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XRD Characteristics of Na-ZSM-5 Synthesized from an Organic-Free System

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XRD profiles of as-synthesized Na- and TPA-ZSM-5 were not identical. They became similar to each other, however, when both zeolites were converted into organic-free or organic-contained forms. In terms of the framework topology, Na-ZSM-5 resembled TPA-ZSM-5 but differed from so-called ZSM-8. SEM images revealed the Na-ZSM-5 crystal to exhibit a hexagonal-lath-shaped morphology. Due to the preferred orientations, the intensities of *(0k0)* and *(h0l)* reflections were intensified and diminished, respectively. The hexagonal flat plane of the Na-ZSM-5 crystal was (010). Therefore, the 10-membered-ring straight channels were strongly indicated to penetrate perpendicularly to the hexagonal flat plane of the as-synthesized Na-ZSM-5 crystal.

Powder X-ray diffraction (XRD) is commonly used for identifying the structure of as-synthesized zeolites, because this technique is very simple and suitable for the small crystals of synthetic zeolites (ca. 0.5—15 μm).

Care should be taken on XRD characterization, since certain zeolites with different frameworks exhibit similar profiles, as has been pointed out previously by Breck[1)] for phillipsite, harmotome and gismondine. Lechert[2)] gave another example recently for structurally related zeolites of ZSM-5, ZSM-8, and ZSM-11, and stated that a splitting of the highest peak (2θ=23.0—23.5°; Cu$K\alpha$ radiation) was observed for ZSM-8 only.

ZSM-5 zeolite has been synthesized generally from the tetrapropylammonium (TPA)-contained aluminosilicate gel;[3)] nevertheless, it is possible to obtain ZSM-5 without adopting expensive and toxic TPA components.[4—8)] Grose et al.[5)] mentioned that the XRD pattern and adsorption property of a novel zeolite synthesized from an organic-free system (designated as Na-ZSM-5 hereafter) resembled those of typical TPA-ZSM-5. According to our preliminary examinations, however, as-synthesized Na-ZSM-5 gave a splitting similar to ZSM-8 in the main peak region (2θ=23.0—23.5°). A new question arises therefore whether as-synthesized Na-ZSM-5 belongs to TPA-ZSM-5 or so-called ZSM-8.

XRD profiles of zeolites are well-known to be affected easily without changing the framework topology. For example, dehydration of chabazite brought about framework distortion.[10)] According to Baerlocher and Meier,[11)] synthetic tetramethylammonium gismondine with tetragonal crystal symmetry changed continuously to a pseudocubic form upon thermal decomposition of the organic cation. Wu et al.[12)] showed that conversion of as-synthesized TPA-ZSM-5 into its ammonium or hydrogen form caused a symmetry change from orthorhombic to monoclinic, whereas the orthorhombic symmetry was regenerated by ammonia adsorption on the hydrogen form. The XRD profiles of zeolites are thus affected by guest substances in the skeleton, such as water or organic species.

The present study is an attempt to attribute the structure of as-synthesized Na-ZSM-5 zeolite to TPA-ZSM-5 or ZSM-8 and also to elucidate the correlation between its characteristic morphology and the crystal structure.

Experimental

Sample Preparation. TPA-ZSM-5 zeolite (designated sample A_1 hereafter) was synthesized from a starting composition of 2.0 TPA_2O-4.0 Na_2O-1.0 Al_2O_3-65 SiO_2-3000 H_2O under hydrothermal conditions of 170 °C for 48 h with stirring. Tetrapropylammonium bromide (TPABr) was adopted as the TPA source. The sample A_1 was calcined in air at 620 °C for 3 h to give a calcined (TPA)-ZSM-5 (sample B_1). The sample B_1 was then treated with 1 M NH_4Cl aqueous solution (1 M=1 mol dm^{-3}) at room temperature for 12 h, followed by calcination at 540 °C for 4 h to convert it into a hydrogen form. After this hydrogen form was degassed in vacuo at 150 °C for 1 h in a glass tube, an excess amount of prepurified diethylamine (DEA) was vacuum-transferred into the glass tube to immerse the zeolite at 15 °C for 12 h, producing a DEA-contained zeolite (sample A_1').

