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FeZSM-5: A Durable SCR Catalyst for NO_x Removal from Combustion Streams

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A convenient method of preparing "overexchanged" FeZSM-5 catalysts is described that minimizes oxidation of Fe^{2+} to Fe^{3+} during base-exchange and inhibits the formation of Brønsted sites. These catalysts are more active than comparable CuZSM-5 preparations and are much more durable. They are not poisoned by up to 20% H_2O and/or 150 ppm of SO_2. A 2500-h durability test, carried out at 500°C, is described. It showed minimal loss of activity in a simulated exhaust gas stream. Moreover, 24-h *in situ* excursions to higher temperatures (up to 800°C) caused no loss in activity on return to 500°C. These findings are contrasted with those obtained with CuZSM-5. Examination of the catalyst at the end of the test showed minimal loss of pore volume and only T_d coordinated ^{27}Al could be detected. The sum of Fe + Na (residual) was equal to the Al. ^1HNMR showed no evidence of Brønsted sites suggesting that $(FeOH)^+$ was exchanged with Na^+ with the corresponding H^+ being removed by the anion of Fe-salt used for exchange, viz., $C_2O_4^{-2}$. Supplemental tests showed that the Fe^{2+} base-exchanged cations could be readily oxidized to Fe^{3+} by O_2 and reduced back to Fe^{2+} with H_2, but could not be further reduced at temperatures as high as 950°C. The results suggest that dealumination and breakdown of the lattice result from the presence of Brønsted sites.

INTRODUCTION

Ever since the selective catalytic reduction of NO by various hydrocarbons in the presence of excess O_2 (SCR) was first reported (1–3), numerous studies have appeared using various zeolites bearing a variety of different base-exchange cations (4). The majority of these have employed CuZSM-5 preparations, which have become the standards against which all other preparations are compared. The MFI zeolites appear to be the most favored structural types and, although a number of divalent or polyvalent cations have been tested, there is a dearth of information concerning FeZSM-5. Our literature research turned up only a few papers on this subject, and none of these reported overexchanged preparations. Indeed, our early attempts to achieve loadings higher than about 70% exchange failed; repeated exchange did not significantly raise the exchange level.

In 1969, Delgass *et al.* (5) pointed out a special problem that exists in the preparation of Fe*Y*, viz., that the Fe^{2+} cation is readily oxidized in aqueous solution to precipitate FeOOH in the zeolite pore systems. With the Faujasite system, this problem could be minimized by maintaining anaerobic conditions in a N_2 flushed glove bag. Following their procedures we also were able to achieve satisfactory results with Fe*Y* and published a series of papers on their catalytic properties. When we attempted to use the same procedures with the *M*FI zeolites, we found them inadequate. Besides decreased pore volumes, it was not possible to achieve high exchange levels. Hence, we have employed more stringent methods as disclosed herein. In this way we have been able to raise the exchange level as high as 185%. These catalysts have proved highly active for SCR and resistant to poisoning with H_2O and SO_2.

In some earlier work (6) we reported that the reaction $NO + CO \rightarrow CO_2 + 1/2\ N_2$, over Fe*Y*, was not severely poisoned by added H_2O. The inhibition was reversible and/or the original activity could be restored by raising the reaction temperature by about 70°C. This was quite different behavior than that reported for the SCR reaction over CoZSM-5 (7) or CuZSM-5 (8). Moreover, Segawa *et al.* (9) found no loss in activity for a period of 40 min when 10% H_2O was added to an SCR stream at 300°C over a 71% exchanged FeZSM-5 catalyst. This work has been extended considerably in the present report.

EXPERIMENTAL

Catalyst Preparation Method

The apparatus shown in Fig. 1 was devised to exclude O_2 to the greatest possible extent during the base-exchange procedure. It consisted of two sealed 250-ml flasks joined at the bottom through a fritted disk sealed into the connecting tube. This allowed ions to freely pass from one chamber to another but prevented the passage of solids. These vessels were filled with freshly distilled deionized H_2O. A stream of ultra-pure N_2 or Ar was bubbled at 100 ml NTP/min into both chambers for a period of about 30 min to wash

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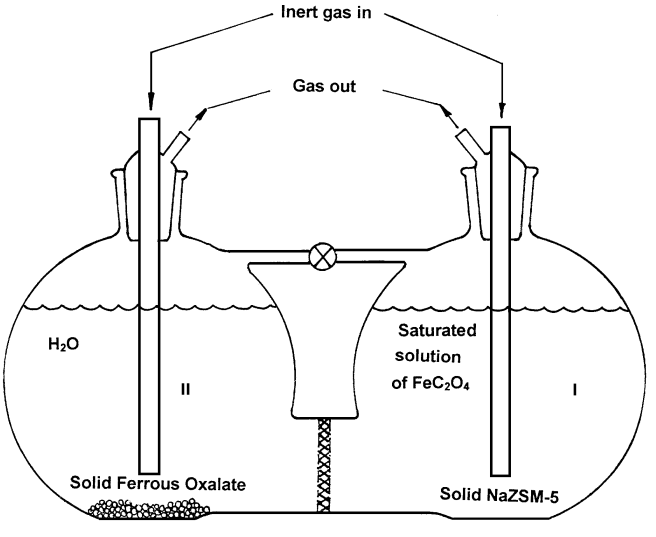

FIG. 1. Apparatus used to exclude traces of O_2 in the preparation of FeZSM-5 by base-exchange of NaZSM-5 with FeC_2O_4.

out traces of O_2. Then 2 g of NaZSM-5 was introduced into Chamber I while flushing continued; finally excess solid FeC_2O_4 was quickly dumped into Chamber II as the flushing continued (usually 1 g of FeC_2O_4 was used per gram of catalyst). Both chambers were severely agitated by the bubbles. FeC_2O_4 has a solubility at room temperature of about $10^{-3}M$. Thus the zeolite found itself in contact with a saturated solution of FeC_2O_4 at room temperature where the exchange was carried out. The preferred pH range was $6.5 < \mathrm{pH} < 7.5$.

