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**Preparation of Nano-Crystalline MFI Zeolite via Hydrothermal Synthesis in
Water/Surfactant/Organic Solvent using Fumed Silica as the Si Source**

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Abstract

The preparation of nano-crystalline MFI zeolites (Silicalite-1 and ZSM-5) was carried out by hydrothermal synthesis in a water/surfactant/organic solvent using fumed silica and aluminum sulfate as the Si and Al source, respectively. It was confirmed that the surfactant in the solution affected the nucleation rate of the MFI zeolite. Moreover, the crystal size of the MFI zeolite decreased with increasing surfactant concentration, and nanometer-sized MFI zeolites was obtained at a surfactant concentration of 0.25 ~ 0.5 mol/L. The successful preparation of MFI zeolite nanocrystals was ascribed to the stabilization of the MFI zeolite precursors and/or crystals by the adsorbed surfactant on their surface. This method was applied to the preparation of nano-crystalline ZSM-5 zeolite. ZSM-5 zeolite with a crystal size of approximately 50 nm was obtained. The nano-crystalline ZSM-5 zeolite was well-crystallized without octahedral Al atoms in the external framework, and exhibited almost the same acidity as a reference ZSM-5 zeolite.

Key words: Nano-crystalline zeolite, MFI, Surfactant, Emulsion

1. Introduction

Zeolites, crystalline aluminosilicates, have attracted significant attention from numerous researchers due to their thermal stability, strong acidity, high surface area, and presence of sub-nanometer spaces within their pores. The sizes of the intracrystalline pores and nanospaces, depending on the type of zeolite providing the framework, are almost the same as the molecular diameters of lighter hydrocarbons. Moreover, strong acid sites exist on the nanopore surfaces, enabling the zeolites to be used as shape-selective catalysts in industrial applications such as fluid catalytic cracking of heavy oil, isomerization of xylene and synthesis of ethylbenzene. However, the crystal size of zeolites is much larger than the micropore size of zeolites exhibiting a molecular sieving effect. A small micropore size results in a low diffusion rate of reactant hydrocarbon molecules leading to limitations of the reaction rate, low selectivity of intermediates, and coke formation followed by a short catalyst life time. Faster mass transfer is required to avoid these serious problems. Two primary strategies have been proposed; one is the formation of meso-pores within zeolite crystals [1–4], and the other is the preparation of nano-crystalline zeolites [5–17].

In nano-crystalline zeolite, the diffusion length for reactant hydrocarbons, assignable to the crystal size, decreases. On the other hand, the outer surface area of the crystal increases with decreasing crystal size. The increase in the outer surface area of a zeolite nanocrystal is effective for improving catalytic activity for isomerization/cracking of hexane and alkylation of phenol [18], and dehydration of glycerol [19]. Since these favorable properties for heterogeneous catalysts appear in nano-crystalline zeolites, preparation methods for several types of zeolite nanocrystals have been reported and reviewed [20, 21]. Recently, there has been growing interest in the synthesis of nano-crystalline zeolites in the presence of a surfactant [18, 22] including water/surfactant/organic solvent mixtures [23, 24]. We successfully prepared MFI- and MOR-type zeolite nanocrystals via hydrothermal synthesis in a water/surfactant/organic

solvent (emulsion method) [25–27]. The non-ionic surfactants adsorbed on the surface of the zeolite precursors likely induced the formation of zeolite nuclei, which enhanced zeolite nucleation in these cases. Moreover, size-controlled synthesis of nano-crystalline MFI and MOR zeolites can be achieved by changing the surfactant concentration in the solutions.

In the emulsion method reported previously, metal-alkoxide compounds are used as the Si and Al sources, and hydrolysis of these alkoxide compounds is carried out in an alkaline water solution containing structure-directing agents (SDA) to form the complexes of Si-Al-SDA. After adding a water solution containing the Si-Al-SDA complex to the surfactant/organic solvent, the zeolite precursor can be stabilized by the adsorption of surfactants in water/surfactant/organic solvent under hydrothermal conditions. In contrast, fumed silica is used as the Si source in conventional zeolite preparation methods. Unlike the metal-alkoxide which is hydrolyzed in the alkaline water solution containing SDA, the fumed silica is first dissolved in an alkaline water solution under hydrothermal conditions, wherein the complex of the SDA and dissolved silica is formed. In this study, fumed silica was used as the Si source, and the preparation of MFI-type zeolite nanocrystals was carried out by hydrothermal synthesis in a water/surfactant/organic solvent (emulsion method). First, in order to investigate the contribution of the surfactant to nano-crystalline zeolite synthesis, the effects of surfactant concentration on the crystallinity and crystal size of Silicalite-1 were examined. These properties were then compared with those of Silicalite-1 prepared by a conventional method without a surfactant. In addition, the emulsion method was applied to the synthesis of ZSM-5 zeolite nanocrystals, and the effect of the molar ratio of water to surfactant (W/S values) on the crystal size of the ZSM-5 zeolite was investigated.

2. Experimental

2.1. Zeolite synthesis by the emulsion method

MFI zeolite (Silicalite-1 and ZSM-5) nanocrystals were prepared via hydrothermal synthesis in a water/surfactant/organic solvent. Fumed silica (Wako, Silicon oxide, purity 99+%, particle size 12 nm) and tetrapropylammoniumhydroxide (TPAOH) (Wako, 10% aqueous solution) were employed as the silica source and structure-directing agent (SDA), respectively. The molar ratio of Si to SDA (Si/SDA) and the Si concentration in water were 3.3 and 1.6 mol/L, respectively. To prepare ZSM-5 zeolite, aluminum sulfate and sodium chloride were added to the water solution as the Al source and counter cations, respectively, with Si/Al molar ratios of 50, 80, and 200, and an Na/Al ratio of 3. The starting water solution was stirred for 24 h. The water solution (4~8 cc) was slowly added to the surfactant-organic solvent (70 cc), and the mixture was magnetically stirred at 323 K for 1 h. Polyoxyethylene(15)oleylether (Nikko Chemical, denoted as O-15 hereafter) and cyclohexane (Wako, C₆H₁₂) were employed as the surfactant and organic solvent, respectively. The concentration of O-15 ([O-15]) in the surfactant/organic solvent was changed within the range of 0.0 to 0.75 mol/L, which affected the molar ratio of water to surfactant (W/S) in the solution. The mixture was then placed in a Teflon sealed stainless steel bottle (100 cc bottle), heated to 393 K, and then held at this temperature for 6 ~ 72 h with stirring to yield MFI zeolite nanocrystals. This method is referred to hereafter as the emulsion method. For comparison, the water solution without surfactant/organic solvent was poured into a Teflon-sealed stainless bottle and the preparation was carried out under the same hydrothermal condition (conventional method). The precipitate of the Silicalite-1 nanocrystals thus obtained was centrifuged, washed thoroughly with 2-propanol, dried at 373 K overnight, and then calcined under an air flow at 773 K to remove the surfactant and the SDA. After the air calcination, the weight of the sample was measured to calculate the yield of zeolite, based on the theoretical MFI and NaZSM-5 weight calculated from the number of Si and Al molecules in the water phase. The reference MFI-type zeolite (Silicalite-1 and ZSM-5) was prepared via hydrothermal synthesis at a high temperature of 423 K for 50 h (conventional method) to obtain

fine MFI crystals.

2.2. Characterization

The morphology and crystallinity of the obtained materials were investigated using a field-emission scanning electron microscope (FE-SEM; JEOL JSM-6500F) and an X-ray diffractometer (XRD; JEOL JDX-8020). Crystal sizes of approximately 300 zeolite crystals were measured from the SEM photographs to obtain the crystal size distribution. The N₂ adsorption and desorption isotherm of the obtained materials was measured (BEL Japan, Inc., Belsorp mini), and the total surface area, external surface area and micropore volume were calculated by the BET and t-methods. The chemical bonds of the aluminum atoms were characterized by ²⁷Al-NMR (Bruker MSL400). The acidity of the obtained samples was evaluated by the ac-NH₃-TPD method [28]. In the TPD experiment, the carrier gas was 1.0 % NH₃ with balance He, the heating rate was 5 K min⁻¹, and the temperature range was 373 to 823 K. The desorption of NH₃ molecules from the acid sites of the zeolite was measured under a 1.0% NH₃-He atmosphere, so that the TPD profile could be measured under complete adsorption equilibrium conditions, which is referred to as the ac-NH₃-TPD method.

