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CRYSTAL SYMMETRY CHANGE OF ZSM-5 BY VARIOUS TREATMENTS

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When a SiO_2/Al_2O_3 ratio was higher than about 170, the crystal structure of ZSM-5 changed from orthorhombic to monoclinic symmetry by mere calcination. The monoclinic symmetry remained unchanged by NH_4-ion exchange, but the symmetry was reformed to orthorhombic in some of the specimens by protonation. The SiO_2/Al_2O_3 ratio was found to play a major role compared with the Na-content.

Zeolite ZSM-5 is a new class of high siliceous zeolite which possesses wide SiO_2/Al_2O_3 ratios from about 20 to more than 8000.1) By X-ray powder diffraction profiles, the crystal system of as-synthesized ZSM-5 is identified to be orthorhombic symmetry. It has also been observed that the orthorhombic symmetry structurally changed to monoclinic one by calcination and ion-exchange.2) Wu and coworkers2) have commented that extra framework matter(a sodium content) and an aluminium content are among the critical variables which control the symmetry change of ZSM-5 from orthorhombic to monoclinic, however quantitative data on the symmetry change have been lacking.

In the present work, various forms of ZSM-5 with different sodium and aluminium contents were prepared, and the role of sodium and aluminium contents on the symmetry change of ZSM-5 was examined in detail.

Various forms of ZSM-5 samples examined have the following designations: as-synthesized, calcined, ammonium-exchanged (NH_4-) and protonated form(H-), and those prepared as described previously.3) The crystal structure of samples was identified by their X-ray powder diffraction profiles, when the data reported by Wu and coworkers2) were employed as a criterion for its identification, and some of their molphologies were observed by electronmicroscopy.

The selected chemical components and the observed crystal symmetry of ZSM-5 samples are listed in Table 1. The X-ray powder diffraction profiles of as-synthesized samples, in which SiO_2/Al_2O_3 ratios varied from 50 to 2000, were very similar to the profiles consisting of orthorhombic symmetry system.
In case of the sample exposed to an ambient atmosphere for 1 h after calcination at 540 °C, the X-ray powder diffraction profiles of the samples with SiO_2/Al_2O_3 ratios below 160 displayed orthorhombic symmetry, while those of the samples with the ratios above 170 showed clearly monoclinic symmetry. When the samples with SiO_2/Al_2O_3 ratios of about 160 were exposed to water vapor at room temperature for 24 h, their X-ray powder diffraction profiles changed from orthorhombic to monoclinic symmetry. The behavior described above is to be compared to that reported by Wu and coworkers.2) They reported that only shortly after calcination at 600 °C for 1 h, the X-ray powder diffraction profiles of the sample with a Na-content of 0.8 wt% and with a SiO_2/Al_2O_3 ratio about 1600 seemed to be orthorhombic and that when the sample was further exposed to an ambient atmosphere for 3 days, its profiles consisted of monoclinic symmetry, while no symmetry change was observed with the sample with a Na-content of 1.6 wt%. They suggested that for such a behavior, water vapor presumably caused relocation of the residual sodium species which enable the framework structure to undergo a symmetry change. For the NH_4-form samples, the X-ray powder diffraction profiles of those with SiO_2/Al_2O_3 ratios above about 170 showed monoclinic symmetry, while those of the samples with SiO_2/Al_2O_3 ratios below about 160 showed orthorhombic symmetry. When the samples with SiO_2/Al_2O_3 ratios between 730 and 860 were transformed to H-form, their X-ray powder diffraction profiles changed from monoclinic to orthorhombic symmetry.

In view of these data, the higher the SiO_2/Al_2O_3 ratio is, the easier it is for the ZSM-5 framework to change from orthorhombic to monoclinic symmetry upon treatments such as calcination and ion-exchange to the NH_4- and/or H-form, which has previously been described by Wu and coworkers.2) For the calcined form, however, our results are significantly different from those of Wu and coworkers,2) that is, it was evident that some samples, as the SiO_2/Al_2O_3 ratio became higher, changed from orthorhombic to monoclinic symmetry by mere calcination, and that the SiO_2/Al_2O_3 ratio played a major role rather than the Na-content did on the symmetry change of ZSM-5. In addition, the reversal change, from monoclinic to orthorhombic symmetry, was also shown to occur in some samples, which has not been reported so

Table 1. Variation in crystal symmetry of ZSM-5 with various treatments.

