

NOTE

## CRYSTALLIZATION OF FERRISILICATE MOLECULAR SIEVE IN THE PRESENCE OF FLUORIDE IONS

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**Abstract**—The ferrisilicate molecular sieve analogue of the ZSM-5 was prepared from the weak alkaline medium (pH 8) in the presence of  $F^-$  ions, which was confirmed by IR, X-ray powder diffraction, EPR, and  $^{29}Si$  MAS NMR studies. The addition of  $F^-$  ion in the preparation of metallosilicate molecular sieves could reduced the pH value of the reaction mixture, and prevent from the precipitation of metal ions which are sparingly soluble in strong alkaline media.

### INTRODUCTION

In recent years, the isomorphous substitution of various metal atoms into the aluminum lattice sites in the pentasil ZSM-5 structure has aroused considerable interest. However, only a limited number of metal-substituted ZSM-5 have been prepared [1-3]. This seems to be due to the low solubility of metal ions in alkaline media, because silica-based zeolites such as ZSM-5 were generally prepared by hydrothermal crystallization of alkaline reaction mixtures (pH > 10) [4].

The ferrisilicate molecular sieve, one of the analogues of the ZSM-5, has been reported recently [5-7]. However, it has been prepared from the strong alkaline media. In this paper, the ferrisilicate molecular sieve has been prepared in the presence of  $F^-$  ions below pH 8.

### EXPERIMENTAL

Ferrisilicate was prepared by hydrothermal crystallization at 175°C for 4 days from the mixture containing colloidal silica (Ludox HS-40,  $SiO_2$  40 wt%),  $Fe(NO_3)_3 \cdot 9H_2O$ , and tetrapropyl ammonium bromide (TPABr), and  $NH_4F$ . The mole ratios of  $SiO_2/NH_4F$ ,  $SiO_2/Fe_2O_3$ , TPABr/ $SiO_2$ , and  $H_2O/SiO_2$  in the reaction mixture were 1.0, 50, 0.15, and 40 respectively. The pH of the reaction mixture was 7.5.

Elemental analyses were done by atomic absorption spectroscopy. X-ray diffraction pattern was taken on a Rigaku D/Max II-A diffractometer using  $K_\alpha$  radiation. IR spectra were recorded with an Analect 6160

Fourier Transformed Spectro-photometer applying the KBr technique. The morphology of the sample was examined by ISI model SX-30E scanning electron microscope. The EPR spectra were recorded on a Bruker model ER-200D-SRC spectrometer. The g-value was calibrated with strong pitch ( $g = 2.0028$ ) and DPPH ( $g = 2.0036$ ). The  $^{29}Si$  NMR spectrum was obtained on a Bruker AM-200 high resolution NMR spectrometer operating at a field of 4.7 T with a standard magic angle spinning (MAS) probe. MAS probe was spun at 3.8 kHz using conical Derlin rotors. The chemical shift was determined from TMS as an external reference.

### RESULTS AND DISCUSSION

It was reported that  $F^-$  ions readily reacted with silica to form complexes in aqueous media [8,9]. Mole ratios of  $SiO_2/Fe_2O_3$  and  $SiO_2/F^-$  in the prepared ferrisilicate from chemical analysis were 66.6 and 89.3, respectively. The X-ray diffraction pattern of the ferrisilicate

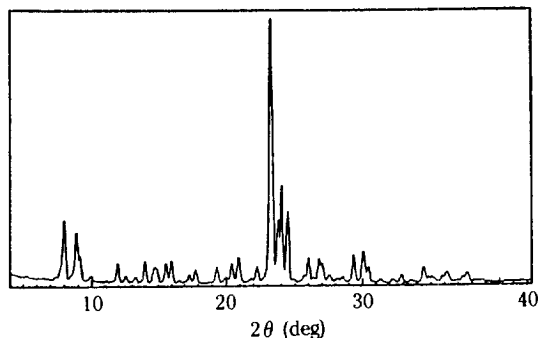


Fig. 1. X-ray diffraction pattern of ferrisilicate.

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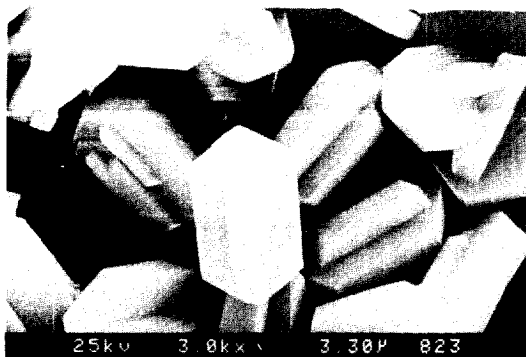


Fig. 2. SEM picture of ferrisilicate.

ilicate was the same as that of ZSM-5 (Fig. 1). Any impurity crystalline structure was not detected from the X-ray diffraction pattern. The color and morphology of ferrisilicate prepared by this method was white and showed twinned single crystals measuring  $6 \times 6 \times 12 \mu$  (Fig. 2.)