FeC_2O_4 was the reagent of choice because the $C_2O_4^{-2}$ anion is more easily oxidized to CO_2 than is Fe^{2+} to Fe^{3+}. Despite the dilute solutions used it usually was found possible to reach 185% exchange in 24 h at room temperature. More soluble ferrous salts such as $FeSO_4$ could be used provided that an equimolar amount of oxalic acid was added to Chamber II prior to adding the Fe salt. In this case, FeC_2O_4 precipitated and the same overall result was obtained. A sampling of the catalysts prepared and used in this work is shown in Table 1. Elementary analyses were carried out by Galbraith Laboratories. This was supplemented here using XFS and ^{23}Na MAS-NMR. Further details may be found elsewhere (10).

Materials and Catalysts

The $FeC_2O_4 \cdot 2H_2O$ was Reagent Grade (99%) from Aldrich; $H_2C_2O_4$ was a 99% preparation obtained from Fisher Scientific Company; $FeSO_4 \cdot 7H_2O$ was from Sigma Chemical Company.

Two NaZSM-5 samples were furnished by Air Products. These had unit cell compositions shown in Table 1 (Items 1 and 2) and each unit cell contained about $16H_2O$ when the pore system was filled. The two CuZSM-5 preparations shown as Items 10 and 11 had been made previously using these same parent zeolites. FeZSM-5-12-37 (Item 8) was a conventional preparation made by ion exchange of NaZSM-5 with 0.1 *N* aqueous solution of ferrous sulfate under N_2 atmosphere. FeZSM-5-12-41 (Item 9) was made by five times ion exchange with 0.1 *N* aqueous solution of ferrous sulfate under N_2. The catalyst was filtered, washed, and dried in air overnight.

The overexchanged FeZSM-5 catalysts were prepared by ion exchange of NaZSM-5 with aqueous solution of ferrous oxalate as described above. The catalyst was filtered, washed, and dried, first on a Buchner funnel and then overnight in air at room temperature.

MAS NMR

^{1}H, ^{27}Al, and ^{23}Na MAS NMR spectra were obtained using a Bruker DMX-300 spectrometer at a proton Larmor frequency of 300 MHz. A Bruker broad-band double channel 7-mm MAS probe was used with the samples spun at 8 KHz at the magic angle. The pulse width used was 1 μs for ^{1}H (about 20 degrees of a $\pi/2$ pulse for ^{1}H), 3 μs for ^{27}Al (about 30 degrees of a $\pi/2$ pulse for ^{27}Al) and 1μs for ^{23}Na (about 30 degrees of a $\pi/2$ pulse). Recycle delay was 10 s for ^{1}H and 5 s for both ^{27}Al and ^{23}Na. Line broadening of 100, 200, and 1000 Hz were used with ^{1}H, ^{27}Al, and ^{23}Na spectra to reduce the high frequency noise. Tetramethylsilane (TMS), $AlCl_3$ (0.1 *M*), and NaCl (0.1 *M*) were used as chemical shift references for ^{1}H, ^{27}Al, and ^{23}Na, respectively. For ^{1}H spectra all samples were pretreated in flowing UHP grade He at 500°C for 24 h. This was followed by a

TABLE 1

Analytical Data for Catalysts Prepared[a]

Item	Code[a,b]	Unit cell composition	(Na + Fe)/Al[c]
1	NaZSM-5-12-108	$Na_{8.0}Al_{7.4}Si_{88.6}O_{192}$	
2	NaZSM-5-19-120	$Na_{5.8}Al_{4.8}Si_{91.2}O_{192}$	
3	FeZSM-5-19-183	$(FeOH)_{4.4}Na_{0.7}Al_{4.8}Si_{91.2}O_{192}$	1.1
4	FeZSM-5-12-20	$(FeOH)_{0.7}Na_{6.8}Al_{7.4}Si_{88.6}O_{192}$	1.0
5	FeZSM-5-12-66	$(FeOH)_{2.5}Na_{5.0}Al_{7.4}Si_{88.6}O_{192}$	1.0
6	FeZSM-5-12-120	$(FeOH)_{4.5}Na_{3.0}Al_{7.4}Si_{88.6}O_{192}$	1.0
7	FeZSM-5-12-190	$(FeOH)_{7.1}Na_{0.4}Al_{7.4}Si_{88.6}O_{192}$	1.0
8	FeZSM-5-12-37	$(FeOH)_{1.4}Na_{6.1}Al_{7.4}Si_{88.6}O_{192}$	1.0
9	FeZSM-5-12-41	$(FeOH)_{1.5}Na_{6.0}Al_{7.4}Si_{88.6}O_{192}$	1.0
10	CuZSM-5-12-103	$(CuOH)_{3.8}Na_{3.6}Al_{7.4}Si_{88.6}O_{192}$	0.9
11	CuZSM-5-12-122	$(CuOH)_{4.5}Na_{2.9}Al_{7.4}Si_{88.6}O_{192}$	0.9

[a] Items 8 and 9 were made using $FeSO_4$ and the glove bag technique (5) and items 10 and 11 were prepared in air.

[b] Nominal composition showing the major cation followed by structure type, then by the Si/Al ratio and finally by the percentage exchange, based on the assumption that $1Fe^{2+} = 2Na^{+}$.

[c] Ratio of cations to Al T-sites shows that Fe was present mainly in the form of a monovalent ion and that the amount of H^{+} put on the lattice was minimal, i.e., within the experimental error. Excess Na^{+} from items 1 and 2 has been deducted.

24 h evacuation at the same temperature. The pretreated samples were sealed in the 7-mm ZrO_2 rotors.

Catalytic Testing and Procedures

The apparatus was essentially the same as used earlier (4, 11). In normal operation four streams of gas were mixed to obtain the desired overall composition. Each stream was metered with a Moore mass flow controller. The gases fed were obtained from BOC; they were 1% NO in He, 10% O_2 in He, 1% isobutane in He, and pure He to make up the desired composition to 1 atm. The overall flow rate was 70 ml/min and the weight of catalyst tested was usually 50 mg although in some cases 100 mg was used. With 50 mg the space velocity was 42,000 h^{-1}. The apparatus was modified slightly to allow a stream of H_2O vapor in He to replace a corresponding amount of the pure He stream. Similarly, an additional stream of 1% SO_2 in He (Scott Specialty Gases-analyzed) was substituted for pure He. The H_2O/He stream was regulated by saturation of a pure He stream with H_2O at 78°C by immersion of the saturator in a regulated temperature bath. By proper manipulation, the flow stream normally contained 2000 ppm NO, 2000 ppm *i*-butane, and 3% O_2. When H_2O was added the amount was about 20% of the total stream and when SO_2 was added the concentration was 150 ppm.

