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Mössbauer Spectroscopic Characterization of Iron Supported on Y Type Zeolites after Sulfiding

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Iron supported on zeolite catalysts, prepared by treating NH_4Y with aqueous solutions containing Fe^{3+} or Fe^{2+} ions followed by calcination in air, were subjected to Mössbauer spectroscopic investigations before and after sulfiding treatments to elucidate the states and properties of Fe species supported. At least three types of Fe^{3+} species could be distinguished in the prepared samples. The first Fe^{3+} species were those located at the cation-exchange sites of zeolite. This type was reduced easily to Fe^{2+} species with the H_2S treatment, but was resistant to aggregation to form $Fe_{1-x}S$. The second Fe^{3+} species were those which had precipitated on the surface of zeolites as hydroxides. These were sulfided to crystalline $Fe_{1-x}S$ after H_2S treatment. Finally, the third Fe^{3+} species were those which were quite resistant to both reduction to Fe^{2+} and sulfiding to $Fe_{1-x}S$. These species were preferentially supported under the conditions where dealumination from zeolite framework took place simultaneously. Thus it was speculated that these species were bonded to zeolite framework to be stabilized. The distribution of the three Fe^{3+} species were quite different depending on the sample preparation. Comparison with the catalytic data clearly indicated that the third Fe^{3+} species acted as highly active sites for the toluene disproportionation reaction in the presence of H_2S.

Recently we reported that the iron supported on Y type zeolite (FeHY-1) prepared by treating NH_4Y with an aqueous $Fe(NO_3)_3$ solution showed high catalytic activity and low coke formation for the toluene disproportionation reaction in a flow of H_2S/H_2.[1] It was also shown that a FeHY-1 based catalyst was highly active for the hydrocracking of the atmospheric residual oil in the presence of H_2S.[2] There has been collected ample evidence to indicate that the iron species supported on FeHY-1 are clearly different from those on the other iron supported on zeolites prepared by conventional methods such as an ion-exchange method.[1,3] However, we still lack definite information as to the nature and state of iron species in FeHY-1.

It is known that Mössbauer spectroscopy is very useful to investigate the state of iron species on zeolites.[4] In this paper, we have studied the state of iron species after sulfiding treatment by using Mössbauer spectroscopy and the correlation between catalytic activity and the state of iron species supported on zeolite in the presence of H_2S.

Experimental

Preparation of Catalyst. To obtain FeHY-1-L, FeHY-1, FeHY-1-H, FeHY-2-L, and FeHY-2, ammonium-ion-exchanged Y type zeolite, NH_4Y (UCC; LZY-82), was mixed with the aqueous $Fe(NO_3)_3$ or $FeSO_4$ solution shown in Table 1 at room temperature, and stirred for 2 h at the specified temperatures. Then the suspension was filtered, washed with distilled water, dried in air at 363 K, and finally calcined in air at 773 K for 3 h.

For FeHY-3 and Fe/SiO_2, NH_4Y or silica gel(Fuji Davison) was suspended in water, to which aqueous $Fe(NO_3)_3$ solution was added as droplets while caution was paid to keep the pH of the suspension at 7 by adding droplets of aqueous ammonia solution simultaneously. This procedure was adopted in order to have Fe^{3+} ions precipitated as $Fe(OH)_3$. The subsequent procedures were the same as the above.

