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Environments of Iron in Fe-Silicates Synthesized by the Rapid Crystallization Method

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Pentasil-type Fe-silicates with different iron contents were synthesized using the rapid crystallization method. The physical and chemical properties of the Fe-silicates were investigated by means of various spectrometries, and the environments of iron in the Fe-silicate crystals are discussed. Almost all of the iron did not exist on the ion-exchange sites in the Fe-silicate crystals. Both the ion-exchange capacity and the unit-cell volume of Fe-silicates increased with an increase in the iron content. The IR spectra of the Fe-silicates showed an absorption band due to the silanol groups which were demonstrated to be formed by elimination of a part of the iron atoms from the framework. The NMR and UV spectra also provided evidence for the isomorphous substitution of iron(III) ions in the silicate framework. © 1993 Academic Press, Inc.

INTRODUCTION

Many workers (*1–7*) throughout the world have synthesized various kinds of metallosilicates with the pentasil open pore structure of ZSM-5 by the conventional crystallization method, and identified the pentasil-type metallosilicates as catalysts having new catalytic functions. Especially, a Ti-silicate catalyst exhibited excellent performance in the epoxidation and hydroxylation of olefins with hydrogen peroxide (*4*). On a B-silicate catalyst, *p*-xylene was produced with high selectivity in the alkylation of toluene with methanol (*5*). The B- and Fe-silicate catalysts were effective in the reaction which took place on the weak acid sites (*6*).

By using our original preparation method, the rapid crystallization method (*8–10*), we have synthesized various kinds of metallosilicates with the pentasil pore structure of ZSM-5, by replacing the aluminum in ZSM-5 with other transition elements at the stage of gel formation before crystallization. We have also investigated the catalytic properties of the metallosilicates. A Ga-silicate catalyst converted methanol or light olefins to more aromatic-rich gasoline than the ZSM-5 catalyst (*8, 11, 12*). A platinum-ion-exchanged Ga-silicate and Zn-silicate catalysts with high metal contents exhibited high selectivity for aromatic hydrocarbons in light paraffin conversion (*13, 14*). An Fe-silicate catalyst converted methanol to lower olefins almost quantitatively (*10, 11*) and produced a high-octane-number gasoline fraction from light olefins in very high space-time yields (*12*).

The chemical and physical properties of Fe-silicate have been studied by many researchers (*3, 15–19*). However, in those studies, because the Fe-silicates were synthesized by a conventional crystallization method, the elements except for silicon and aluminum were excluded from the silicate lattice. Therefore, the local concentration of iron in the silicate crystal increases from the center toward the outer portion of the

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crystallites regardless of the imposed atomic ratio of silicon to iron. Iron ions in the Fe-silicates are liable to be oxidized and reduced, and dissolved in acid solutions. In the case of the rapid crystallization method, because its crystallization rate is much faster than that of the conventional crystallization method, it is possible to incorporate many kinds of other elements in the silicate lattice in large quantity. In our previous papers, Fe-silicates were prepared using different valence ions, Fe^{3+} ($Fe(NO_3)_3$) and Fe^{2+} ($FeSO_4$) as the starting metal salts and the extent of Fe incorporation into the framework was compared (*20*). A sharp contrast between H-ZSM-5 and H-Fe-silicate in the oligomerization reaction of light olefins was observed and the reason for this was discussed in relation to the acidic properties of the zeolites (*21*). In this paper, the chemical and physical properties of the Fe-silicate synthesized by the rapid crystallization method were investigated in order to better resolve the environments of iron in the Fe-silicate crystals.