As before, analysis was by GLC using the apparatus described in detail by Petunchi (11). The conversion of NO to N_2 could be calculated directly from the N_2 produced using the known concentration of NO in the feed. Similarly, the conversion of isobutane to CO_2 could be measured from the latter peak or by disappearance of isobutane. In this work the behavior of "overexchanged" FeZSM-5 was compared with that of conventionally prepared samples and with CuZSM-5.

Postreaction Testing

Following the reaction, several postexperimental measurements were made to determine whether any changes occurred during testing. These included ^{1}H and ^{27}Al NMR and pore volume measurements made both with the initial preparation and the same preparation after use.

Pore filling factors were measured in a standard BET system from the condensation of O_2 at −195°C calculated as liquid O_2 from the value obtained at $P/P_0 = 0.5$. Also the redox chemistry: oxidation in pure O_2 and reduction in pure H_2 were determined at various temperatures using a Cahn Microbalance Model RG as in previous work (12).

RESULTS

Overexchanged FeZSM-5-19-183 and FeZSM-5-14-22

The temperature dependence of the conversion of NO into N_2 and i-C_4H_{10} into CO_2 over these two catalysts is shown in Fig. 2. The integral reaction rates may be calculated by multiplying these conversions by the flow rates of NO and dividing by the weight of the catalyst used. Thus at 400° and 450°C, these rates were 0.063 and 0.12 mmol of NO per minute converted to N_2 per gram of catalyst. Since 1 g of this catalyst contains 0.79 mmol of Fe/g zeolite, the corresponding turnover frequencies (based on total Fe^{2+}) were 1.3×10^{-3} and 2.6×10^{-3} s^{-1}, respectively. The rather broad window of the former between 450 and 550°C will be useful for this work. Note that the selectivity is high; isobutane is still not fully reacted at 500°C. Above 550°C the conversion to N_2 fell as the hydrocarbon was fully consumed. However, this window of opportunity will vary depending upon the interrelationships between the external variables. Changes in the chemical structure of the reducing agent or the relative concentrations of O_2 and NO in the feed as well as the catalyst composition may lead to important changes in this rather ideal situation. For example, this window was moved by about 100°C to lower temperature when FeZSM-5-12-190 was used. Moreover, underexchanged FeZSM-5-14-22 (dashed lines) showed similar selectivities below 500°C, but only about 40% maximum conversion of NO to N_2. When the conversion of NO to N_2 was less than 100%, N_2O amounting to about 10% of the unconverted NO was formed. In our experience, isobutane is the most facile reducing agent so far tested (4). Further, SCR using this reducing agent is relatively clean; we have reason to think that the use of olefins will involve coking and mechanistically be more complicated.

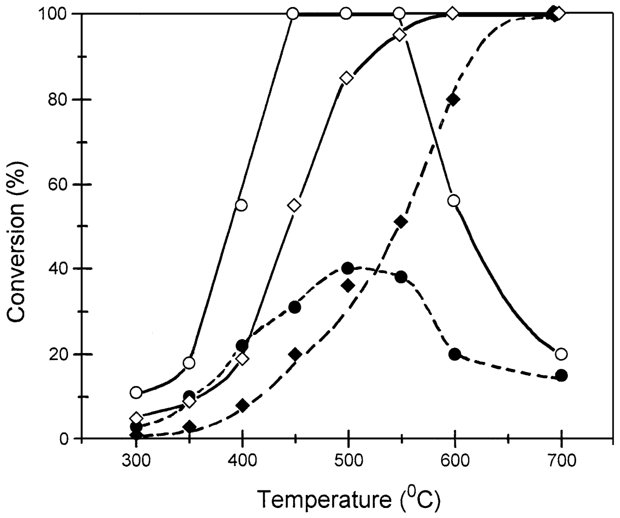

FIG. 2. Reaction profiles for conversion of NO to N_2 (circles) and of i-C_4H_{10} to CO_2 (diamonds) over Catalysts FeZSM-5-19-183 (open symbols) and FeZSM-5-14-22 (closed symbols) as a function of temperature. The feed gas composition in both cases was: NO, 2000 ppm; i-C_4H_{10}, 2000 ppm; O_2, 3%, with He to 1 atm. The flow rate was 70 cc (NTP)/min and the catalyst weight was 50 mg corresponding to SVH = 42,000 h^{-1}.

