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Remarkable N_2 affinity of a steam-activated FeZSM-5 catalyst: a ^{57}Fe Mössbauer study

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Abstract

^{57}Fe Mössbauer spectroscopy was used to investigate the redox behavior of iron species in steam-treated FeZSM-5, a catalyst material with outstanding properties in benzene-to-phenol oxidation as well as nitrous oxide decomposition. It was found that Fe^{3+} ions in isolated extraframework sites and in extremely small oxo–iron clusters are easily converted into Fe^{2+} species using a thermal treatment at 623 K. Fe^{3+} ions in larger iron oxide particles of 2 nm in diameter located at the outer surface of the zeolite are less prone to reduction. Some of the iron species in the FeZSM-5 catalyst show an unusual affinity for N_2 leading to redox changes ($Fe^{3+} \rightarrow Fe^{2+}$) at temperatures as low as 300 K. In addition, it has been observed that some of the Fe^{2+} species, which are present in the catalyst after thermal reduction, reversibly adsorb N_2.

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1. Introduction

FeZSM-5 zeolites have been known for over two decades [1,2]. They are of considerable interest for different catalytic applications, including the catalytic decomposition or reduction of nitrous oxide (N_2O) [3–5], the deNO_x selective catalytic reduction (HC-SCR) [6], the benzene to phenol oxidation [7], and the selective oxidation of methane to methanol [8,9]. Different preparation methods have been reported to result in FeZSM-5 materials with a high catalytic performance for the various applications. These methods vary from classical ion-exchange [4] to chemical vapor deposition of volatile iron compounds [6] or isomorphous substitution of iron in the MFI-type framework [10,11].

In 1988 it was discovered that ZSM-5 zeolites are very efficient in the oxidation of benzene to phenol using N_2O [12–14]. Panov and co-workers continued to develop this system and found a correlation between the amount of iron in the ZSM-5 zeolite and the conversion of benzene to phenol with N_2O [15,16]. They optimized the synthesis of FeZSM-5 and achieved high selectivity ($> 95\%$) for phenol production at a typical temperature of 623 K. It was suggested that the active site of the catalyst is a binuclear iron species, immobilized in the pores of ZSM-5, which resembles the active iron oxidant in the enzyme methane monooxygenase [7]. This enzyme is capable of transferring one oxygen atom activated on a binuclear iron center to a C–H bond [17].

Following the pioneering work of Panov and co-workers, we published the characterization of steamed, isomorphously substituted FeZSM-5, used as a catalyst for the selective oxidation of benzene to phenol with N_2O [18]. This FeZSM-5 catalyst with a typical Si/Al ratio of 31–34 and an iron content of 0.6 wt% displayed an activity of 0.8 mmol of phenol/(h g_{cat}), which lasted for more than 7 h time on stream. The zeolite was characterized by XRD, SEM, TEM, FT-IR, UV–Vis spectroscopy, and EPR. Spectroscopic studies indicated that during the steaming process Fe–O–Si bonds were broken and iron migrated toward extraframework positions, resulting in well-dispersed iron centers. EPR revealed that after steaming new iron centers were formed, which we proposed to be involved with N_2O [18].

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Here we report a closer study of the redox behavior of the iron centers in a steamed FeZSM-5 catalyst by using ^{57}Fe Mössbauer spectroscopy. This follows a recent publication in which we investigated the iron species of the FeZSM-5 catalyst with this technique after subsequent steps in the preparation [19]. There, we concluded that steaming of calcined FeZSM-5 material leads to complete removal of Fe^{3+} ions from the zeolite framework and forms mononuclear and small oligonuclear oxo–iron complexes as well as larger iron oxide particles of ca. 2 nm in diameter. In addition, it was found that a small fraction of the Fe^{3+} ions was reduced to the divalent state.

Mössbauer spectroscopy offers several advantages for the study of iron zeolites. First, in a solid there are no forms of iron that are Mössbauer silent (unlike EPR). Secondly, iron present in different environments results in different subspectra that together form the observed spectrum. This favors Mössbauer spectroscopy over bulk-averaging techniques, such as magnetic susceptibility.

In Mössbauer spectroscopy three hyperfine interactions are important in obtaining chemical and structural information of iron-containing materials: the isomer shift, the quadrupole splitting, and the magnetic or Zeeman splitting. The isomer shift, which is a measure for the s-electron density at the nucleus, yields information on the oxidation state of the iron atoms. The quadrupole splitting is determined by the interaction of the quadrupole moment of the iron nucleus with the electric field gradient and reflects symmetry distortions in the ligand environment of the iron atom. The magnetic or Zeeman splitting arises from an interaction between nuclear magnetic dipole moments and the magnetic field at the iron nucleus. This hyperfine interaction enables us to probe magnetic properties of iron-containing materials, such as superparamagnetism or paramagnetism, which in turn provide information on particle size or iron concentration.

Despite these advantages Mössbauer spectroscopy has not been used very often as a characterization tool in the analysis of FeZSM-5 catalysts prepared via isomorphous substitution. Most of the Mössbauer studies have been focused on Fe–silicalite [20–23]. Meagher and coworkers [21] showed that calcination of isomorphously substituted Fe–silicalite leads to partial removal of Fe^{3+} ions from framework positions. Subsequent steaming of the calcined Fe–silicalite strongly enhanced the loss from the framework of Fe^{3+} ions, which clustered together to form large iron oxide particles at the exterior surface of the silicalite crystals. Lázár and co-workers noted that part of the Fe^{3+} ions reduced to Fe^{2+} upon thermal treatment of the material under high-vacuum conditions [22,23]. This so-called autoreduction behavior has been known to occur on Fe^{3+} ions in extraframework positions [24,25].

Recently, a few Mössbauer studies appeared that deal with FeZSM-5 catalysts [26–28]. These studies revealed that after high-temperature vacuum or steaming treatments almost all iron in the FeZSM-5 catalysts is in the divalent state. By reaction of this material with N_2O, i.e., loading with α-oxygen, a considerable fraction of the divalent iron ions oxidizes to Fe^{3+}. Unfortunately, these studies did not include low-temperature (4.2 K) Mössbauer measurements, so that information about the iron dispersion over the ZSM-5 zeolite is limited.