As-synthesized Na-ZSM-5 was prepared from a composition of 8.75 Na_2O-1.0 Al_2O_3-70 SiO_2-3150 H_2O by following the procedure reported previously.[8)] Conversion of as-synthesized Na-ZSM-5 into its hydrogen form (sample B_2) was carried out by ion-exchange with 1 M NH_4Cl aqueous solution, followed by calcination at 540 °C for 4 h. Immersion with DEA changed the sample B_2 into another DEA-contained zeolite (sample A_2). The other organic-free ZSM-5 (sample B_2') was prepared by calcining the sample A_2 at 620 °C for 3 h.

Characterization. The XRD profiles of zeolites were measured by an X-ray diffractometer (Rigaku Denki Co. Ltd., D-9 C, equipped with a scintillation counter) under the conditions: Cu$K\alpha$ radiation (Ni-filter) at the intensity of 30 kV-10 mA with the slit system of RS=0.15 mm and DS=SS=1/2°; the 2θ scanning rate of 1/4 or 1/8° min^{-1}.

Silicon powder (300 mesh-pass) was adopted as the internal standard for adjusting 2θ values (22—25°) accurately with reference to the Si(111) reflection.

Crystal morphologies of zeolites were observed by means of scanning electron microscopy (SEM) (Akashi Co., Ltd., Alpha-10).

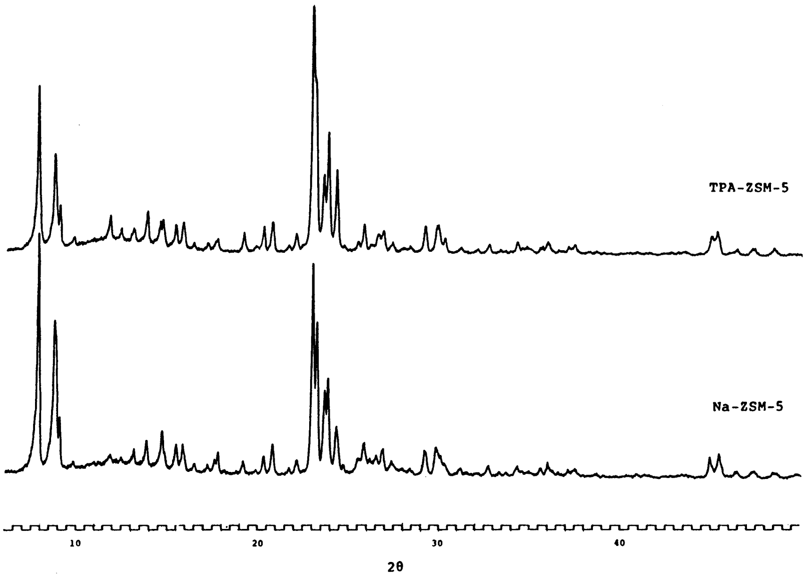

Fig. 1. XRD profiles of Na-ZSM-5 and TPA-ZSM-5 synthesized from organic-free and TPABr systems, respectively; XRD 2θ scanning rate of 1/4° min^{-1}.

Results and Discussion

Effects of Organic Species on XRD Profiles. Typical XRD profiles of as-synthesized TPA-ZSM-5 and Na-ZSM-5 are contrasted in Fig. 1. Although it was once stated that almost all the diffraction peaks of as-synthesized Na-ZSM-5 coincided with those of typical TPA-ZSM-5,[5] these XRD profiles were not exactly identical. Firstly, peak intensity differences were apparent at 2θ=7.94, 8.87, 11.90, 12.50, 13.19, 14.70—14.88 (doublet), 20.34, 23.68, and 23.91°. Secondly, the splitting in the main peak region (2θ=23.0—23.5°) was much clearer for Na-ZSM-5 than for TPA-ZSM-5. Calcination of as-synthesized TPA-ZSM-5, however, resulted in a well-resolved profile of the main peak splitting,[13] accompanying the intensified peaks at 2θ=7.94, 8.87, 13.19, and 14.82°, and the diminished ones at 11.90, 12.50, 20.34, 23.68, and 23.91°.[14] Consequently, the XRD profile of calcined-(TPA)-ZSM-5 (B_1) well resembles that of as-synthesized Na-ZSM-5.