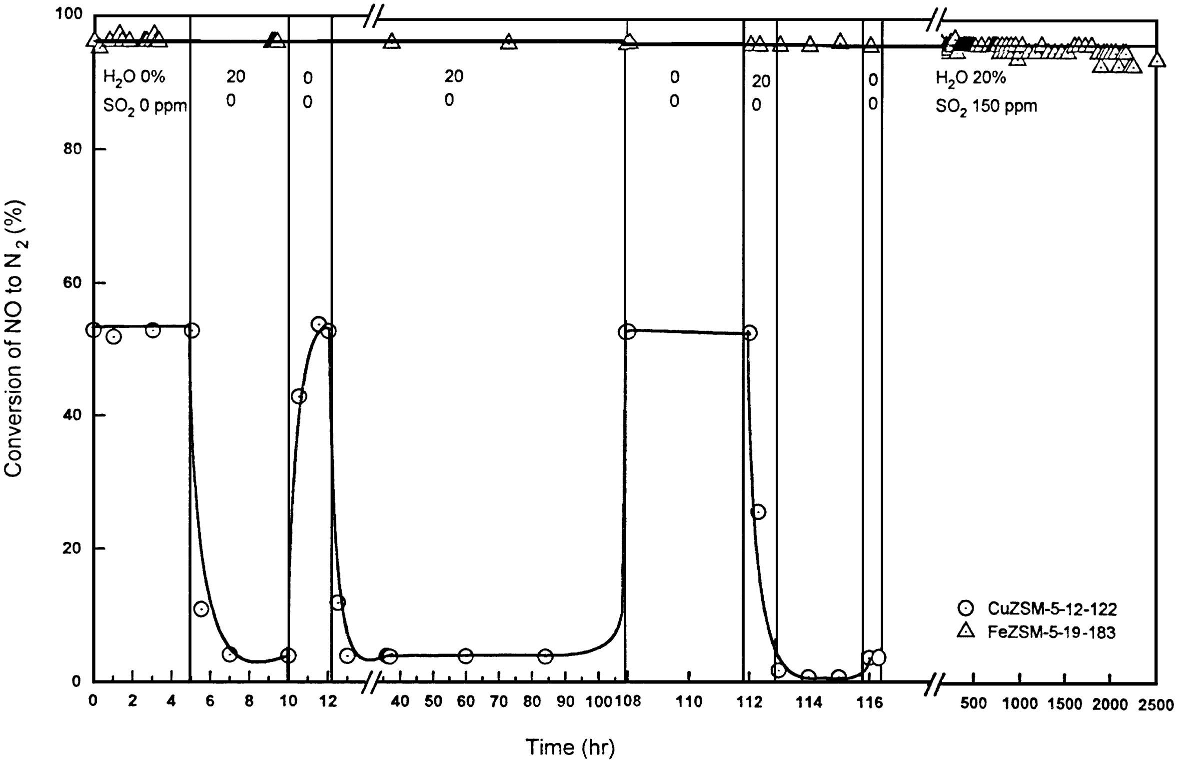

FIG. 3. Effects of H_2O and SO_2 on the conversions over CuZSM-5-12-122 vìs-a-vìs FeZSM-5-19-183 compared as a function of time on stream. The weight of catalyst was 50 mg in each case and the standard feed gas composition and flow rate were the same as in Fig. 2; H_2O vapor (20%) and SO_2 (150 ppm) were added in separate metered feed streams and were substituted for a portion of the He carrying gas. The calculated SVH was 42,000 h^{-1}. See text for further details.

Comparison of FeZSM-5-19-183 and CuZSM-5-11-122 in Durability Tests and the Effects of Poisons

The conversion of NO to N_2 at 500°C is shown in Fig. 3 as a function of time on stream. Parallel tests were carried out with the two catalysts under comparable conditions. The effects of H_2O vapor and SO_2 were determined periodically. First the normal "dry" testing stream was introduced for a period of 5 h. The data show that the FeZSM-5 catalyst was about twice as active for N_2 formation as the CuZSM-5. At this point 20% H_2O was substituted for He. The conversion over the CuZSM-5 fell precipitously while the FeZSM-5 was unaffected over the next 5 h. At this point the H_2O was removed from the feed. Again no effect was observed with the Fe-catalyst, but the Cu-catalyst recovered activity to its initial value over the next 2 h showing that the observed poisoning was reversible. This experiment was repeated, but with a longer time frame (~100 h with 20% H_2O); similar results were obtained. The activity of the Cu catalyst recovered to its initial value while the Fe catalyst was unaffected by H_2O. However, when H_2O was again added, together with SO_2, the activity of CuZSM-5 did not recover, whereas the FeZSM-5 was still unaffected by this combination of poisons as the test was extended to 2500 h (equivalent to the federally mandated 100,000 miles at 40 mph). Note that 20% H_2O and 150 ppm of SO_2 are both higher than the concentrations produced within an internal combustion engine. Most significantly, the FeZSM-5 catalyst showed no significant loss in activity during this entire reaction period despite the temperature excursions described below.

During the lifetime of a practical automobile catalyst, high temperature excursions for short periods of time may occur. To test the durability of the FeZSM-5 catalyst, the temperature was raised for periods of about 24 h and then returned to the original reaction temperature of 500°C. These experiments were made between 400 and 500 h during the durability test of Fig. 3. The results showed that the catalyst remained undamaged by these extended times at these higher temperatures. These data are outlined on Fig. 4, where the points were taken on return to 500°C following the high temperature excursion. These tests were carried out in the presence of 20% H_2O and 150 ppm SO_2. The 24-h period at 800°C under these conditions may be considered a severe steaming, yet there was no loss in catalytic activity nor any appreciable loss in pore volume, *vide infra*.

Another interesting feature is shown in Fig. 5. Here the conversion of NO to N_2 and the conversion of isobutane

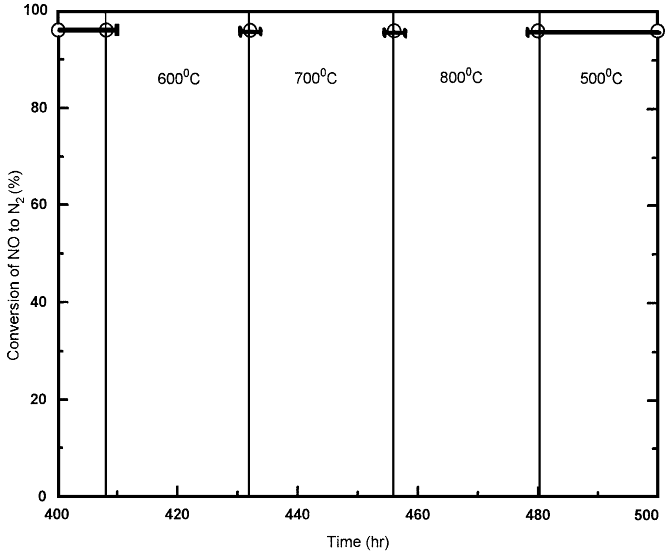

FIG. 4. Data showing that FeZSM-5-19-183 was undamaged by 24-h temperature excursions to 600°, 700°, or 800°C in the simulated exhaust gas stream. The points shown were taken on return to 500°C following the high temperature excursions. Gases and conditions as specified on Fig. 3.