Measurements of Physicochemical and Catalytic Properties. The amount of supported Fe as well as the SiO_2/Al_2O_3 molar ratio of each sample were measured by Fluorescence spectrometer (Rigaku Denki; 3080E). The specific surface area was determined by BET method. The

Table 1. Preparation Methods of Catalysts

Catalyst	Starting Fe solution	Zeolite / Fe solution/g l^{-1}	Temp/K	Time/h
FeHY-1-L	0.10 M[b] $Fe(NO_3)_3$	8	323	2
FeHY-1	0.25 M $Fe(NO_3)_3$	8	323	2
FeHY-1-H	0.25 M $Fe(NO_3)_3$	8	373	2
FeHY-2-L	1.00 M $FeSO_4$	40	323	2
FeHY-2	1.00 M $FeSO_4$	40	363	2
FeHY-3	0.25 M $Fe(NO_3)_3+NH_4OH$	8	R.T.	1
Fe/SiO_2	0.25 M $Fe(NO_3)_3+NH_4OH$	8[a]	R.T.	1

a) SiO_2/Fe solution. b) 1 M=1 mol dm^{-3}.

unit cell dimension of zeolite lattice was determined by X-ray (Cu *Kα*) powder diffraction.

The toluene disproportionation reaction was carried out in a high-pressure fixed catalyst bed reactor. The loaded catalyst (1.8 g) was sulfided in a flow (60 cm^3 m^{-1}) of H_2S(0.2 vol%)/H_2 mixture at 523 K and 3 MPa for 16 h, before toluene was fed at a rate of 10 cm^3 (liquid) h^{-1} in a flow (200 cm^3 m^{-1}) of H_2S(0.2 vol%)/H_2 at 623 K and 6 MPa. The effluent, consisting mostly of unconverted toluene, xylene, and benzene was analyzed by FID gas chromatography. The amounts of coke deposition on spent catalysts were determined from increases in weight.

Mössbauer Measurement. Mössbauer spectroscopy was carried out by using a constant-acceleration spectrometer (Elscint, Inc.). Data were stored in a 1024-channel pulse height analyzer, TN-7200 (Tracor Northen, Inc.). A cobalt-57 source of 10 mCi diffused into a palladium foil (Amersham, Inc.) was used for the absorption measurement. Some of the spectra were fitted to the Lorentzian line shape by using a least-squares analysis. Isomer shift was referred to the center of the spectrum of metallic iron. In many cases samples were subjected to sulfiding treatments prior to the measurements: Samples were exposed to a flow of either H_2S(10 vol%)/He at 473 K or H_2S(10 vol%)/H_2 at 673 K for 2 h unless noted otherwise. The sulfied samples were measured in nitrogen atmosphere to prevent the reoxidation of sulfided iron species if any.

Results and Disscusion

Physicochemical Properties and Catalytic Activities. Some physicochemical and catalytic properties of the prepared samples as well as those of NH_4Y and HY are compared in Table 2. We have shown already that the treatment of NH_4Y with an aqueous solution of $Fe(NO_3)_3$ results in dealumination from zeolite framework.[1)] The dealumination proceeds through

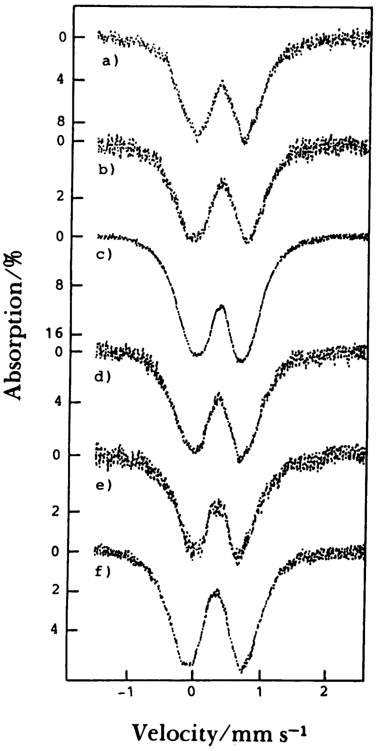

Fig. 1. Mössbauer spectra of iron supported on zeolites after calcination at 773 K.
a) FeHY-1-L, b) FeHY-1, c) FeHY-1-H, d) FeHY-2-L, e) FeHY-2, f) FeHY-3.