Readsorption of organic species onto either calcined-(TPA)-ZSM-5 or as-synthesized Na-ZSM-5 was attemped therefore to clarify the effect of organic guest substances on XRD profiles.

The XRD region of 2θ=22—25° was enlarged and shown in Figs. 2 and 3. Hydrogen forms of both kinds of as-synthesized ZSM-5 were prepared in order to minimize the steric hindrances for the adsorption of organic species. Diethylamine (DEA) was adopted as absorbate, because its molecule size is small enough to diffuse freely into the zeolite channel (size of ZSM-5 window: 5—6 Å).[15]

The XRD profile of five significant peaks of as-synthesized TPA-ZSM-5 was varied by sequential treatments of $A_1 \rightarrow B_1 \rightarrow A_1'$ (Fig. 2).

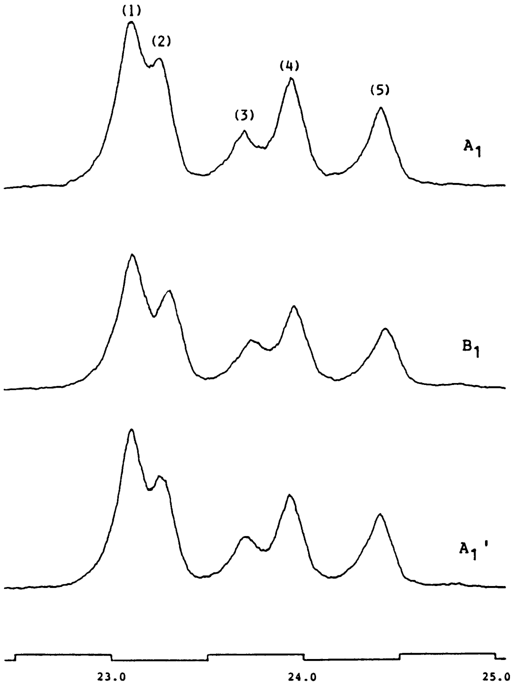

Fig. 2. Variation of XRD profiles: as-synthesized TPA-ZSM-5 (A_1) changed to calcined-TPA-ZSM-5 (B_1) by calcination at 620°C for 3 h, and finally to DEA-ZSM-5 (A_1') by loading diethylamine (DEA) at 15°C for 12 h; XRD 2θ scanning rate of 1/8° min^{-1}.

As converting A_1 into B_1, the position of the strongest peak (marked as (1)) remained unchanged, whereas the others of (2)—(5) were shifted slightly toward high angles. As the peak (2) shifted to higher angle, the profile became well-resolved, which was accepted as grounds for the ZSM-8 assignment. On the contrary, incorporation of DEA into H-ZSM-5 (B_1) induced peak shifts again toward lower angles, as shown for the (2)—(5) peaks of DEA-ZSM-5 (A_1'). The XRD profile was thus changed reversibly between as-synthesized TPA-ZSM-5 (A_1) and DEA-ZSM-5 (A_1').

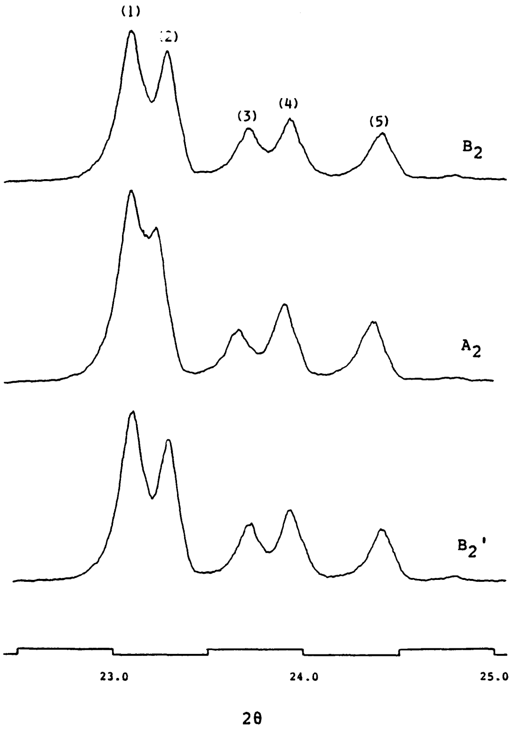

Fig. 3. Variation of XRD profiles: H-ZSM-5 (B_2), ion-exchanged from as-synthesized Na-ZSM-5, changed to DEA-ZSM-5 (A_2) by loading diethylamine (DEA) and finally to calcined-DEA-ZSM-5 (B_2') by calcination at 540 °C for 4 h; XRD measurement conditions are the same as those of Fig. 2.

