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A NEW METHOD FOR THE PREPARATION OF ZEOLITE ZSM-5 BY USING SODIUM n-DODECYLBENZENE SULFONATE

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Zeolite ZSM-5 was easily synthesized by using sodium n-dodecylbenzene sulfonate (SDBS) in place of organic ammonium and/or phosphonium ions. A well-crystallized ZSM-5 was obtained by the mild hydrothermal treatment of a reaction mixture composed of SDBS and alumina-silica gel at about 180 °C and $P_{H_2O} \approx 10$ kg/cm^2 for 4 h.

Recently, Mobil Oil Corp. has successively synthesized a new type of zeolite, so called ZSM-5, by using organic bases such as tetra-n-propyl ammonium ion (TPA).[1] This zeolite has interesting properties for the conversion of methanol and other compounds to higher hydrocarbons, being considered to be a powerful catalyst for the production of high-quality gasoline from methanol in one step.[2-4] The aluminosilicate framework of ZSM-5 is unique in that it has straight channels with 10-membered ring apertures along the b-axis and sinusoidal channels with the same apertures in the ac plane of the orthorhombic cell. These channels intersect each other and the TPA ions are believed to be occluded in the pore structure as templates. According to Mobil Oil Corp,s patents, ZSM-5 can be synthesized by using other organic ammonium and/or phosphonium ions besides TPA. However, there are not any reports which describe the synthesis of ZSM-5 by using other organic materials. The present paper will describe a new route to the fruitful preparation of ZSM-5 by using one of the familier detergents, i.e., sodium n-dodecylbenzene sulfonate (SDBS) in place of N- and/or P- bearing organic bases.

A stainless steel autoclave (300 ml, SUS 316) was used under hydrothermal conditions up to 150 kg/cm^2 and 250 °C for the preparation of ZSM-5. This autoclave has a magnet-induced stirrer inside the reactor. The rotation rate of the stirrer was set to be 500 rpm in each run. An X-ray diffractometer with a Ni-filtered Cu Kα radiation (Rigaku Denki, D-3F) was used to identify each sample prepared in this work. Scanning speeds of a goniometer and a recorder were 2°2θ/min and 2 cm/min, respectively. Morphology of synthetic zeolites was observed by using a scanning electron microscope (JEOL, JSM-2).

Silica was in the form of five types of stable aqueous sodium silicate solutions (Nippon Kagaku Kogyo, water glass, No. 1, 2, 3, 4, and 4') whose molar ratios of SiO_2/Na_2O were 2.0, 2.5, 3.0, 3.5, and 4.3, respectively. They had traces of iron (below 0.02 wt%) and water insolible materials (below 0.05 wt%) as impulities. Alumina was introduced as aluminium sulfate (Kokusan Kagaku Kogyo, guaranteed reagent, $Al_2(SO_4)_3.16\text{-}18H_2O$). A 10 wt% SDBS solution was obtained by dissolving SDBS (Tokyo Kasei Kogyo, extra-pure reagent, $(n\text{-}C_{12}H_{25})C_6H_4SO_3Na$) in water.

Table 1 Hydrothermal Reaction Condition for Preparation of Each Product

Run	Water Glass (g)	Aluminium Sulfate (g)	SiO_2/Al_2O_3	SDBS (g)	Temp. (°C)	Product
1	No.1, 39.6	1.62	56	0.23	180	analcite
2	No.2, 41.9	1.62	45	0.23	180	mordenite
3	No.3, 50.6	1.62	56	0.23	180	ZSM-5
4	No.4, 61.1	1.62	56	0.23	180	ZSM-5
5	No.4',61.1	1.62	50	0.23	180	ZSM-5
6	No.4, 61.1	1.62	56	0.23	180	ZSM-5
7	No.4, 61.1	1.62	56	none	180	amorphous
8	No.4, 61.1	1.62	56	0.23	120	amorphous
9	No.4, 61.1	1.62	56	0.23	160	ZSM-5
10	No.4, 61.1	1.62	56	0.23	180	ZSM-5
11	No.4, 61.1	1.62	56	0.23	200	α-quartz
12	No.4, 61.1	1.62	56	0.23	220	α-quartz