Table 2. Physicochemical Properties and Catalytic Activity

Catalyst	Physicochemical properties			
	Fe_2O_3/wt%	SiO_2/Al_2O_3 (molar ratio)	Surface area/m^2 g^{-1}	UD[a)]/Å
NH_4Y	tr.	5.4	543	24.57
HY	tr.	5.4	427	24.51
FeHY-1L	4.8	6.6	463	24.50
FeHY-1	9.0	10.6	456	24.40
FeHY-1H	16.2	10.6	477	n[d)]
FeHY-2L	4.1	5.7	443	24.51
FeHY-2	11.8	6.3	437	24.51
FeHY-3	10.0	5.9	451	24.51
Fe/SiO_2	9.2	—	96	—

Catalyst	Tol. dispro.[b)]		
	Converted toluene/mol%	Sel.[c)]/mol%	Coke deposited/wt%
NH_4Y	—	—	—
HY	5.5	100	14.6
FeHY-1L	12.9	76.0	11.6
FeHY-1	45.3	92.0	0.5
FeHY-1H	32.4	70.1	1.2
FeHY-2L	12.1	71.1	11.5
FeHY-2	18.2	72.5	8.0
FeHY-3	16.9	70.4	9.6
Fe/SiO_2	—	—	—

a) Unit cell dimension of zeolite lattice. b) Toluene disproportion. Sulfiding; H_2S(0.2 vol%)/H_2, 523 K, 3 MPa, 16 h. Reaction; H_2S(0.2 vol%)/H_2, 623 K, 6 MPa, LHSV: 4.0 h^{-1}. c) Selectivity to benzene and xylene. d) Not measured.

the attack of the protons which are produced from the hydrolysis of Fe^{3+} ions. As a result of the dealumination, SiO_2/Al_2O_3 molar ratio increases while the unit cell dimension of zeolite decreases. As seen from Table 2, FeHY-1 and FeHY-1-H showed larger SiO_2/Al_2O_3 ratios and smaller unit cell dimensions than the other samples, indicating the progress of significant degrees of dealumination. The amounts of supported Fe_2O_3 varied considerably with the samples, but these amounts were not directly related with the catalytic properties. As seen from the table, FeHY-1 and FeHY-1-H showed very high activities and very low coke depositions in a flow of H_2S(0.2 vol%)/H_2 compared with the other catalysts.

This clearly shows the importance of dealumination during the catalyst preparation. As stated previously, it is considered that the Fe species loaded on zeolite under the dealuminating conditions are present in a state significantly different from those loaded under the non-dealuminating conditions, and thus show unique acidic properties in the presence of H_2S.[1)]

Mössbauer Spectra of Fresh Catalysts. Mössbauer spectra of prepared samples after calcination are shown in Fig. 1. The Mössbauer parameters estimated for the samples listed in Table 3. The spectra consisted of broad quadrupole doublets, denoted Type A hereafter. The doublets showed isomer shift (IS) 0.33—0.36 mm s^{-1} and quadrupole splitting (QS) 0.76—0.90 mm s^{-1}, which were in the anticipated ranges for octahedrally coordinated Fe^{3+} species.[5)] However, the isomer shifts denied the existence of significant amounts of tetrahedrally coordinated Fe^{3+} ions in the samples. The absence of Zeeman splitting in the spectra assured that the particle sizes of the Fe^{3+} species were very fine, being 50—100 Å or less.[6)]

As for the octahedrally coordinated Fe^{3+} species, several types are possible, such as Fe^{3+} ions located at the cation-exchange sites of zeolite,[4,7)] oligomerized iron(III) oxide clusters located in supercages or on outer surface of zeolite, and fine Fe_2O_3 particles. The proportion of each type would depend on the sample preparation but more than a single type are likely to be loaded in each sample, as suggested from the broadness of the quadrupole doublet.