3. Results and Discussion

3.1. Preparation of zeolite nanocrystals in water/surfactant/organic solvent

Silicalite-1 samples were prepared in a water/surfactant/organic solvent (emulsion method) under the following conditions; the hydrothermal temperature was 393 K, concentration of surfactant in cyclohexane was 0.5 mol/L. The concentration of Si in water was 1.6 mol/L, and the molar ratio of water (8 cc) to surfactant (W/S) was 10. Silicalite-1 samples were also

prepared by a conventional method without a surfactant/organic solvent for comparison. Figures 1 and 2 show the X-ray diffraction (XRD) patterns and SEM images of the obtained samples respectively with different hydrothermal synthesis times.

In the sample prepared by the conventional method, an amorphous pattern was observed for a hydrothermal time of 24 h, and peaks corresponding to MFI zeolite were observed from the samples at 50 h and 72 h, indicating that the nucleation of MFI zeolite occurred after the hydrothermal time of 24 h. In contrast, the sample prepared by the emulsion method at 12 h showed peaks corresponding to MFI zeolite, and the intensity of the peaks increased with increasing hydrothermal times. The difference in diffraction patterns of the samples prepared by both methods resulted from the difference in the nucleation rate of the zeolites. Since the nucleation of zeolite is enhanced in the emulsion method, as we have reported previously [25–27], the nucleation occurred during the early stage of hydrothermal synthesis between 6 to 12 h, and the growth of the crystals proceeded, leading to an increase in intensity of the diffraction peaks.

Though the XRD patterns of these samples showed peaks corresponding to MFI zeolite, the difference in nucleation rate affected the morphology of the samples as shown in Figs. 2. From Figs. 2(a) and 2(b), crystalline zeolites larger than 500 nm and smaller than 100 nm were observed in the samples prepared by the conventional method. This broad size distribution resulted from simultaneous nucleation and crystal growth. Moreover, as shown in Fig. 2(a), two types of morphology were observed, particles with (a-1) crystalline and (a-2) spherical shapes. Since crystallization was not completed at 50 h in the conventional method, it was considered that amorphous silica species were deposited on the surface of Silicalite-1 crystals to form the spherical particles.

In contrast, in the samples prepared by the emulsion method at 12 h, nanocrystals with the sizes of approximately 30-40 nm could be observed, and the sizes gradually increased with increasing hydrothermal times. Since the nucleation rate in the emulsion method was much

higher than that in the conventional method, it was considered that the nucleation of Silicalite-1 was completed by the hydrothermal time of 12 h, followed by crystal growth, leading to mono-dispersed Silicalite-1 nanocrystals. This result is in good agreement with the XRD patterns. The obtained Silicalite-1 yields at hydrothermal synthesis times of 12, 24 and 50 h were 62%, 66% and 78%, respectively. Figure 3 shows the size distribution of the Silicalite-1 nanocrystals at 50 h (Fig. 2(e)). Approximately 73% of the Silicalite-1 nanocrystals fell in the range 40 to 60 nm, and the average crystal size was approximately 50 nm.

N₂ adsorption isotherms of the samples by both methods with different hydrothermal times are shown in Fig. 4. The surface areas and micropore volumes calculated by the BET method and t-method, respectively, are listed in Table 1. As shown in Fig. 4(a), the sample prepared by the conventional method for 24 h exhibited large N₂ adsorption around P/P_0 of 0.2~1.0 with a small micropore volume of approximately 0.03 cm³/g. From X-ray diffraction analysis and the N₂ adsorption isotherm, it was apparent that the sample was amorphous silica. As the hydrothermal synthesis proceeded, the amount of N₂ adsorption around P/P_0 of 0.2~1.0 was significantly decreased and the micropore volume increased. The silicalite-1 sample obtained by the conventional method at 50 h showed that the amount of N₂ adsorption around the relative pressure P/P_0 of 0.0 was larger than that of the reference Silicalite-1, which was confirmed by the micropore volume listed in Table 1. It was considered that the amorphous layer was formed on the surface of the Silicalite-1 crystal as shown in Fig. 2(a), and hence the large micropore volume was ascribed to the micropores of Silicalite-1 as well as amorphous silica. At 72 h, the N₂ adsorption isotherm agreed well with that of the reference sample, and the micropore volume also reached almost the same value as the reference sample.

In contrast, as shown in Fig. 4(b), the sample prepared by the emulsion method at 12 h exhibited a steep increase in the amount of N₂ adsorption around P/P_0 of 0.0, and the micropore volume reached 0.13 cm³/g. As the hydrothermal synthesis proceeded to 24 and 50 h, the adsorption isotherms were almost the same as that of the reference Silicalite-1. The micropore

volumes increased to approximately 0.15~0.17 cm³/g, whereas the external surface areas slightly decreased from 80 to 60 m²/g. These slight changes in micropore volumes and external surface areas resulted from the growth of Silicalite-1 nanocrystals shown in Fig. 2.

From the above discussion, the major difference between the conventional and emulsion methods was the nucleation rate of zeolite. In the conventional method, though crystal growth was completed at 72 h, nucleation and crystal growth occurred simultaneously, leading to the broad size distribution of zeolite. In contrast, in the emulsion method, the nucleation rate was much higher than that in the conventional method, and the nucleation of Silicalite-1 was likely completed early during the hydrothermal time, followed by crystal growth, leading to the formation of mono-dispersed Silicalite-1 nanocrystals. The silicalite-1 sample prepared by the emulsion method at 72 h showed a lower amount of N₂ adsorption around P/P_0 of 0.0 than that of the reference Silicalite-1. This was ascribed to re-dissolution of Silicalite-1 crystals. Accordingly, the hydrothermal synthesis time was set at 50 h subsequently in order to avoid *Ostwald ripening*.

3.2. Effect of the surfactant concentration

It was hypothesized that the surfactant in the solution affected the nucleation and crystal growth of Silicalite-1 nanocrystals, hence the effects of surfactant concentration on the morphology and crystallinity of the Silicalite-1 were investigated. Silicalite-1 samples were prepared by the emulsion method with different surfactant concentrations [O-15]. The hydrothermal temperature and time were 393 K and 50 h, respectively, and the surfactant concentration was changed in the range of 0~0.75 mol/L. The concentration of Si in water was 1.6 mol/L, and the molar ratio of water (8 cc) to surfactant (W/S) was changed in the range of 7~52 in accordance with the surfactant concentration.

Figures 5, 6 and 7 show the effects of surfactant concentration on the X-ray diffraction

patterns, morphology and N₂ adsorption isotherms of the prepared samples, respectively. The SEM image of the sample with surfactant concentration of 0.5 mol/L is shown in Fig. 2(d). Though the X-ray diffraction patterns of these samples showed peaks corresponding to MFI zeolite, the morphology and crystal sizes shown in Fig. 6 are different, depended on the surfactant concentration regardless of the composition of the water solution, including the case wherein the concentrations of SDA and the silica source are the same.

The crystal size of Silicalite-1 synthesized without a surfactant was approximately 700 nm, as shown in Figs. 6(a). At the low surfactant concentration of 0.1 mol/L in the emulsion method, a large amount of debris on Silicalite-1 with a large crystal size was observed. The large crystal size was attributed to the low nucleation rate of Silicalite-1. Moreover, since the amount of nitrogen adsorption around P/P_0 of 0.0, which was indicative of the micropore volume, was lower than that of the reference Silicalite-1, it was considered that the crystallinity of the sample was insufficient, which was attributed to the debris being amorphous silica.