The aim of the present paper is to probe the redox behavior of the different iron sites that we identified in a steamed FeZSM-5 catalyst described in an earlier paper [19]. For that purpose in situ Mössbauer measurements have been carried out at temperatures that vary from 4.2 K to ambient. The catalyst has been exposed to several gas treatments (N_2, O_2, N_2O, or Ar) at temperatures ranging from ambient to 623 K. From these measurements we show that the FeZSM-5 catalyst has a remarkable affinity for N_2 resulting in a reduction of extraframework, mononuclear Fe^{3+} species at room temperature.

2. Experimental

2.1. Catalyst preparation

In order to obtain good quality Mössbauer spectra ^{57}Fe-enriched (to 95%) FeZSM-5 was prepared according to a procedure described in a previous paper [19]. The details of the ratios applied in the synthesis gel are given in Table 1. The enriched iron nitrate was synthesized by dissolving metallic ^{57}Fe foil in concentrated nitric acid followed by the addition of ammonium hydroxide to neutralize the solution. Next, aluminum nitrate nona-hydrate (Merck 98.5%) was added. To this solution was added dropwise a solution of the silica source (tetraethylorthosilicate, Acros, 98%), the template (tetraethylammonium hydroxide, Fluka ∼20% in water), and sodium hydroxide (Aldrich 97%). The ratios are depicted in Table 1. To validate this procedure, samples were prepared in the same manner using natural iron powder. These samples were used for catalytic testing.

The synthesis gel was transferred into a stainless-steel autoclave with Teflon lining and placed in a static oven at 448 K for 5 days. The crystalline material was separated by filtration and washed with water until the latter was free of nitrate. To ensure that the catalyst is in the acidic form, the material was exchanged three times with a 0.1 M ammonium nitrate solution followed by calcination in air at 823 K for 5 h. In the final step, the catalyst was steamed (water partial pressure of 300 mbar and a total flow of 30 ml/min) at 873 K for 5 h. The sample was stored at ambient temperature in dry air.

2.2. Mössbauer experiments

The ^{57}Fe Mössbauer spectra were recorded using a constant acceleration spectrometer in triangular mode with a ^{57}Co:Rh source. Isomer shift values are reported relative

Table 1
Molar ratios of the gel and crystalline FeZSM-5 sample, as determined by ICP-OES[a]

	Si/Al[b]	Si/Fe[b]	TPAOH/Si[b]	NaOH/Si[b]	Si/Al[c]	Si/Fe[c]	Fe (wt%)
^{57}FeZSM-5$_{as}$[d]	36	152	0.1	0.2	34.1	131.1	0.57
^{57}FeZSM-5$_{calc}$[d]	36	152	0.1	0.2	35.6	150.0	0.58
^{57}FeZSM-5$_{steam}$[d]	36	152	0.1	0.2	35.9	150.6	0.60

[a] The error in the values obtained by ICP-OES for the molar ratios amounts to ±2%.

[b] Molar ratios of the gels.

[c] Molar ratios of the crystalline samples.

[d] as, as-synthesized; calc, calcined; steam, steamed sample.

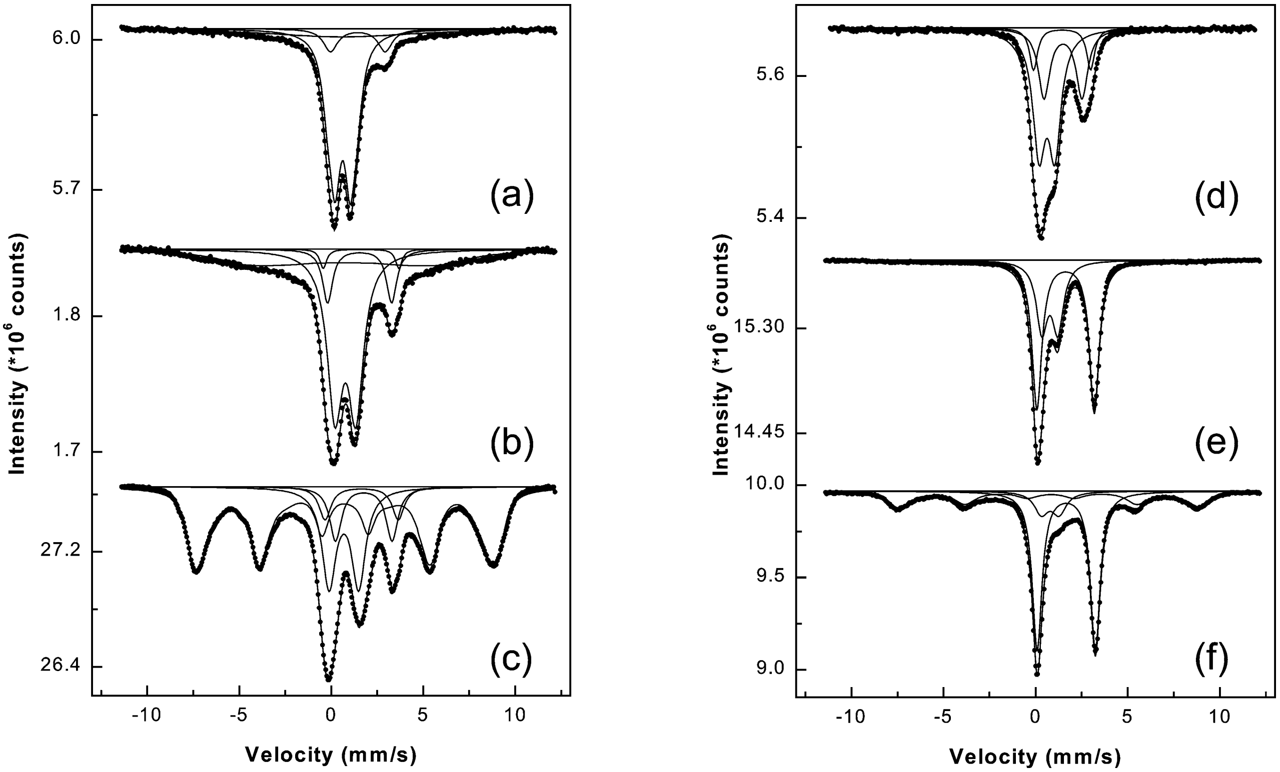

Fig. 1. ^{57}Fe Mössbauer spectra together with the accompanying fits of steamed FeZSM-5, before (left) and after (right) thermal treatment in N_2 for 1.5 h at 623 K. The spectra are recorded at 300 K (a and d), 77 K (b and e), and 4.2 K (c and f).

