

# Preparation of Overexchanged Fe–ZSM-5 Zeolites Using the Ferrous Oxalate Method: Why Does It Fail?

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A plausible explanation of why the ferrous oxalate method is unsuitable for the preparation of overexchanged Fe–ZSM-5 is proposed on the basis of TG–DSC, FTIR, and <sup>27</sup>Al MAS NMR results. Iron is precipitated onto the zeolite mainly as an FeC<sub>2</sub>O<sub>4</sub> complex, which blocks the pores and impedes a complete exchange of the Na<sup>+</sup> cations. Most of the precipitate is removed by extensively washing the zeolite, whereas most of the remaining iron species is transformed into iron oxide during the subsequent thermal treatment. A small number of iron species may also occupy ion-exchange positions (Fe/Al << 0.5). IR spectroscopy revealed the formation of Brønsted acid sites, both during the exchange and upon drying of the zeolite. These results suggest that overexchanged iron zeolites cannot be prepared easily by conventional ion exchange in aqueous solution. The effectiveness of this method does not seem to depend on the source of the parent ZSM-5 used. © 2000 Academic Press

**Key Words:** overexchanged Fe–ZSM-5; deNO<sub>x</sub> catalysts; Brønsted acid sites.

## INTRODUCTION

Overexchanged Fe–ZSM-5, i.e., a zeolite with a Fe<sup>II</sup>/Al molar ratio >0.5, has recently been shown to be a promising catalyst for the selective catalytic reduction (SCR) of nitrogen oxides with hydrocarbons under lean burn conditions (1, 2). Besides higher activities than Cu–ZSM-5 catalysts and a remarkable durability under hydrothermal conditions, the activity of overexchanged Fe–ZSM-5 was not impaired by up to 150 ppm of SO<sub>2</sub> and 20% H<sub>2</sub>O in a simulated vehicular exhaust stream (1). The ion-exchange procedure applied by Feng and Hall (1) for the preparation of Fe–ZSM-5 comprised the use of a ferrous oxalate solution under exclusion of air. Their apparatus consisted of two flasks containing the zeolite and ferrous oxalate, respectively, connected through a fritted disk, which allowed ions to freely pass from one flask to another but impeded the passage of solids. Both chambers were flushed with N<sub>2</sub> or Ar to exclude traces of O<sub>2</sub>. This device prevented the oxidation of Fe<sup>II</sup> into Fe<sup>III</sup> and the ensuing precipitation of iron

hydroxide which would cause the blockage of the pores of the zeolite (3). The authors reported that the sodium cations of the parent material were almost completely replaced with iron species whose nature, however, is still unclear. Subsequent reports, as well as our own studies, questioned the reproducibility of this preparation method (2, 4, 5). The performance of Fe–ZSM-5 prepared by the oxalate method was shown to depend markedly on the synthesis history of the starting material (2). In a more recent communication, Hall and co-workers also accounted for these problems in the preparation of Fe–ZSM-5 (6). One way to overcome these drawbacks has been suggested by Chen and Sachtler, who reported the preparation of active Fe–ZSM-5 by the sublimation of FeCl<sub>3</sub> onto the proton form of a ZSM-5 zeolite (2). The catalyst obtained with this method exhibited somewhat lower activity for the SCR of NO with *i*-butane than the catalyst originally prepared by Feng and Hall, but the preparation method seemed to be less sensitive to the origin of the zeolite. The sublimation method was successfully applied by Kucherov *et al.* in the preparation of Fe–ZSM-5 as well as Fe–SAPO-34 (4). The results of their *in situ* ESR investigation showed that Fe-exchanged zeolites hardly chemisorb water above 200°C, which was concluded to lead to the observed resistance towards water vapor during the SCR reaction (1, 2). Additionally, they observed the irreversible formation of an agglomerated ferromagnetic species induced by reducing condition on both Fe–ZSM-5 and Fe–SAPO-34.

Ma and Grünert observed very good catalytic activity in the SCR with ammonia on an Fe–ZSM-5, which was prepared using a somewhat modified sublimation technique (7). Their catalyst, however, exhibited lower activity in the SCR with *i*-butane compared to that reported by Feng and Hall and was also less active than Cu–ZSM-5. They suggested that different sites might be active for the two reactions.

Solid-state ion exchange (SSIE) was employed by Turek and co-workers for the preparation of Fe–ZSM-5 in the presence of air (8, 9). Although they did not apply oxygen-free conditions during the catalyst preparation, the activity of their catalysts was still remarkably high. Overexchange

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(i.e.,  $\text{Fe}^{\text{II}}/\text{Al} > 0.5$ ), however, was not reached by this method regardless of the type and amount of Fe sources and the conditions applied during the exchange (heating *in vacuo* or inert atmosphere). Whenever the iron content exceeded the ratio  $\text{Fe}^{\text{II}}/\text{Al} = 0.5$ , precipitation of hematite occurred, which was concluded to be inactive in the reduction of nitrogen oxides.

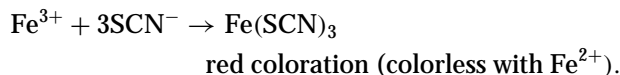
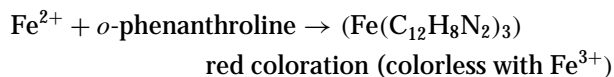
As of today the actual nature of the active species of these catalysts has not been completely elucidated and different models have been proposed. Feng and Hall claimed that the  $\text{Fe}(\text{OH})^+$  complex was the predominant species in the ferrous oxalate solution used for the exchange and therefore replaced the  $\text{Na}^+$  cations at ion-exchange positions (1). This procedure was furthermore claimed to prevent also the formation of Brønsted acid sites, which were considered responsible for the hydrothermal breakdown of the catalyst (10). On the other hand, Chen and Sachtler suggested an oxygen-bridged binuclear complex as a plausible model for the active species (2, 11). A third model was put forward by Joyner and Stockenhuber, who prepared Fe-ZSM-5 using the conventional aqueous exchange procedure. From EXAFS analyses they concluded that the active species was present on the zeolite as clusters of iron and oxygen atoms with a structure similar to that of  $\text{Fe}_3\text{S}_4$  (12).