As the surfactant concentrations increased above 0.25 mol/L, the crystal size decreased, and the average size of the Silicalite-1 nanocrystal was approximately 50 nm. This was ascribed to an increase in the nucleation rate. The formation of nanocrystalline zeolite was also confirmed by the large external surface area of 96.8 m²/g indicated in Table 1 as well as the increase in the amount of N₂ adsorption around P/P_0 of 0.2~1.0, which resulted from the adsorption of N₂ on the mesopore surfaces among crystals. In contrast, the sample obtained for the surfactant concentration of 0.75 mol/L exhibited a small external surface area of 21.1 m²/g, which was ascribed to marked aggregation of Silicalite-1 nanocrystals shown in Fig. 6(d). Accordingly, the appropriate surfactant concentration to obtain mono-dispersed Silicalite-1 nanocrystals was decided to be 0.25~0.5 mol/L.

In the emulsion method, the increase in surfactant concentration was effective for preparing Silicalite-1 nanocrystals due to enhancement of zeolite nucleation. The dependence of the crystal size on the surfactant concentration is in agreement with our previous results for the

preparation of Silicalite-1 [26] and MOR zeolite nanocrystals [27] using tetraethylorthosilicate as a Si source. In contrast, the fumed silica which was used as the Si source in this study, unlike the metal-alkoxide being hydrolyzed in water solution, dissolves in an alkaline water solution to form a complex of Si-Al-SDA, so that higher hydrothermal temperatures as well as longer hydrothermal synthesis times are required to prepare well-crystallized MFI nanocrystals compared to our previous work [25, 26].

3.3. Preparation of ZSM-5 nanocrystals

The above discussion indicates that nano-crystalline Silicalite-1 can be prepared in a water/surfactant/organic solvent (emulsion method) at a surfactant concentration of 0.5 mol/L. This method was applied to the preparation of nano-crystalline ZSM-5 zeolites. Aluminum sulfate as the Al source was added to the water solution. The hydrothermal conditions used were: Si/Al ratio; 50, 80, and 200, hydrothermal synthesis time; 50 h, hydrothermal temperature; 393 K. Moreover, the effects of the molar ratio of water to surfactant *W/S* on the morphology of the ZSM-5 zeolite were also examined, since it was revealed that the surfactant in the solution affects the morphology and crystal sizes of Silicalite-1. A reference ZSM-5 zeolite sample with an Si/Al ratio of 80 was also prepared at 423 K for 50 h by a conventional method.

Figures 8 and 9 show the X-ray diffraction patterns and FE-SEM photographs for the ZSM-5 samples, respectively. Though the X-ray diffraction patterns showed the peaks corresponding to MFI zeolite, the morphologies of these ZSM-5 zeolites were different. Figure 9(a) shows aggregation of nanocrystals in the ZSM-5 zeolite with the Si/Al ratio of 50. As the concentration of Al increased during the preparation of ZSM-5 with a low Si/Al ratio, this caused excessive enhancement in the crystallization rate of zeolite, leading to the simultaneous nucleation and crystal growth and thereby aggregating large particles of ZSM-5, as shown in Fig. 9(a). As

shown in Figs. 9(b) and 9(c), ZSM-5 nanocrystals with a size of approximately 50 nm could be obtained by the emulsion method. At W/S of 10, the crystal sizes of the ZSM-5 zeolite increased to approximately 100-150 nm, as seen in Figs. 9(d) and 9(e), implying that the crystals sizes could be changed by varying the water/surfactant (W/S) ratio regardless of the same concentrations of Si and Al sources and SDA in the water solution. In the preparation of Silicalite-1 nanocrystals without Al, Silicalite-1 nanocrystals with a size of 50 nm could be obtained at a W/S of 10 (Fig. 2), whereas much more surfactant was required to synthesize nano-crystalline ZSM-5 zeolites, because the Al in the solution likely accelerates the crystallization rate.

Figure 10 shows the *ac*-NH₃-TPD [28] profile of the ZSM-5 nanocrystal with an Si/Al ratio of 80. The NH₃ desorption peak observed at temperatures above 600 K is associated with strong acid sites. The TPD profile of the reference ZSM-5 with an Si/Al ratio of 80 is also shown for comparison. The reference ZSM-5 and the ZSM-5 nanocrystal with an Si/Al ratio of 80 prepared by the emulsion method exhibited almost the same peak position and area, indicating that these ZSM-5 zeolites possessed almost the same acidity regardless of the different crystal morphology. When aromatic chemicals with larger molecular diameters than the pore size are adsorbed on the ZSM-5 zeolites, these molecules are adsorbed on acid sites located on or near the outer surface of the crystals, where the dependence of the adsorption properties on the crystal sizes can be observed [29, 30]. In contrast, since the molecular size of NH₃ is smaller than the pore size of the ZSM-5 zeolite, the NH₃ molecules are adsorbed on all the acid sites located on the outer surface as well as inside the pores, followed by adsorption equilibrium of NH₃ on the acid sites. Accordingly, ZSM-5 zeolites with the same Si/Al ratio and different crystal sizes exhibited almost the same TPD profiles.

To confirm the positions of Al in the zeolite lattice, ²⁷Al-NMR spectra of the zeolites were measured. Figure 11 shows the ²⁷Al-NMR spectra of the ZSM-5 nanocrystal prepared by the emulsion method and the reference ZSM-5. The presence of a signal resonance centered at

approximately 55 ppm is assigned to the tetrahedral Al atoms located in the internal framework of the zeolite. A signal resonance at 0 ppm is characteristic of the octahedral Al atoms located in the external framework of the zeolite. The ^{27}Al -NMR spectrum of ZSM-5 nanocrystals prepared by the emulsion method only indicated the presence of tetrahedral Al atoms. The ^{27}Al -NMR spectrum of the ZSM-5 nanocrystal was in good agreement with the ^{27}Al -NMR spectrum of the reference ZSM-5. This result confirmed the same acidity of the ZSM-5 zeolites with different crystal sizes.

4. Conclusions

Nano-crystalline MFI zeolites (Silicalite-1 and ZSM-5) were prepared by hydrothermal synthesis in a water/surfactant/organic solvent mixture (emulsion method) using fumed silica and aluminum sulfate as the Si and Al sources, respectively. It was confirmed that the surfactant in the solution affected the nucleation rate. Moreover, as the surfactant concentrations increased, the crystal size of the MFI zeolite decreased and nanometer-sized MFI zeolites were obtained at a surfactant concentration of 0.5 mol/L. The successful preparation of the MFI zeolite nanocrystals was ascribed to stabilization of the MFI zeolite precursors and/or crystals by the adsorbed surfactant on the surface.

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Fig. 1. The effects of hydrothermal synthesis time on the crystallinity of samples prepared in water (conventional method) and in a water/surfactant/organic solvent (emulsion method) at a hydrothermal temperature of 393 K. Concentrations of the surfactant in an organic solvent and that of Si in water were 0.5 and 1.6 mol/L, respectively.

Fig. 2. FE-SEM micrographs of silicalite-1 samples prepared by the conventional method (a, b) and the emulsion method (c ~ e) with different hydrothermal times. The Si concentration in water was 1.6 mol/L and the molar ratio of water to surfactant (W/S) was 10.

Fig. 3. Crystal size distributions of Silicalite-1 prepared by the emulsion method at a hydrothermal synthesis time of 50 h. The concentrations of Si in water and the surfactant in an organic solvent were 1.6 and 0.5 mol/L, respectively.

Fig. 4. The effects of hydrothermal synthesis time on nitrogen adsorption isotherms of samples prepared by (a) conventional and (b) emulsion methods. The concentrations of Si in water and the surfactant in an organic solvent were 1.6 and 0.5 mol/L, respectively.