Fig. 3 showed the IR spectra of the ferrisilicate and ZSM-5 prepared in this work. All the bands of ferrisilicate were slightly shifted to lower frequencies as compared with those of ZSM-5. In previous IR study [10] the band of the symmetric Si-O-Si stretching vibrations within the ZSM-5 structure was observed at  $798 \text{ cm}^{-1}$  and was not differentiated from that of symmetric Si-O-Al stretching vibrations because of the small difference in the mass between Al atom and Si atom. However, it can be expected that the symmetric Si-O-Fe stretching vibrations are observed at the lower wavenumber than the Si-O-Si vibrations because of Fe atom heavier than Al atom. Szostak and Thomas [7] reported that a weak band at  $656 \text{ cm}^{-1}$  in the IR study on their ferrisilicates ( $\text{SiO}_2/\text{Fe}_2\text{O}_3 = 15\text{-}30$ ) prepared in the strong alkaline media was due to the symmetric Si-O-Fe stretching vibrations. The IR spectrum of our ferrisilicate showed a weak band at  $650 \text{ cm}^{-1}$ , which can be assigned to the symmetric Si-O-Fe stretching vibration. This result confirmed the presence of iron atom in the tetrahedral sites of the ZSM-5 structure. The most strong band around  $1100 \text{ cm}^{-1}$  is assigned to the asymmetric stretching vibrations of T-O bond, where T is Al or Si atom [11]. However, this band [Fig. 3(b)] was observed at  $1085 \text{ cm}^{-1}$  with a shoulder around  $1030 \text{ cm}^{-1}$ , which was shifted to lower frequency and was splitted into doublet for ferrisilicate as compared with ZSM-5 when Al atom is replaced with Fe atom heavier than Al atom. This seems to be due to the substitution of Fe atom into the ZSM-5 structure, resulting in that the band of  $\text{TO}_4$  units having Fe atom was shifted to the lower wavenumber than that of  $\text{TO}_4$  units having Si atom because of longer Fe-O bond distance ( $1.84 \text{ \AA}$ ) as

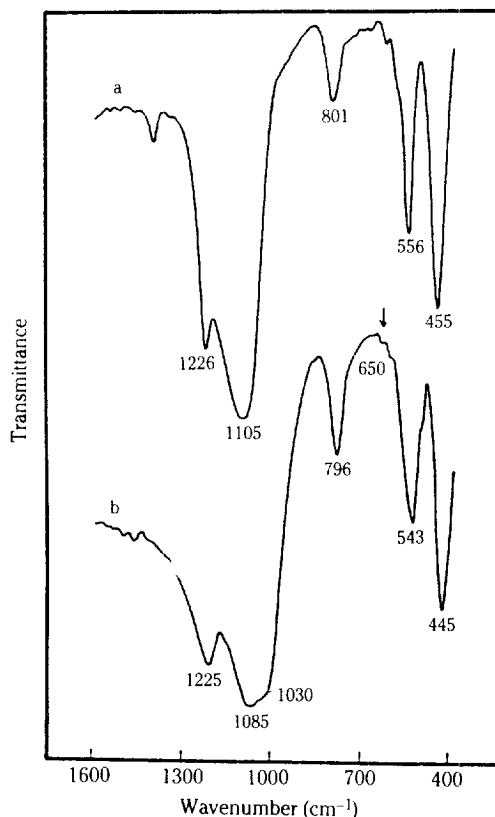


Fig. 3. IR spectra of (a) ZSM-5 and (b) ferrisilicate.

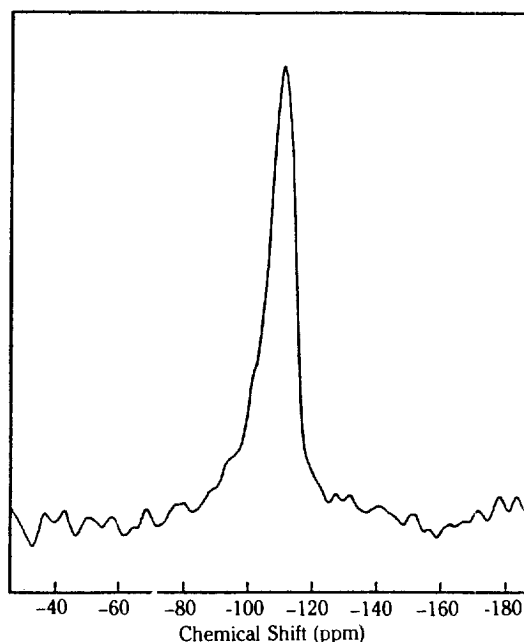


Fig. 4.  $^{29}\text{Si}$  MAS NMR spectrum of ferrisilicate.

compared with the Si-O bond distance (1.60 Å).

Further evidences for the substitution of iron atom into the ZSM-5 structure were provided by EPR and  $^{29}\text{Si}$  NMR results. The band at  $g = 4.3$  in the EPR spectrum indicated the presence of the  $\text{Fe}^{+3}$  ions tetrahedrally coordinated in the ZSM-5 structure [12,13]. The  $^{29}\text{Si}$  NMR band of the prepared ferrisilicate as shown in Fig. 4 appeared at  $-109.5$  ppm with a shoulder around  $105$  ppm. Ball et al. [12] reported that the half-band width of  $^{29}\text{Si}$  NMR band increased with increasing the paramagnetic ion content in the zeolite structure. The half-band width ( $=380$  Hz) of the band at  $-109.5$  ppm also indicated the presence of paramagnetic iron in the ZSM-5 structure. A shoulder around  $-105$  ppm in the NMR spectrum of ferrisilicate is closely to the value for  $\text{Si}(1\text{Al}, 3\text{Si})$  in the ZSM-5 and can be tentatively assigned to  $\text{Si}(1\text{Fe}, 3\text{Si})$  [12].

Application of this method,  $\text{NH}_4\text{F}$  were added to the reaction mixture, to preparing metallosilicates has two advantages. The major advantage is that metal ions, sparingly soluble in the strong alkaline medium, can be isomorphously incorporated into the zeolite framework in the mild pH condition. The minor is that it is possible to prepare the  $\text{NH}_4^+$  form of the metallosilicates directly. Substitution of the other transition metals in the presence of  $\text{F}^-$  ions is being prepared in our laboratory.

#### ACKNOWLEDGEMENT

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