The aim of the present paper is to contribute to the understanding of the peculiarity of the iron-exchanged zeolites, focusing mainly on the aqueous chemistry of the iron ions. We will show results of our attempts at preparing an Fe-ZSM-5 catalyst through the exchange method based on a ferrous oxalate solution. A large amount of iron was found to precipitate onto the zeolite in the form of iron oxalate complex. Upon extensive washing a small fraction of the iron migrates to the ion-exchange sites, but no overexchange was achieved. Formation of Brønsted acid sites occurred during both the exchange and the subsequent washing. Through a renewed analysis of the distribution of species present in a ferrous oxalate solution we could account for such results. The application of the method to another ZSM-5 zeolite provided by a different manufacturer led to similar results.

## EXPERIMENTAL METHODS

Na-ZSM-5 samples were provided by CU Chemie Uetikon (Zeocat PZ-2/40,  $\text{Si}/\text{Al} = 18$ ) and Süd-Chemie AG (Na-MFI-46 P,  $\text{Si}/\text{Al} = 20$ ). The zeolites were calcined at  $550^\circ\text{C}$  overnight in static air under shallow bed conditions prior to use, and then exchanged with a 1 M aqueous solution of  $\text{Na}_2\text{SO}_4$  for 2 h under reflux conditions. The ion exchange of the Na-ZSM-5 (Chemie Uetikon) with ferrous oxalate ( $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , Fluka) was carried out following exactly the description given by Feng and Hall (1). In order to avoid the presence of oxygen and therefore the oxidation of  $\text{Fe}^{\text{II}}$  into  $\text{Fe}^{\text{III}}$  a glass apparatus identical to that described

in (1) was used. Two grams of zeolite was exchanged with a saturated solution of ferrous oxalate (1 g of  $\text{FeC}_2\text{O}_4$  per gram of zeolite) that had been previously purged with nitrogen. The pH during exchange reached values between 5–6 and was not corrected to neutrality to avoid exposure of the preparation to air. After a 24-h exchange at ambient temperature the sample (with a yellowish color) was repeatedly washed with hot ( $50^\circ\text{C}$ ) deionised water (36 times, 500 ml each). After each washing, the solutions were qualitatively tested for the presence of iron cations using the following reactions (13):



Fractions of the sample were collected separately after 4, 9, 17, and 36 washings, and will be hereafter referred to as Fe(CU)-4, Fe(CU)-9, Fe(CU)-17, and Fe(CU)-36, respectively. After the washings, the zeolites were allowed to dry in air at ambient temperature overnight.

The procedure was repeated using as starting material the Na-ZSM-5 received from Süd Chemie AG. After the exchange the zeolite was washed with hot deionised water until no iron cations were detected in the washing solution (16 washings, 500 ml each). Fractions of the sample were collected separately after 4 and 16 washings, and will be hereafter referred to as Fe(SC)-4 and Fe(SC)-16, respectively. Since it has been suggested that the treatment in an inert atmosphere rather than in air at an elevated temperature prior to reaction would result in an active catalyst (6), a part of the preparation (still wet) was separated after four washings, dried, and heated in He at  $500^\circ\text{C}$  for 2 h (Fe(SC)-4-He).

The chemical composition of all zeolites was determined by atomic absorption spectroscopy on a Varian SpectrAA-10 after dissolution in hydrofluoric acid. The thermogravimetric analyses combined with differential scanning calorimetry (TGA-DSC) of the samples Fe(CU) were performed on a Polymer Laboratories STA 1500H instrument under air flow in the temperature range  $25\text{--}800^\circ\text{C}$  (heating ramp,  $10^\circ\text{C}/\text{min}$ ). For the samples Fe(SC) the thermogravimetric analyses combined with single differential thermal analyses (TGA-SDTA) were performed on a TGA/SDTA 851e Mettler Toledo instrument under identical conditions.

Solid-state MAS NMR measurements were carried out using a Bruker AMX400 spectrometer at a magnetic field of 9.4 T.  $^{27}\text{Al}$  MAS NMR spectra were recorded on fully hydrated samples at a resonance frequency of 104.26 MHz. The  $^{27}\text{Al}$  chemical shifts were referenced to  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  in a 1 M aqueous solution of  $\text{Al}(\text{NO}_3)_3$ . For each spectrum 2160 scans were acquired with a recycling time of 10 s. Rotors were spun at 5 kHz with pulse lengths of 1  $\mu\text{s}$ , corresponding

to a flip angle  $<\pi/12$ . These parameters ascertained quantitative determination of Al species.

Infrared spectra of self-supporting zeolite wafers were recorded at ambient temperature on a Mattson Galaxy 6020 IR spectrometer equipped with a MCT detector at a resolution of  $4\text{ cm}^{-1}$ . Prior to IR measurements samples were outgassed *in situ* at a pressure below  $10^{-6}$  mbar either at  $150^\circ\text{C}$  (1 h) in order to avoid decomposition of the oxalate species or at  $500^\circ\text{C}$  (overnight). For the calculation of the distribution of Fe species in aqueous solution the software MINEQL+ from Environmental Research Software was used. The thermodynamic data were either provided directly by the software or taken from the literature (see Table 2).

## RESULTS

### Elemental Analysis (AAS)

The results of the elemental analyses of the samples studied are summarised in Table 1. As for the Fe(CU) zeolites, the most evident result is the decrease of the iron content with the amount of water used for washing the zeolites. During the first 17 washings the amount of Fe present on the zeolite strongly decreased from 3.8 to 2.3 wt%, whereas the subsequent washing diminished the iron content less markedly (2.0 wt% for Fe(CU)-36). Leaching of iron from the zeolite in the form of Fe(II) was confirmed by the qualitative test reactions carried out after each washing. No Fe(III) ions were detected in the washing solutions according to the thiocyanate test, thus confirming the effectiveness of the apparatus used for the exchange at preventing the oxidation of the Fe(II) ions in solution. As indicated by the residual sodium content of Fe(CU)-4, the exchange procedure did not completely replace the original counteranions of the parent zeolite. However, replacement of Na cations proceeded during the subsequent washing of the zeolite and was complete on the sample Fe(CU)-36 ( $\text{Na}/\text{Al} < 0.05$ ).

TABLE 1

Chemical Composition of the Zeolites Investigated

	Fe/Al	Na/Al	Fe wt% <sup>a</sup>	Calcd Fe wt% <sup>b</sup>
Na-ZSM5 (CU)	—	0.9	—	—
Na-ZSM5 (SC)	—	0.9	—	—
Fe(CU)-4	0.9	0.4	3.8	4.6
Fe(CU)-9	0.7	0.2	3.2	2.6
Fe(CU)-17	0.5	0.1	2.3	1.5
Fe(CU)-36	0.4	<0.05	2.0	1.2
Fe(SC)-4	0.3	0.4	1.1	0.6
Fe(SC)-16	0.2	0.3	0.8	0.3
Fe(SC)-4-He	0.3	0.4	1.1	—

<sup>a</sup> Determined by AAS analysis.