to sodium nitroprusside. The overall spectra were deconvoluted with calculated Mössbauer spectra that consisted of Lorentzian-shaped lines. In the case of quadrupole doublets the linewidth and the absorption areas of the constituent lines were constrained equal. The magnetically split lines were fitted with several components in order to simulate a distribution of hyperfine fields. Therefore, the hyperfine field given in the tables is the average hyperfine field. In the figures only the sum of the magnetically split components is given. Positional parameters were not constrained in the fitting procedure.

Samples of typically 150–200 mg were used for the Mössbauer measurements. Mössbauer measurements, which included measurements at 4.2 K, were carried out using a specially designed in situ reactor. A detailed description of this in situ reactor has been given elsewhere [29]. A second series of Mössbauer measurements with recordings down to 100 K have been carried out using a different in situ Mössbauer reactor. This setup has been used to expose the FeZSM-5 catalyst to different gases up to 773 K.

3. Results and discussion

3.1. Thermal treatment at 623 K

The sensitivity of the different iron species in freshly steamed FeZSM-5 toward redox changes was studied first by subjecting the catalyst material to a thermal treatment in N_2 at 623 K. Therefore, a sample of the FeZSM-5 catalyst was mounted in the in situ reactor and heated to 623 K in a flow of N_2 (30 ml/min) following a temperature ramp of 5 K/min. The sample was held at this temperature for 1.5 h. Then, it was cooled down to room temperature, the sample holder of the in situ reactor was sealed, and Mössbauer

Table 2
Mössbauer fitting parameters of spectra in Fig. 1

Spectrum No.	Isomer shift (mm/s)	Quadrupole splitting (mm/s)	Hyperfine field (T)	Spectral contribution (%)	Oxidation state
1a	0.60			19.4	Fe^{3+}
	0.61	1.02		71.0	Fe^{3+}
	1.45	2.99		9.6	Fe^{2+}
1b	0.67			28.7	Fe^{3+}
	0.77	1.14		55.4	Fe^{3+}
	1.54	3.48		12.8	Fe^{2+}
	1.62	4.11		3.1	Fe^{2+}
1c	0.68	1.62		22.5	Fe^{3+}
	0.76		48.8	60.0	Fe^{3+}
	1.65	3.99		6.0	Fe^{2+}
	1.77	3.08		11.5	Fe^{2+}
1d	0.73	0.65		56.3	Fe^{3+}
	1.32	2.39		26.9	Fe^{2+}
	1.45	3.17		16.8	Fe^{2+}
1e	0.77	0.87		34.0	Fe^{3+}
	1.63	3.12		66.0	Fe^{2+}
1f	0.77	0.01	50.2	28.7	Fe^{3+}
	0.79	0.97		11.6	Fe^{3+}
	1.66	3.16		59.7	Fe^{2+}

spectra were recorded at room temperature, 77 and 4.2 K. In Fig. 1, Mössbauer spectra of the freshly steamed FeZSM-5 catalyst before and after the thermal treatment are presented together with the fits. The corresponding fit parameters are collected in Table 2.

A full explanation of the different iron species that could be distinguished in the freshly steamed FeZSM-5 catalyst has already been presented in a previous paper [19]. The four different spectral contributions that are observed in Figs. 1a–1c have been assigned to: (1) isolated extraframework Fe^{3+} ions, which display paramagnetic hyperfine splitting and give rise to the very broad lines at room temperature and 77 K. At 4.2 K these lines become much narrower and form a sextuplet: (2) small oligonuclear oxo–iron complexes that result in a high-spin Fe^{3+} doublet with a relatively large quadrupole splitting (QS) of 1.62 mm/s at 4.2 K, and (3) iron oxide particles of about 2 nm in diameter at the exterior surface of the zeolite crystals that display superparamagnetic behavior at 77 K and above, leading to a Fe^{3+} doublet in the Mössbauer spectra and to a magnetically split sextuplet at 4.2 K. The latter component strongly overlaps with the magnetically split sextuplet of the isolated extraframework Fe^{3+} ions. In addition (4) a small percentage of high-spin Fe^{2+} ions was observed (two spectral components with IS of 1.65 and 1.77 mm/s; QS of 3.99 and 3.08 mm/s, respectively). The observation of only a small fraction of Fe^{2+} is remarkable since Dubkov et al. [28] found that the iron species in a steamed FeZSM-5 catalyst (steamed at 923 K) contained exclusively Fe^{2+} ions.

The Mössbauer spectra that were recorded after the thermal treatment in N_2 clearly show that a considerable fraction of the Fe^{3+} ions is reduced to Fe^{2+}. The Mössbauer spectra reveal the presence of two high-spin Fe^{2+} doublets (see Figs. 1d–1f) that are separated at ambient temperature and strongly overlap at lower temperatures. Therefore, these Fe^{2+} components are fitted with a single high-spin Fe^{2+} doublet at 77 K and 4.2 K (see Table 2). A comparison of the spectra in the left and right column of Fig. 1 shows that the thermal treatment in N_2 leads to complete removal of the broad component ($\pm 10\ \mathrm{mm\,s^{-1}}$). In addition, a strong decrease in spectral contribution of the sextuplet lines has taken place (compare Figs. 1c and 1f). Furthermore, a comparison of the high-spin Fe^{3+} doublets at 4.2 K also shows a reduction of the quadrupole splitting from 1.62 mm/s before heat treatment to 0.97 mm/s after heat treatment. The spectral contribution of the Fe^{3+} quadrupole doublet changes from 22.5% before the heat treatment to 11.6%, after the heat treatment. It should be emphasized that thermal treatment carried out at 350 °C in Ar instead of N_2 gives rise to similar changes, and thus also leads to the disappearance of the broad component ($\pm 10\ \mathrm{mm\,s^{-1}}$) and reduction of the sextuplet contribution (results not shown).