EXPERIMENTAL

Preparation of Fe-Silicate

Fe-silicates with different iron contents were prepared by adopting the rapid crystallization method (*11*). The observed iron concentrations in the products were almost equal to those of the charged concentration of iron in the starting materials upto a silicon to iron ratio of 12 (10 wt% as iron(III) oxide). X-ray diffraction patterns of the Fe-silicates were the same as the pattern of ZSM-5 only, and their BET surface areas were more than 350 m^2/g. Moreover, the physical properties of the Fe-silicate did not change upon thermal treatment. These results indicate that these Fe-silicate samples do not contain amorphous or layer-type ferrisilicates. The color of Fe-silicate (milk-white even for the catalyst with the highest iron content) and the negligible activity for CO hydrogenation are in accord with this idea. TPD (temperature-programmed desorption) spectra of ammonia from the Fe-silicates indicated that the iron ion incorporated in the crystal was responsible for the formation of acid sites and that the acid strength of Fe-silicate was weaker than that of H-ZSM-5. Furthermore, SEM (scanning electron microscope) and EPMA (electron probe micro-analysis) measurements indicated that a small amount of iron acted as the nuclei in the growth of high-silica crystals to change the morphology and that the iron concentration inside a given crystal was higher than the concentration at the outer surface layers of the crystal particle. Detailed data for these observations have been described in our previous paper (*11*).

Dissolution Measurement of Iron Ions in Fe-Silicates

The treatment of Fe-silicates with nitric acid was carried out as follows. A 15-mg portion of the H-Fe-silicate powder was weighed out into a porcelain crucible. To the crucible was added 30 ml of 4 *N* nitric acid (guaranteed grade; Wako Pure Chemical Industries, Ltd.), and then the crucible was gently heated by a Bunsen burner for 30 min. After cooling to room temperature, the sample was filtered and washed with distilled water. The filtrate and all the washings were transferred into a 100-ml measuring flask, and then the total volume was exactly adjusted to 100 ml with distilled water.

Atomic absorption spectrophotometry (Shimadzu atomic absorption/flame emission spectrophotometer AA-640-01) was carried out using an acetylene-air flame.

Determination of Ion-Exchange Capacity of Fe-Silicate

A 0.5-g portion of H-Fe-silicate powder was suspended in 50 ml of 0.1 *N* sodium hydroxide aqueous solution at room temperature for 2 h, then the sample was filtered and washed with distilled water until the pH of the wash water was 8. The washed crystals were dried overnight at 120°C.

Atomic absorption spectrophotometry (Shimadzu AA-640-01) was carried out using an acetylene-air flame.

Characterization of Fe-Silicate

X-ray diffraction (XRD) analysis was carried out using a Rigaku-Denki Geigerflex-2013 with Ni-filtered monochromatic Cu$K\alpha$ radiation. Unit-cell parameters were obtained by a least-squares fit to the interplanar spacings of 25–28 reflections, accurately measured in the 13°–46° 2θ angular region, using α-alumina as an internal standard. ^{29}Si-MAS-NMR spectra were registered using a JEOL JNMGSH-270 spectrometer at 53.54 MHz. UV spectra were registered using a Shimadzu MPS-2000 spectrometer in the range of 190–900 nm. IR absorption measurements of the silicate framework were made with KBr-pressed wafers on a Shimadzu IR-435 spectrometer in the region of 400–4000 cm^{-1}. As for the silanol group in Fe-silicates, the samples were pretreated at 400°C for 1 h, and then diffuse reflectance IR spectra in the region of the fundamental stretching vibrations of hydroxy groups (3000–4000 cm^{-1}) were measured using a JEOL JIR-3510 spectrophotometer equipped wtih diffuse reflectance attachments.

RESULTS AND DISCUSSION

Chemical Properties of Fe-Silicate

The Fe-silicate crystals with various silicon-to-iron ratios were heated in 4 *N* nitric acid for 30 min. The amount of iron dissolved in the nitric acid from the Fe-silicate crystal was determined by the atomic absorption method. The results of the analysis are summarized in Table 1. The concentrations of iron impurity in both acids were less than 0.00005%, and therefore, the effect of iron as an impurity could be ignored. The amount of iron(III) ions dissolved by the nitric acid treatment was less than 20%. Especially, in the case of Fe-silicates with a silicon to iron ratio less than 100, only a few percent of the total iron(III) ions was dissolved out by hot nitric acid. These results support the belief that the Fe-silicate framework of the pentasil structure is quite stable toward the acid treatment, as is the case for silica-rich aluminosilicate with a pentasil pore structure (ZSM-5), and that almost none of the iron existed on the ion-exchange sites in the Fe-silicate crystal.