Fig. 5. X-ray diffraction patterns of Silicalite-1 samples prepared in a water/surfactant/organic solvent (emulsion method) with different surfactant concentrations. The hydrothermal synthesis time and temperature were 50 h and 393 K, respectively, and the Si concentration in water was 1.6 mol/L.

Fig. 6. FE-SEM micrographs of silicalite-1 samples prepared by the emulsion method with different surfactant concentrations. The hydrothermal synthesis time and temperature were 50 h and 393 K, respectively, and the Si concentration in water was 1.6 mol/L. The molar ratio of

water to surfactant (*W/S*) were (b) 52, (c) 21, (d) 7.0.

Fig. 7. Effect of surfactant concentration on the nitrogen adsorption isotherm of silicalite-1 samples prepared by the emulsion method. Hydrothermal synthesis time and temperature were 50 h and 393 K, respectively, and the Si concentration in water was 1.6 mol/L.

Fig. 8. X-ray diffraction patterns of ZSM-5 samples with different Si/Al ratios prepared by the emulsion method ((a) ~ (e)) and that of the reference ZSM-5 (f). In the emulsion method, the hydrothermal synthesis time and temperature were 50 h and 393 K, respectively, and the Si concentration in water was 1.6 mol/L.

Fig. 9. FE-SEM micrographs of ZSM-5 samples with different Si/Al ratios prepared by the emulsion method ((a) ~ (e)) and that of the reference ZSM-5 (f). In the emulsion method, the hydrothermal synthesis time and temperature were 50 h and 393 K, respectively, and the Si concentration in water was 1.6 mol/L.

Fig. 10. NH₃-TPD profiles of the ZSM-5 nanocrystal prepared by the emulsion method and the reference sample.

Fig. 11. ²⁷Al-NMR spectra of the ZSM-5 nanocrystal prepared by the emulsion method and the reference sample.

Table 1. Surface area and micropore volume of prepared samples.

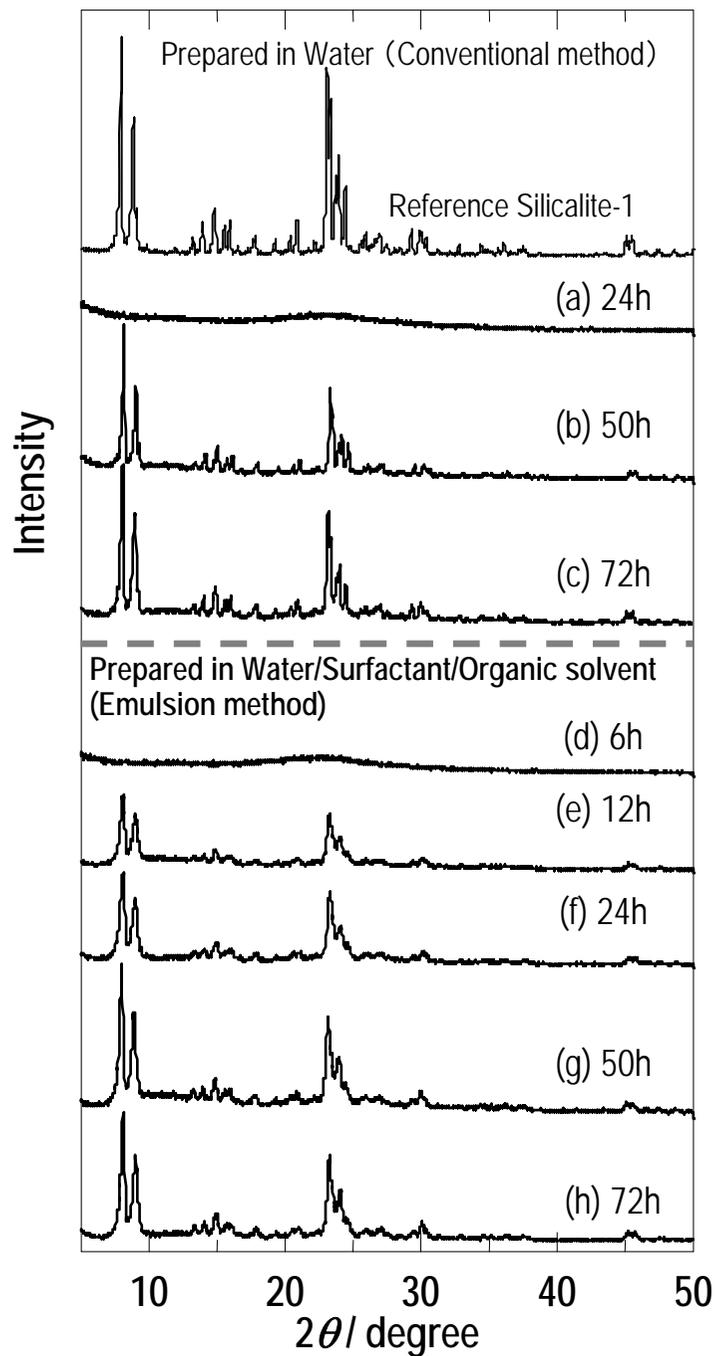


Fig. 1. The effects of hydrothermal synthesis time on the crystallinity of samples prepared in water (conventional method) and in a water/surfactant/organic solvent (emulsion method) at a hydrothermal temperature of 393 K. Concentrations of the surfactant in an organic solvent and that of Si in water were 0.5 and 1.6 mol/L, respectively.

