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Structural Investigation on Crystallization of ZSM-5-Type Ferrisilicate

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Hydrothermal synthesis of ferrisilicate of ZSM-5 structure was followed by FT-IR, XRD, XPS, XRF, TG, and EXAFS. It was found that the micro-structure around Fe formed before instantaneous crystallization of the bulk.

It is well-known that Fe is isomorphously substituted for Si in the lattice of zeolites.[1,2] Iron in hydrothermally synthesized zeolites is atomically dispersed. Such an ultra-high dispersion of Fe could not be obtained by conventional impregnation techniques. Ferrisilicate of ZSM-5 structure, thus prepared, has weaker acid sites than ZSM-5 (Al-silicate),[3,4] and catalyzes selective conversion of methanol to light olefins.[5] Moreover, the Fe particles in the silicate matrix are thermally stabilized, and show high selectivity for light olefins in the Fischer-Tropsch (F-T) reaction at an extraordinary high temperature,[6] at which conventional F-T catalysts are easily deactivated by coking. In order to improve the catalytic properties, a new generation ferrisilicate is to be designed at atomic level. For this purpose, it is of great importance to reveal how the ferrisilicate is crystallized in detail, and which stages should be precisely controlled. In the present investigation, the crystallization was followed by FT-IR, XRD, XPS, X-ray fluorescence analysis (XRF), TG and EXAFS, and the micro-structure around Fe is discussed.

Appropriate amounts of colloidal silica, ferric nitrate, tetrapropylammonium (TPA) bromide, sodium hydroxide, and distilled water were mixed together to form ferrisilicate gel having the following compositions; SiO_2/Fe_2O_3 = 60, SiO_2/TPABr = 10, SiO_2/OH = 10. The gel was autoclaved at 433 K. The crystallinity of the products was evaluated by XRD intensity of a spacing, d(501). The bulk and surface were analyzed by XRF and XPS, respectively. The infrared spectra were recorded with diffuse reflection method. Thermogravimetric analysis was carried out from 323 to 973 K with a heating rate of 10 K/min in an air flow. The Fe K-edge EXAFS spectra were measured at about 20 K. The EXAFS measurements were conducted at Photon Factory (BL-7C) of National Laboratory for High Energy Physics.

The crystallization profiles of ferrisilicates are depicted in Fig. 1. The XRD intensities indicate that the crystallization was completed during a short period of time after 16 hours of hydrothermal reaction; the silicate was almost amorphous within 16 h, and was almost completely crystalline after 16.5 h. The XRF results show that the Fe-content (Fe_2O_3/SiO_2) decreased immediately after crystallization, suggesting that a high-silica ferrisilicate was crystallized at first.

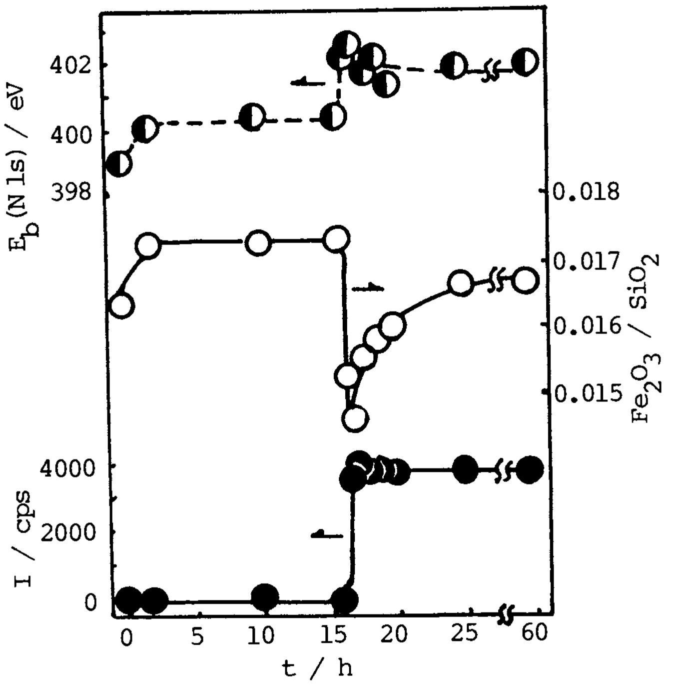

Fig. 1. Crystallization Profiles by XRD Intensity (●), Fe-Content(○), and XPS N 1s Binding Energy (◐) of Ferrisilicates.