Mössbauer Spectra after H_2S/He Treatment at 473 K. The fresh samples were treated with H_2S(10 vol%)/He at 473 K (at 573 K for FeHY-1) and atmospheric pressure. Their Mössbauer spectra are

Table 3. Mössbauer Parameters of Quadrupole Doublets of Iron Supported on Zeolites

Catalyst	Treatment[a)]	Isomer shift/mm s^{-1} (±0.02)	Quadrupole splitting/mm s^{-1} (±0.05)	Relative amount/%	
FeHY-1-L	Fresh	0.36	0.79	A	100
	I	0.30	0.74	A+C	32
		1.13	2.10	B	68
	II	0.35	0.85	A	27
		1.16	2.08	B	73
FeHY-1	Fresh	0.35	0.87	A	100
	I′	0.35	1.02	A	61
		1.17	2.17	B	39
	II	0.36	0.95	A	42
		1.12	1.99	B	58
FeHY-1-H	Fresh	0.34	0.76	A	100
	I	0.30	0.54	C	67
		0.39	1.00	A	19
		1.70	1.77	B	15
	II	Hyperfine splitting		D	—
FeHY-2-L	Fresh	0.35	0.83	A	100
	I	0.27	0.69	C	17
		1.15	2.11	B	83
	II	0.30	0.78	C	13
		1.14	2.10	B	87
FeHY-2	Fresh	0.34	0.77	A	100
	I	0.28	0.58	C	67
		1.13	2.05	B	33
	II	Hyperfine splitting		D	—
FeHY-3	Fresh	0.33	0.90	A	100
	I	0.28	0.42	C	93
		0.92	2.31	B	7
	II	Hyperfine splitting		D	—
Fe/SiO_2	I	0.30	0.61	C	100

a) Conditions I and I′: exposure to a flow of H_2S(10 vol%)/He at 473 K (I) or 573 K (I′) for 2 h. Conditions II: exposure to a flow of H_2S(10 vol%)/H_2 at 673 K for 2 h. b) A: Octahedrally coordinated Fe^{3+} ions. B: Fe^{2+} ions located at cation-exchange sites. C: $Fe_{1-x}S$ showing a quadrupole splitting. D: $Fe_{1-x}S$ showing a hyperfine structure.

shown in Fig. 2. The Mössbauer parameters are listed in Table 3. The spectra are all composed of two or three types of quadrupole doublets.

A type of quadrupole doublet (Type B), with large IS of 0.92—1.70 mm s^{-1} and large QS of 1.77—2.31 mm s^{-1}, was typically observed in FeHY-1-L and FeHY-2-L. These samples were prepared by treating NH_4Y with either a dilute Fe^{3+} solution or a Fe^{2+} solution, conditions where the ion exchange of NH_4^+ with Fe^{3+} or Fe^{2+} was favored over the other types of loading. It has also been reported that such Fe^{3+} ions are easily reduced.[8] Thus Type B doublet is likely to be assigned to Fe^{2+} ions located at the cation-exchange sites of zeolite. This doublet was far weaker in FeHY-1 and FeHY-2, almost unvisible in FeHY-1-H and FeHY-3, and not visible in Fe/SiO_2.

A quadrupole doublet (Type C), with IS of 0.27—0.30 mm s^{-1} and QS of 0.54—0.77 mm s^{-1} appeared typically in FeHY-1-H, FeHY-2, FeHY-3, and Fe/SiO_2, and was assigned to fine particles of nonstoichiometric iron sulfide ($Fe_{1-x}S$) according to literature.[9] These samples were prepared under such conditions that the precipitation of iron hydroxides on zeolite was facilitated more or less. It is inferred that the precipitate changed to fine particles of Fe(III) oxide with the calcination and then to ferric sulfide with the H_2S/H_2.