<sup>b</sup> Calculated from TG patterns assuming the weight loss to be completely related to the decomposition of  $\text{FeC}_2\text{O}_4$ .

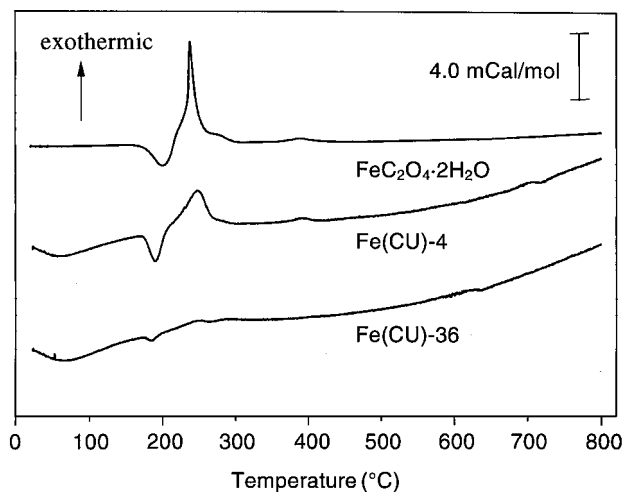


FIG. 1. DSC patterns for the samples Fe(CU)-4 and Fe(CU)-36 compared with that of pure ferrous oxalate.

The AAS results for the Fe(SC) samples showed basically the same trend as that observed for the Fe(CU) samples, the only difference being the lower amount of iron introduced into the zeolite (Fe(SC)-4,  $\text{Fe}/\text{Al} = 0.3$ ). After the exchange the iron content was 1.1 wt% and it decreased upon further washing (0.8 wt% for Fe(SC)-16).

### Thermal Analysis

In Fig. 1 the results of the DSC analyses on the Fe(CU) samples are shown. The curve of pure ferrous oxalate used for the exchange is given as a reference. The similar thermal patterns observed for Fe(CU)-4 and Fe(CU)-36 suggest substantial amounts of iron oxalate to be present on the zeolite Fe(CU)-4 and to a smaller extent on the zeolite Fe(CU)-36. This result indicates that the iron hosted in the zeolite pores formed a complex with oxalate anions. In order to quantify the amount of iron oxalate present on the various samples the weight loss curves, as determined by TGA, were evaluated (Fig. 2). For all the samples three main temperature domains could be distinguished: ambient temperature– $150^\circ\text{C}$ ,  $150$ – $240^\circ\text{C}$ , and  $240$ – $350^\circ\text{C}$ . The weight loss observed up to  $150^\circ\text{C}$  was due to the removal of the water adsorbed on the zeolite. Between  $150$  and  $240^\circ\text{C}$ , the removal of crystallisation water took place while above  $240^\circ\text{C}$  release of  $\text{CO}$  and  $\text{CO}_2$  occurred upon combustion of the oxalate anions (incidentally, the absence of weight loss in the range  $150$ – $240^\circ\text{C}$  on Fe(CU)-9 (Fig. 2c) is due to an evacuation treatment carried out at  $150^\circ\text{C}$  before the measurement, which removed the crystal water without decomposing the oxalate species). Beyond  $350^\circ\text{C}$  no further weight loss was detected. From a comparison of the weight loss of the samples with that of pure ferrous oxalate in the temperature range  $150$ – $350^\circ\text{C}$  an estimation of the amount of iron present in the zeolite as ferrous oxalate was made

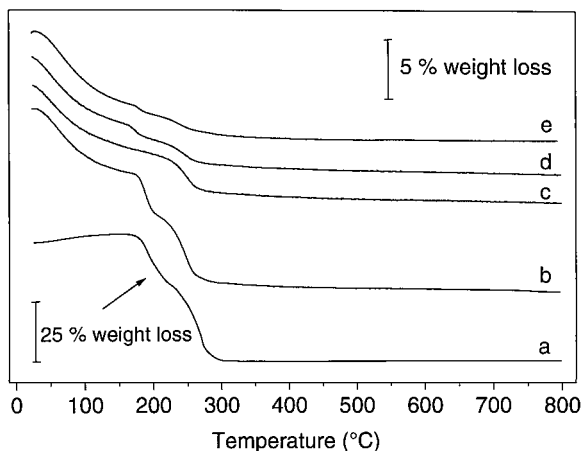


FIG. 2. TGA profiles of the samples: (a)  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , (b) Fe(CU)-4, (c) Fe(CU)-9, (d) Fe(CU)-17, and (e) Fe(CU)-36.

(see Table 1). The effect of washing on the concentration of different iron species in the ferrous oxalate-exchanged ZSM-5 is depicted in Fig. 3.

The ferrous oxalate content calculated for Fe(CU)-4 ( $\text{Fe} = 4.6 \text{ wt}\%$ ) was found larger than that determined by AAS analysis ( $\text{Fe} = 3.8 \text{ wt}\%$ ). This means that all the iron present on the zeolite at this stage of the preparation was in the form of ferrous oxalate. This result was accounted for in Fig. 3 (full circles coinciding with open triangles). The excess weight loss could originate from other oxalate species. The more extensively washed samples showed a decrease of both the total iron content and the amount of  $\text{FeC}_2\text{O}_4$  complex. However, in the samples Fe(CU)-9, Fe(CU)-17, and Fe(CU)-36,  $\text{FeC}_2\text{O}_4$  still accounted for more than 50% of all the iron present. The remainder of the iron, namely the difference between the total iron content and the amount of iron oxalate complex (closed triangles) could be any type of Fe species. Nevertheless, even when it is assumed that all

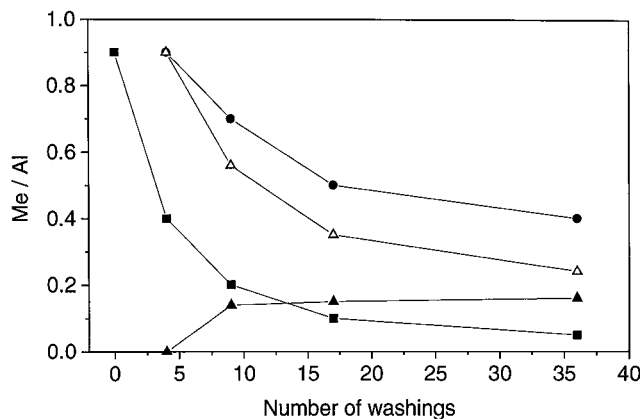


FIG. 3. Effect of washing upon composition of Fe(CU) zeolites: (■) Na content, (●) total Fe content, (△) Fe as  $\text{FeC}_2\text{O}_4$ , and (▲) other Fe species.

the iron that was not present as iron oxalate was located at ion-exchange positions, overexchange was not achieved and a maximum exchange ratio of only  $\text{Fe}/\text{Al} = 0.2$  can be envisaged.

