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Trial of Zeolite Synthesis in Non-Aqueous Solvent

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The synthesis of zeolites in non-aqueous solvent such as methanol, xylene and 2-propanol was carried out with various procedures. Using tetraethoxysilane, aluminum triisopropoxide and sodium hydroxide, the crystals developed sufficiently were not formed in these solvents. But the crystals were developed by addition of trace amounts of water. In 2-propanol, the excellent crystal was formed with fumed silica for the first time. Silica sodalite was prepared according to D. M. Bibby et al. 's method. The several properties of these crystals were surveyed.

1. Introduction

In general, zeolites are hydrothermally synthesized with silicon, aluminum, alkali and water as a solvent. Zeolite crystals are produced under metastable condition.1) Recently, the synthesis of zeolites has been carried out in non-aqueous solvent,2) so much attention has been attracted on it.3-7) As many zeolites are hydrothermally crystallized under metastable condition, the crystals of new structure or crystals having new surface properties are expected.

Because the authors have originally used metallic alcoholates as a starting material, the authors have given attention to the alcohol molecules derived from hydrolysis of metallic alcoholates in the reaction system.8-9) In this experiment, the synthesis of zeolites using some organic solvents was carried out under mild condition. And some subjects concerning the synthesis in non-aqueous solvents were pointed out.

Silica sodalite that was synthesized by D. M. Bibby et al.2) in ethyene glycol was prepared according to their procedure. In this experiment, the synthesis of sodalite crystals was successful in 2-propanol in perfect-non-aqueous system. These crystals obtained were characterized by XRD, IR spectra, adsorption of gas and vapor, heat of immersion and DTA-TGA measurents and some knowldges were obtained.

2. Experimental

2.1 Reagents

In the synthesis, aluminum triisopropoxide as a source of alminum, tetraethoxysilane and fumed silica as a source of silicon and sodium hydroxide as a source of alkali were used. As solvents, 2-propanol, methanol, xylene and ethlene glycol were used. Ethylene glycol was used only in D. M. Bibby et al. 's method.

At first all solvents that are commercial-guaranteed reagents were used in the synthesis without further purification. As will be seen later, trace amounts of water included as impurity influenced significantly the crystallization of zeolites. So the reagents purified carefully were used in the later experiments. The authors paied close attention to prevent mixing of water.

2.2 Procedure of synthesis

The mol ratios of starting materials were decided from the preliminary experiment. And they were $SiO_2/Al_2O_3=2$, $Na_2O/Sio_2=5$ and solvent/$Na_2O=90-104$. The procedure of the synthesis was as follows.

[Ⅰ] Method The mol ratios of starting materials were $SiO_2/Al_2O_3=2$, $Na_2O/SiO_2=5$ and solvent/$Na_2O=98$. Xylene (20 ml) was placed in a flask and aluminum triisopropoxide (1.0212 g) was dissolved in xylene, and tetraethoxysilane (1.11 ml) was poured in the flask. 2-propanol (100 ml) was placed in another flask, and sodium hydroxide (2.00 g) was added and the solution was stirred throughly and then it was poured into the former flask. In addition, 2-propanol (76 ml) was added and shaken mildly, and then the solution was stirred mechanically at room temperature. After stirring for a fixed time, the flask was kept in an air-oven at a fixed temperature in the range of 60 to 80°C. The crystals produced were filtered off and washed with distilled water and dried at 110°C for 24hr.

[Ⅱ] Method The mol ratios of staring materials were $SiO_2/Al_2O_3=2$, $Na_2O/SiO_2=5$ and solvent/$Na_2O=90$. This method was nearly same as [Ⅰ]. Aluminum triisopropoxide (1.0212 g) was mixed directly with tetraerthoxysilane (1.11 ml) without using xylene. Then, 2-propanol dispersed sodium hydroxide (2.00 g) and the residual 2-propanol (77 ml) were added into the flask. The solution was stirred mechanically for a fixed time at room temperature and was kept in an air-oven at 80°C for a fixed time.

[Ⅲ] Method The mol ratios of starting materials were $SiO_2/Al_2O_3=2$, $Na_2O/SiO_2=5$ and solvent/$Na_2O=90$. This method was nearly same as [Ⅱ]. After aluminum triisopropoxide (1.0212 g) was dispersed into 2-propanol (50 ml), tetraethoxysilane (1.11 ml) was poured into the solution. After 2-propanol (100 ml) dispersed sodium hydroxide (2.00 g) and residual 2-propanol (22 ml) were added into the solution, the solution was stirred mechanically at room temperature and was kept at 80°C for a fixed time.

[Ⅳ] Method The mol ratios of starting materials were $SiO_2/Al_2O_3=2$, $Na_2O/SiO_2=5$ and solvent/$Na_2O=104$. This method was nearly same as [Ⅰ]. Aluminum triisopropoxide (1.0212 g) was dissolved into xylene (50 ml) and tetraethoxysilane (1.11 ml) was mixed. And then methanol (100 ml) dissolved sodium hydroxide (2.00 g) and 2-propanol (2 ml) were added into the solution. After the solution was stirred mechanically at room temperature for a fixed time, the solution was kept in an air-oven at 67°C for a fixed time.

[Ⅴ] Method In the [Ⅳ] Method, sodalite crystals were formed in non-aqueous solvent, but the reproducibility of the crystals was poor. The authors considered that trace amounts of water included in solvent may contribute to the poor reproducibility of the crystals. Therefore, in [Ⅲ] Method, 0.6-6 vol% of water to solvent was added.

[Ⅵ] Method This includes addition of water in the [Ⅰ] Method.