The hydrogen form of Na-ZSM-5 was loaded with DEA, then calcined to reproduce the organic-free form. These treatments brought the changes of XRD profiles as $B_2 \rightarrow A_2 \rightarrow B_2'$ (Fig. 3).

Conversion of H-ZSM-5(B_2) to DEA-ZSM-5(A_2) induced peak shifts toward lower angles except for the main peak (1). The splitting profiles due to the main peaks of (1) and (2) were similar between DEA-ZSM-5 (A_2) and as-synthesized TPA-ZSM-5 (A_1 in Fig. 2). Thermal decomposition of guest organic substances contained in the sample A_2 yielded the sample B_2', which gave again the XRD profile similar to H-ZSM-5 (B_2).

The following aspects are deduced from Figs. 2 and 3.

(1) Either occluded during hydrothermal synthesis or absorbed by ammine immersion, organic species inside the zeolite skeleton exert an influence upon XRD profiles, irrespective of the ZSM-5 zeolite synthesized from the system with or without using organic templates.

(2) The adsorption and decomposition of guest organic subtances induce XRD profiles to change reversibly, as apparent from the resemblance between A_1' and A_1 (Fig. 2) or between B_2 and B_2' (Fig. 3).

(3) The shape of the main peaks around $2\theta=$ 23.0—23.5° is sensitive to the involvement of organic species in the zeolite skeleton; the well-resolved profile of the organic-free form (B_1, B_2, and B_2') is in sharp contrast to the poorly-resolved profile of those incorporated with organic species (A_1, A_1', and A_2).

(4) Certain diffraction peaks are induced to shift by the incorporation of organic species into both kinds of ZSM-5 skeletons.

Since both kinds of silicious zeolites exhibit high

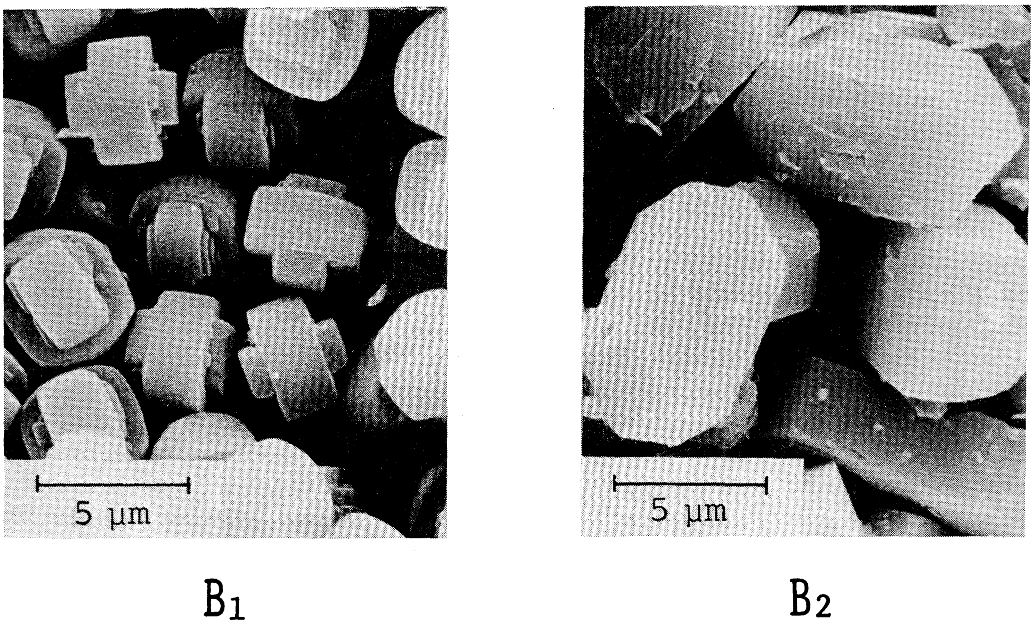

Fig. 4. Typical SEM morphologies of ZSM-5 zeolites synthesized from TPABr (B_1) and organic-free (B_2) systems; notations are common to those of Figs. 2 and 3.

