in the fresh state, after silanization and after aging at 650 °C and 800 °C, respectively.

Both the Brønsted acidity and the number of active iron sites were reduced by hydrothermal aging. The loss of Brønsted acidity can thereby ascribed to dealumination and the loss of surface area [3,43–47]. The NH_3 spectrum shown in Fig. 7 shows that hydrothermal aging lowered the Lewis acidity as well as Brønsted acidity. The loss of active iron sites is due to migration of the iron species out of the ionic exchange sites. As a consequence, inactive metal-oxide particles with reduced oxidation activity are formed [38,48–51].

In contrast to the hydrothermal aging, the silanization process should only impact the Brønsted acid sites, whereas it is reasonable

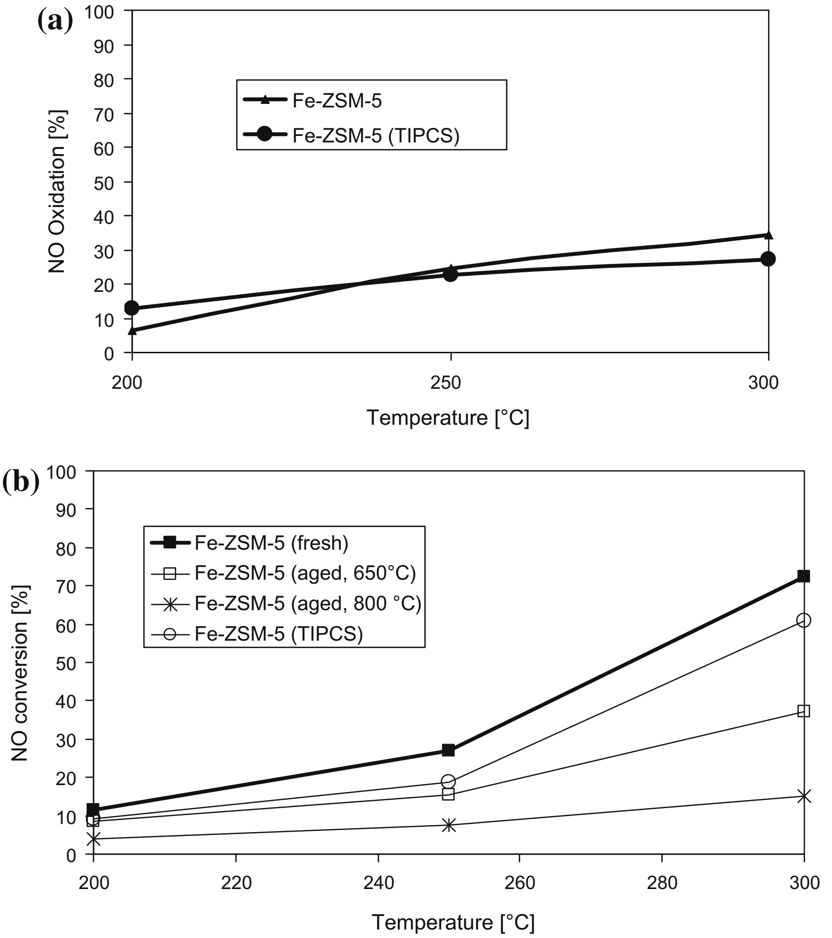

Fig. 8. (a) NO oxidation activity of fresh and silanized Fe-ZSM-5 (0.3). (b) NO reduction efficiency as a function of temperature over Fe-ZSM-5 catalysts with equal exchange degree Fe/Al = 0.3, but with different Brønsted acidities ranging from 52% for the fresh sample, 4% after silanization with TIPCS, 0.7% after aging at 650 °C, and 0.6% after aging at 800 °C, relative to the parent H-ZSM-5. Reaction conditions: 1000 ppm NO, 1000 ppm, NH_3, 10% O_2, without H_2O, remaining gas feed consists of N_2. GHSV = 52,000 h^{-1}.

to assume that the Lewis acid sites and active iron sites remain almost unaffected. Please note that the NH_3–TPD of the silanized sample shown in Fig. 7 does not reflect the proportion of the Lewis acidity and Brønsted acidity correctly. During the TPD experiment, the O–SiR_3 bond is thermally degraded, which releases Brønsted acid sites. The NH_3 desorbing from Lewis acid sites may readsorb on these freed sites. Niwa et al. have shown that this readsorption of NH_3 on Brønsted acid sites is possible under the applied experimental conditions [52]. Consequently, the Brønsted acidity is increased at the expense of the Lewis acidity.