The FT-IR spectra are shown in Fig. 2. By crystallization, a band suddenly appeared at 1180 cm^{-1}, which was assigned to a lattice vibration of pentasil-type silicate.[7] The shapes of O-H bands also changed discontinuously by crystallization. These results support the fact that the bulk crystallization was completed during a short period of time.

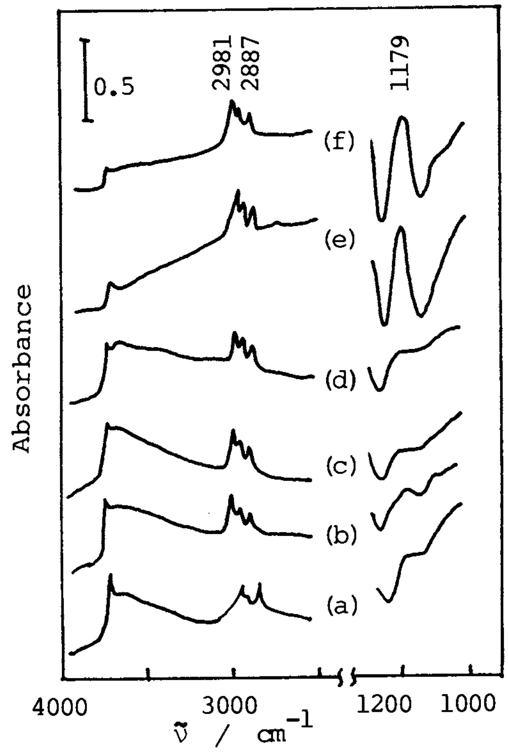

Fig. 2. FT-IR Spectra of Ferrisilicates after Hydrothermal Reaction of (a) 0 h, (b) 2 h, (c) 10 h, (d) 16 h, (e) 16.5 h, and (f) 20 h.

The C-H bands were, on the contrary, transfigured in a very early stage of hydrothermal reaction, within 2 h, and were almost unchanged any more. This result suggests the possibility that TPA cation was occluded within a precursor to form a clathrate like structure[8] in the early stage of crystallization, even if the bulk was not yet crystallized. The XPS results indicated that the N 1s binding energies of TPA shifted to high energy side in two stages, as shown in Fig. 1; about 1 eV in the early stage of hydrothermal reaction, and another 1.5 eV at crystallization. This fact suggests that the form of occluded TPA might change in these two stages.

The TG profiles are illustrated in Fig. 3. Two sharp peaks were observed at 703 K and 728 K on the samples after crystallization. These peaks were assigned to the combustion of TPA at the ion-exchangeable sites and at the channel intersections of the ferrisilicate.9) The hydrothermal products before 16 h showed two broad peaks at about 590 and 720 K. The latter peak position is similar to that of crystalline ferrisilicate, implying that TPA was interacting with silicate gel, even before bulk crystallization. Another broad peak at lower temperature may correspond to TPA weakly interacting with silicate gel. The starting gel mixture (a) did not show any of these peaks, implying that TPA was free from gel mixture at first. It is supposed from these results that TPA was occluded in a precursor of ferrisilicate at an early stage of reaction to form clathrate-like structure.

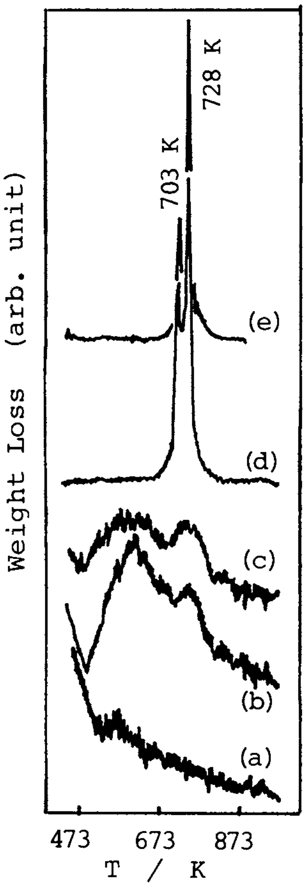

Fig. 3. Thermogravimetric Analysis of Ferrisilicates after Hydrothermal Reaction of (a) 0 h, (b) 2 h, (c) 16 h, (d) 16.5 h, and (e) 20 h.