Reaction conditions-

Reaction Time : 4 h, Heating Rate : 3 °C/min

The compositions of the reaction mixtures of starting materials and the crystallization conditions of runs 1-5 are summarized in Table 1. 0.3 ml of a 10-wt% SDBS was added to both solutions A and B, prior to mixing of their solutions. Following to this procedure, both solutions were transferred to a 500-ml beaker with vigorous stirring. The reaction mixture thus obtained was placed into the reactor of the autoclave, and treated under the hydrothermal conditions described in Table 1. Table 1 shows optimum or typical composition of raw materials to prepare each product. The hydrothermal pressure was the one determined by the chemical composition of the reaction mixture and the volume of the autoclave employed in this study, so that it was maintained 27 kg/cm^2 at the highest. After hydrothermal treatment, the solid material deposited in the reactor was collected by centrifusing and washing with water repeatedly, and then dried at 100 - 110 °C for the subsequent studies of X-ray and electron microscopic analysis. In order to investigate the effects of SDBS and temperature on the reaction products, seven other similar experiments (runs 6 and 7, and runs 8-12) were conducted.

The types of water glasses (solution A) were varied in the experiments of runs 1-5, whereas the quantity of alumina (solution B) and the crystallization conditions were unchanged. As a result, runs 3-5 gave the essentially same product. This product was assigned to be ZSM-5 from the X-ray diffractogram (Fig. 1), and the crystal habit observed by scanning electron microscopy (Fig. 4). On the other hand, runs 1 and 2 gave analcite and mordenite, respectively. These X-ray diffractograms are shown in Figs. 2 and 3. From these data, it has been elucidated that the less basisty or the sodium content in a reaction mixture, the more preferably ZSM-5 crystal is to be produced.

Run 6 gave the zeolite ZSM-5 whereas run 7 gave no zeolite but an amorphous material. As shown in Table 1, the reaction mixture of run 6 contains SDBS whereas that of run 7 does not. Subsequently, it is concluded that the addition is necessary

for the crystallization of ZSM-5, and that SDBS has an important role in forming the unique pore structure of ZSM-5, just as TPA does.

Effects of reaction temperatures on products are also shown in Table 1 (runs 8-12), which clarifies that ZSM-5 crystallizes in the temperature range between 160 and 180 °C, whereas amorphous product is obtained at lower temperature (120 °C) and α-quartz tends to yield at higher temperature (200 and 220 °C). Therefore, it is suggested that at lower temperature it takes quite a long time enough to crystallize ZSM-5, whilst at higher temperature SDBS as a template of the ZSM-5 structure becomes to decompose itself and the resulting reaction mixture tends to deposit non-zeolitic material such as α-quartz.

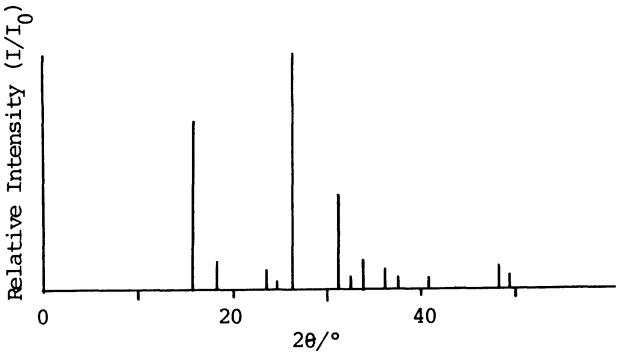

Fig. 1 X-ray Diffractogram for Product Obtained from Runs 3,4, and 5.