Quite remarkably, Type C doublet was hardly visible in FeHY-1. The spectrum was dominated by Type A doublet responsible for Fe^{3+} species, with a minor contribution of Type B. The survival of Fe^{3+} species is still more remarkable when it is taken into account that the H_2S/H_2 treatment was carried out at a higher temperature (573 K) than that for the other samples (473 K). This fact indicates that a prevailing part of the Fe^{3+} ions in FeHY-1 are situated in a form which is quite resistive to reduction. Type A doublet was also present, but far less visible, in FeHY-1-H. It is considered that the reduction-resistant property arises from a strong interaction of Fe^{3+} species with zeolite lattice, and that such Fe^{3+} species are formed when Fe^{3+} ions are loaded on zeolite under the dealuminating conditions. The relative intensities of the three types of quadrupole doublets were estimated from the areas under the doublets and are indicated in Table 3.

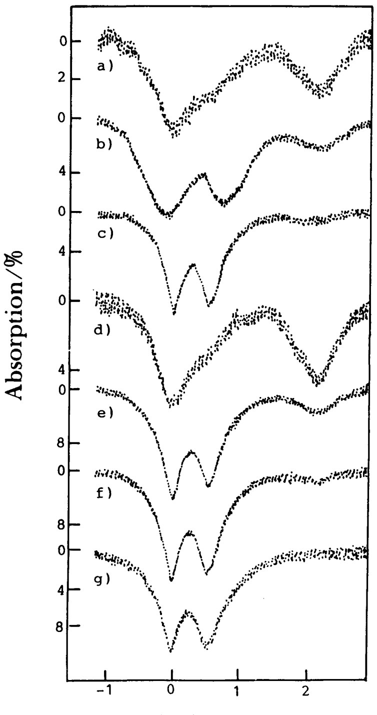

Fig. 2. Mössbauer spectra of iron supported on zeolites after sulfiding in H_2S(10 vol%)/He flow at 473 K or 573 K for 2 h.
a) FeHY-1-L, b) FeHY-1, c) FeHY-1-H, d) FeHY-2-L, e) FeHY-2, f) FeHY-3, g) Fe/SiO_2.

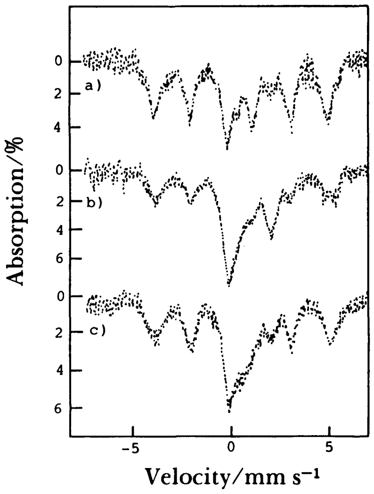

Fig. 3. Mössbauer spectra of iron supported on zeolites after sulfiding in H_2S(10 vol%)/H_2 flow at 673 K for 2 h.
a) FeHY-1-H, b) FeHY-2, c) FeHY-3.

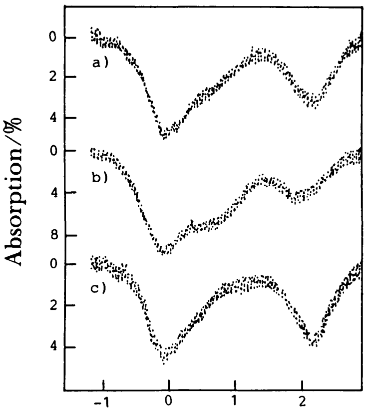

Fig. 4. Mössbauer spectra of iron supported on zeolites after sulfiding in H_2S(10 vol%)/H_2 flow at 673 K for 2 h.
a) FeHY-1-L, b) FeHY-1, c) FeHY-2-L.

Mössbauer Spectra after H_2S/H_2 Treatment at 673 K. Mössbauer spectra after H_2S(10 vol%)/H_2 treatment at 673 K are shown in Figs. 3 and 4, and Mössbauer parameters are listed in Table 3. Most of these spectra were drastically different from those described in the previous sections.