The Fourier transforms of Fe K-edge EXAFS with phase-shift correction are depicted in Fig. 4. The spectrum of the gel mixture showed two peaks at 2.0 Å and 3.2 Å, similar to those of α-FeO(OH), assigned to Fe-O and Fe-O-Fe, respectively. By hydrothermal reaction of 2 h, these peaks shifted to 1.9 Å and 3.1 Å, respectively, and another peak appeared at 3.6 Å. The intensity of the peak at 1.9 Å increased by further reaction, whereas that at 3.1 Å decreased. During the hydrothermal reaction up to 16 h, the positions nor the intensities of the peaks hardly changed. By crystallization, the intensities of the peaks at 1.9 Å and 3.6 Å increased discontinuously, and another peak appeared at 4.0 Å. An increase of the peak intensities suggests that an increase of the configurational symmetry around Fe.

It is reported that the Fe atoms in ferrisilicate of ZSM-5 structure are homogeneously dispersed in tetrahedral framework sites of silica matrix.10) Therefore the peaks at 3.1 Å, 3.6 Å, and 4.0 Å may be assigned to Fe-O-Si. The shifts of peak positions before bulk crystallization suggest that the second neighbors of Fe atom were turned into Si, instead of Fe, to form Fe-silicate in a very early stage. Similar changes in EXAFS spectra by forming metal-silicate are also reported in a Ni/SiO_2 system.$^{11)}$

In conclusion, it is suggested from these results that the micro-structure of ferrisilicate precursor containing TPA was formed in the early stage of hydrothermal reaction, before instantaneous crystallization of the bulk, and that the regularity of local structure around Fe increased with the reaction time. Therefore, the control of the first step of micro-structure formation, as well as the crystallization, will be a key-technology for controlling the regularity of ferrisilicate.

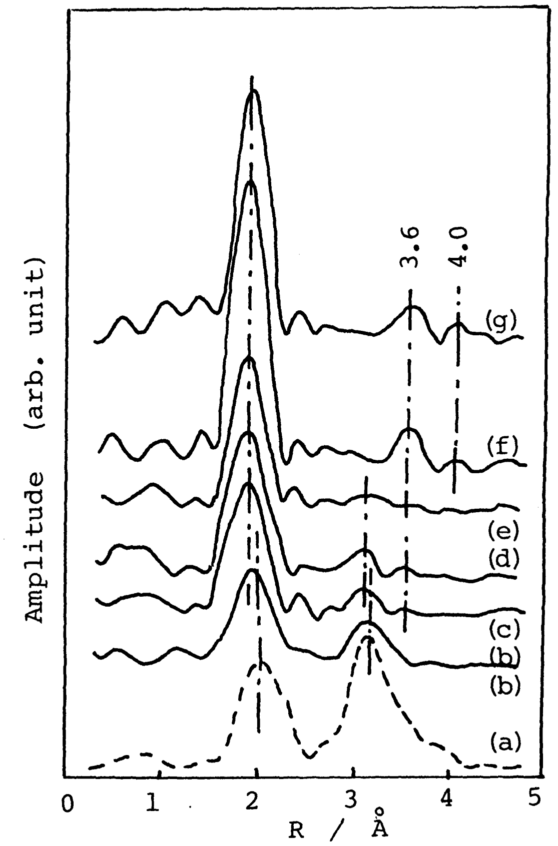

Fig. 4. Fourier Transforms of Fe K-Edge EXAFS of (a) α-FeOOH, and Ferrisilicates after Hydrothermal Reaction of (b) 0 h, (c) 2 h, (d) 10 h, (e) 16 h, (f) 16.5 h, and (g) 20 h.

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