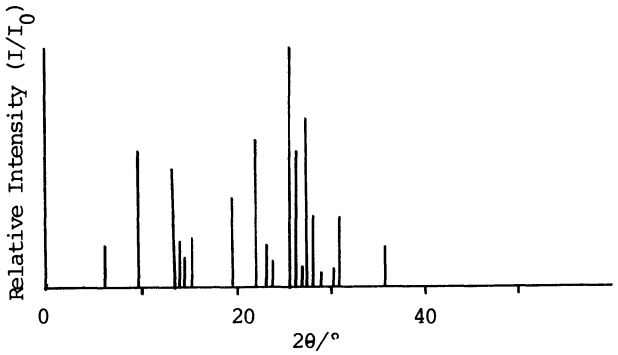

Fig. 2 X-ray Diffractogram for Product Obtained from Run 1.

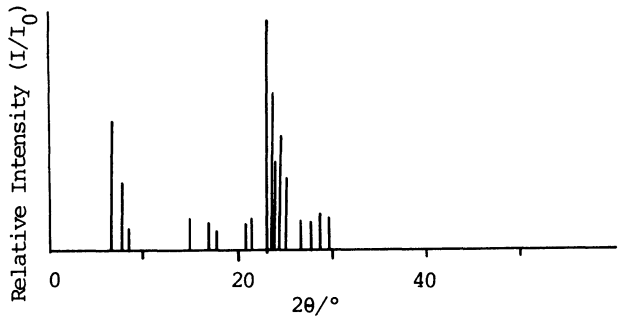

Fig. 3 X-ray Diffractogram for Product Obtained from Run 2.

In the present study, ZSM-5 has been easily synthesized by using sodium n-dodecylbenzene sulfonate, one of the familier detergents, together with water glass and aluminium sulfate under mild hydrothermal conditions. Moreover, a well-crystallized zeolite ZSM-5 observed using electron microscope could be obtained for only 4 hours of reaction. Therefore, it is considered that this new method is an alternative one for the preparation of ZSM-5. Further studies will be required to fully understand the effect of sodium n-dodecylbenzen sulfonate and reaction conditions such as temperature or basicity of solution on the preparation of the novel zeolite.

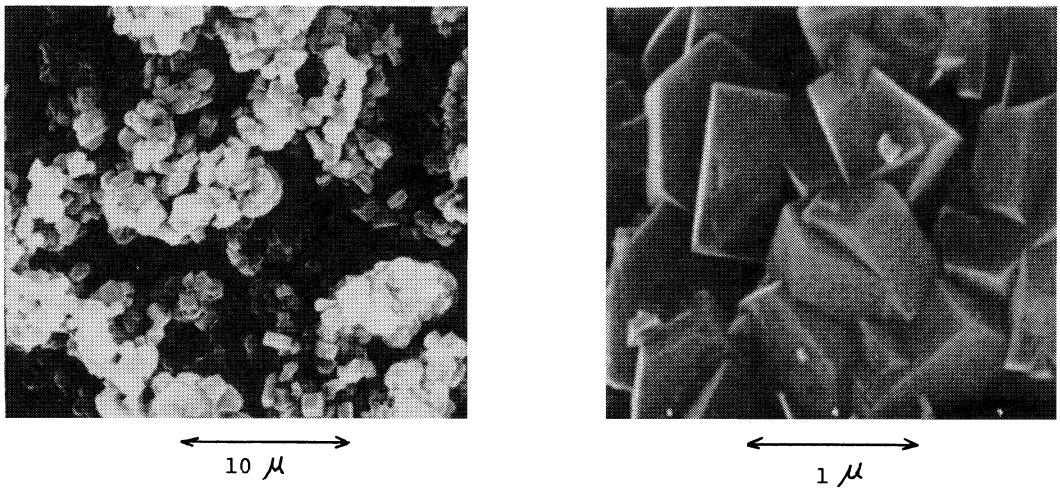

Fig. 4 Shape of ZSM-5 Measured by Electron Microscope

References

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