TABLE 2

Pore Volume Measurements of Catalysts Tested

Item[a]	Sample	O_2 Physisorption (ml/g)	Note
1	NaZSM-5-12-108	0.155 ± 0.003	Parent zeolite
10	CuZSM-5-12-103	0.151 ± 0.002	$Cu(Ac)_2$
7	FeZSM-5-12-190	0.153 ± 0.003	FeC_2O_4 preparation
7a	FeZSM-5-12-190 (Calcined at 500°C)	0.155 ± 0.002	Two hours in 10% O_2/He
8	FeZSM-5-12-37	0.138 ± 0.005	$FeSO_4$ preparation
9	FeZSM-5-12-41	0.136 ± 0.005	$FeSO_4$ preparation by multiple exchange
2	NaZSM-5-19-120	0.150 ± 0.002	Parent zeolite
3	FeZSM-5-19-183	0.151 ± 0.005	FeC_2O_4
3a	FeZSM-5-19-183 (Calcined at 500°C)	0.149 ± 0.002	Two hours in 10% O_2/He
3b	FeZSM-5-19-183 (After 2500 h on stream)	0.128 ± 0.010	20% H_2O, 150 ppm SO_2, 2000 ppm i-C_4H_{10}, 2000 ppm NO, 3% O_2, 77% He

[a] The numbers correspond to those in Table 1. When remeasured after another step, these are denoted as 7a, 3a, and 3b.

to CO_2 are compared for the poisoned and the unpoisoned gases. In both cases the conversion to N_2 was higher than the conversion of isobutane into CO_2, and when H_2O was added into the gas stream the combustion was further repressed, whereas the conversion to N_2 was unaffected. Thus the selectivity was enhanced by these poisons. This is a valuable asset. Moreover, it supports the earlier postulate of Lukyanov *et al.* (11) that combustion and N_2 formation follow independent pathways.

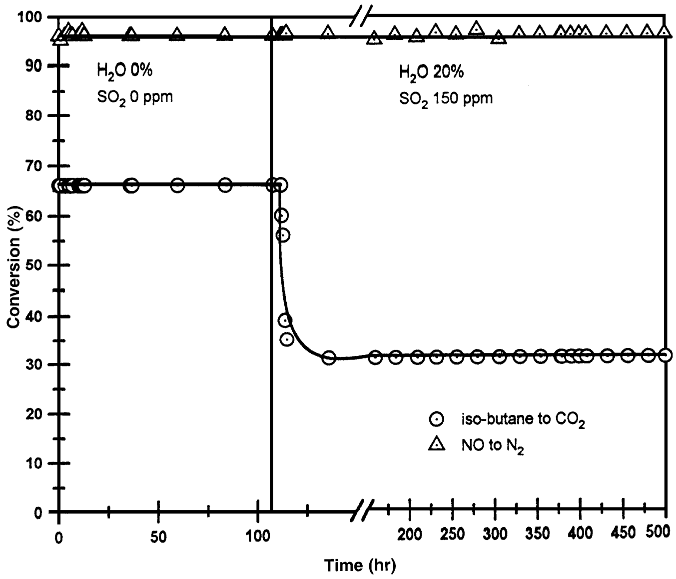

FIG. 5. Effect of H_2O and SO_2 on selectivity over catalyst FeZSM-5-19-183 at 500°C. The conversion of i-C_4H_{10} was strongly repressed by $H_2O + SO_2$ while formation of N_2 was unaffected. Conditions were the same as those used in Figs. 2 and 3.

Pore volumes were measured for a number of catalysts and are listed in Table 2. Those preparations made in the normal fashion using the anaerobic conditions specified by Delgass *et al.* (5), using $FeSO_4$ (Items 8 and 9) had significantly lower volumes than the parent NaZSM-5 or those prepared using FeC_2O_4. The result of the first exchange was FeZSM-5-12-37 and after repeating the exchange five times the result was FeZSM-5-12-41. A catalyst prepared by the method described herein using FeC_2O_4 yielded FeZSM-5-12-190 in a single exchange, a striking difference. It may be supposed that this difference was brought about by the precipitation of a small amount of FeOOH in the pore system, utilizing oxygen not excluded using the glove bag technique. It is easy to understand why the small port MFI structure would be much easier to plug with a small amount of this precipitate than the much larger channels of the *Y*-zeolite system.

Figure 6 shows a comparison of the ^{27}Al MAS NMR spectra of the freshly pretreated FeZSM-5-19-183 (a) with that after the 2500-h durability test (b). These spectra have been normalized to the same catalyst weight; they show no real evidence of any O_h coordinated Al (near 0 ppm), and only a small loss (<10%) in the intensity of the T_d signal (at about 52 ppm). This is close to the experimental error.

Similarly, ^{1}H MAS NMR spectra were obtained from the hydroxyls contained in the catalyst after the 2500-h run (Fig. 7a). Also shown in Fig. 7b is the spectrum taken from a sample spiked with 5% HZSM-5. Clearly the bands for the

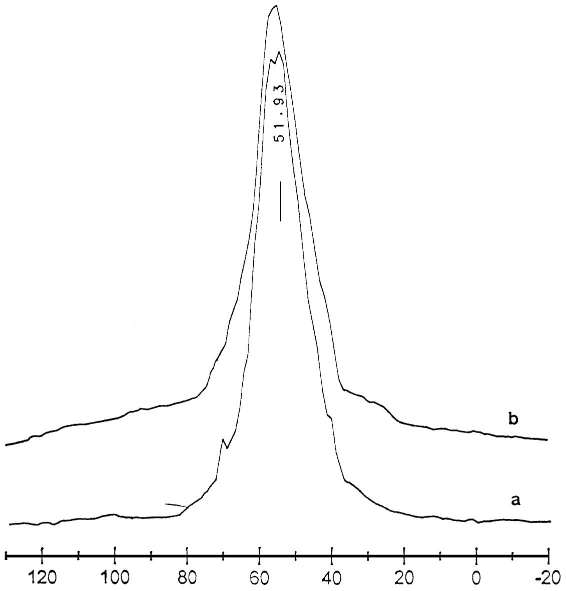

FIG. 6. (a) ^{27}Al MAS NMR spectrum of freshly prepared FeZSM-5-19-183 compared with (b) the spectrum after the 2500-h test shown in Fig. 3. The integrated intensities for (a) and (b) were 0.7 and 0.6 mmol Al/g, respectively.

