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PREPARATION OF ZSM-4 AND -5 ZEOLITES BY USING SLUDGE OBTAINED FROM GEOTHERMAL POWER PLANT

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Zeolites such as ZSM-5 or -4 were easily synthesized by using sludge obtained from geothermal power plants in place of some chemicals. Zeolites prepared were characterized by an X-ray diffractometer and a scanning electron microscope.

The effort for the development of geothermal energy is to be made for the establishment at an early data of exploration and extraction technology to permit development on a large scale and in a wide area of deep geothermal reservoir.[1)] Geothermal hot water contains about 600 - 1500 ppm of silicate including small amounts of aluminium and calcium.[2)] These inorganic materials in geothermal hot water have to be removed in order to prevent pipes of geothermal power generation from plugging or clogging by the deposition of silicate. Accordingly, a large amount of inorganic materials are produced as sludge in the geothermal power generation. The purpose of the work reported here is to apply the sludge as a starting material to prepare zeolites such as ZSM-5 or -4 in place of some chemicals.

A preparation of zeolites was carried out by using a stainless steel autoclave (300 ml, SUS 316) under hydrothermal conditions up to 2.5 MPa and 220 °C. The autoclave has a magnet-induced stirrer inside the reactor. The rotation rate of the stirrer was set at 500 rpm in each run. An X-ray diffractometer (Philips PW-1710) was used to identify each sample prepared. Scanning speeds of a goniometer and a recorder were 2° 2θ/min and 2 cm/min, respectively. The morphology of zeolites synthesized in this work was observed by using a scanning microscope (Shimazu ASM-SX).

Table 1. Chemical composition of sludge[a)]

	SiO_2	Al_2O_3	Na_2O	Fe_2O_3	CaO	K_2O
Sludge 1	92.3	3.7	3.7	0.08	0.09	0.18
Sludge 2	59.9	32.4	3.6	0.06	2.37	1.67

a) Analyses were made by using an atomic absorption spectrometer after heating sludge at 500 °C for 3 h.

Table 2. Hydrothermal reaction condition for preparation of each product

Run	Sludge[a)] / g	SiO_2/Al_2O_3	NaOH / g	Additive / g	t / °C	p / MPa	Product
1	15	43	10	TPA-Br,10	100	0.1	amorphous
2	15	43	10	TPA-Br,10	120	0.2	ZSM-5
3	15	43	10	TPA-Br,10	150	0.5	ZSM-5
4	15	43	10	TPA-Br,10	180	1.0	ZSM-5
5	15	43	10	TPA-Br,10	220	2.5	ZSM-5+α-quarts
6	10 b)	7	10	TMA, 2.5	150	0.5	ZSM-4
7	10 b)	7	10	BTMA-Cl,10	150	0.5	sodalite
8	15	3	20	TPA-Br,10	150	0.5	analcime

a) Sludge was treated under the hydrothermal condition for 20 h.
b) $Al_2(SO_4)_3$ was added to 10 g of sludge.
TPA-Br : Tetra-n-propylammonium bromide, TMA : Tetramethylammonium hydroxide,
BTMA-Cl : Benzyltrimethylammonium chloride.

Two types of sludge (Sludge 1 and 2) obtained from the geothermal generation plant at Ohtake in Kyushu were used to prepare zeolites. Compositions of these sludge are shown in Table 1. Sludge 1 contains about 93 wt% of SiO_2 basing on oxide and small amounts of Al_2O_3 and Na_2O in it. On the other hand, Sludge 2 contains more than 30 wt% of Al_2O_3 because of the addition of aluminium ions in geothermal hot water. Molar ratios of SiO_2/Al_2O_3 for sludge 1 and 2 are 42.7 and 3.1, respectively. Organic ammonium solutions such as tetra-n-propylammonium bromide (TPA-Br) were prepared by dissolving them in distilled water. These sludge were dried at 110 °C for 20 h before preparation. Distilled water and the sludge were placed into a 300 ml beaker and vigorously stirred. Then an organic ammonium solution and a sodium hydroxide solution were added in the beaker. The reaction mixture thus obtained was set in the reactor of the autoclave, and treated under the hydrothermal condition for 20 h. Optimum or typical compositions of raw materials to prepare each product are summarized in Table 2. After hydrothermal reaction, the solid materials deposited in the reactor was collected by centrifusing and washing with water repeatedly. Each product was dried at 110 °C for 10 h, and then examined by using the X-ray diffractometer and the electron microscope.