The negligible Na content of Fe(CU)-36 indicated that complete exchange of Na was reached. From the maximum possible amount of iron present at exchange positions on Fe(CU)-36 ( $\text{Fe}(\text{II})/\text{Al} = \text{ca. } 0.2$ ) it was inferred that the remainder of the cationic sites had to be occupied by protons. Similar calculations carried out for the Fe(SC) samples revealed that a low degree of exchange was also achieved on this zeolite ( $\text{Fe}(\text{II})/\text{Al} = 0.15$ ). In contrast to the case for Fe(CU)-4, not all the iron could be accounted for as oxalate complex, suggesting that some Fe ions may have already been located at the ion-exchange sites during the exchange. The ferrous oxalate that precipitated on the zeolite was also leached upon extended washing. The sodium content decreased with washing as well, but replacement of the sodium cations did not reach completion even after extended washing (Fe(SC)-16,  $\text{Na}/\text{Al} = 0.3$ ). Since the maximum total cation content ( $\text{Na} + \text{Fe}$ ) accounted only for ca. 50% of all the available ion-exchange sites, the formation of Brønsted acid sites during the exchange was concluded.

#### FTIR Spectroscopy

In Fig. 4 the spectra of the Fe-exchanged zeolites in the range  $1250\text{--}2100 \text{ cm}^{-1}$  are shown. Spectra were recorded at ambient temperature after the samples were outgassed *in vacuo* at  $150^\circ\text{C}$  (1 h) in order to avoid decomposition of the oxalate species. Besides the weak bands at  $1880$  and  $2000 \text{ cm}^{-1}$  observed for all samples, which are the overtone bands of the vibration modes of the lattice T-O-T units, for Fe(CU)-4 four bands were clearly distinguished at  $1314$ ,  $1359$ ,  $1467$ , and  $1630 \text{ cm}^{-1}$ . The broad absorption

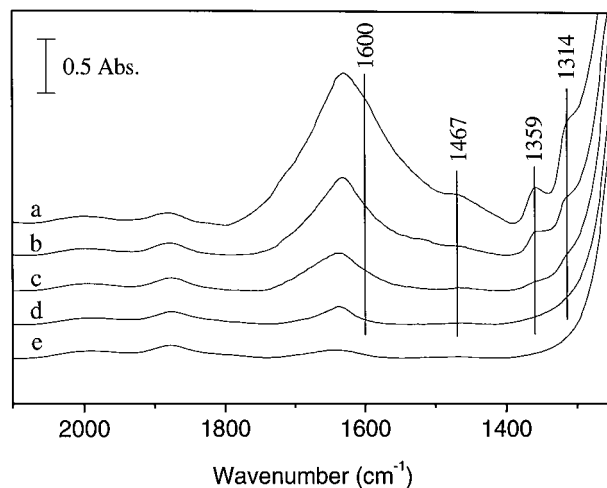


FIG. 4. FTIR spectra at room temperature after evacuation at  $150^\circ\text{C}$  (1 h) of (a) Fe(CU)-4, (b) Fe(CU)-9, (c) Fe(CU)-17, (d) Fe(CU)-36, and (e) Na-ZSM-5 (CU).

at  $1630\text{ cm}^{-1}$ , which is due to the bending mode of the O-H bonds of the water molecules adsorbed on the zeolite, exhibited a shoulder at about  $1600\text{ cm}^{-1}$ . The bands at  $1314$ ,  $1359$ , and  $1600\text{ cm}^{-1}$  were already visible upon evacuation at ambient temperature, whereas the band at  $1467\text{ cm}^{-1}$  appeared only during the thermal treatment. We attribute the bands at  $1314$ ,  $1359$ , and  $1600\text{ cm}^{-1}$  to the stretching vibration modes of oxalate species ( $\nu(\text{C-C}) = 1314\text{ cm}^{-1}$ ,  $\nu_{\text{sym}}(-\text{CO}_2) = 1359\text{ cm}^{-1}$ , and  $\nu_{\text{asym}}(-\text{CO}_2) = 1600\text{ cm}^{-1}$ ), while the band at  $1467\text{ cm}^{-1}$  is assigned to the doubly degenerate  $\nu_{\text{asym}}(\text{CO}_3)$  stretching mode of carbonate species (the symmetric stretching modes of the carbonates species are either IR inactive or show up around  $1100\text{--}1300\text{ cm}^{-1}$ , which is beyond the frequency range of our instrument) (14). Formation of carbonate species upon heating *in vacuo* at  $150^\circ\text{C}$  of a mechanical mixture  $\text{NH}_4\text{-Y/FeC}_2\text{O}_4$  has been also reported in the literature (15). Samples Fe(CU)-9, Fe(CU)-17, and Fe(CU)-36 exhibited similar spectra, the only difference being the intensities of the oxalate bands. The signals at  $1614$ ,  $1359$ , and  $1314\text{ cm}^{-1}$  decreased in intensities with the extent of washing, becoming barely visible on the sample Fe(CU)-36 (Fig. 4). The fact that the more the zeolite is washed the more these species are leached out suggests that the oxalate species are loosely bound to the lattice, if at all.

In all Fe(CU) samples a band at  $3612\text{ cm}^{-1}$  was detected as well. The presence of this band indicates the formation of Brønsted acid sites and, therefore, is clear evidence for protons replacing sodium cations at ion-exchange positions. The concentration of the Brønsted sites slightly increased on going from Fe(CU)-4 to Fe(CU)-36 (Fig. 5, spectra b, c, d, and e). On Fe(CU)-36 the integrated intensity of the band of the Brønsted hydroxyls was roughly comparable with that of the corresponding band in H-ZSM-5 (spectrum f).