Following our earlier assignment on freshly steamed FeZSM-5 [19], the Fe^{3+} ions that are reduced to Fe^{2+} ions by the thermal treatment are those in isolated extraframework positions and oligonuclear oxo–iron complexes. The Fe^{3+} ions in the iron oxide particles of 2 nm are not affected by the thermal treatment.

The parameters of the high-spin Fe^{2+} doublet at 77 K (see Fig. 1e and Table 2) are similar to those observed by Panov, Ovanesyan, and co-workers ($IS = 1.63\ \mathrm{mm\,s^{-1}}$, $QS = 3.19\ \mathrm{mm\,s^{-1}}$ at 85 K) [26]. In that particular case, Panov and co-workers prepared FeZSM-5 by loading a ZSM-5 zeolite with $FeCl_3$ followed by activation via a high-temperature treatment under vacuum conditions and subsequent air exposure. The similarity of the spectral parameters suggests a strong resemblance of the reduced Fe^{2+} phases in both iron-containing zeolites. Panov, Ovanesyan, and co-workers relate this phase to binuclear iron complexes present in methane monooxygenase (MMO) for which almost equal Mössbauer parameters have been obtained [30]. However, based on our Mössbauer results we conclude that there cannot be a similarity between the active Fe species in the steamed FeZSM-5 and the binuclear Fe clusters in MMO. First of all, we show that both mononuclear Fe^{3+} species and Fe^{3+} ions in oligonuclear oxo–iron clusters, both of which we have identified in the freshly steamed catalyst, reduce to Fe^{2+} species. Upon oxidation at 350 °C with N_2O the lines of both mononuclear Fe^{3+} and oligonuclear oxo–iron (Fe^{3+}) clusters return in the Mössbauer spectrum (vide infra). Secondly, the overlapping Fe^{2+} components can be separated from each other by exposure of the reduced FeZSM-5 catalyst to different gases at room temperature (see next paragraph), thus indicating that we are dealing with chemically different Fe^{2+} species.

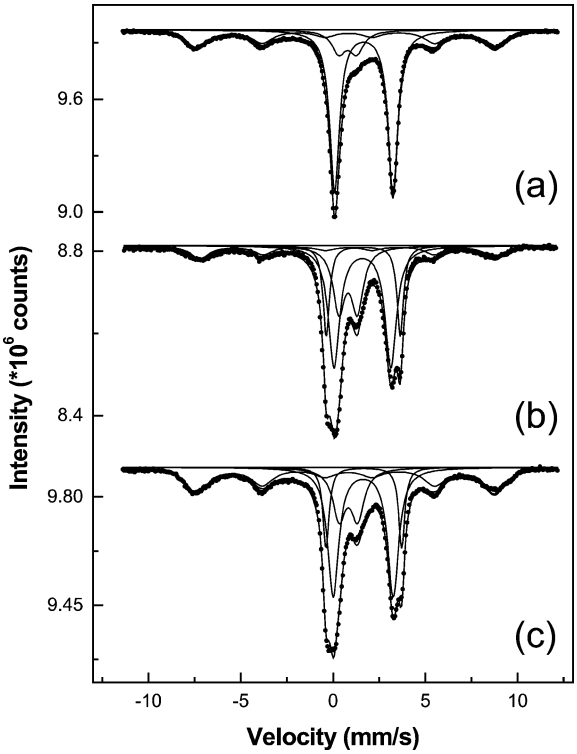

Fig. 2. ^{57}Fe Mössbauer spectra recorded at 4.2 K together with the accompanying fits of “reduced” FeZSM-5: (a) in contact with N_2, (b) at 1×10^{-6} mbar, and (c) in contact with Ar.

3.2. Study of the Fe^{2+} species formed by thermal reduction

The measurements after thermal treatment as presented in Fig. 1 were obtained with the sample in contact with N_2 in a closed sample holder. Opening of the sample holder and pumping on the sample to 1×10^{-6} mbar led to a separation of the high-spin Fe^{2+} doublets at 4.2 K. This effect is shown in Figs. 2a and 2b. While one of the Fe^{2+} doublets remains virtually unchanged, the second Fe^{2+} doublet shows an increased QS of 4.04 mm/s (see Fig. 2b and Table 3). It is possible that these two Fe^{2+} components represent the mononuclear extraframework Fe^{2+} ions and Fe^{2+} ions in oxo–iron clusters, respectively.

It is remarkable that N_2 is not inert toward the Fe^{2+} species inside the FeZSM-5 catalyst. To show this, the in situ reactor containing the thermally treated FeZSM-5 catalyst was flushed with Ar at 300 K followed by sealing of the cell. Mössbauer spectra were recorded at ambient temperature, 77 and 4.2 K. Only the spectrum recorded at 4.2 K is shown (see Fig. 2c). The Mössbauer parameters in Table 3 show that the Fe^{2+} components are similar in case of Ar exposure and high-vacuum conditions but differ in the presence of N_2. These experiments strongly suggest the reversible adsorption and desorption of N_2 to one of the Fe^{2+} species.

Table 3
Mössbauer fitting parameters of spectra in Fig. 2

Spectrum No.	Isomer shift (mm/s)	Quadrupole splitting (mm/s)	Hyperfine field (T)	Spectral contribution (%)	Oxidation state
2b	0.81	0.04	49.7	15.0	Fe^{3+}
	0.82	1.00		23.5	Fe^{3+}
	1.60	3.10		43.2	Fe^{2+}
	1.65	4.04		18.3	Fe^{2+}
2c	0.76	0.08	49.7	29.9	Fe^{3+}
	0.83	1.00		17.4	Fe^{3+}
	1.63	3.25		39.2	Fe^{2+}
	1.67	4.10		13.6	Fe^{2+}

The fitting parameters of spectrum 2a can be found in Table 2, spectrum 1f, which spectrum is identical.