As shown in Fig. 3, the spectra of FeHY-1-H, FeHY-2, and FeHY-3 clearly showed a sextet of magnetic hyperfine structure with a paramagnetic doublet weakly superposing on it. The sextet was assigned to crystalline $Fe_{1-x}S$ of sufficiently large domains because the internal magnetic field (H_{int}) of about 28 T as well as the spectral shape coincided with those of commercially obtained $Fe_{1-x}S$ (Nippon Chikagaku Co., Ltd.).

As estimated from the area under the sextet, about 70% or more of iron species on these samples could be assigned to this kind of crystalline $Fe_{1-x}S$. It is considerd that fine particles $Fe_{1-x}S$, formed after sulfiding in H_2S(10 vol%)/He at 473 K, grew to large particles during sulfiding in H_2S(10 vol%)/H_2 at 673 K.

On the contrary, such a sextet magnetic hyperfine structure was not observed for FeHY-1-L, FeHY-1, and FeHY-2-L as shown in Fig. 4. This suggests that the crystal growth of $Fe_{1-x}S$ hardly proceeded. For FeHY-1-L and FeHY-2-L, a quadrupole doublet (Type B) due to Fe^{2+} ions at the cation-exchange sites of zeolite, remained predominant. While FeHY-1 exhibited not only this kind of quadrupole doublet (Type B) due to Fe^{2+} ions but also a quadrupole doublet (Type A) due to Fe^{3+} ions. As shown in Fig. 3, more than 40% of Fe^{3+} ions supported on FeHY-1 could survive after the treatment in H_2S(10%)/H_2 at 673 K. These results again indicate that the Fe^{3+} ions supported on FeHY-1 are resistant to reduction. This resistance should come from a strong interaction between the Fe^{3+} ions and zeolite lattice as described before.

States and Catalytic Activities of Supported Iron Species. The Mössbauer measurements mentioned above revealed that the states and properties of supported Fe^{3+} ions were largely different, depending on the preparation conditions.

When NH_4Y was treated with a dilute aqueous solution containing Fe^{3+} or Fe^{2+} at 323 K, as in the cases of FeHY-1-L and FeHY-2-L, most iron ions were loaded on zeolite by ion exchange and situated at the cationic sites. These Fe^{3+} ions were easily reduced to Fe^{2+} under the sulfiding conditions, but they were resistant to aggregation into crystalline $Fe_{1-x}S$.

When NH_4Y was treated with a Fe^{2+} or Fe^{3+} solution at higher temperature (363 or 373 K), as in the cases of FeHY-1-H and FeHY-2, a major part of Fe ions seemed to be loaded on zeolite by precipitation as hydroxides. Like FeHY-3 and Fe/SiO_2, the samples prepared in this way showed a superparamagnetic doublet due to finely dispersed $Fe_{1-x}S$ particles after the low temperature sulfiding (473 K) and a sextet hyperfine structure due to large particles of $Fe_{1-x}S$ after the high temperature sulfiding (673 K).

In contrast to these samples, FeHY-1 was shown to be very unique in the stability of Fe^{3+} ions loaded. In fact, more than 40% of the loaded Fe^{3+} ions could remain as Fe^{3+} even after the sulfiding treatment with H_2S(10%)/H_2 at 673 K. FeHY-1 was prepared under the conditions where dealumination from zeolite lattice took place. The hydrolysis of Fe^{3+} ions in the solution should produce protons and Fe^{3+} complexes. The released protons should attack zeolite lattice to dealuminate while the dealuminated sites would tend to be compensated by the Fe^{3+} complexes. In this way, Fe^{3+} complexes should be incorporated and partially bonded to zeolite lattice. It is assumed that such bonding should result in the remarkable resistivity of the Fe^{3+} ions to reduction.