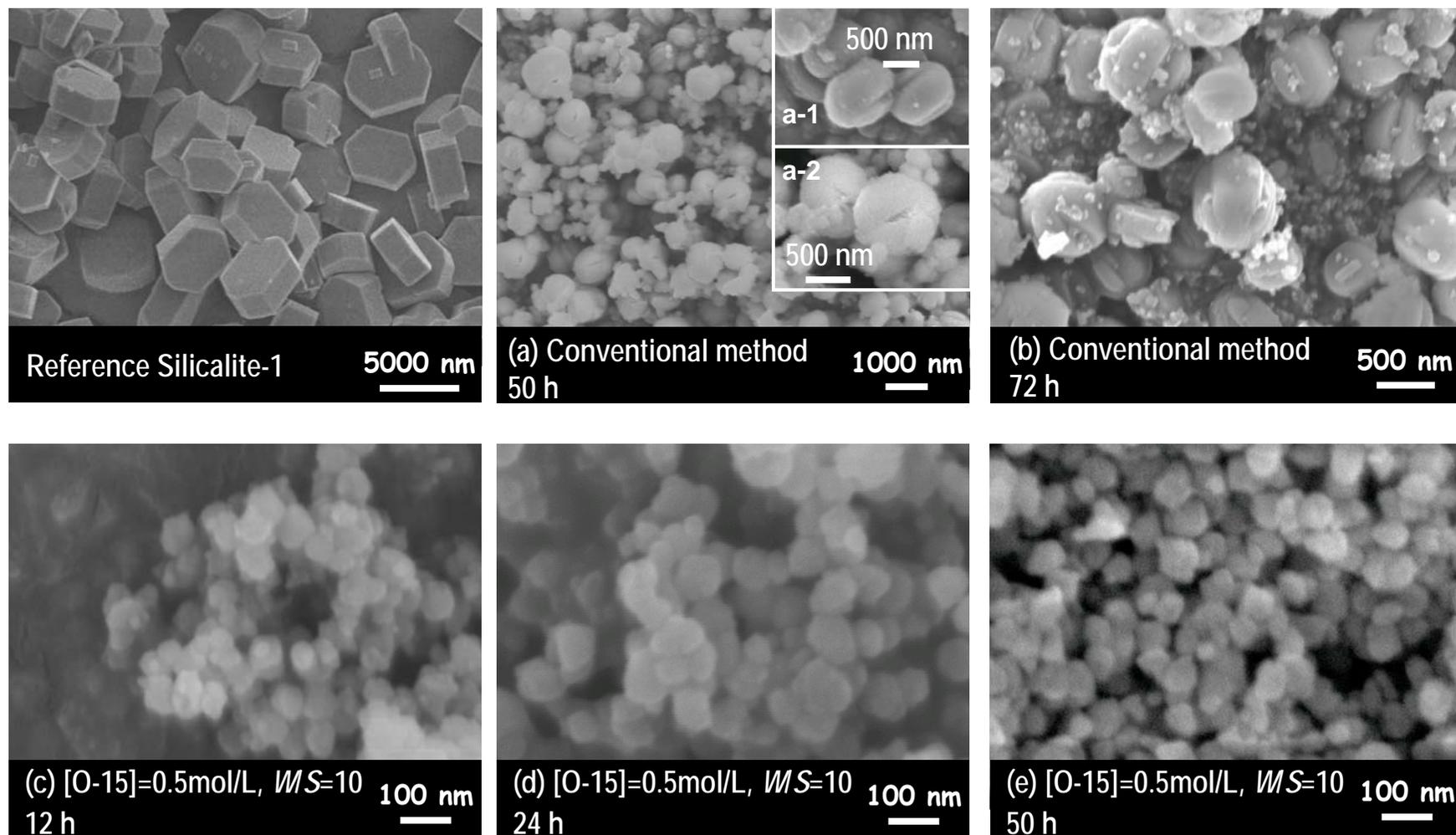


Fig. 2. FE-SEM micrographs of silicalite-1 samples prepared by the conventional method (a, b) and the emulsion method (c ~ e) with different hydrothermal times. The Si concentration in water was 1.6 mol/L and the molar ratio of water to surfactant (W/S) was 10.

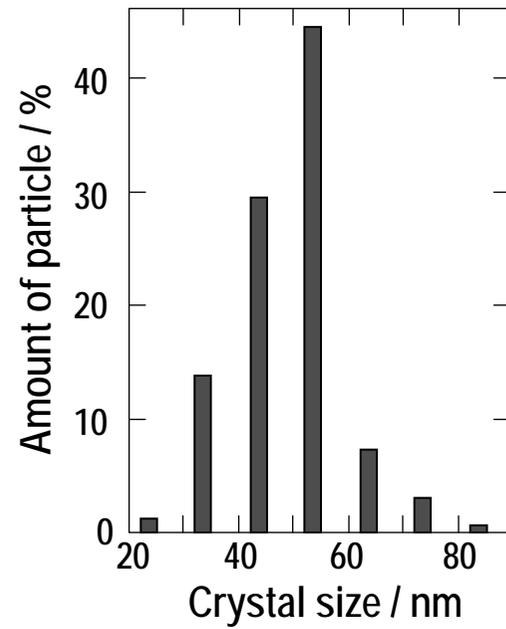


Fig. 3. Crystal size distributions of Silicalite-1 prepared by the emulsion method at a hydrothermal synthesis time of 50 h. The concentrations of Si in water and the surfactant in an organic solvent were 1.6 and 0.5 mol/L, respectively.

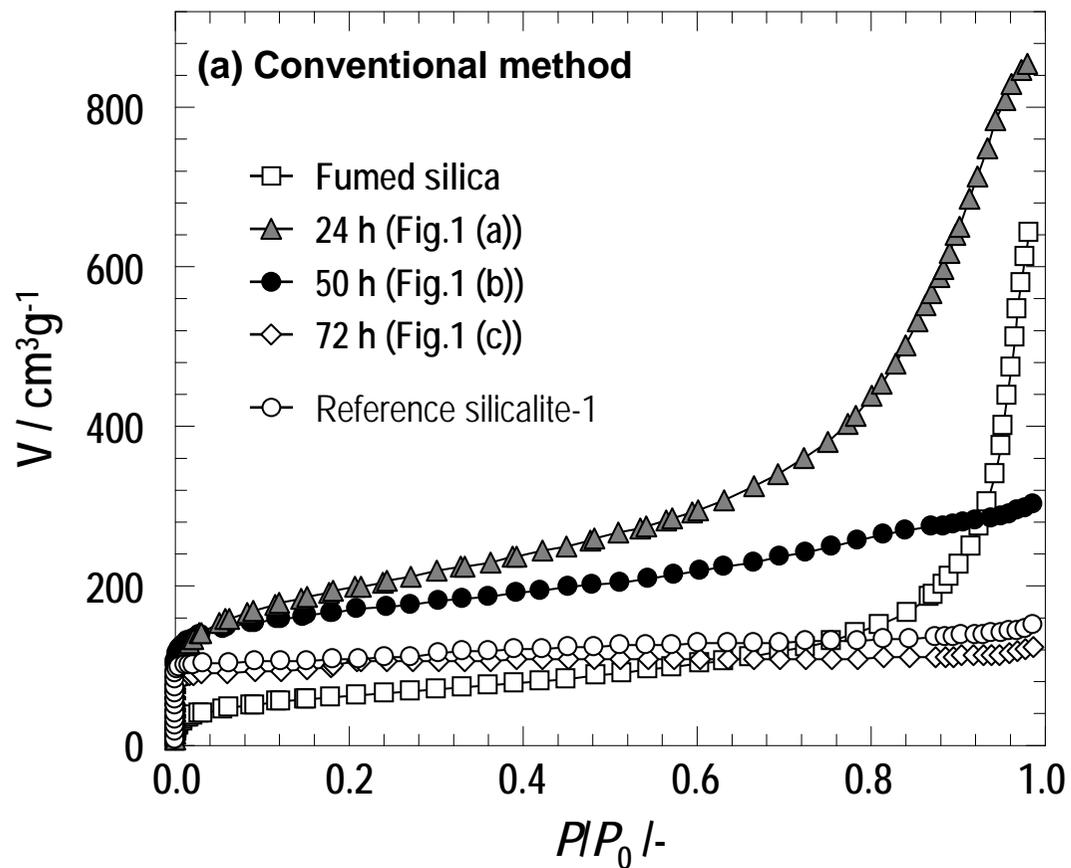


Fig. 4. The effects of hydrothermal synthesis time on nitrogen adsorption isotherms of samples prepared by (a) conventional and (b) emulsion methods. The concentrations of Si in water and the surfactant in an organic solvent were 1.6 and 0.5 mol/L, respectively.