Sample No.	Chemical Analysis (as-synthesized form)		Crystal Symmetry				
	Na (dry wt%)	SiO_2/Al_2O_3 (molar ratio)	as-synthesized form	calcined form (1)	calcined form (2)	NH_4-form	H-form
1	0.57	53	O(3)	O	O	O	O
2	0.59	86	O	O	O	O	O
3	0.50	95	O	O	O	O	O
4	0.54	128	O	O	O	O	O
5	0.61	147	O	O	O	O	O
6	0.88	159	O	O	M(4)	O	O
7	0.94	163	O	O	M	O	O
8	0.94	169	O	M	M	M	M
9	0.73	249	O	M	M	M	M
10	0.79	470	O	M	M	M	M
11	0.79	729	O	M	M	M	O
12	0.73	862	O	M	M	M	O
13	0.57	912	O	M	M	M	M
14	0.63	1607	O	M	M	M	M
15	0.64	2066	O	M	M	M	M
16	1.55	130	O	O	O	O	O
17	1.29	150	O	O	O	O	O

(1) Exposure to ambient conditions for 1 h after calcination at 540 °C.

(2) Exposure to water vapor at room temperature after calcination at 540 °C.

(3) Orthorhombic symmetry

(4) Monoclinic symmetry

far. The particle size and morphology of samples have no relation to the symmetry change. The particle size of samples is about 0.2 to 6 μm and their morphology is characteristic as shown in Fig. 1. It seemed probable that some samples, although being apparently identical in terms of X-ray diffraction profiles, could display substantial differences in their nature of framework structure.

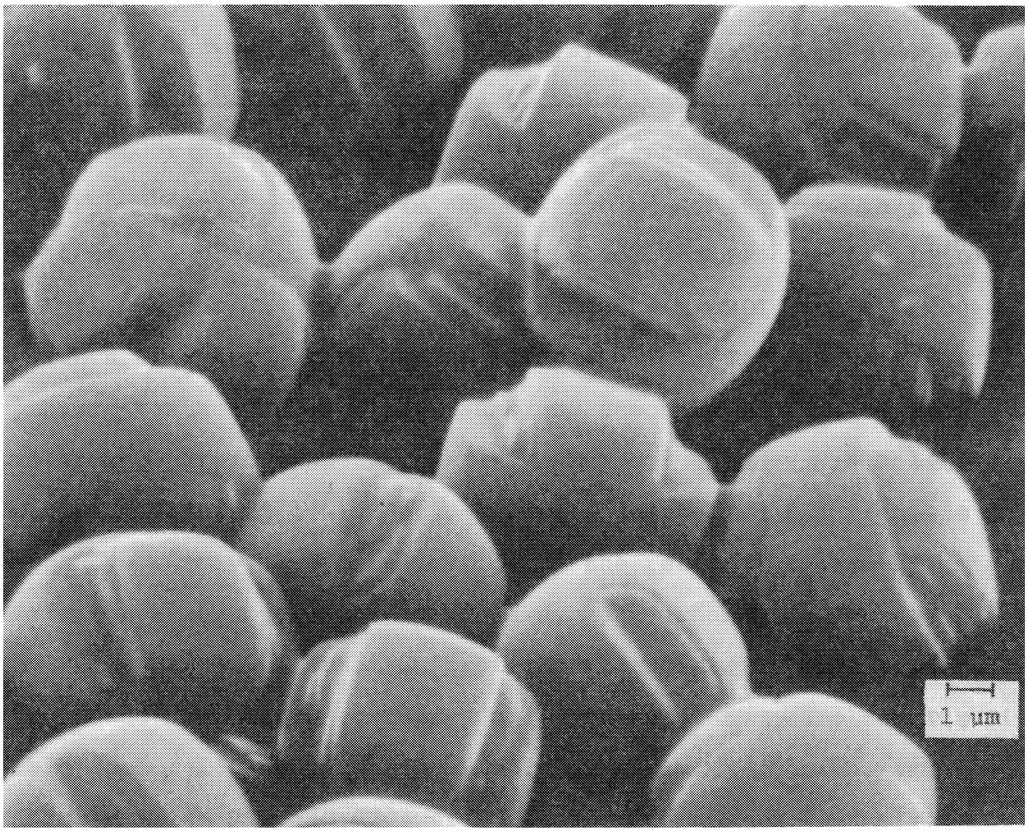

Fig. 1. Scanning electronmicrograph of ZSM-5(sample No.8).

References

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