It is interesting to compare these results with the catalytic activities for the toluene disproportionation reaction in the presence of H_2S. As already stated, FeHY-1 was the most active among the tested samples. This indicates the importance of the reduction-resistant Fe^{3+} species just mentioned. Moreover, the other two species dominating in the other samples, i.e., the ion-exchanged Fe^{3+} ions at the cation-exchange sites and the Fe species deposited on zeolite surface, which were easily reduced to Fe^{2+} or to crystalline $Fe_{1-x}S$ in the H_2S atmosphere, are judged to be not so active as the above one. A comment may be necessary for FeHY-1-H, which was active next to FeHY-1. Although the reduction-resistant Fe^{3+} could not be clealy revealed in this sample, probably due to the excessive amounts of the other species, one can expect its presence from the extent of dealumination of the sample. Therefore the high activity of FeHY-1-H can be assumed to result also from the reduction-resistant Fe^{3+} species.

Previously we estimated that the unique acidic properties of the Fe supported on zeolite in the toluene disproportionation reaction in the presence of H_2S were not associated with the formation of iron sulfide ($Fe_{1-x}S$) but with the adsorption of H_2S on a certain type of supported Fe^{3+} species.[1] This estimation has been confirmed with the above observation that the active sites are provided by the reduction-resistant Fe^{3+} species, although the mechanism for generating the unique acidity remains to be studied further.

Conclusion

Three types of Fe^{3+} species could be distinguished in the Fe supported on zeolite catalysts prepared. The Fe^{3+} located at cation-exchange sites of zeolite (the first type), dominating in FeHY-1-L and FeHY-2-L, are easily reduced to Fe^{2+} with the H_2S treatment, to give a characteristic quadrupole doublet with a large isomer shift. The second type, dominating in FeHY-

1-H, FeHY-2 and FeHY-3, consists of those which have precipitated on zeolite surface as iron hydroxides and have changed into Fe(III) oxide after calcination in air. This type is changed easily into well dispersed $Fe_{1-x}S$ with the H_2S treatment at 473 K, which further grows into sufficiently large particles of $Fe_{1-x}S$ to give a sextet hyperfine structure at higher temperature (673 K). The third type, typically formed in FeHY-1, is very resistant to chemical change, remaining almost intact even after the H_2S treatment at 673 K. The remarkable stability of this type is considered to arise from a strong interaction with the zeolite framework.

Comparison of these results with the catalytic performances, clearly indicates that it is the third type Fe^{3+} species which provide the highly active sites for the toluene disproportionation reaction in the presence of H_2S. The adsorption of H_2S on these Fe^{3+} species seems to produce the unique acidity required to the catalysis.

References

1) S. Hidaka, A. Iino, K. Nita, Y. Maeda, K. Morinaga, and N. Yamazoe, Proceedings of 7th International Zeolite Conference ed by Y. Murakami, A. Iijima, and J. W. Ward, Tokyo (1986), p. 329.

2) S. Hidaka, H. Shimakawa, A. Iino, T. Mibuchi, S. Nakay, and K. Nita, Ketjen Catalyst Symposium'86, H-9, 1986.

3) S. Hidaka, I. Iino, T. Mibuchi, K. Nita, and N. Yamazoe, *Chem. Lett.*, **1986**, 1213.

4) For example, R. L. Garten, W. N. Delgass, and M. Boudart, *J. Catal.*, **18**, 90 (1970).

5) H. Sano, "Mössbauer Spectroscopy," Koudan-sha Scientific (1972), p. 144.

6) W. N. Kundig, H. Bommel, G. Constabaris, and R. H. Lindquist, *Phys. Rev.*, **142**, 467 (1986).

7) K. Segawa, Y. Chen, J. E. Kubsh, W. N. Delgass. J. A. Dumesic, and W. K. Hall, *J. Catal.*, **76**, 112 (1982).

8) B. Wichterlova, *Zeolites*, **1**, 181 (1981).

9) P. P. Vaishnava, P. A. Montano, R. E. Tischer, and S. S. Pollack, *J. Catal.*, **78**, 454 (1982).