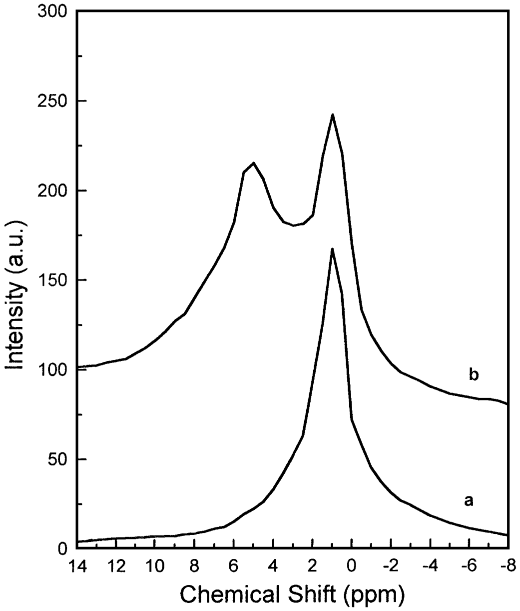

FIG. 7. (a) The ^{1}H MAS NMR spectrum of catalyst FeZSM-5-19-183 after 2500-h time on stream. Please note that a peak was not found for an OH adjacent to Al^{3+} which, as shown in (b), should appear at about +5 ppm. Here 5 wt% of HZSM-5 was added to a fresh sample of the same zeolite. The integrated intensity of the Si–OH peak shown in (a) amounted to only 0.08 spins/Al.

two kinds of OH groups are present in agreement with the work of Freude *et al.* (13). Moreover, only small concentrations ($\sim 4 \times 10^{19}$ OH/g) were obtained; these corresponded to the terminal SiOH groups. No evidence of any bridged Brønsted OH between Si and Al T sites was found in Fig. 7a.

An interesting feature of the analytical data is shown in Table 1. The sum of the Fe and the residual Na was almost precisely equal to the lattice Al after correction for the excess Na^+ present in the parent NaZSM-5 zeolites. This, together with the ^{1}H spectra, suggests that Brønsted sites have been largely excluded from these preparations.

The adsorption of H_2O was studied briefly in hopes of shedding light on the mechanism of hydrolytic breakdown in steam; H_2O isotherms taken at room temperature were obtained for FeZSM-5-19-183, CuZSM-5-12-103, and HZSM-5-12-100. The resulting data are presented in Fig. 8, where they are compared with an isotherm determined for *n*-pentane. It was anticipated that these data would indicate the relative hydrophobicity versus lyophilicity of these surfaces. This test failed. The H_2O isotherms for the cation exchanged zeolites were not convex to the pressure axis, as expected for a truly hydrophobic surface. Instead, they appeared to follow Henry's law (CuZSM-5) or were weakly concave (FeZSM-5) to the pressure axis. The HZSM-5 sample appeared to reach a limit at quite low relative pressure and was flat thereafter. This isotherm is quite interesting. It has the appearance of a site-selective chemisorption. The total uptake in this flat region, however, amounted to about 0.4 H_2O/Al-T site or, if each site retains an accessible OH, 0.4 H_2O/Brønsted site, where hydrogen-bonding might be expected. Furthermore, there is no evidence of capillary condensation below $P/P_0 = 0.7$. The total pore volumes listed in Table 2 (~ 0.152 ml/g = 8.4 mmol/g for H_2O) are very much higher than any of these H_2O isotherm data. Even the *n*-pentane isotherm (also flat) indicates that only about 28% of the pore volume is filled.

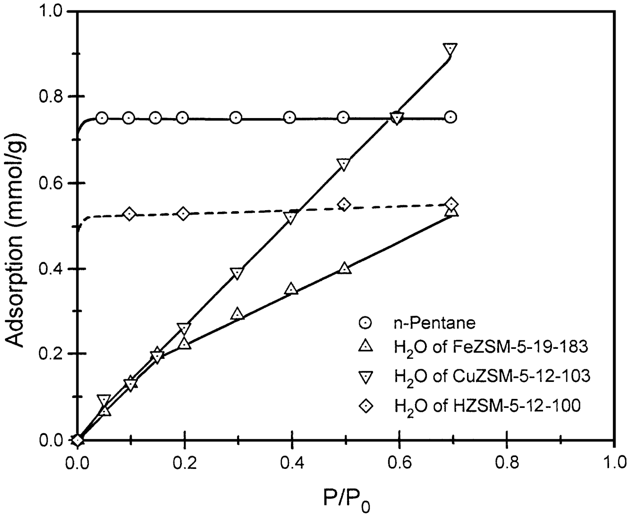

FIG. 8. Water (H_2O) adsorption isotherms taken at room temperature on HZSM-5, CuZSM-5-12-103, and FeZSM-5-19-183. The *n*-pentane isotherm for FeZSM-5 is shown for comparison.

TABLE 3

Microbalance Studies of Oxidation-Reduction Cycle with FeZSM-5 Samples[a]

Temperature °C	Treatment	Weight change (mg)		ΔO/Fe	
		FeZSM-5-19-183	FeZSM-5-19-198	FeZSM-5-19-183	FeZSM-5-19-198
500°C	O_2	+0.562	+0.655	+0.46	+0.49
	He	−0.061	−0.005	−0.05	−0.01
	H_2	−0.512	−0.645	−0.42	−0.48
	He	−0.011	−0.02	−0.01	−002
950°C	O_2	+0.549	+0.650	+0.45	+0.49
	He	−0.061	−0.005	−0.05	−0.01
	H_2	−0.537	−0.645	−0.44	−0.48
	He	−0.010	−0.02	−0.01	−0.02
1050°C	O_2	+1.147	NA	+0.94	NA
	H_2	NA	−1.295	NA	−0.97
	He	−0.085	−0.02	−0.07	−0.02
	H_2	−1.232	NA	−1.01	NA
	O_2	NA	+1.465	NA	+1.09

[a] Freshly prepared sample was treated in UHP grade He with a temperature ramp of 25°C/h to 500°C. Subsequently all treatments were 24 h.

The cation exchanged zeolites were different in character, but here too the numerical relationships at $P/P_0 = 0.7$ are comparable with those given above for HZSM-5. Perhaps they correspond to a very slow restoration of the hydration spheres of the cations on exposure to H_2O at room temperature. It has been reported (14) that this process proceeds nearly to completion with CuZSM-5. At $P/P_0 = 0.7$ the uptake is far removed from this state. The data of Fig. 8 show that this process is pressure dependent for the cation-exchanged zeolites, and the data show that at lower partial pressures rehydration is far from complete. HZSM-5, perhaps because of the stronger interactions involved, behaved differently. The data do suggest that dealumination is induced by attack of H_2O on the Brønsted sites and that elimination of these will tend to stabilize the lattice.