Generally, in the case of the Fe-silicates synthesized by the conventional crystallization method, the elements except for silicon and aluminum, are subject to exclusion from the silicate crystal. Therefore, the concentration of iron in the silicate crystal becomes higher from the center toward the outer portion of the silicate regardless of the charged atomic ratio of silicon to iron (*22*), and the iron ions in the Fe-silicates are easily dissolved in acid solutions. On the other hand, in the case of the Fe-silicates synthesized by the rapid crystallization method, the concentration of iron in the center of a typical silicate crystal became higher than that in the outer portion of the silicate crystal at low silicon-to-iron ratios. This indicates that iron ions play a role as nuclei of crystal growth in the preparation of high-silica Fe-silicate (*11*). In the case of the Fe-silicate using the rapid crystallization method, the framework of the pentasil structure is quite stable toward acid treatment, as is the case for silica-rich aluminosilicate with a pentasil pore structure (ZSM-5), and almost none of the iron exists in the ion-exchange sites in the Fe-silicate crystal.

The iron-content-dependence on the ion-exchange capacity in Fe-silicate crystal is shown in Fig. 1. The ion-exchange capacity increased in proportion to an increase in iron content. However, when the silicon-to-iron ratio was less than 40, the slope of the line became gentler. This indicates that the silicate framework became charged negatively as iron(III) ions, similar to aluminum(III) ions, were incorporated into the silicate framework. Thus, the ion-exchange capacity increased with an increase in iron content. Moreover, in the region of low iron content, the slope of the line became more than 1. As will be mentioned later, this attributed to the terminal silanol groups formed by the elimination of part of the iron functioning similar to the ion-exchange

TABLE 1

Results of Dissolution of Iron Ions from Fe-silicates by Nitric Acid

Si/Fe ratio[a]	Fe concn. (g-Fe/g-sample)		Si/Fe ratio[b]	Dissolution (wt%)
	Nitric acid	Hydrofluoric acid		
1178	1.52×10^{-4}	7.88×10^{-4}	1460	19.3
467	2.16×10^{-4}	1.83×10^{-3}	529	11.8
226	4.21×10^{-4}	3.68×10^{-3}	255	11.4
117	1.84×10^{-4}	6.89×10^{-3}	120	2.67
36	1.29×10^{-3}	2.23×10^{-2}	38	5.78
24	1.60×10^{-3}	3.31×10^{-2}	25	4.83

[a] Before nitric acid treatment.

[b] After nitric acid treatment.

sites. The line in Fig. 1 became curved for a sample with an iron concentration of more than 0.40 mmol/g-catalyst. This indicates that, as reported in our previous paper (*11*), the amount of acid sites becomes constant for H-Fe-silicates with a silicon-to-iron ratio of less than 40, considering the increase in the amount of terminal silanol groups. A similar tendency was observed in the case of H-Ga-silicate (*23*). Moreover, according to the following result for the unit cell volume of Fe-silicate, iron(III) ions were incorporated into the silicate framework up to 0.63 mmol/g-catalyst. Therefore, based on the result of the ion-exchange capacity in Fe-silicates, it is considered that not all of the iron incorporated in the Fe-silicate framework with a high iron content is contributing to the ion-exchange capacity.