However, we found the total NH_3 adsorption capacities of Fe-ZSM-5 (0.3) and Fe-ZSM-5 (0.3) TIPCS to be 2.8 and 2.2 mol/kg, respectively (Table 1). The difference of 0.6 mol/kg between these two values is equivalent to the 0.56 mol/kg of NH_3 desorbed at 490 °C for Fe-ZSM-5 (0.3). This proves that the Brønsted acid sites are consumed almost completely due to the silanization. Using in situ DRIFT experiments, we could show that the O–SiR_3 group is stable up to about 300 °C under anhydrous SCR conditions. Using DRIFT spectroscopy, we measured the Brønsted acidity relative to the parent H-ZSM-5 to be 52% for the fresh sample, 4% after silanization with TIPCS, 0.7% after aging at 650 °C, and 0.6% after aging at 800 °C (Table 1). It is interesting to note that the NH_3–TPD of the aged 650 °C sample shows a considerable amount of NH_3 desorbing at about 490 °C, whereas the DRIFT measurement reports that the Brønsted acid sites disappeared almost completely. This may serve as evidence that some new Lewis acid sites may be formed during the thermal aging process, which is a known process for steam-treated alumina [31] that desorbs NH_3 at about 490 °C.

To draw reliable conclusions from the experiments, it is important that the iron sites remain unaffected by the silanization. In order to prove that there is no migration of iron ions out of the ion exchange sites due to the silanization, the SCR activity before silanization was compared with the activity after silanization and the subsequent hydrolysis of the O–SiR_3 bond accomplished at 500 °C in an atmosphere with 5% H_2O. The SCR activity was completely restored after hydrolysis (data not shown). Moreover, the NO oxidation activity of the silanized and fresh Fe-ZSM-5 (0.3) samples demonstrate that the oxidation activity remains almost constant (Fig. 8a).

Fig. 8b shows the SCR activity of the fresh catalyst, the two aged Fe-ZSM-5 samples and the Fe-ZSM-5 sample silanized with TIPCS. In order to avoid hydrolysis of the Si–O bond, the SCR measurements were performed in an anhydrous atmosphere. Remarkably, the silanized sample with only 4% acidity, containing about 10 times more iron sites than Brønsted sites, showed only a slightly lower NO conversion, reduced by about 20% compared to the fresh Fe-ZSM-5 (0.3). Note that the formation of CO and CO_2 is negligible in all experiments (data not shown), which excludes oxidation of the isopropyl group. The hydrothermally aged samples, which lost about 99% of their Brønsted acidity, show a remarkably low activity compared to the silanized sample, which lost about 96% of its Brønsted acidity. This may suggest that the loss of redox active iron