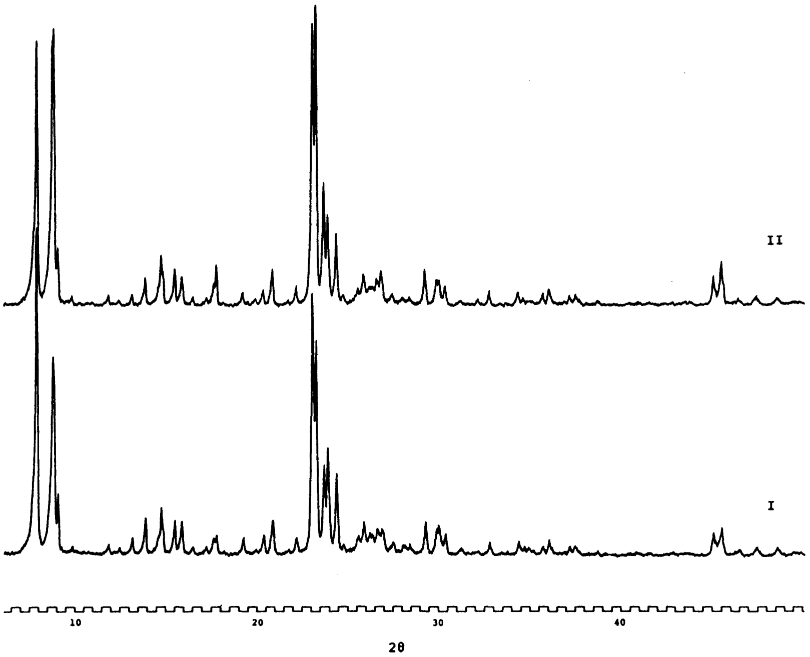

Fig. 5. Variation of XRD profiles for H-ZSM-5, ion-exchanged from as-synthesized Na-ZSM-5: specimen set with the normal manner (I) and extremely pressurized manner (II); XRD 2θ scanning rate of 1/4° min^{-1}.

thermal stability against calcination (620 °C for 3 h), as evident from the reversible changes of those XRD profiles (point (2)), no topological changes occur throughout these conversion processes. These XRD profile changes (Figs. 2 and 3) can therefore be attributed to lattice expansion induced by the guest organic amine.

Throughout the XRD region of 2θ=5—50°, all the peak positions of calcined-(TPA)-ZSM-5 (B_1) coincided well (within an error of ±0.02°) with those of H-ZSM-5 (B_2). No doublet peaks were observed at the regions around 24.4, 29.2, and 48.6° for either Na-ZSM-5 or TPA-ZSM-5 during the conversion processes, suggesting both of them to belong commonly to the orthorhombic symmetry.[12] On these grounds, as-synthesized Na-ZSM-5 is concluded to possess an isostructure with TPA-ZSM-5, different from the so-called ZSM-8[9] in framework topology.

Crystal Characteristics of Na-ZSM-5 Synthesized from Organic Free System. Crystal Morphology. Typical SEM morphologies of Na- and TPA-ZSM-5 zeolites are shown in Fig. 4. Spherical-like or crossed-discus crystals (B_1) were easily formed with use of TPABr, whereas hexagonal-lath-shaped crystals (B_2) were always obtained from the organic-free system. Each crystal morphology remained unchanged throughout sequential treatments of ammonium ion exchange, calcination and DEA adsorption.

Effect of Preferred Orientation on XRD Profiles. Characteristic to the hexagonal-lath-shaped ZSM-5 crystals (B_2) synthesized from the organic-free system, certain XRD peak intensities were sensitive to the manner of mounting the specimen onto an X-ray sample holder. With regard to the spherical-like ZSM-5 zeolite (B_1), such changes of XRD spectra have never been experienced previously.