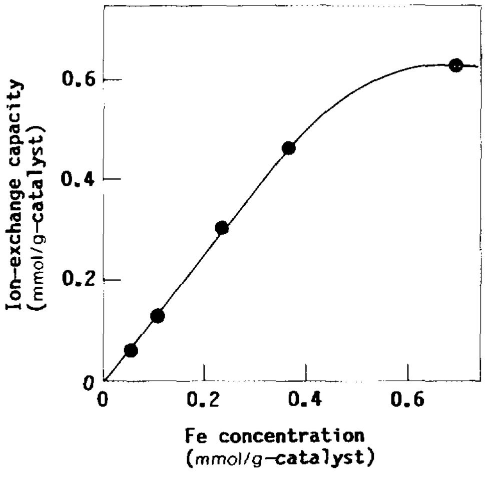

FIG. 1. Change in ion-exchange capacity with iron content in Fe-silicate.

Physical Properties of Fe-Silicate

According to XRD patterns of Fe-silicates with various iron contents, the monoclinic lattice symmetry was preserved up to 1.3 wt% as iron(III) oxide; for a higher content of iron, orthorhombic symmetry was detected. The unit-cell volume of the Fe-silicate crystal, as shown in Fig. 2, increased linearly with an increase in iron content. This result is attributed to the difference in bond lengths between Si–O (1.61 Å) and Fe–O (1.88 Å). Therefore, this result supports the assumption that the iron ions are incorporated in the silicate framework.

The ^{29}Si-MAS-NMR peaks of Fe-silicates with various iron content are shown in Fig. 3. The peaks were at −113.05 ppm for a silicon-to-iron ratio of ∞, −112.68 ppm for 100, and −112.55 ppm for 40 and 20. The peak shifted to a lower magnetic field with an increase in the iron content. The linewidth is plotted as a function of the iron content of the Fe-silicate in Fig. 4. The linewidth spread proportionally with an increase in iron content. The spread of the

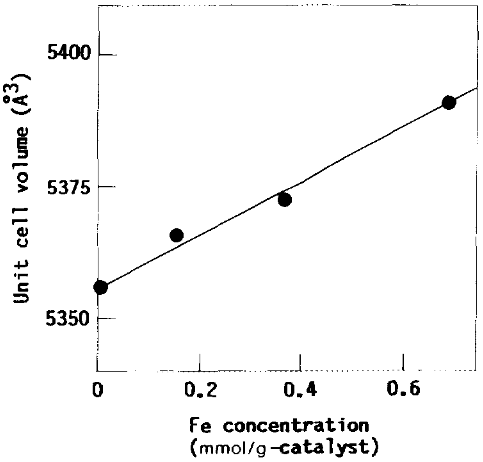

FIG. 2. Change in unit cell volume with iron content in Fe-silicate.

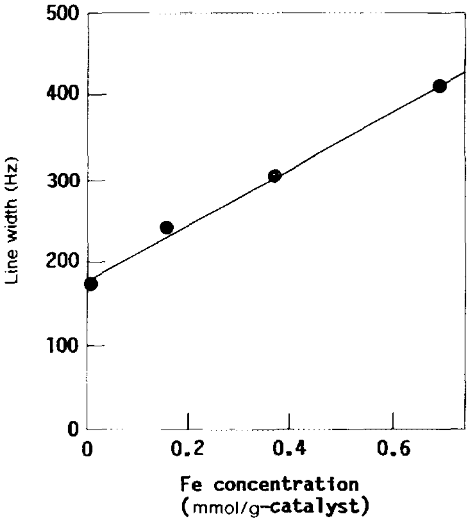

FIG. 4. Change in line width on ^{29}Si-MAS-NMR spectra with iron content in Fe-silicate.

linewidth is attributed to the effect of paramagnetic iron(III) ions. When magnetic iron oxides such as magnetite and maghemite existed as impurity phases in the Fe-silicate crystal, as shown in Fig. 4, a good linear relationship must not be obtained. Therefore, this result supports the belief that iron ions are dispersed in the silicate crystal homogeneously.

