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BRIEF COMMUNICATIONS

The Influence of the Templating Agent on the Unit Cell Volume of ZSM-5 Zeolite

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The XRD technique was used to study the lattice parameters *a*, *b*, and *c* and unit cell volume *V* of several groups of zeolite ZSM-5 synthesized with different templating agents. When the templating agent was changed, the *V* changed greatly and the *a* parameter increased greatly whereas *b* and *c* did not change significantly. This result supports the conclusion that the ZSM-5 crystal grows through one by one combination of *bc* sheets along the *a* direction. © 1990 Academic Press, Inc.

Since it was first prepared in the presence of tetrapropylammonium (TPA) (*1*), ZSM-5 zeolite has been synthesized with some amines and alcohols as templating agents; the mechanism of ZSM-5 zeolite synthesis has been widely investigated (*2–4*). In this paper the crystal growth during formation of ZSM-5 zeolite is studied by X-ray diffraction for polycrystalline materials.

ZSM-5 zeolite samples with a variety of SiO_2/Al_2O_3 ratios were prepared in the system $Na_2O–Al_2O_3–SiO_2–H_2O$, using waterglass as the source of silicon, $Al_2(SO_4)_3$ as the source of aluminum, and TPA, butylamine, 1,6-hexanediol, tetrahexylammonium (THexA), tetraheptylammonium (THepA), and tetraoctylammonium (TOctA) as the templating agents, respectively.

The determination of the lattice parameters of ZSM-5 samples was carried out by using Rigaku D/MAX-IIIA X-ray diffractometer operating with Cu*Kα* radiation at 40 kV and 30 mA and at a scanning rate of 1°/16 min. The lattice parameter *a*, *b*, and *c* and *V* (volume of unit cell) were determined from the 2θ values corresponding to 002, 102, 131, 312, 203, 051, 501, 133, 432, and 352 diffraction peaks, using the formula for orthorhombic symmetry:

$$\mathrm{Sin}^2\,\theta(hkl) = \left(\frac{1}{4}\right)^2\left[h^2\left(\frac{1}{a}\right)^2 + k^2\left(\frac{1}{b}\right)^2 + l^2\left(\frac{1}{c}\right)^2\right].$$

These values are shown in Table I.

It is known that the larger the number of Al atoms in the unit cell, the larger the unit cell volume becomes because the Al–O bond length is longer than that of Si–O.

From Table I, the following facts can be ascertained:

First, within the same group the ratio SiO_2/Al_2O_3 of all ZSM-5 samples are very

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TABLE I

THE LATTICE PARAMETERS AND RATIO SiO_2/Al_2O_3 OF ZSM-5 SAMPLES

Group	No.	Templating agent	SiO_2/Al_2O_3	a (Å)	b (Å)	c (Å)	V (Å^3)
1	1-1	TPA	94.2	20.0870	19.9519	13.4189	5377.95
1	1-2	Butylamine	95.0	20.1659	19.9665	13.4488	5415.04
2	2-1	TPA	74.8	20.0875	19.9582	13.4376	5387.27
2	2-2	Butylamine	74.6	20.1561	19.9779	13.4606	5420.00
2	2-3	1,6-Hexanediol	77.4	20.2415	19.9733	13.4545	5439.51
3	3-1	TPA	55.6	20.1175	19.9896	13.4528	5409.93
3	3-2	Butylamine	60.0	20.1824	19.9898	13.4641	5431.99
3	3-3	1,6-Hexanediol	57.2	20.2041	20.0137	13.4770	5449.57
4	4-1	TPA	40.1	20.1474	19.9938	13.4528	5419.07
4	4-2	Butylamine	39.2	20.2031	19.9904	13.4682	5439.36
5	5-1	TPA	55.6	20.1175	19.9896	13.4528	5409.93
5	5-2	THexA	64.4	20.1674	20.0003	13.4843	5438.96
5	5-3	THepA	56.0	20.1914	20.0167	13.4632	5441.35
5	5-4	TOctA	74.1	20.2229	20.0051	13.4619	5446.16

close, but their unit cell volumes are very different, which effect is caused by the difference in pore volume, not by the difference in kind or number of atoms. The volume of pores in each zeolite depends on the size of the templating agents.

Second, within the same group, with changing unit cell volume the increases in a, b, and c (Δa, Δb, and Δc) are very different from each other: the value of Δa is very large but changes in b and c are not significant.

This result supplies further evidence to the view that crystal growth of ZSM-5 occurs through the combination of bc sheets, one by one, along the a direction. The formation of the bc sheet is not related to the size of templating agents; therefore, the values of b and c do not change greatly with templating agents. The combination of bc sections along the a axis occurs through the attraction of the positively charged tetrahedron templating agents (*4*) which are located between two bc sheets. Therefore, the size of the templating agents influences the distance between the two sections bc, so that the value of a is very large with unit cell volume changes.

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