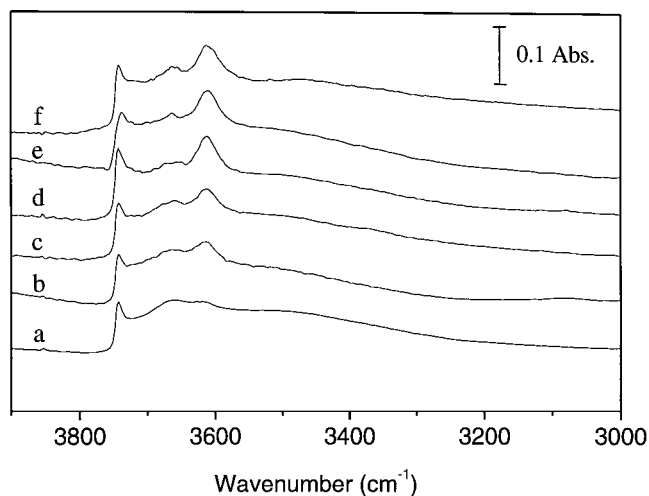


FIG. 5. FTIR spectra at room temperature after evacuation at  $500^\circ\text{C}$  of (a) Na-ZSM-5 (CU), (b) Fe(CU)-4, (c) Fe(CU)-9, (d) Fe(CU)-17, (e) Fe(CU)-36, and (f) Na-ZSM-5 (CU).

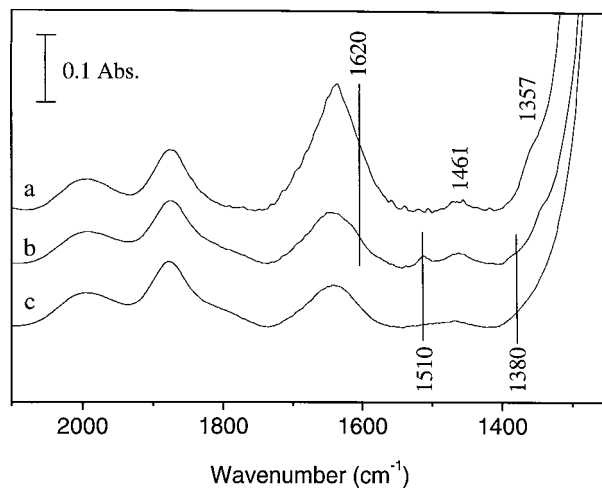


FIG. 6. FTIR spectra at room temperature after evacuation at  $150^\circ\text{C}$  (1 h) of (a) Fe(SC)-4, (b) Fe(SC)-16, and (c) Na-ZSM-5 (SC).

The Fe(SC) zeolites exhibited the same spectral features as the Fe(CU) zeolites, although all the bands were somewhat shifted in frequency and much less intense (Fig. 6). The bands at  $1357\text{ cm}^{-1}$  and the shoulder at  $1620\text{ cm}^{-1}$  were assigned to oxalate species, although the  $\nu(\text{C-C}) = 1314\text{ cm}^{-1}$  was not detected, probably due to the lower concentration of oxalate anions on this zeolite. The band at  $1461\text{ cm}^{-1}$ , as well as the two additional bands at  $1380$  and  $1510\text{ cm}^{-1}$ , indicated the presence of carbonate species. The former band (doubly degenerate) is due to carbonate species in which the symmetry around  $\text{CO}_3$  ions is retained (14). The latter bands are due to carbonate species in which the symmetry is not retained and the degeneration is therefore resolved (14). Upon washing of the samples, the intensities of these signals decreased. The band at  $3612\text{ cm}^{-1}$  again showed the formation of Brønsted acid sites whose concentration increased with the extent of washing (Fig. 7). In this respect

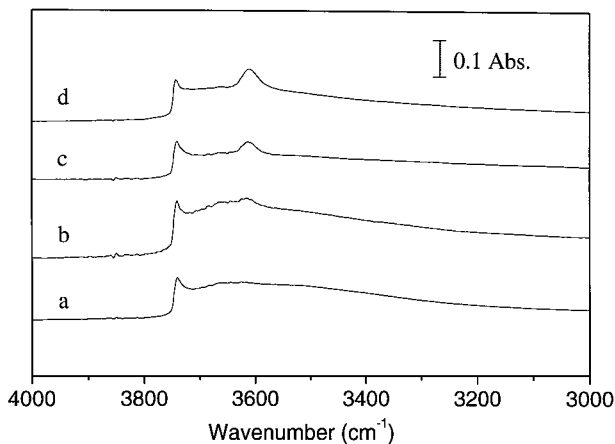


FIG. 7. FTIR spectra at room temperature after evacuation at  $500^\circ\text{C}$  of (a) Na-ZSM-5 (SC), (b) Fe(SC)-4, (c) Fe(SC)-16, and (d) H-ZSM-5 (SC).

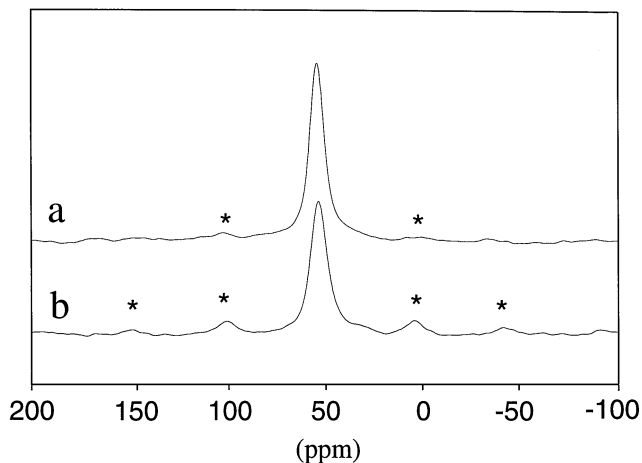


FIG. 8.  $^{27}\text{Al}$  MAS NMR spectra of (a) parent zeolite Na-ZSM-5 (SC) and (b) Fe(SC)-4. Asterisks indicate spinning side bands.

it should be noted that drying and calcining the zeolite in flowing He at  $500^\circ\text{C}$  after the exchange (still wet) (6) did not prevent the formation of the Brønsted acid sites, since the spectrum of Fe(SC)-4-He (not reported here) was identical with that of Fe(SC)-4 (Fig. 7, spectrum b).