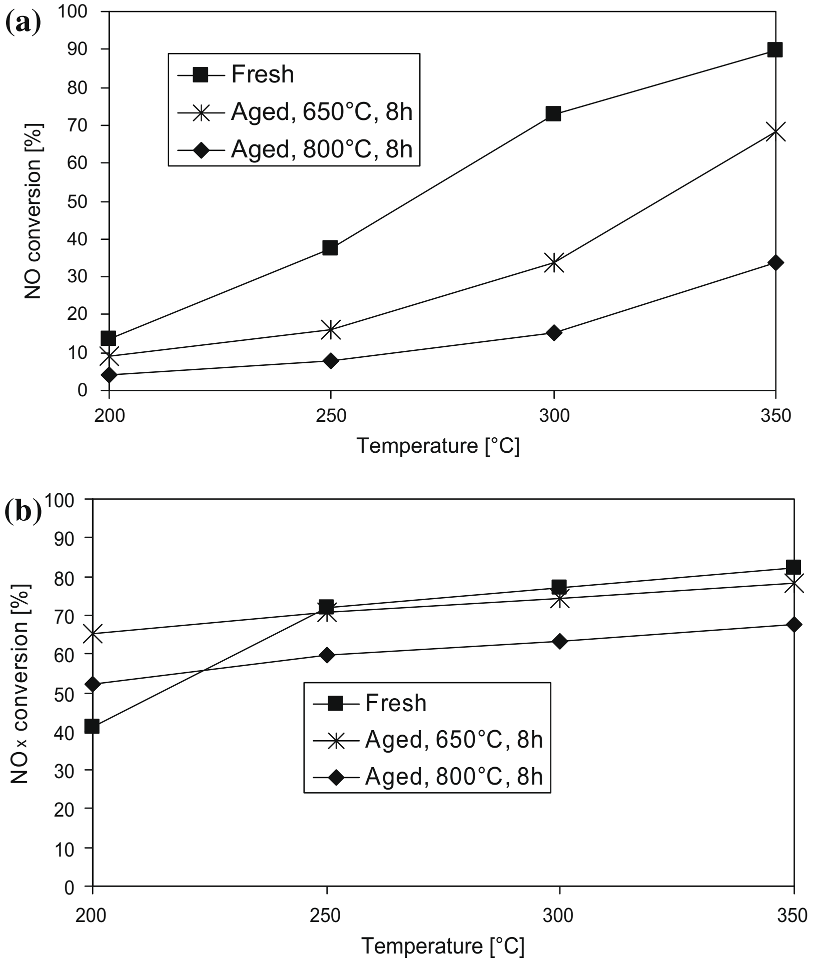

Fig. 9. NO_x reduction as a function of temperature over Fe-ZSM-5 (0.3) catalysts with various exchange degrees (Fe/Al). (a) Standard SCR. Reaction conditions: 1000 ppm NO, 1000 ppm, NH_3, 10% O_2, 5% H_2O, remaining gas feed consists of N_2. GHSV = 52,000 h^{-1}. (b) Fast SCR. Reaction conditions: 500 ppm NO, 500 ppm NO_2, 1000 ppm, NH_3, 10% O_2, 5% H_2O, remaining gas feed consists of N_2. GHSV = 280,000 h^{-1}.

sites is responsible for the decreased activity rather than the loss of Brønsted acidity.