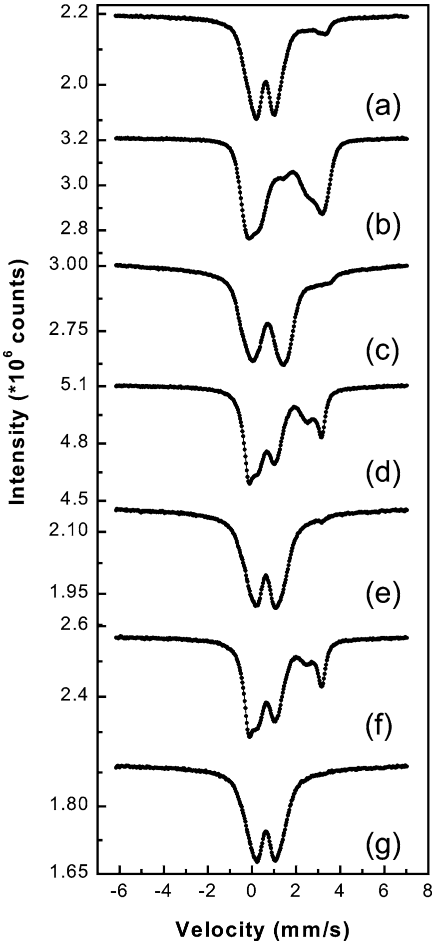

Fig. 3. In situ ^{57}Fe Mössbauer spectra of steamed FeZSM-5 after subsequent treatments: (a) at 300 K in Ar; (b) at 108 K in N_2, after heat treatment at 623 K, 1.5 h in N_2; (c) at 108 K in N_2, after heat treatment at 623 K, 2.5 h in N_2O; (d) at 300 K in N_2; (e) at 300 K in N_2O, after heat treatment at 623 K, 1.5 h in N_2O; (f) at 300 K in N_2; (g) at 300 K in Ar, after heat treatment at 623 K, 1.5 h in N_2O.

3.3. In situ studies with N_2 and N_2O

In Fig. 3, Mössbauer spectra are presented that are recorded after subsequent treatments of the steamed catalyst. The corresponding Mössbauer parameters are given in Table 4. Initially, the sample was measured at 300 K in Ar (see Fig. 3a). Apart from a high-spin Fe^{3+} doublet, the spectrum reveals a Fe^{2+} species. Subsequently, the sample was

Table 4
Mössbauer fitting parameters of spectra in Fig. 3

Spectrum No.	Isomer shift (mm/s)	Quadrupole splitting (mm/s)	Hyperfine field (T)	Spectral contribution (%)	Oxidation state
3a	0.62	0.91		83.4	Fe^{3+}
	1.23	2.87		7.4	Fe^{2+}
	1.50	3.58		9.2	Fe^{2+}
3b	0.79	1.15		24.5	Fe^{3+}
	1.46	2.21		37.6	Fe^{2+}
	1.50	3.45		37.9	Fe^{2+}
3c	0.74	1.43		93.3	Fe^{3+}
	1.44	3.84		6.7	Fe^{2+}
3d	0.59	1.01		54.1	Fe^{3+}
	1.48	3.35		19.1	Fe^{2+}
	1.50	2.08		26.8	Fe^{2+}
3e	0.65	1.19		97.7	Fe^{3+}
	1.32	3.71		2.3	Fe^{2+}
3f	0.62	0.99		64.3	Fe^{3+}
	1.49	3.35		20.1	Fe^{2+}
	1.51	2.03		15.6	Fe^{2+}
3g	0.64	1.14		100.0	Fe^{3+}

heated to 623 K using a ramp of 5 K/min and a N_2 flow of 30 ml/min. The sample was held at this temperature for 2.5 h and then cooled down to room temperature. Upon this treatment the Mössbauer spectrum shows a strong increase in the contribution of Fe^{2+} components (see Fig. 3b). Thereafter, the sample was heated to 623 K at 5 K/min in N_2O (flow 30 ml/min), held at this temperature for 2.5 h, and rapidly cooled to 108 K. Then, the gas was switched from N_2O to N_2 and a Mössbauer spectrum was recorded (see Fig. 3c). Apart from a high-spin Fe^{2+} doublet, it is noted that the high-spin Fe^{3+} doublet shows an increased quadrupole splitting of 1.43 mm/s compared to the starting value (0.91 mm/s). We will address this aspect later on when the oxidation with N_2O is treated in more detail (vide infra). Heating up the FeZSM-5 sample to 300 K in the N_2 atmosphere leads to a strong increase in the contribution of the Fe^{2+} components from 6.7 to 45.9% (see Fig. 3d). This spectral change points to a change in the oxidation state. Namely, the recoil-free fractions of the Fe^{2+} species show a much stronger temperature dependence than the recoil-free fractions of the Fe^{3+} species. Therefore, if the sample is not changed, a diminished contribution of the Fe^{2+} components is expected on raising the temperature. Since the opposite is observed, the spectral changes reflect a change in the oxidation state of part of the iron atoms. This change in the oxidation state of the iron atoms by exposure to N_2 at room temperature could be repeated as illustrated by the Mössbauer spectra given in Figs. 3e and 3f. First, in Fig. 3e the FeZSM-5 catalyst was reoxidized by treating it with N_2O (30 ml/min) at 623 K (ramp 5 K/min) for 2.5 h and then cooled to 300 K under N_2O. The Mössbauer spectrum predominantly reveals Fe^{3+} (see Fig. 3e). Next, at 300 K N_2O was replaced by N_2 and another Mössbauer spectrum was recorded (see Fig. 3f). Immediately, a strong increase of the Fe^{2+} contribution is observed in the spectrum (35.7% total spectral area compared to 2.3% in the oxidized case). This reduction did not take place if Ar (see Fig. 3g) replaced N_2O. The sample was oxidized again using the conditions noted in the previous experiment but instead of switching to N_2 the sample holder was flushed with Ar at ambient temperature (flow: 30 ml/min). Control experiments with potential reducing contaminants such as H_2 and CH_4 were performed but exposure to these gases at ambient temperature only leads to a limited fraction of Fe^{2+} ions (less than 10%). These observations clearly show that the $Fe^{3+} \rightarrow Fe^{2+}$ transition is caused by the presence of N_2. It must be emphasized that the oxidation with N_2O prior to exposure to N_2 is crucial in order to observe this reduction behavior. Pretreatment with an O_2/Ar mixture at 623 K for 2 h as the oxidant did not give reduction of Fe^{3+} upon exposure to N_2. This is illustrated by the spectra included in Fig. 4 (fits in Table 5).