#### $^{27}\text{Al}$ MAS NMR

In Fig. 8 the  $^{27}\text{Al}$  MAS NMR spectra of the parent Na-ZSM-5 (SC) zeolite and Fe(SC)-4 are depicted. A distinct signal at about 54 ppm was detected on both Na-ZSM-5 (SC) and Fe(SC)-4 and attributed to tetrahedrally coordinated Al atoms in lattice positions. Due to the quadrupolar interactions of  $^{27}\text{Al}$  nuclei, two additional spinning side bands at 5 and 105 ppm, respectively, were detected on the Na-ZSM-5 (SC) zeolite. For Fe(SC)-4 the anisotropy of the spectrum was more pronounced and spinning side bands were visible over a wider spectral range. This enhanced anisotropy, which is a direct consequence of the paramagnetic nature of the iron nuclei present in the zeolite, has already been observed in natural aluminosilicate (16) and in MnAlPO<sub>5</sub> systems (17). The integrated intensities of the peaks between 160 and -60 ppm were essentially the same on both samples. The spectra of Fe(CU)-ZSM-5 zeolites (not shown) were similar to those shown in Fig. 8.

## DISCUSSION

The attempts at preparing overexchanged Fe-ZSM-5 following the ferrous oxalate method described in the literature (1) were not successful. Low degrees of exchange were obtained irrespective of the parent zeolite used. However, based on the results of this study a plausible explanation for the inadequacy of this method at locating iron at ion-exchange positions can be put forward.

As revealed by AAS analysis, a substantial amount of iron was loaded onto the zeolite using a saturated ferrous oxalate solution under anaerobic conditions. A large fraction of the iron, however, was leached out by simply washing the preparation, which means that iron species were not bound to the zeolite lattice at ion-exchange sites, right after the exchange. The DTA patterns of the Fe(CU) samples, being very similar to that of pure ferrous oxalate (Fig. 1), show that iron was precipitated as FeC<sub>2</sub>O<sub>4</sub> on the zeolite. The reason for such a precipitation is related to the formation of dissolved iron oxalate complexes in the solution used for the exchange (see below). The quantitative analysis of the weight loss curves revealed that in the case of Fe(CU)-4 100% of the iron was present as FeC<sub>2</sub>O<sub>4</sub> after the exchange (ca. 60% on the sample Fe(SC)-4). These findings, together with the fact that a substantial amount of the original sodium ions was replaced only during the washing, strongly suggest that iron did not substitute at all sodium counterions. Most likely the precipitate blocked the zeolite pores, favouring the exchange of protons rather than iron. Indeed, high concentrations of Brønsted acid sites were detected using IR spectroscopy on all the zeolites investigated. The presence of iron species at ion-exchange positions, nonetheless, cannot be ruled out *a priori*. As a consequence of the leaching of FeC<sub>2</sub>O<sub>4</sub> during the washing, the zeolite pores became accessible again and further exchange of the sodium occurred. The fraction of iron that is not in the oxalate form (Fig. 3, closed triangles) may then have reached the ion-exchange positions and replaced sodium cations. In this respect, it is worthwhile noting that, even assuming that all the iron species were located at the ion-exchange sites, overexchange would not have been achieved. The maximum degrees of exchange that would have been obtained were approximately Fe(II)/Al = 0.2 and 0.15 on Fe(CU)-ZSM-5 and Fe(SC)-ZSM-5, respectively.

$^{27}\text{Al}$  MAS NMR provided indirect confirmation of the low degree of exchange attained with this method. We have previously shown (5) that the signal at 54 ppm in the  $^{27}\text{Al}$  NMR spectrum of overexchanged Fe-ZSM-5 prepared by vapor-phase loading with FeCl<sub>3</sub> was almost totally suppressed, probably as a consequence of Fermi contact interaction and/or dipolar pseudocontact interactions between Al atoms and the paramagnetic iron nuclei. The same type of modification of the spectrum was observed in the case of sodalite zeolites containing paramagnetic species in close vicinity to the framework Al atoms, namely at ion-exchange positions (18). The small differences observed in the  $^{27}\text{Al}$  NMR spectra of the Fe-ZSM-5 zeolites prepared using the ferrous oxalate method and the parent Na-ZSM-5 (Fig. 8) therefore indicate that only a few iron species were exchanged.

Thermal treatment of the zeolites impregnated with FeC<sub>2</sub>O<sub>4</sub> carried out under different conditions can lead to iron species of different natures. Most of the iron that is

hosted in the zeolite, however, is bound to be transformed into oxide species. By analogy with the chemical transformation of pure ferrous oxalate, formation of  $\text{Fe}_2\text{O}_3$  is expected during calcination in air already at relatively low temperatures ( $T < 400^\circ\text{C}$ ), whereas  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ , and metallic iron are the products obtained when thermal treatment is done in an inert atmosphere (above  $630^\circ\text{C}$ ) (19). In any case the formation of such oxide species cannot lead to any further solid-state ion exchange, since their very low solubilities and high lattice enthalpies markedly limit the mobility of iron ions within the zeolite cavities (4, 20). Nevertheless, secondary solid-state ion exchange may be promoted to a certain extent by carrying out the thermal treatment in an inert atmosphere or *in vacuo*. As reported by Lázár *et al.* (15), during the treatment *in vacuo* iron is first transformed into  $\text{FeCO}_3$  between 150 and  $550^\circ\text{C}$  and then, above  $550^\circ\text{C}$ , into  $\text{Fe}_3\text{O}_4$  and metallic Fe. At  $T > 450^\circ\text{C}$  ion exchange of Fe(II) species also occurred but only to a limited extent (15% of the total iron loaded) (15). Mild conditions, such as low heating ramps and long dwell times at low temperatures, may thus facilitate the migration of  $\text{FeCO}_3$  towards ion-exchange sites by stripping its coordinatively bonded water without decomposition taking place. The solubility of ferrous carbonate in water, which is low but still higher than that of the iron oxides, may contribute to the exchange. In this regard, the claims in the literature of enhanced SCR activities of Fe-ZSM-5 catalysts pretreated in an inert atmosphere seem to be in line with this hypothesis (6, 21).