With an $NO/NO_2 = 1/1$ gas feed, the SCR of NO with NH_3 reaches the highest rate, and is therefore called fast SCR. At this point, the oxidation activity of the catalyst is no longer required [5,53]. This interesting feature of the fast SCR reaction gives us the opportunity to measure SCR activities independent of the oxidation functionality in the catalyst. In order to differ between the influence of oxidation activity and Brønsted acidity, the standard SCR activity (Fig. 9a) was compared with NO_x conversion under fast SCR conditions (Fig. 9b) before and after aging at 650 °C and 800 °C, respectively. Fig. 9a shows that aging at 650 °C and 800 °C strongly reduces the NO conversion efficiency, decreasing at 250 °C from 37.4 to 15.9 and 7.7% for the fresh, aged at 650 °C and aged at 800 °C samples, respectively. In contrast, Fig. 9b demonstrates that under fast SCR conditions the NO_x conversion is almost unchanged after aging at 650 °C and only reduced by 15% after aging at 800 °C. At 200 °C, the fast SCR conversion for the fresh sample is decreased to some extent. It is worth mentioning that we observed a high initial SCR activity when measuring this data point, which, however, decreased within 15 min to the final steady-state activity reported in Fig. 9b. This observation is in line with the accumulation of NH_4NO_3 deposits in the pores of Fe-ZSM-5 already at 200 °C, thereby blocking the active sites [2,54]. The reaction rate constants were calculated from the measured NO_x conversion shown in Fig. 9a and b at 250 °C and compared with the Brønsted acidity shown in Fig. 10. Interestingly, the sample aged at 650 °C exhibited a very similar Brønsted acidity, but significantly higher standard and fast SCR activities than the sample aged at 800 °C. In order to understand this observation the oxidation activities of the fresh and aged catalysts have to be compared, but unlike the experiment described in Fig. 8a, the NO oxidation activity cannot be used to assess this difference. It seems that the NO_2 produced from NO in the oxidation process over the iron in the sample desorbs at different rates from the various iron sites. For instance, NO_2 adsorbs on Fe sites attached to the zeolite framework but not on Fe-oxide particles [4,11,55,56]. As the iron sites are altered during aging, and due to the fact that the rate of the NO oxidation reaction is controlled by the desorption of NO_2, [4] no meaningful comparison of fresh and aged Fe-ZSM-5 samples could be made. Therefore, we measured the CO oxidation activity because the interaction of CO with Fe-ZSM-5 is very weak and the oxidation product CO_2 is not adsorbed, [57] which simplifies the interpretation. The results shown in Fig. 11 illustrate that the evolution of CO oxidation activity follows the trend found in SCR activity.

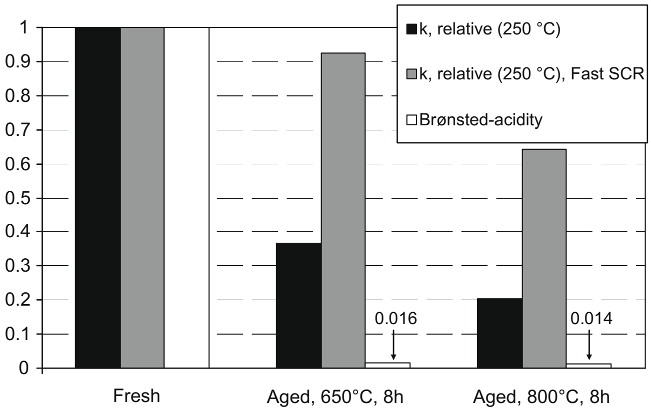

Fig. 10. Relative Brønsted acidity and relative first-order rate constants for the standard SCR reaction and fast SCR reaction, calculated from Fig. 9 for fresh and 650 °C and 800 °C aged Fe-ZSM-5 (0.3).

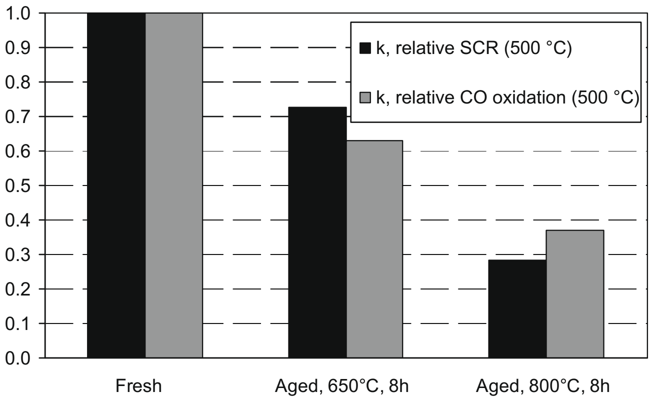

Fig. 11. CO oxidation activity at 500 °C and relative first-order rate constants for the standard SCR reaction at 500 °C for fresh and 650 °C and 800 °C aged Fe-ZSM-5 (0.3).

4. Discussion

The NH_3–TPD experiments (Fig. 1a and b) and DRIFTS measurements (Fig. 2) show that the concentration of Brønsted acid sites decreases with an increase in Fe loading, suggesting thereby that up to Fe/Al = 0.39, about one Brønsted acid site is substituted by one Fe site (Fig. 3). This let us conclude that most of the iron is dispersed as cations and that the Fe complexes, located in the ion exchange sites, have in average a single positive charge which is in line with the results from Marturano et al. [58].