In the experiments of Runs 1-5, the reaction temperature of the hydrothermal treatments varied from 100 °C to 220 °C, whereas the composition of the raw materials (Sludge 1), an additive (tetra-n-propylammonium bromide), and other reaction conditions were not changed. As a result, Run 1 gave no crystalline product. Runs 2-4 gave essentially the same product. This product was assigned to be ZSM-5 from the X-ray diffractogram (Fig. 1) and the crystal habit observed by the scanning electron microscopy (Fig. 2). On the other hand, Run 5 gave both ZSM-5 and α-quartz. From these data, it was found that ZSM-5 crystallizes in the temperature range between 120 °C and 180 °C, whereas an amorphous product is obtained at lower temperature (100 °C) and α-quartz tends to yield at a higher

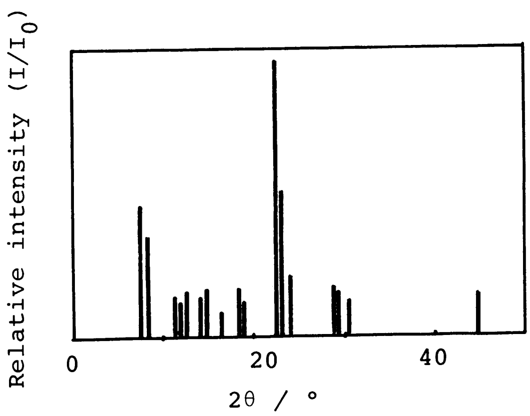

Fig. 1. X-ray diffractogram for product obtained from Runs 2,3, and 4.

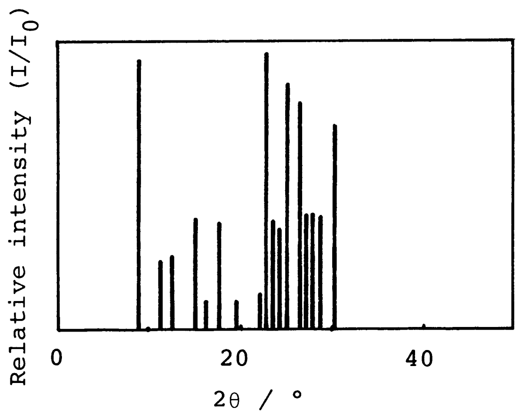

Fig. 3. X-ray diffractogram for product obtained from Run 6.

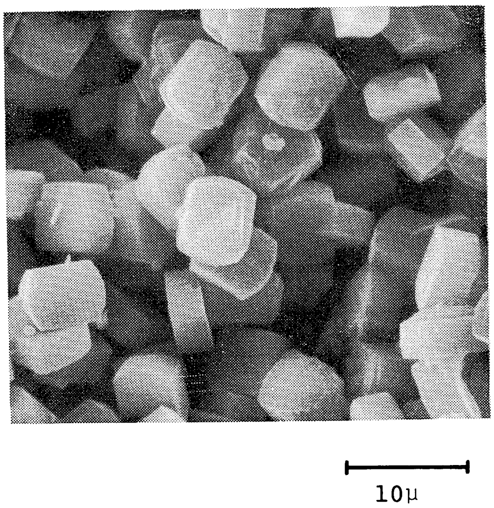

Fig. 2. Shape of ZSM-5 measured by electron microscope.

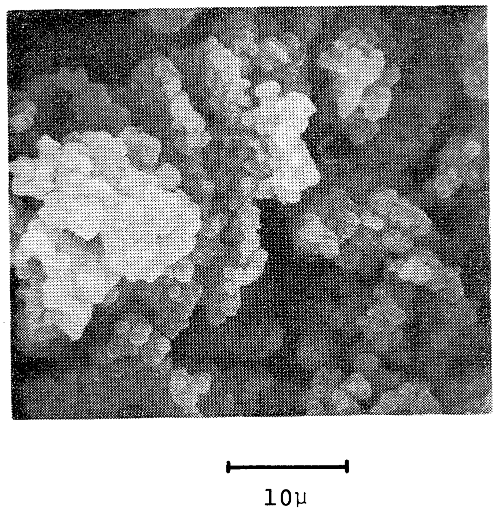

Fig. 4. Shape of ZSM-4 measured by electron microscope.