To shed light on the reasons for the precipitation of  $\text{FeC}_2\text{O}_4$  onto the zeolite, the distribution of species in a saturated solution of ferrous oxalate was calculated using the equilibrium reactions reported in Table 2. Equilibria involving Fe(III) species were not included since the device used for the exchange assured a low concentration of oxygen. The results of the calculation are reported in Fig. 9. From the plot it appears that the Fe(II) aquo ion is the predominant species in solution in the range  $4 < \text{pH} < 7$ . In

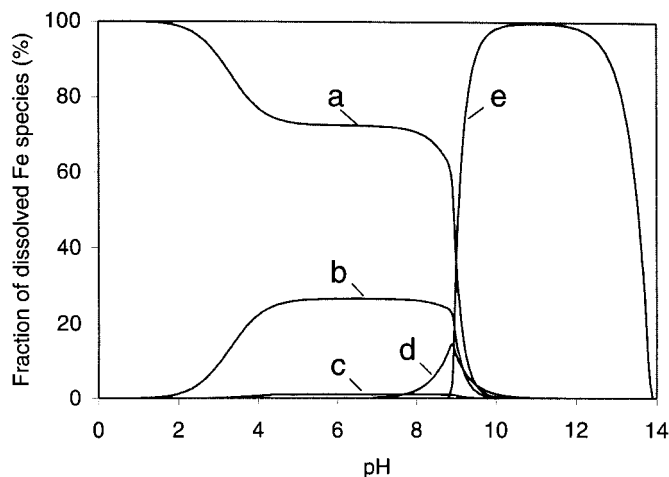


FIG. 9. Distribution of Fe species as a function of pH in a saturated solution of  $\text{FeC}_2\text{O}_4$  at  $25^\circ\text{C}$ , calculated from the data of Table 2: (a)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , (b)  $[\text{Fe}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4]_{(\text{aq})}^{1-}$ , (c)  $[\text{Fe}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ , (d)  $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^+$ , and (e)  $\text{Fe}(\text{OH})_{2(\text{s})}$ .

the same pH range, however, a significant fraction of iron forms complexes with the oxalate ions. Particularly, at pH 6 the uncharged species  $[\text{Fe}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4]$  accounts for ca. 30% of the total amount of iron in solution and the negatively charged complex  $[\text{Fe}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$  for ca. 1.0%. The formation of substantial amounts of dissolved iron oxalate complexes is most likely the reason for the massive precipitation of  $\text{FeC}_2\text{O}_4$ . During the exchange these iron complexes come in contact with the zeolite crystals, which may act as a crystallisation seed and cause the precipitation of the iron species.

According to the calculation, the relative fraction of the  $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^+$  species, which was reported to be predominant above pH 4 (1), was found to be negligible at neutral pH and around 11% at pH 9. This result is in remarkable contrast with the distribution of species reported

TABLE 2

Equilibrium Reactions Used for the Calculation of the Distribution of Species for a Saturated Ferrous Oxalate Aqueous Solution

Eq. [1]	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}_{(\text{s})} + 4\text{H}_2\text{O}$	$\text{Log } K = 6.68$	(22)
Eq. [2]	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{C}_2\text{O}_4^{2-} \rightleftharpoons [\text{Fe}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4]_{(\text{aq})}^{1-} + 2\text{H}_2\text{O}$	$\text{Log } K = 3.05$	(23)
Eq. [3]	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + 2\text{C}_2\text{O}_4^{2-} \rightleftharpoons [\text{Fe}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-} + 4\text{H}_2\text{O}$	$\text{Log } K = 5.15$	(23)
Eq. [4]	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^+ + \text{H}_3\text{O}^+$	$\text{Log } K = -9.5$	(24)
Eq. [5]	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + 2\text{H}_2\text{O} \rightleftharpoons [\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4]_{(\text{aq})}^{0} + 2\text{H}_3\text{O}^+$	$\text{Log } K = -20.6$	(24)
Eq. [6]	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + 3\text{H}_2\text{O} \rightleftharpoons [\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3]^- + 3\text{H}_3\text{O}^+$	$\text{Log } K = -31.0$	(24)
Eq. [7]	$\text{Fe}(\text{OH})_{2(\text{s})} + 2\text{H}_3\text{O}^+ + 2\text{H}_2\text{O} \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$\text{Log } K = 12.85$	(24)
Eq. [8]	$\text{C}_2\text{O}_4^{2-} + \text{Na}^+ \rightleftharpoons [\text{Na}(\text{C}_2\text{O}_4)]^-$	$\text{Log } K = 0.49$	(23)
Eq. [8]	$\text{C}_2\text{O}_4^{2-} + \text{H}_3\text{O}^+ \rightleftharpoons \text{HC}_2\text{O}_4^- + \text{H}_2\text{O}$	$\text{Log } K = 4.19$	(22)
Eq. [9]	$\text{C}_2\text{O}_4^{2-} + 2\text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$	$\text{Log } K = 5.42$	(22)
Eq. [10]	$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$	$\text{Log } K = -14.0$	(23)

Note. The number in the last column indicates the literature source of the thermodynamic constant.

in Ref. (1), the reason being the different series of equilibrium reactions considered for calculation. In contrast with Ref. (1), the possibility of formation of dissolved iron oxalate complexes was also taken in consideration, being substantiated by the rather high value of the formation constants found in the literature (see references in Table 2). Second, the log  $K$  value for Eq. [4] used in our calculation differs by several orders of magnitude from that reported in Ref. (1).<sup>2</sup>

The presence of Brønsted acid sites seems to be in contradiction with the distribution of species shown in Fig. 9.  $\text{Fe}^{2+}$  species, in fact, are largely available in solution and their absolute concentration exceeds that of  $\text{H}^+$  in the range  $4 < \text{pH} < 7$  by about 2 orders of magnitude ( $\text{FeC}_2\text{O}_4$  solubility in water, ca.  $10^{-3}$  M). Therefore, factors other than the concentration of  $\text{H}^+$  species must favour the formation of the Brønsted acid sites with respect to the exchange for iron species. Possible factors that can be envisioned are the small dimension of protons and their particular mechanism of diffusion in solution (Grotthus or chain mechanism) (25). The former would facilitate the formation of Brønsted sites in the presence of  $\text{FeC}_2\text{O}_4$ , whose precipitation blocks the pores of the zeolite and impedes the access of the bulkier iron species to the ion-exchange sites. The latter increases noticeably the diffusion rate of protons through the solution, as it does not involve the actual migration of  $\text{H}^+$  species (the charge of the proton is transferred from one point of the solution to another just by reorientation of the surrounding water molecules). Besides kinetic reasons, formation of Brønsted acid sites may be related to the mechanism of compensation of the negative charge of the zeolite lattice. A double positively charged ion, which in principle can replace two  $\text{Na}^+$  ions during the exchange, requires the presence of a sufficient number of water molecules in order to delocalise the positive charge of the counterion (e.g.,  $[\text{Me}^{\text{II}}(\text{H}_2\text{O})_6^{2+}]$ ) (26). Thermal treatments remove the hydration sphere of the in-going species, which as a consequence become more localised. The associated electrostatic field of the bare ions, therefore, may induce dissociation of the remaining coordinated water molecules, producing hydrolysed species and protons (e.g.,  $\text{Me}^{\text{II}}(\text{H}_2\text{O})_6^{2+} \rightarrow \text{Me}^{\text{II}}(\text{OH})^+ + \text{H}^+ + 5\text{H}_2\text{O}$ ). Such a mechanism of formation of Brønsted acid sites is well documented on faujasite zeolites (26) and can be of crucial importance in the preparation of overexchanged zeolites. Whenever water is present during the exchange, the hydrolysis takes place and overexchange can hardly be achieved. Recent investigations by Turek and co-workers