Fig. 4 shows that at $T > 500$ °C, the NO reduction efficiencies of Fe-ZSM-5 catalysts decrease with rising iron content (with the exception of the zeolite with Fe = 0.74). This is related to more pronounced NH_3 oxidation activity with rising iron content leading to a decreased NO reduction efficiency. The oxidation activity goes thereby trough a maximum for sample Fe-ZSM-5 (0.39) and decreases again with rising iron content for sample Fe-ZSM-5 (0.74) because of the formation of higher clustered iron species, which are less active in NH_3 oxidation as we have proposed elsewhere [1]. At temperatures below 350 °C, NO conversion increases with rising iron content (with the exception of the zeolite with Fe = 0.74) and decreasing Brønsted acidity. This is in line with the expected trend that the SCR activity is a function of the iron concentration as well as the assumption that the oxidation of NO to NO_2^{ads} over the iron sites is the rate-limiting step. The relatively low activity of Fe-ZSM-5 (0.74) can be explained by the low concentration of isolated iron ions, responsible for NO oxidation at low temperature as proposed from us in another study [1].

The consequently rising activity with decreasing Brønsted acidity shown in Fig. 5 may interpreted in such a way that a high Brønsted acidity is not decisive for high activity. This assumption is supported by the results shown in Fig. 6: It is clearly seen that over the whole temperature range both catalysts show the same SCR activity, although the Brønsted acidity of sample Fe-ZSM-5 (0.04)* is only about 1/4 of the acidity of sample Fe-ZSM-5 (0.04). By choosing a very low exchange degree, the formation of isolated iron ions was strongly favored in both catalysts [59–61], which ensures that both catalysts contain Fe sites of the same structure regardless of the Brønsted acidity. One may argue that for high activity just low Brønsted acidity is required because NH_3 is known to adsorb strongly on the zeolite surface [6]. Moreover, there are still about five times more Brønsted sites than iron sites in sample Fe-ZSM-5 (0.04)*. In this light, the 22% of Brønsted acidity remaining in Fe-ZSM-5 (0.04)* relative to the parent H-

ZSM-5 material may be still sufficient. However, Fig. 8b shows that a silanized sample exhibits only a slightly decreased SCR activity with respect to the fresh sample even though the Brønsted acidity is depleted by about 96% (Table 1). This result implies that Brønsted acidity is indeed of minor importance for SCR activity. The slightly lower activity of the silanized sample relative to the fresh one cannot be caused by an alteration of the redox site by silanization because the NO oxidation activity remains almost unaffected (Fig. 8a). Furthermore, the original SCR activity was restored after hydrolysis of the O–SiR_3 bond (data not shown). A more likely explanation is that either the diffusion of the reactant is hindered due to the large isopropyl groups, or that there is a slightly promoting effect of Brønsted acid sites in the SCR reaction as recently proposed by Schwidder et al. [16].

Fig. 8b also shows that the aged samples show a remarkable lower activity compared to the silanized sample even though both lost Brønsted acidity to a similar extent (≈96% for Fe-ZSM-5 TIPCS and ≈99% for aged samples). During hydrothermal aging, the Brønsted acidity and the number of active iron sites were reduced, but the silanization only affects the Brønsted acidity, whereas the oxidation activity can be assumed to be unaffected. Therefore, the activity pattern shown in Fig. 8b indicates that the primary feature affected by hydrothermal aging is the redox activity, which is of particular importance for the SCR reaction. The comparison of NO_x conversion under standard SCR conditions (Fig. 9a) and fast SCR conditions (Fig. 9b) before and after aging is fully compatible with this assumption. After aging at 650 °C and 800 °C, the efficiency under standard SCR conditions strongly decreases, whereas at $NO/NO_2 = 1/1$, where oxidation activity is not required, the efficiency is almost unchanged after aging at 650 °C and only slightly decreased after aging at 800 °C.