It was shown (Fig. 4) that the catalyst was not damaged by temperature excursions up to 800°C. Higher temperatures were not investigated for fear of ruining the catalyst before the 2500-h mark was achieved. Therefore, following these experiments the flow microbalance was used to test the effect of temperature in a number of O_2/H_2 redox cycles. Some results are listed in Table 3. These show a reversible oxidation-reduction redox couple of about 1 e/Fe, stable to 950°C. This could be repeated many times and extended reductions at this temperature did not effect a deeper reduction. However, when the temperature was raised to 1050°C, the swing in weight doubled, both on oxidation and on reduction (Table 3) and corresponded to about a 2 e/Fe change. This was accompanied by a concomitant destruction of the lattice. Metallic iron or Fe_3O_4 could be separated from the resulting oxide layer using a simple horseshoe magnet, demonstrating the presence of ferromagnetism.

DISCUSSION

The results presented demonstrate the relatively high activity for SCR and the hydrothermal stability of the FeZSM-5 made from FeC_2O_4. How can this stabilization be rationalized? Based on earlier studies with CuZSM-5 (11), it was recognized that (a) dealumination resulting from steaming is one probable cause of structural decay and (b) that H_2O attacks preferentially the Brønsted hydroxyls. Therefore as a working hypothesis it was assumed that if Brønsted sites could be eliminated from the zeolite, this source of decay could be suppressed. Furthermore, Brønsted sites may be introduced by reduction of a divalent cation to a lower valence state, particularly to the metal. Depending upon circumstances this may be reversible (11) (but not if dealumination occurs first). To circumvent this problem Fe^{2+} was selected because it may be oxidized to Fe^{3+}, but not readily reduced to Fe^0 (5). Note that on reduction of Fe^{3+}ZSM-5 extralattice oxygen (ELO) is removed, but is reincorporated on treatment with O_2. It is interesting that one atom of ELO/Fe^{2+} is introduced during exchange; this is not reducible. A second atom of ELO is incorporated on oxidation of the Fe^{2+} cations to Fe^{3+}, and this portion is removable by reaction with H_2 at 550°C. Some of the suggestions appearing in the following paragraphs are admittedly speculative, but hopefully will serve to generate further research.

In order to understand the special role of FeC_2O_4 in stabilizing the zeolite, it is necessary to consider the chemistry of base-exchange. The solubility of FeC_2O_4 in H_2O is about $10^{-3}M$. From the literature (15), the equilibrium constants and reduction potentials listed in Table 4 were

TABLE 4

Equilibrium Constants and Reduction Potentials for FeC_2O_4 aq. at 25°C

Eq. [1]	$FeC_2O_4 \leftrightarrow Fe^{2+} + C_2O_4^{2-}$	$K_{6\text{-}p} = 5.0 \times 10^{-6}$
Eq. [2]	$H^+ + C_2O_4^{2-} \leftrightarrow HC_2O_4^-$	$K_{a2} = 2.0 \times 10^4$
Eq. [3]	$H^+ + HC_2O_4^- \leftrightarrow H_2C_2O_4$	$K_{a1} = 2.6 \times 10^1$
Eq. [4]	$Fe^{2+} + OH^- \leftrightarrow FeOH^+$	$K_{b2} = 5.6 \times 10^{10}$
Eq. [5]	$Fe^{2+} + 2OH^- \leftrightarrow Fe(OH)_2\downarrow$	$K_1 = 5.6 \times 10^{14}$
Eq. [6]	$Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3\downarrow$	$K_2 = 1.7 \times 10^{37}$
Eq. [7]	$H_2O \leftrightarrow H^+ + OH^-$	$K_w = 1.0 \times 10^{-14}$
Eq. [8]	$Fe^{2+} + 1/4O_2 + 1/2H_2O + 2OH^- \leftrightarrow Fe(OH)_3$	6.015 V
Eq. [9]	$2H_2C_2O_4 + O_2 \leftrightarrow 4CO_2\uparrow + 4H_2O$	2.209 V
Eq. [10]	$HC_2O_4^- + 2Fe^{3+} \leftrightarrow 2Fe^{2+} + 2CO_2 + H^+$	2.032 V
Eq. [11]	$FeOH^+ + \text{Na Zeolite} \leftrightarrow \text{FeOH Zeolite} + Na^+$	

obtained. These data define the distribution of various ions in solution. The first three equations show that the $C_2O_4^{-2}$ released when FeC_2O_4 is dissolved will react with H^+ available in the aqueous solution forming $HC_2O_4^-$ along with a lesser amount of $H_2C_2O_4$. The next two equations show that the Fe^{2+} released will react with the available OH^- to form $Fe(OH)^+$ and $Fe(OH)_2$. Taking K_w into account, these data make it possible to calculate the distribution of iron ions in the bulk solution as a function of pH (Fig. 9). Below $pH = 2$, Fe^{2+} is the dominant ion in the solution but by $pH = 4$, $Fe(OH)^+$ becomes the chief, and above $pH = 5$ almost the sole ion present. The H^+ ions produced from H_2O, corresponding to the OH^- used in the formation of $Fe(OH)^+$, were thus "gettered" by the oxalate ions produced by Eq. [1] as shown by Eqs. [2] and [3]. Consequently they were not available to form Brønsted sites. This was our chief objective.

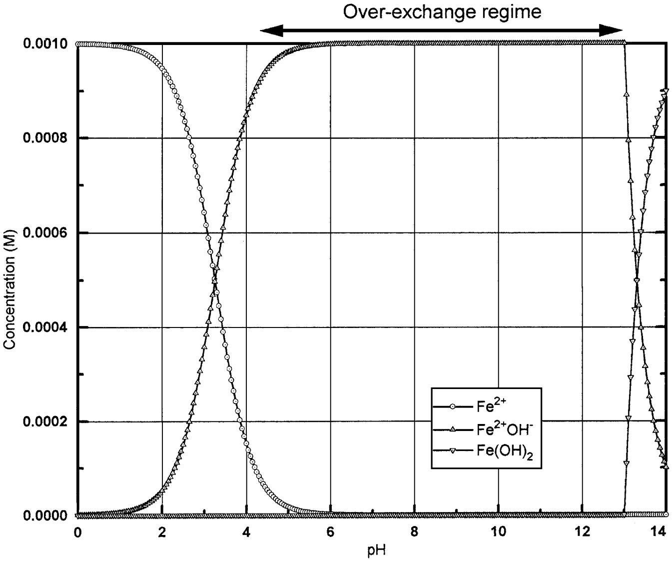

FIG. 9. Hydrolysis equilibria of Fe-containing ions in a 10^{-3} *M* FeC_2O_4 solution at 25°C as a function of pH calculated from the data of Table 4.