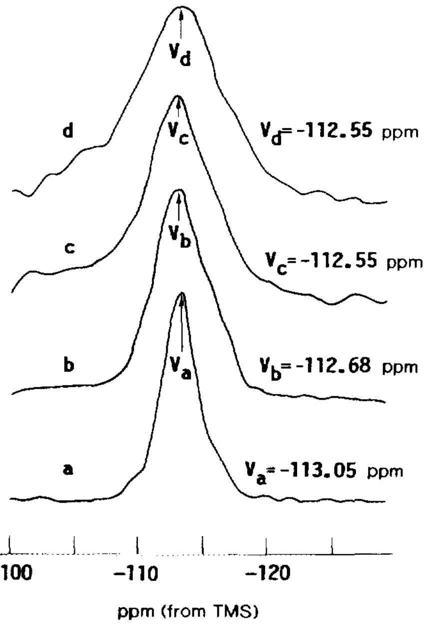

FIG. 3. ^{29}Si-MAS-NMR spectra of Fe-silicates: (a) silicalite, (b) Si/Fe = 100, (c) Si/Fe = 40, and (d) Si/Fe = 20.

The UV spectra of the as-synthesized Fe-silicates with various iron contents are shown in Fig. 5. In the spectra, the absorptions which were not observed in the UV spectra of amorphous gels before hydrothermal treatment were observed at 370, 405, and 435 nm. The strength of these absorptions became greater with an increase in iron content. As shown in Fig. 5d, these absorptions were observed on the protonated Fe-silicate, although it became difficult for these absorptions to be observed because of overlap of the absorption by the charge transfer from oxygen to iron after every calcination. In the case of iron(III) ion, the $d \rightarrow d$ transition is forbidden. However, because the absorption strength of the tetrahedral was generally greater than that of the octahedral, sharp absorptions were observed.

The IR spectra of Fe-silicates calcined after hydrothermal treatment are shown in Fig. 6. In these spectra, the absorptions originating from iron hydroxides and iron

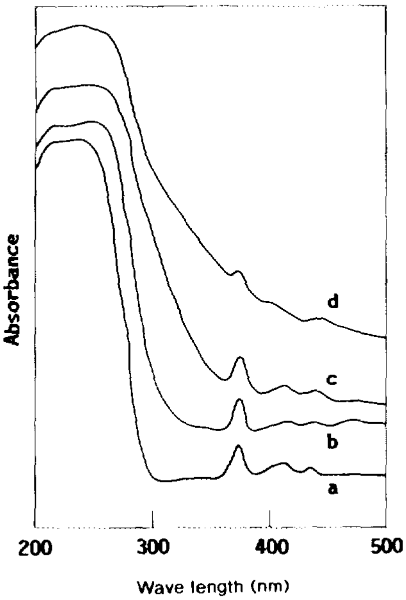

FIG. 5. UV spectra of Fe-silicates. (a) Si/Fe = 100, (b) Si/Fe = 40, (c) Si/Fe = 20, and (d) Si/Fe = 40 (as ion-exchanged).

oxides were not observed, and therefore, no evidence that iron existed as an independent phase such as iron oxides was obtained. Szostak and Thomas (*15*) reported that the absorption originated from the vibration of Fe–O–Si observed at 656 cm^{-1} in the spectra of "Ferrisilicate ZSM-5" which they synthesized. However, in the spectra of Fe-silicate samples prepared using the rapid crystallization method, the absorption originating from the Fe–O–Si vibration was not observed. Flanigen (*24*) has pointed out that the vibrations of Si–O–Si and Al–O–Si in a zeolite framework do not have a different frequency. Similar to the case of aluminum, because iron substituted in the silicate crystal is regarded as a T atom, the new absorption originating from the Fe–O–Si vibration does not appear.