The change in activity can be expressed by a relative comparison of the apparent first-order rate constants in order to make the situation clearer (Fig. 10). The comparison shows that the NO conversion during standard SCR decreases by about 63% after aging at 650 °C, but the performance in fast SCR is almost unchanged and is reduced by only 7% after the hydrothermal treatment even though the Brønsted acidity disappeared almost completely. Moreover, during aging at 800 °C, the Brønsted acidity remained almost constant relative to the acidity change during aging at 650 °C, but the standard SCR as well as the fast SCR activity still decreases. Both observations support the hypothesis that Brønsted acidity is of minor importance, but that the oxidation activity may be of major importance or even define standard SCR activity. This conclusion agrees with the results shown in Fig. 11; revealing that at 500 °C the evolution of the CO oxidation activity follows the trend of the SCR activity. Even though this interpretation is somewhat speculative because there might be different active sites responsible for CO oxidation and NO oxidation, this result provides evidence that altered oxidation activity is one of the main factors responsible for decreased SCR activity after hydrothermal aging of the catalysts.

Of course, the presence of Brønsted acid sites is necessary to bind and disperse the metal ions. They may also prevent the aggregation of exchanged metal ions. However, both weak and strong Lewis acid sites in the zeolite framework might act as an adsorption site for NH_3 and therefore as a reservoir of the reductant. Table 1 shows that the total NH_3 adsorption capacity is still 1.2 mol/kg after aging at 650 °C and 0.6 mol/kg after aging at 800 °C.

Another interesting conclusion of our study is that the cooperative contribution of two adjacent Brønsted acid sites in the NH_3–SCR of NO, as mentioned in Section 1, is cast into doubt and may even be impossible. The probability of finding two acid sites in proximity is very small in ZSM-5 zeolites with reduced Brønsted acidity such as the silanized sample or in Fe-ZSM-5 (0.04)*. In other words, if two adjacent Brønsted acid sites were required for the SCR reaction, the SCR activity of catalysts with reduced Brønsted acidity would be expected to be very low. However, our experiments found no such effect.

5. Conclusion

Fe-ZSM-5 samples with equal metal exchange degrees, but with different Brønsted acidities have been prepared in such a way that the active iron sites can be assumed to be identical. Moreover, we reduced the Brønsted acidity in two different ways: by poisoning the Brønsted acid sites by silanization and by aging the Fe-ZSM-5 (0.3) sample at 650 °C or 800 °C under hydrothermal conditions (10% H_2O). The activity of fresh and aged samples with reduced Brønsted acidity and a reduced concentration of active iron sites have been compared under standard SCR conditions. We also performed a similar investigation under fast SCR conditions, where oxidation activity provided by the iron ions is not required. Using NH_3–TPD–FTIR and DRIFT spectroscopy, we measured the Brønsted acidity of the samples and found both methods well suited to quantify the acidity in an accurate manner.

Our experimental results allow us to conclude the following:

- Brønsted acidity is not required for adsorbing or activating the ammonia, but it is necessary in order to bind and disperse the metal ions. Thereby, a maximum of about 55% of all Brønsted acid sites can be exchanged in aqueous Fe^{2+} solution.
- During liquid ion exchange about one Brønsted acid proton is replaced by one Fe atom up to an exchange degree of $Fe/Al = 0.39$, proving the monovalence of the exchanging iron complexes.
- At low temperatures, the acidic function of the Fe-ZSM-5 is not a prerequisite for high activity in the SCR reaction of NO with NH_3.
- The form in which ammonia is held by the support is not crucial and the support acts mainly as a reservoir for ammonia, which then migrates to the active site in order to undergo a reaction with NO.
- The oxidation function of the Fe-ZSM-5 is one of the main factors that control the activity in the standard SCR reaction.
- Altered oxidation activity is responsible for the decreased SCR activity after hydrothermal aging.

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