The ability of Fe^{3+} in iron-containing zeolites to reduce to Fe^{2+} at temperatures as low as 300 K is unusual. Also, the supporting role of N_2 on the redox behavior of the iron centers is uncommon and has not been reported in the literature. Meagher et al. [21], who studied the behavior of steamed Fe–silicalite, did not find any evidence for the existence of Fe^{2+} in their samples. Lázár and co-workers [23], on the other hand, also studying Fe–silicalite observed reduction of the Fe^{3+} species in these materials. This reduction occurred under high-vacuum conditions at an elevated temperature of 573 K. Lamberti et al. [31] observed a $Fe^{3+} \rightarrow Fe^{2+} \rightarrow Fe^{3+}$ redox cycle in a 1 wt% Fe–silicalite upon thermal treatment and subsequent exposure to N_2O. These changes were monitored using XANES and IR spectroscopy. Ovanesyan et al. [26] showed that their FeZSM-5 catalyst, which was activated by a high-temperature vacuum treatment and subsequently oxidized by N_2O, did show reduction of a fraction of Fe^{3+} ions to Fe^{2+} at room temperature upon exposure to CH_4.

3.4. Identification of Fe species upon oxidation with N_2O at 623 K

From the previous experiments it is clear that pretreatment of the FeZSM-5 catalyst with N_2O leads to a different state of the iron species compared to freshly steamed FeZSM-5. This is similar to what has been observed by Lamberti and co-workers [31], who noted that the isolated extraframework iron species obtained after oxidation with N_2O displayed a less coordinative unsaturation, exemplified by an inhibition of the capacity of the iron species to adsorb NO at room temperature.

In our case, the material that was oxidized in N_2O has been examined in more detail with low-temperature Mössbauer measurements. A freshly steamed catalyst was first “reduced” by thermal treatment at 623 K according to conditions noted before (vide supra) and subsequently oxidized with N_2O for 1.5 h at 623 K. Mössbauer spectra were

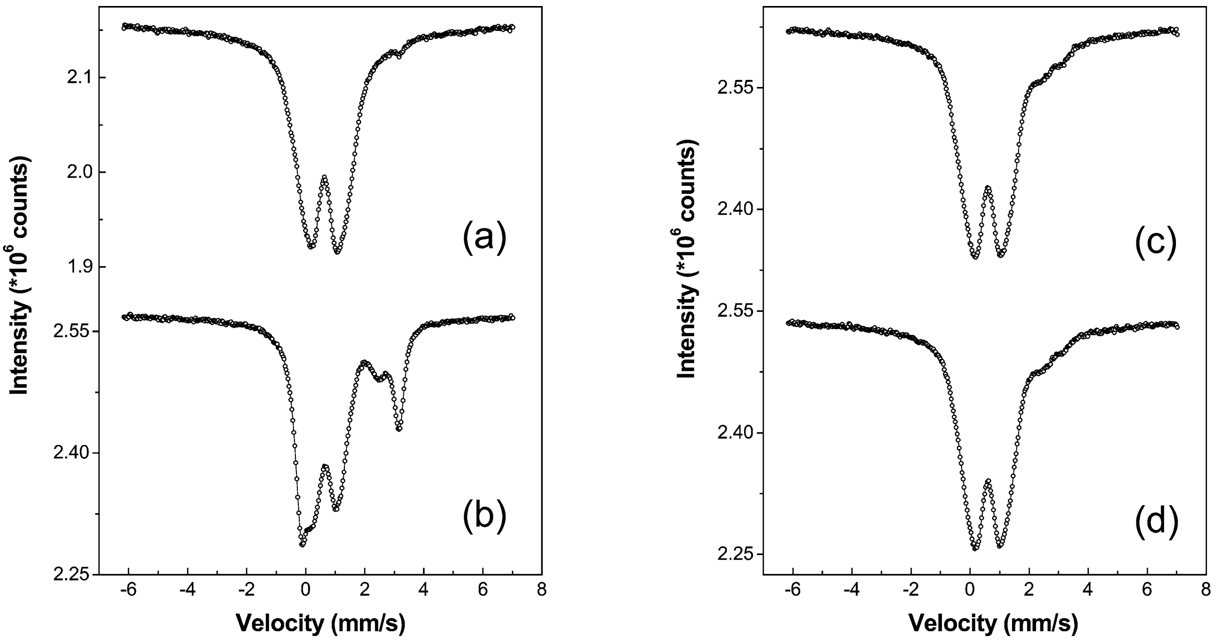

Fig. 4. ^{57}Fe Mössbauer spectra recorded at 300 K of steamed FeZSM-5 after oxidation in N_2O (left column) or O_2/Ar mixture (right column), respectively. Spectra a and c are recorded in the presence of the oxidizing agents, spectra b and d are recorded in the presence of N_2.

recorded at ambient temperature, 77 and 4.2 K (see Figs. 5a–5c and Table 6). Similar to the freshly steamed material, but unlike the "reduced material," FeZSM-5 oxidized in N_2O shows a broad featureless component (± 10 mm s^{-1}) at room temperature and 77 K. However, at 4.2 K a complex pattern of magnetically split lines is observed. From a comparison of this spectrum with the 4.2 K Mössbauer spectra of freshly steamed FeZSM-5 and "reduced" FeZSM-5 it is concluded that the iron oxide particles of 2 nm in diameter are not affected by the N_2O treatment. The 4.2 K spectra of these three materials have been grouped together (see Figs. 5d–5f) and dotted lines have been drawn to mark the positions of the four outer peaks of the sextuplet that we attribute to the 2-nm iron oxide particles. The comparison makes clear that additional magnetically split components have appeared in the N_2O treated sample with relatively small hyperfine fields (ca. 44 T). Up to now it is not clear whether these components originate from isolated Fe^{3+} species which exhibit paramagnetic hyperfine splitting or from highly disordered iron oxide particles. Future Mössbauer measurements with an applied external field will enable us to distinguish between these possibilities.