Base-exchange of the NaZSM-5 with $Fe(OH)^+$ allows up to 200% exchange to be achieved (calculated on the basis of $1Fe^{2+} = 2Na^+$). As shown in Table 1 the sum of the $Fe(OH)^+$ and the residual Na^+ almost exactly balanced the Al T- sites. Hence, few if any Brønsted sites were produced during the exchange and extralattice oxygen (ELO) equivalent to 1 atom for every 2Fe remained after heating in flowing He to 500°C. Moreover, as noted above this ELO was not reducible at 950°C.

The oxalate method simultaneously accomplished another important function. It has been known for many years that Fe^{2+} in aqueous solution is readily oxidized to Fe^{3+} by trace amounts of O_2 unavoidably present. Fe^{3+} readily hydrolyses to gelatinous FeOOH partially blocking the pores of the zeolite. Delgass *et al.* (5) showed that the larger pores of the *Y*-zeolite could be protected satisfactorily by the "anaerobic conditions" maintained in a glove box or glove bag flushed with pure N_2. However, this did not prove successful with the smaller port MFI systems. As shown in Table 2, all the fresh preparations except those made using $FeSO_4$ by the conventional method had pore volumes of 0.152 ± 0.003 ml/g. The latter had volumes 10% lower (0.137 ± 0.002 ml/g) demonstrating pore blocking and, hence, loss of accessible sites. It is supposed that the $C_2O_4^{2-}$ acts to prevent oxidation of Fe^{2+} to Fe^{3+} since it is more easily oxidized to CO_2 than is Fe^{2+} to Fe^{3+}. Indeed Eq. [10] shows that $H_2C_2O_4$ oxidation to CO_2 by Fe^{3+} is strongly favored thermodynamically. Interestingly Catalyst FeZSM-5-19-183 lost only about 15% of its pore volume in 2500 h of operation.

A final interesting feature is shown by the microbalance data of Table 3. Although the first half of the ELO introduced during preparation was not reducible below about 950°C, a second and about equal portion could be added by oxidation of Fe^{2+} in the "as prepared" sample to Fe^{3+}. This ELO could then be removed by reduction with H_2 or CO, as observed previously with Fe*Y* (6). Evidently, there is much to be learned about the internal structure of these materials. Iron, like cobalt, does not have an accessible monovalent state as does copper. If redox chemistry is operative, the former would necessarily need to be reduced to the metal, yet with FeZSM-5 the Fe^{2+} ion has been shown to be extremely difficult to reduce. Oxidation to Fe^{3+}, on other hand, has been shown to be easy and reversible. Oxidation of Co^{2+} to Co^{3+} is feasible, but reduction to Co^0 with regeneration to Co^{2+} is apparently not difficult (12). A careful study of these processes with other systems (16) and involving other physical means is needed.

The present work has explored only a small portion of parameter space. It is to be expected that changes in the composition of the feed and the external variables may profoundly affect the activity and selectivity, e.g., it was shown herein that addition of H_2O strongly suppressed combustion to CO_2. CH_4 was found to be a satisfactory reducing agent, but only above 650°C. Hence other systems must be optimized for activity and selectivity. Finally, tests should realistically reflect real conditions for any potential application. The salient features of the present work are twofold, viz., the resistance to poisoning by H_2O and the long-term durability of these preparations. Under our conditions the selectivity at temperatures up to 500°C favored N_2 formation over combustion to CO_2. It is to be expected that this would be reversed with lower NO/O_2 ratios in the feed or by working at higher temperatures.

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REFERENCES

1. Held, W., and Koening, A., Ger. Offen. DE 3 642018, 1989; SAE Paper 900496, 1990 (unpublished).
2. Hamada, H., Kintaichi, Y., Sasaki, M., and Ito, X., *Appl. Catal.* **64**, L1 (1990); **70**, L15 (1991); **75**, L1 (1991).
3. Iwamoto, M., and Hamada, H., *Catal. Taday* **17**, 94 (1991).
4. Witzel, F., Sill, G. A., and Hall, W. K., *J. Catal.* **149**, 229 (1994).
5. Delgass, W. N., Garten, R. L., and Boudart, M., *J. Phys. Chem.* **73**, 2970 (1969).
6. Petunchi, J. O., and Hall, W. K., *J. Catal.* **80**, 403 (1983).
7. Li, Y., Battavio, P. J., and Armor, J. N., *J. Catal.* **142**, 561 (1993).
8. Feng, X., and Hall, W. K., *Catal. Lett.* **41**, 45 (1996).
9. Segawa, K., Watanabe, K., and Kunugi, R., private communication.
10. Feng, X., and Hall, W. K., United States Patent Application Serial Number 08-634,233; filed April 18, 1996.
11. Petunchi, J. O., Sill, G. A., and Hall, W. K., *Appl. Catal. B* **2**, 303 (1993); Lukyanov, D. B., Sill, G. A., d'ltri, J. L., and Hall, W. K., "Proc. 11th Int. Cong. Catal.," Part A, p. 651, Studies in Surface Science and Catalysis, Elsevier, Amsterdam, 1996.
12. Fierro, G., Eberhardt, M. A., Houalla, M., Hercules, D. M., and Hall, W. K., *J. Phys. Chem.* **100**, 8468 (1996) and earlier references cited therein.
13. Freude, D., Hunger, M., Pfeifer, H., and Schwieger, W., *Chem. Phys. Lett.* **128**, 62 (1986).
14. Larsen, S. C., Aylor, A., Bell, A. T., and Reimer, J. A., *J. Phys. Chem.* **98**, 11533 (1994).
15. Skoog, D. A., and West, D. M., "Fundamentals of Analytical Chemistry," 2nd ed., Holt, Rinehart, Winston, New York, 1969.
16. Fu, C. M., Deeba, M., and Hall, W. K., *I&EC Product Res. Dev.* **19**, 299 (1980).