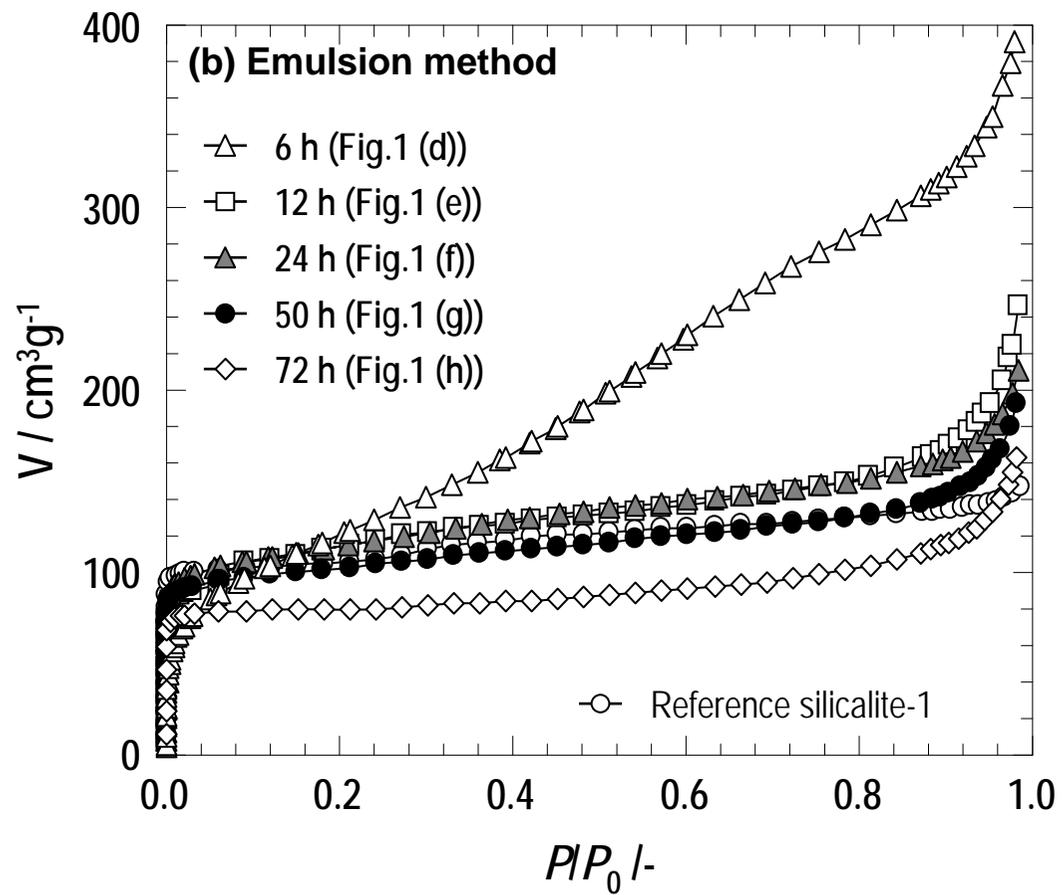


Fig. 4. The effects of hydrothermal synthesis time on nitrogen adsorption isotherms of samples prepared by (a) conventional and (b) emulsion methods. The concentrations of Si in water and the surfactant in an organic solvent were 1.6 and 0.5 mol/L, respectively.

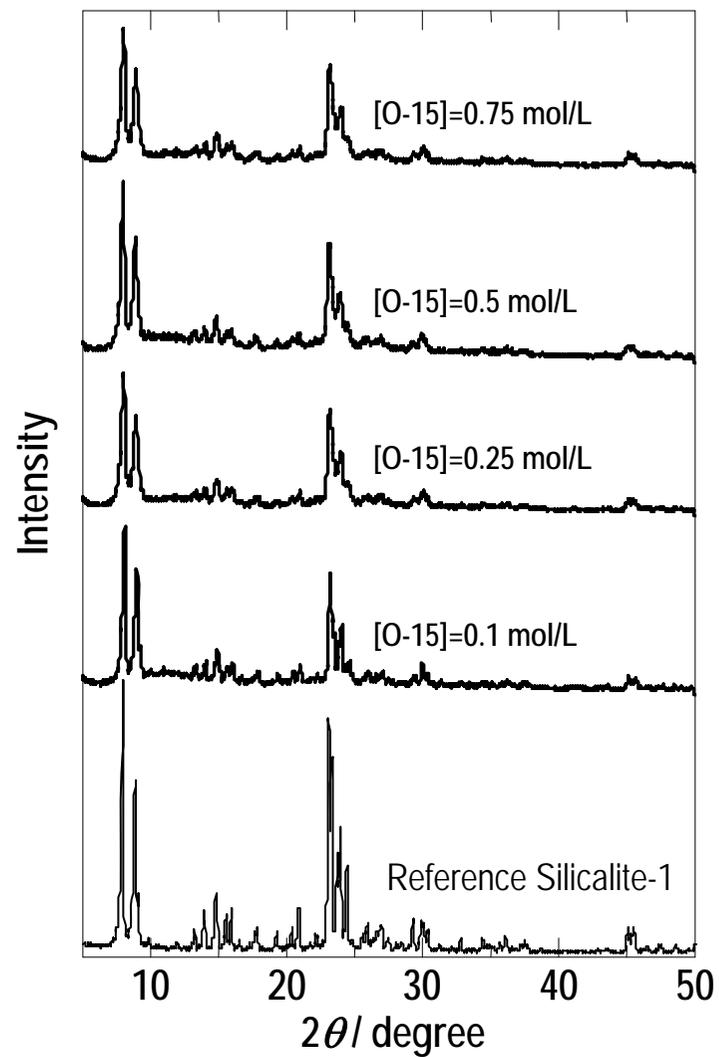
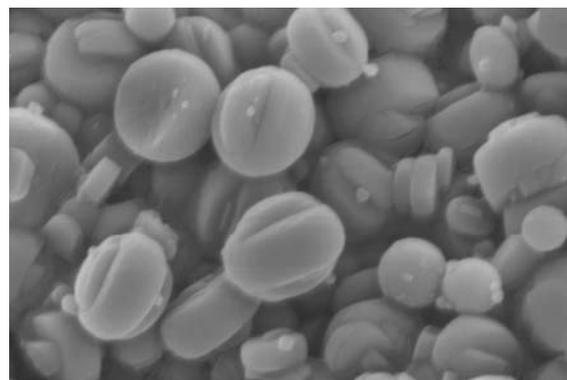
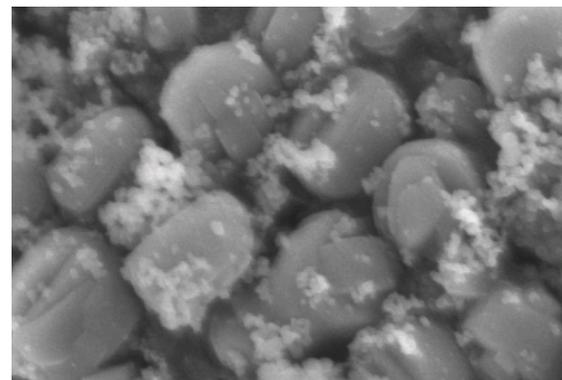


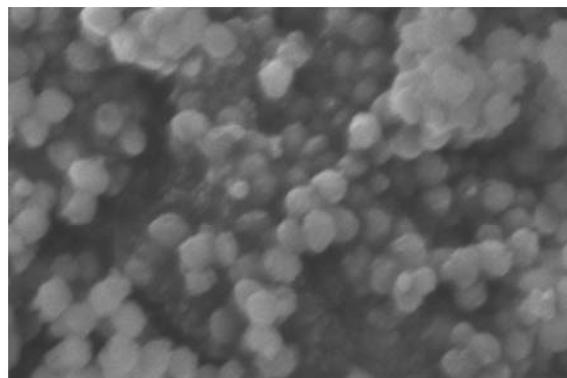
Fig. 5. X-ray diffraction patterns of Silicalite-1 samples prepared in a water/surfactant/organic solvent (emulsion method) with different surfactant concentrations. The hydrothermal synthesis time and temperature were 50 h and 393 K, respectively, and the Si concentration in water was 1.6 mol/L.



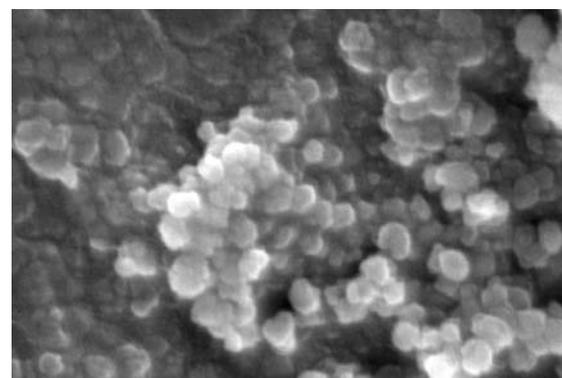
(a) [O-15]=0.0 mol/L 500nm
(H₂O/Organic solvent without surfactant)



(b) [O-15]=0.1mol/L, W/S=52 500nm



(c) [O-15]=0.25mol/L, W/S=21 500nm



(d) [O-15]=0.75mol/L, W/S=7.0 100nm

Fig. 6. FE-SEM micrographs of silicalite-1 samples prepared by the emulsion method with different surfactant concentrations. The hydrothermal synthesis time and temperature were 50 h and 393 K, respectively, and the Si concentration in water was 1.6 mol/L. The molar ratio of water to surfactant (*W/S*) were (b) 52, (c) 21, (d) 7.0.