The quadrupole splitting of the high-spin Fe^{3+} doublet increases with decreasing temperature of the measurement. This is explained by the well-known phenomenon that the quadrupole splitting of high-spin Fe^{3+} ions increases with decreasing particle size [32,33]. At room temperature all iron oxide particles of the FeZSM-5 catalyst are superparamagnetic, which is reflected by the presence of a high-spin Fe^{3+} doublet. At 77 K the temperature gets below the superparamagnetic blocking temperature for the largest iron oxide particles and the Mössbauer lines for these particles become magnetically split; i.e., they form a sextuplet. On a further decrease of the temperature to 4.2 K only the superparamagnetic blocking temperature of the smallest iron oxide particles is still below the temperature of the measurement. This results in a high-spin Fe^{2+} doublet with a relatively large quadrupole splitting of 1.55 mm s^{-1}, while the other iron oxide particles give magnetically split lines.

Table 5
Mössbauer fitting parameters of spectra in Fig. 4

Spectrum No.	Isomer shift (mm/s)	Quadrupole splitting (mm/s)	Hyperfine field (T)	Spectral contribution (%)	Oxidation state
4c	0.64	1.04		82.6	Fe^{3+}
	1.43	3.48		5.5	Fe^{2+}
	1.47	2.21		11.9	Fe^{2+}
4d	0.64	1.01		84.6	Fe^{3+}
	1.44	2.23		8.0	Fe^{2+}
	1.48	3.39		7.4	Fe^{2+}

The fitting parameters of spectra 4a and 4b can be found in Table 4, spectra 3e and 3f, respectively.

Table 6
Mössbauer fitting parameters of spectra in Fig. 5

Spectrum No.	Isomer shift (mm/s)	Quadrupole splitting (mm/s)	Hyperfine field (T)	Spectral contribution (%)	Oxidation state
5a	0.66	1.26		87.5	Fe^{3+}
	0.92			12.5	Fe^{3+}
5b	0.64			32.8	Fe^{3+}
	0.75	1.39		67.2	Fe^{3+}
5c	0.75	1.55		44.2	Fe^{3+}
				55.8	Fe^{3+}

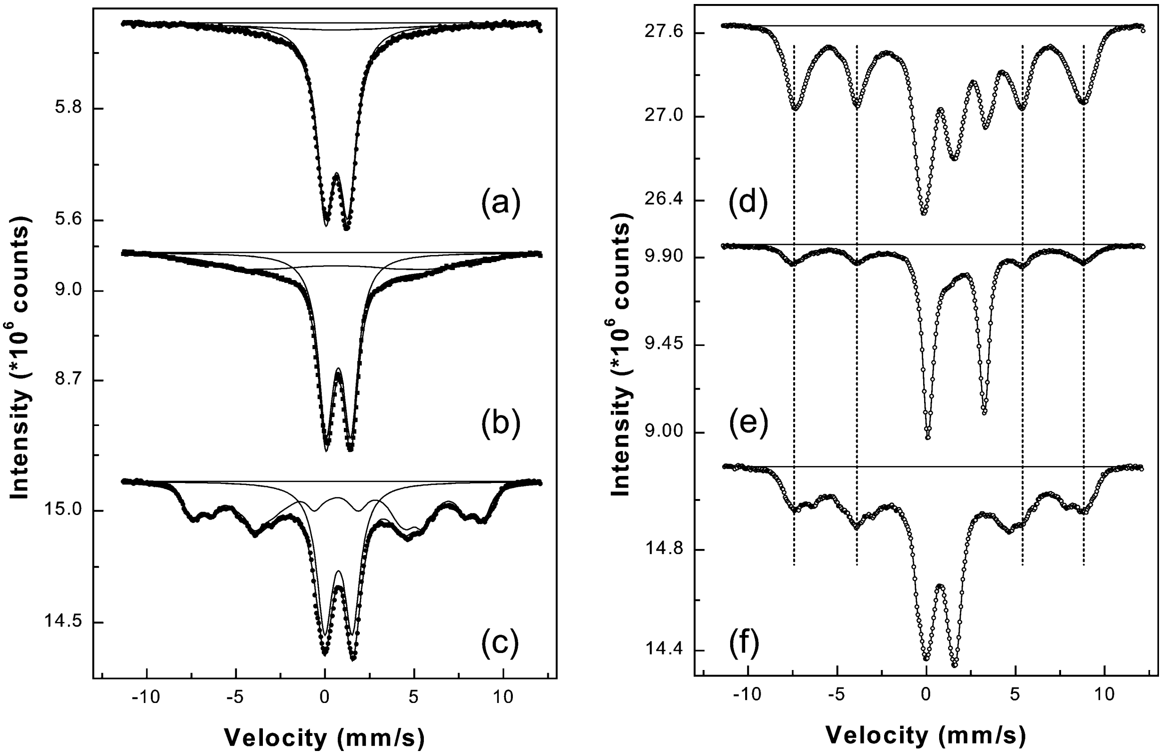

Fig. 5. ^{57}Fe Mössbauer spectra together with the accompanying fits of steamed FeZSM-5, after reduction in N_2 at 623 K for 1.5 h, and subsequent oxidation in N_2O at 623 K for 1.5 h, measured at (a) 300 K, (b) 77 K, and (c) 4.2 K and comparison of Mössbauer spectra recorded at 4.2 K of (d) freshly steamed FeZSM-5, (e) "reduced" FeZSM-5, and (f) "oxidized" FeZSM-5.

Therefore, a gradual increase in the quadrupole splitting of the high-spin Fe^{3+} doublet is expected.