Table 1. Specific XRD Peak Intensities of Hexagonal-Lath-Shaped Na-ZSM-5 Crystals Sensitive to Specimen Setting Manner

(h	k	l)[a]	2θ[b]	(I/I_0)[c] Normal setting	Extreme pressing
1	0	2	13.90	76	47
2	0	2	15.86	69	49
1	0	3	20.34	40	28
3	0	3	23.91	219	156
0	4	0	17.79	38	69
0	5	1	23.25	436	526
1	5	1	23.68	186	213
0	10	0	45.46	57	73

a) See Ref. 18. b) Cu$K\alpha$ radiation ±0.02°. c) The intensity of isotropic (111) reflection (2θ=9.08°) was adopted as I_0, because this was the strongest peak insensitive to the preferred orientation.

Figure 5 illustrated the XRD profiles of hexagonal-lath-shaped ZSM-5 (B_2) measured in different conditions; one of the specimen was set by a standard procedure[16] (I) and the other was set in excess amount with extra pressure(II). The peaks located at 2θ=8.85, 17.79, 23.25, 23.68, 26.85, and 45.46° were intensified, whereas those of 7.92, 13.90, 15.86, 20.34, 23.01, and 23.91° were diminished, by pressing. Extra pressure induced the change of the total peak area within the region of 2θ=22.0—25.0°. Improper specimen pressing must be avoided, since the peak area is often adopted for estimating the degree of crystallization.[17]

The diffraction peaks sensitive to the specimen pressing were specified (Table 1), together with the corresponding Miller Indices of ZSM-5.[18]

As evident from Table 1, the peaks diminished in intensity were classified to the group of (*h*0*l*) reflection, whereas the peaks intensified belonged to the (0*k*0) group.

Since the lath-shaped crystals were apt to deviate from random orientation, it is conceivable that the orientation of hexagonal-flat planes become parallel to the plane of the XRD sample holder. The XRD peaks of the diffraction planes parallel to the hexagonal-flat surface would therefore be intensified. This supports the view that the hexagonal-flat plane of Na-ZSM-5 crystal belong to the (010) plane.

In the ZSM-5 skeleton, the straight 10-membered-ring channel elongates along the 'b' axis, whereas the zigzag channel extends toward the 'a' axis.[15] Since the diffraction planes with (0*k*0) Miller Indices intersect perpendicularly with the 'b' axis, the straight channels are concluded to penetrate perpendicularly to the flat plane of the hexagonal-lath-shaped crystals.

Conclusion

(1) Na-ZSM-5 possesses an isostructure with TPA-ZSM-5 but differs from the so-called ZSM-8 in framework topology. XRD profiles of Na- and TPA-ZSM-5 were controlled by incorporation or decomposition of organic amine in the ZSM-5 skeleton.

(2) XRD intensities of (0*k*0) and (*h*0*l*) reflections for hexagonal-lath-shaped Na-ZSM-5 are sensitive to the preferred orientation. The hexagonal-flat plane of Na-ZSM-5 crystal is (010). Therefore, the 10-membered-ring straight channels of ZSM-5 are strongly indicated to penetrate perpendicularly to the hexagonal-flat plane of the crystal.

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9) The structure of ZSM-8 remains uncertain due to lacking of the single crystal analysis. It is suggested, however on the basis of ^{29}Si-MAS NMR study that "ZSM-8 crystal could be a mixture of ZSM-5 and ZSM-11 or an intergrowth of these two kinds of structure. See, for example, Z. Gabelica, J. B. Nagy, P. Bodart, G. Debras, E. G. Derouane, and P.A. Jacobs, *NATO ASI Ser., Ser. E, No. 80,* "Zeolite: Science and Technology," **1984**, pp. 193—210.

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13) The splitting profile of the main peaks is also observed for hydrated ZSM-5, as shown in 18, and for NH_3-loaded H-ZSM-5 in 12.

14) Peak intensity changes were pointed out previously by Wu et al., when a highly silicious, as-synthesized TPA-ZSM-5 was converted to its ammonium-exchanged form.[12]

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