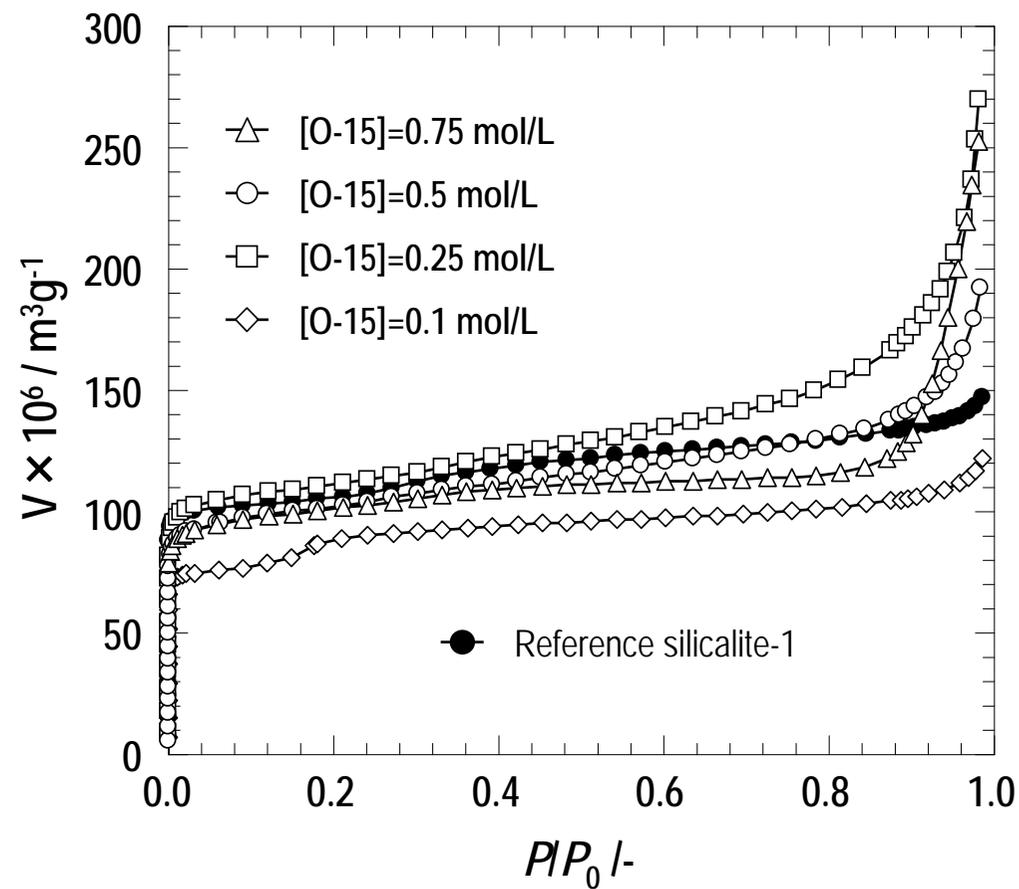


Fig. 7. Effect of surfactant concentration on the nitrogen adsorption isotherm of silicalite-1 samples prepared by the emulsion method. Hydrothermal synthesis time and temperature were 50 h and 393 K, respectively, and the Si concentration in water was 1.6 mol/L.

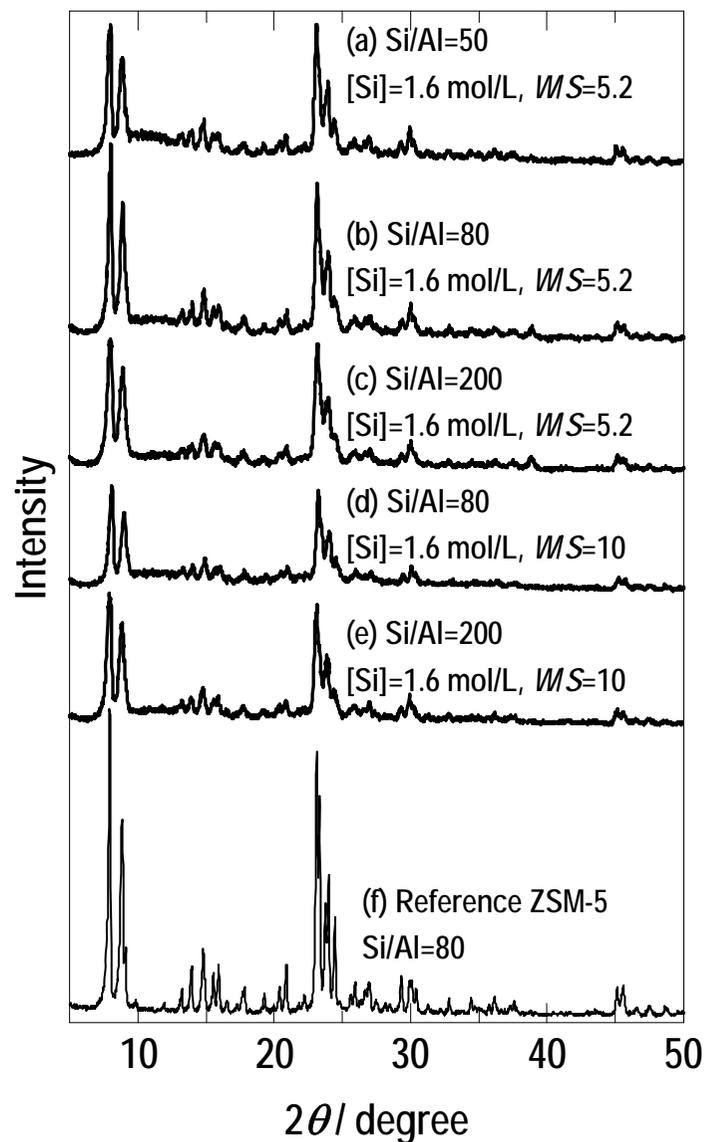


Fig. 8. X-ray diffraction patterns of ZSM-5 samples with different Si/Al ratios prepared by the emulsion method ((a) ~ (e)) and that of the reference ZSM-5 (f). In the emulsion method, the hydrothermal synthesis time and temperature were 50 h and 393 K, respectively, and the Si concentration in water was 1.6 mol/L.