temperature (220 °C). The effect of reaction temperatures on the preparation of ZSM-5 was similar to our previous study in which ZSM-5 was prepared by using a familiar detergent in place of organic ammonium ions.[3)]

The reaction temperature of hydrothermal treatments was fixed at 150 °C in the experiments of Runs 6-8. A solution of aluminium sulfate was added to Sludge 1 in order to change molar ratios of SiO_2/Al_2O_3 in the experiment of Runs 6 and 7. Tetramethylammonium hydroxide (TMA) was used in the experiment of Run 6 as an additive of an organic ammonium ion. The crystalline product obtained from Run 6 was different from that obtained from Runs 2-4. The product was found to be ZSM-4. The X-ray and the electron microscopic analyses of zeolite ZSM-4 are shown in Fig. 3 and Fig. 4, respectively. When benzyltrimethylammonium chloride was used as an additive in place of TMA (Run 7), sodalite was synthesized as shown in Figs. 5 and 6.

Sludge 2 was applied as a starting material for the experiments of Run 8.

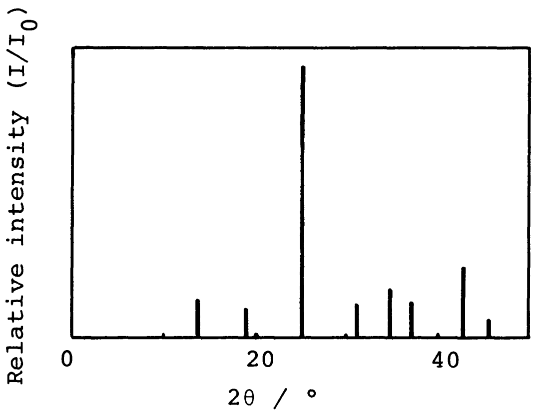

Fig. 5. X-ray diffractogram for product obtained from Run 7.

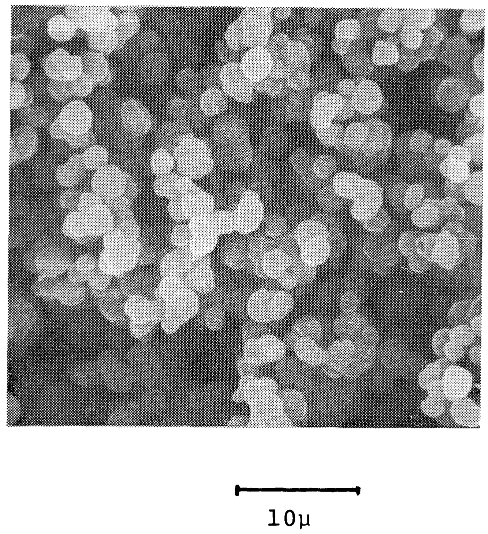

Fig. 6. Shape of sodalite measured by electron microscope.

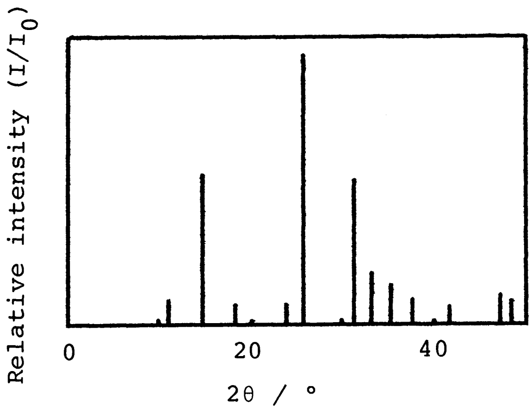

Fig. 7. X-ray diffractogram for procuct obtained from Run 8.

Analcime was obtained from Run 8 (Fig. 7).

In the present work, zeolite ZSM-5 was easily synthesized by using sludge, which was obtained from the geothermal generation plant, in place of some chemicals under mild hydrothermal conditions. Moreover other zeolites such as ZSM-4 whose molar ratio is different from that of ZSM-5 were successively synthesized by adding alminium ions and/or using different types of sludge. These results seem to indicate that many kinds of zeolites will be made from sludge by changing the molar ratios of starting materials and using proper organic ammonium ions.[4)] The zeolites prepared will be used for petroleum purification. The sludge is inexpensive and readily available. Therefore, it is considered that this new method will be an alternative one for the preparation of zeolites.

References

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