4. Conclusions

In this work, we have probed the redox behavior of the different iron species in a steamed FeZSM-5 catalyst with the use of ^{57}Fe Mössbauer spectroscopy. It was shown that Fe^{3+} ions in isolated, extraframework sites and in small oxo–iron clusters reduce to Fe^{2+} ions using a thermal treatment at 623 K in N_2 or Ar and back into Fe^{3+} by an oxidative treatment with N_2O at 623 K. Fe^{3+} ions in the iron oxide particles of 2 nm in diameter did not show reduction to Fe^{2+} under these conditions. A remarkable affinity toward N_2 has been observed leading to reduction of a fraction of the Fe^{3+} ions (most likely in isolated mononuclear sites) to Fe^{2+} species at room temperature. This reduction only occurred if prior to the exposure to N_2 the FeZSM-5 catalyst was oxidized with N_2O. Moreover, this reduction at room temperature did not happen if Ar was used instead of N_2, thus emphasizing the importance of the presence of N_2. Additionally, it was observed that N_2 reversibly adsorbs to only one of the Fe^{2+} species that is present in the catalytic material after thermal treatment at 623 K.

Oxidation of steamed FeZSM-5 with N_2O gives rise to a notably different state of the catalyst, which makes it very sensitive to redox changes. It could be concluded that the iron oxide particles of 2 nm at the outer surface of the zeolite catalyst were not affected by the oxidation reaction. However, identity of the newly formed Fe^{3+} species is unknown at present and will be the topic of future investigations.

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References

[1] B.D. McNico, G.T. Pott, J. Catal. 25 (1972) 223.
[2] R. Szostak, V. Nair, T.L. Thomas, J. Chem. Soc., Faraday Trans. 1 83 (1987) 487.
[3] J. Pérez-Ramírez, J.M. García-Cortés, F. Kapteijn, M.J. Illán-Gómez, C. Salinas-Martínez de Lecea, J.A. Moulijn, Appl. Catal. B 25 (2000) 191.
[4] R. Joyner, M. Stockenhuber, J. Phys. Chem. B 103 (1999) 5963.
[5] J. Pérez-Ramírez, F. Kapteijn, G. Mul, J.A. Moulijn, Appl. Catal. B 35 (2002) 227.
[6] H.-Y. Chen, W.M.H. Sachtler, Catal. Today 42 (1998) 73.
[7] G.I. Panov, A.K. Uriarte, M.A. Rodkin, V.I. Sobolev, Catal. Today 41 (1998) 365.

[8] V.I. Sobolev, K.A. Dubkov, O.V. Panna, G.I. Panov, Catal. Today 24 (1995) 251.
[9] K.A. Dubkov, V.I. Sobolev, G.I. Panov, Kinet. Catal. 39 (1998) 72.
[10] G.I. Panov, G.A. Sheveleva, A.S. Kharitonov, V.N. Romannikov, L.A. Vostrikova, Appl. Catal. 82 (1992) 31.
[11] P. Kubánek, B. Wichterlová, Z.J. Sobalík, J. Catal. 211 (2002) 109.
[12] E. Suzuki, K. Nakashiro, Y. Ono, Chem. Lett. (1988) 953.
[13] M. Gubelmann, P.-J. Tirel, French Patent 2630735, 1988.
[14] A.S. Kharitonov, T.N. Alexandrova, L.A. Vostrikova, K.G. Ione, G.I. Panov, Russian Patent 4445646, 1988.
[15] G.I. Panov, V.I. Sobolev, A.S. Kharitonov, J. Mol. Catal. 61 (1990) 85.
[16] G.I. Panov, A.S. Kharitonov, V.I. Sobolev, Appl. Catal. A 98 (1993) 1.
[17] B.J. Waller, J.D. Libscomb, Chem. Rev. 96 (1996) 2625.
[18] A. Ribera, I.W.C.E. Arends, S. de Vries, J. Pérez-Ramírez, R.A. Sheldon, J. Catal. 195 (2000) 287.
[19] J. Pérez-Ramírez, G. Mul, F. Kapteijn, J.A. Moulijn, A.R. Overweg, A. Doménech, A. Ribera, I.W.C.E. Arends, J. Catal. 207 (2002) 113.
[20] G. Calis, P. Frenken, E. de Boer, A. Swolfs, M.A. Hefni, Zeolites 7 (1988) 319.
[21] A. Meagher, V. Nair, R. Szostak, Zeolites 8 (1988) 3.
[22] K. Lázár, A.N. Kotasthane, P. Fejes, Catal. Lett. 57 (1999) 171.
[23] P. Fejes, J.B. Nagy, K. Lázár, J. Halász, Appl. Catal. A 190 (2000) 117.
[24] S. Bordiga, F. Buzzoni, F. Geobaldo, C. Lamberti, E. Giamello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzola, J. Catal. 15 (1996) 486.
[25] L. Lobree, I.-C. Hwang, J.A. Reimer, A.T. Bell, J. Catal. 186 (1999) 242.
[26] N.S. Ovanesyan, A.A. Shteinman, K.A. Dubkov, V.I. Sobolev, G.I. Panov, Kinet. Catal. 39 (1998) 792.
[27] N.S. Ovanesyan, K.A. Dubkov, A.A. Pyallin, A.A. Shteinman, J. Radianal. Nucl. Chem. 246 (2000) 149.
[28] K.A. Dubkov, N.S. Ovanesyan, A.A. Shteinman, E.V. Starokon, G.I. Panov, J. Catal. 207 (2002) 341.
[29] J.W. Niemantsverdriet, C.F.J. Flipse, A.M. van der Kraan, J.J. van Loef, Appl. Surf. Sci. 10 (1982) 302.
[30] J.G. DeWitt, J.G. Bentsen, A.C. Rosenzweig, B. Hedman, J. Green, S. Pilkington, G.C. Papaeftymiou, H. Dalton, K.O. Hodgson, S.J. Lippard, J. Am. Chem. Soc. 113 (1991) 9219.
[31] G. Berlier, G. Spoto, P. Fisicaro, S. Bordiga, A. Zecchina, E. Giamello, C. Lamberti, Microchem. J. 71 (2002) 101.
[32] W. Kündig, K.J. Ando, R.H. Lindquist, G. Constabaris, J. Phys. B 17 (1967) 467.
[33] A.M. van der Kraan, Phys. Status Solidi 18 (1973) 215.