of Fe-ZSM-5 zeolites prepared through solid-state ion exchange support this conclusion (8, 9), since they also only reached a maximum degree of exchange of  $\text{Fe}^{\text{II}}/\text{Al} = 0.5$ . Furthermore, the occurrence of water dissociation upon drying of the catalyst suggests that the existence of stable monovalent metal complexes in solution is a fundamental prerequisite to prepare metal overexchanged zeolites in aqueous media. Alternatively, dissolved positively charged polynuclear species may be considered good candidates to achieve overexchange as they may satisfy simultaneously more than one lattice charge, providing one Fe atom for each Al site. In Fe(II) aqueous solutions, however, the presence of such polynuclear moieties can be neglected (24).

## CONCLUSIONS

Preparation of overexchanged Fe-ZSM-5 using the ferrous oxalate ion-exchange method proposed in the literature (1) was not successfully attained.  $\text{FeC}_2\text{O}_4$  was precipitated from the solution onto the zeolite, thus blocking the pores and preventing thorough exchange of the original  $\text{Na}^+$  counterions. A large part of the iron oxalate complex was removed by washing the zeolite with water, whereas the remainder was transformed into iron oxide during the subsequent thermal treatment.

Precipitation was found to be related to the formation of dissolved neutral  $[\text{Fe}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4]$  oxalate species, as shown by the calculation of the distribution of species for a ferrous oxalate solution. It could not be excluded that a small amount of iron may also occupy the ion-exchange positions ( $\text{Fe}/\text{Al} \ll 0.5$ ). Brønsted acid sites were detected by IR spectroscopy. These hydroxyl groups are formed both during the exchange and upon drying the zeolite because of the bivalent charge of the Fe species (26). These results suggest that overexchanged iron zeolites can hardly be prepared by conventional ion exchange in aqueous solution. The results do not seem to depend on the history of the parent ZSM-5 used since they were reproduced on the same type of zeolite provided by different manufacturers.

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## REFERENCES

1. Feng, X., and Hall, W. K., *J. Catal.* **166**, 368 (1997).
2. Chen, H.-Y., and Sachtler, W. M. H., *Catal. Today* **42**, 73 (1998).
3. Delgass, W. N., Garten, R. L., and Boudart, M., *J. Phys. Chem.* **73**, 2970 (1969).
4. Kucherov, A. V., Montreuil, C. N., Kucherova, T. N., and Shelef, M., *Catal. Lett.* **56**, 173 (1998).
5. Marturano, P., Kogelbauer, A., and Prins, R., *Stud. Surf. Sci. Catal.* **125**, 619 (1999).
6. Hall, W. K., Feng, X., Dumesic, J., and Watwe, R., *Catal. Lett.* **52**, 13 (1998).

<sup>2</sup> The source of the thermodynamic constants for the equilibrium reactions (Skoog, D. A., and West, D. M., "Fundamentals of Analytical Chemistry," 2nd ed. Holt, Rinehart, Winston, New York, 1969) reported in Ref. (1) was not available to us. Since also the subsequent editions of the book do not report them, the values of the constants used for the calculation were obtained from Refs. (22-24).



7. Ma, A.-Z., and Grünert, W., *Chem. Commun.* 71 (1999).
8. Rauscher, M., Kesore, K., Mönnig, R., Schwieger, W., Tissler, A., and Turek, T., *Appl. Catal. A* **184**, 249 (1999).
9. Kögel, M., Mönnig, R., Schwieger, W., Tissler, A., and Turek, T., *J. Catal.* **182**, 470 (1999).
10. Petunchi, J. O., and Hall, W. K., *Appl. Catal. B* **3**, 239 (1994).
11. El-Malki, E.-M., van Santen, R. A., and Sachtler, W. M. H., *J. Phys. Chem. B* **103**, 4611 (1999).
12. Joyner, R. W., and Stockenhuber, M., *Catal. Lett.* **45**, 15 (1997).
13. Svehla, G., "Vogel's Qualitative Inorganic Analysis." Longmann, New York, 1987.
14. Colthup, N. B., Daly, L. H., and Wiberley, S. E., "Introduction to Infrared and Raman Spectroscopy." Academic Press, London, 1990.
15. Lázár, K., Pál-Borbély, G., Beyer, H. K., and Karge, H. G., *Stud. Surf. Sci. Catal.* **91**, 551 (1995).
16. Oldfield, E., Kinsey, R. A., Smith, K. A., Nichols, J. A., and Kirkpatrick, R. J., *J. Magn. Reson.* **51**, 325 (1983).
17. Goldfarb, D., *Zeolites* **9**, 509 (1989).
18. Engelhardt, G., in "Solid-State NMR Spectroscopy of Inorganic Materials" (J. J. Fitzgerald, Ed.), Vol. 717, p. 266. Am. Chem. Soc., Washington, DC, 1999.
19. Broadbent, D., Dollimore, D., and Dollimore, J., *J. Chem. Soc. (A)* 451 (1967).
20. Kucherov, A. V., and Slinkin, A. A., *Zeolites* **8**, 110 (1988).
21. Joyner, R., and Stockenhuber, M., *J. Phys. Chem. B* **103**, 5963 (1999).
22. Weast, R. C., "CRC Handbook of Chemistry and Physics." 63rd ed. CRC Press, Boca Raton, FL, 1982.
23. Martell, A. E., and Smith, R., "Critical Stability Constants." Plenum, New York, 1977.
24. Baes, C. F. J., and Mesmer, R. E., "The Hydrolysis of cations." Wiley, New York, 1976.
25. Atkins, P. W., "Physical Chemistry." 5th ed. Oxford Univ. Press, London, 1994.
26. Ward, J. W., in "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), Vol. 171, p. 118. Am. Chem. Soc., Washington, DC, 1976.