The diffuse reflectance IR spectra from 3000 to 4000 cm^{-1} on Fe-silicate samples calcined after hydrothermal treatment are shown in Fig. 7. A change in the IR spectra before and after the calcination was observed. The difference between *b* and *c* in Fig. 7 is attributed to the change in silanol groups (ca. 3730 cm^{-1}) before and after the calcination. The absorption strength of the silanol groups increased with an increase in iron content, and moreover, in the spectra of silicalite, the absorption originating from the silanol groups was not observed. Thus, the formation of the silanol group by calcina-

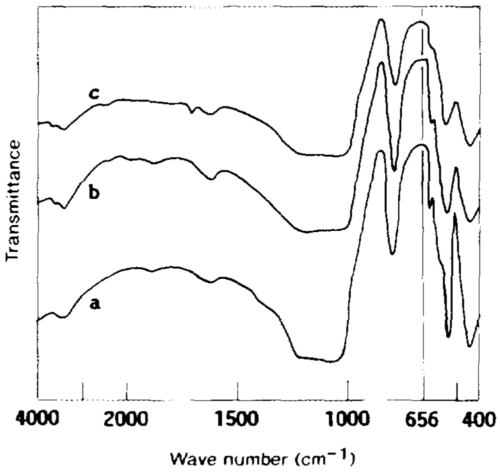

FIG. 6. IR spectra of Fe-silicates. (a) Si/Fe = 20, (b) Si/Fe = 100, and (c) Si/Fe = ∞.

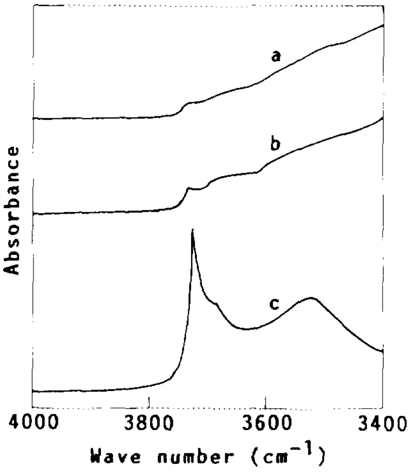

FIG. 7. Change in diffuse reflectance IR spectrum by removal of part of the iron in Fe-silicate. (a) silicalite, (b) Fe-silicate (as synthesized), and (c) Fe-silicate (as calcined).

tion was attributed to iron in silicate framework. On the other hand, it is found that the silanol group was formed because of the elimination of aluminum from the framework by means of steaming of the zeolite (*25*). In the case of Fe-silicate, the silanol groups were also formed due to the elimination of part of iron incorporated in the silicate framework by calcination of Fe-silicate. The elimination of iron from the silicate framework during the combustion removal of the organic template was the largest amount in the preparation procedures for all Fe-silicates. This was attributed to the fact that incomplete combustion occurred at the step in which the organic template was oxidized in the Fe-silicate pores. Iron in the silicate framework was then exposed to the redox cycle by the by-products having a strong reductivity such as carbon monoxide, and also to steaming of the silicate crystal with water produced by the combustion of the organic template. This result agreed with the observations that 0.5 wt% of the amount of iron in an Fe-silicate sample after hydrothermal treatment, was detected in ammonium nitrate aqueous solution and wash water from ion-exchange after calcination to remove the template (atomic ratio of silicon to iron, 12) and that the strength of the absorption owing to the charge transfer from oxygen to iron increased in the UV spectra of Fe-silicate whenever Fe-silicate was calcined.

CONCLUSION

For the Fe-silicates with iron contents up to 3.2 wt% as iron(III) oxides synthesized by the rapid crystallization method, almost all of the iron(III) ions had tetrahedral coordination and were incorporated in the silicate framework. Moreover, in the ESR spectra of Fe-silicates, the signal ($g = 4.4$) which Derouane *et al.* (*27*) assigned to substitutional iron ions was observed, and therefore, the ESR measurement also supported this conclusion (*11*). We previously pointed out that the Fe-silicate had a high diffusion coefficient which was the reason why Fe-silicate catalysts exhibited high selectivity for lower olefins in methanol conversion (*26*). The increase in unit cell volume by the isomorphous substitution on iron and the formation of silanol groups by the elimination of part of the iron results in an increase in pore diameter and an increase in the intraporous effective diffusion coefficient. This results in the depression of oligomerization by accelerating the elimination of the lower olefins produced from the reaction, thus causing the highly selective synthesis of lower olefins from methanol.

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