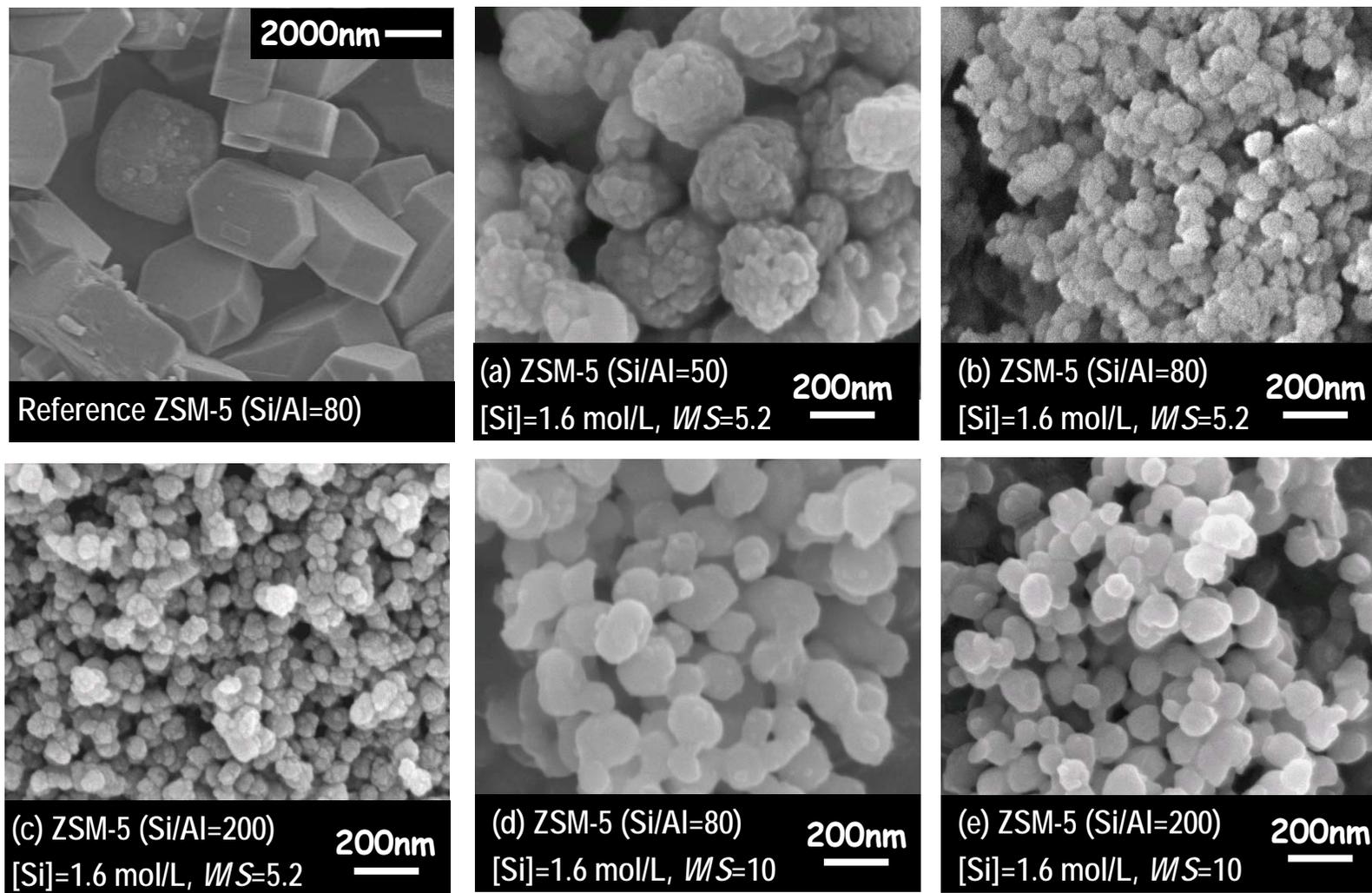


Fig. 9. FE-SEM micrographs of ZSM-5 samples with different Si/Al ratios prepared by the emulsion method ((a) ~ (e)) and that of the reference ZSM-5 (f). In the emulsion method, the hydrothermal synthesis time and temperature were 50 h and 393 K, respectively, and the Si concentration in water was 1.6 mol/L.

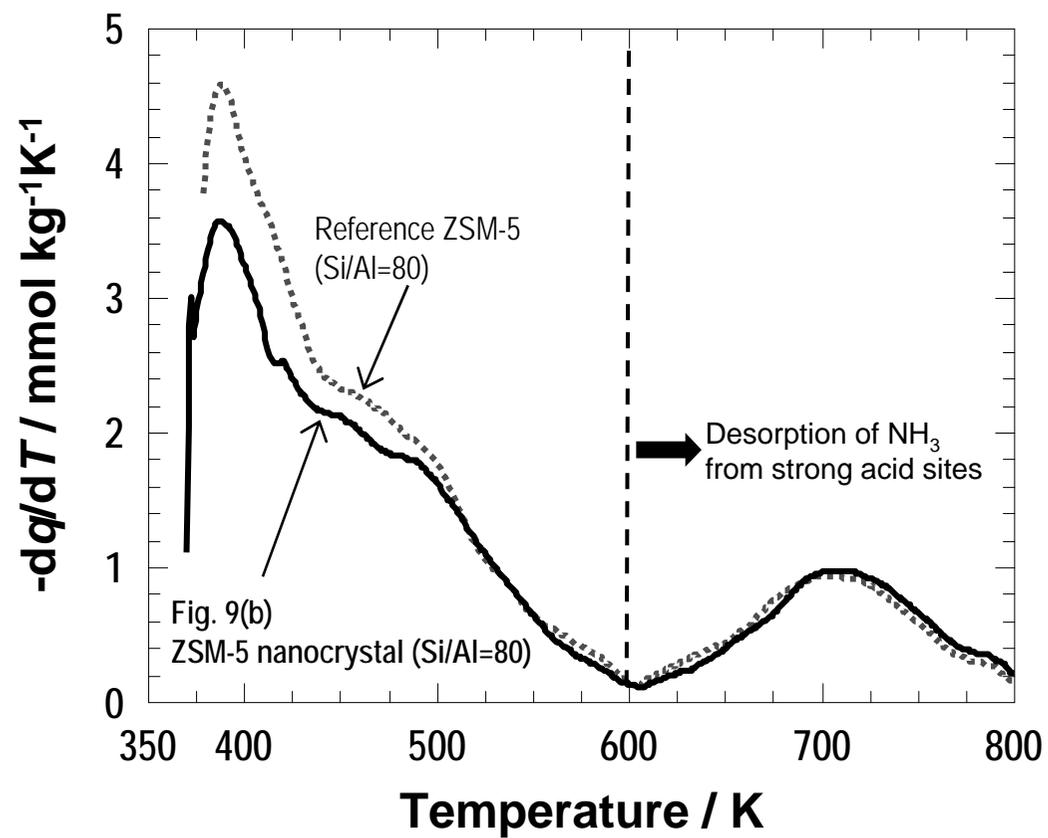


Fig. 10. NH₃-TPD profiles of the ZSM-5 nanocrystal prepared by the emulsion method and the reference sample.

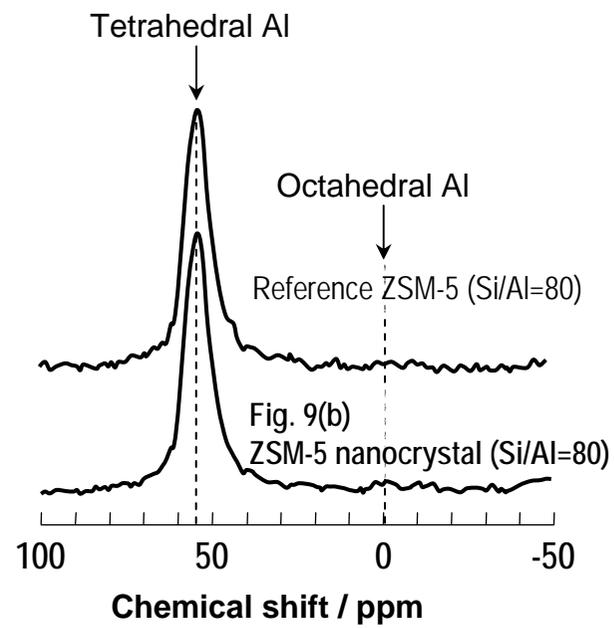


Fig. 11. ^{27}Al -NMR spectra of the ZSM-5 nanocrystal prepared by the emulsion method and the reference sample.

Table1. Surface area and micropore volume of prepared samples

sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_t ($\text{m}^2 \text{g}^{-1}$)	S_{ext} ($\text{m}^2 \text{g}^{-1}$)	V_m ($\text{cm}^3 \text{g}^{-1}$)
Fumed silica	220	220	220	0
Reference Silicalite-1	420	563	25.9	0.17
Conventional method, 24 h	681	693	620	0.03
Conventional method, 50 h	591	678	106	0.28
Conventional method, 72 h	363	486	10.1	0.16
[O-15]=0.5 mol/L, 12 h	377	496	80.8	0.13
[O-15]=0.5 mol/L, 24 h	414	528	60.2	0.17
[O-15]=0.5 mol/L, 50 h	390	513	60.8	0.15
[O-15]=0.5 mol/L, 72 h	326	430	58.0	0.10
[O-15]=0.1 mol/L, 50 h	317	421	22.2	0.14
[O-15]=0.25 mol/L, 50 h	431	564	96.8	0.14
[O-15]=0.75 mol/L, 50 h	390	511	21.1	0.16

S_{BET} : surface area by BET method, S_t : surface area by t-method

S_{ext} : external surface area by t-method, V_m : micropore volume by t-method