[Ⅶ] Method The mol ratios of starting materials were $SiO_2/Al_2O_3=\infty$, $Na_2O/SiO_2=0.75$ and solvent/$Na_2O=26.7$. This is the D. M. Bibby et al. 's method. This method was carried out using fumed silica (aerosil 200), sodium hydroxide, and ethylene glycol. In this method, the source of aluminum was not used. Ethylene glycol (37.11 ml) and sodium hydroxide (2.00 g) were placed in a flask, and the flask was stirred mechanically for 8-12hr. And fumed silica (2.002 g) dried at 110°C for 1hr was added into the flask, and the solution was stirred at 30°C for 24hr. And then, the solution was kept in an air-oven at 150°C for 480hr. The product was unique crystals consisted of 4 and 6 oxygen rings only, though silica was rich.

[Ⅷ] Method The mol ratios of starting materials were $SiO_2/Al_2O_3=2$, $Na_2O/SiO_2=5$ and solvent/$Na_2O=90$. 2-propanol (172 ml) was placed in a flask and sodium hydroxide (2.00 g) was dispersed in the solvent. The solution was stirred for 8-12hr at 30°C. Aluminum triisopropoxide (1.0212 g) and fumed silica (aerosil 200, 0.3004 g) dried at 110°C for 1hr were added into the solution and stirred thoroughly. The solution was stirred mechanically at 30°C for 24hr and was kept in an air-oven at 80°C for 120hr.

Aside from above experiments, in the Bibby et al. 's method ([Ⅶ] Method), surface Si-OH of fumed silica and water molecules adhered to the surface or Si-OH by hydrogen bond must be considered, so fumed silica had been heated at 500°C for 1hr prior to use. In this case the crystallinity of products was very poor, that is, silica sodalite did not develop sufficiently. Therefore, the effect of pretreatment of fumed silica by heating at 110°, 200°, 300°, 400° and 500°C on the crystallinity of silica sodalite was surveyed.

Moreover, in the [Ⅷ] Method, fumed silica was used after pretreatment by heating as same manner as above.

The relation between aging time and degree of crystallinity in [Ⅲ] Method using 2-propanol contained 1.2% water was surveyed.

2.3 Characterization of samples

The products were identified by XRD (Toshiba ADG301, Cu-Kα 30 Kv, 20 mA, Ni filter, G. M. Detector). The surface properties of crystals were surveyed by adsorption of volumetric method using nitrogen and oxygen gas at 77 K, and by adsorption of gravimetric method using water, methanol, benzene, cyclohexane and pyridine vapour at 60 mmHg. The DTA-TGA was carried out using Shimazu DTG 40. IR spectra were measured by KBr wafer technique using Hitachi infrared spectrometer model 260-50. Furthermore, the heat of immersion with water was measured. The measurement was carried out by twin-conduction type calorimeter (Tokyo Riko TCC-2 type).

3. Results and discussion

3.1 Synthesis

The authors tried to synthesize zeolites in organic solvent that was not purified, using the [Ⅰ]~[Ⅳ] Method. As shown in Table 1, the crystals, B, ΔA and A were produced by [Ⅰ] and [Ⅱ] Method. As the crystals, B and ΔA, had low crystallinity, these crystals were not identified by XRD.[10] The crystals A had low crystallinity, but it turned out sodalite crystals by XRD. It became apparent that the crystals B and ΔA were precursor or intermediate of sodalite crystals. Therefore, B was termed a prrcursor of sodalite, ΔA was termed a

Table 1 Reaults of Synthesis

Method	Mechanical stirring(hr)	Temperature of aging(℃)	Time of aging(hr)	Product
I *	24	60	72	B
	24	60	97	ΔA
	24	60	116	ΔA
	24	60	145	A
	24	60	165	B
I	120	60	135	B
	123	60	164	B
	60	80	237	B
	24	80	248	B
	60	80	308	B
II *	24	80	58	B
	24	80	73	ΔA
	48	80	116	A
	48	80	165	A
II	120	80	135	B
	25	80	189	B
	42	80	237	B
	24	80	243	B
	25	80	265	B
	42	80	308	B
III	45	80	48	B
	45	80	105	B
	24	80	116	B
	24	80	137	B
	24	80	161	B
	24	80	167	B
	48	80	195	B
	24	80	236	B
	45	80	259	B
	48	80	264	B
	24	80	267	B
	24	80	336	B

IV		147	67	140	B
		48	67	159	B
		24	67	167	A
		24	67	236	B
		66	67	329	B
		99	67	329	B
V	0.6	24	80	140	B
	0.6	24	80	168	B
	1.2	25	80	5	B
	1.2	25	80	43	A
	1.2	31	80	75	A**
	1.2	31	80	98	A**
	1.2	26	80	168	A**
	1.2	31	80	242	A**
	1.8	43	80	216	A*
	2.4	43	80	163	A*
	3.0	24	80	168	A*
	6.0	24	80	168	A*
VI	0.6	24	80	165	B
	0.6	24	80	260	B
	0.6	24	80	333	B
	3.0	24	80	165	A*
	3.0	24	80	260	A*
	3.0	24	80	333	A*
	6.0	26	80	168	A*

I*, II* : Solvents were used in the synthesis without purification.

The figures in the first column represent the amount of water contained in solvent.

intermediate of sodalite and *A* was termed sodalite-like material.

From this fact, it was believed that sodalite crystals were crystallized in the non-aqueous solvent. Then the solvents were further purified in order to synthesize the crystals with much higher crystallinity and purity. But crystal *B* only was produced by the [I]~[IV] Method as shown in Table 1.

Crystals *A* were once obtained by the [IV] Method but the reproducibility was poor. It may be attributable to trace amounts of water included in methanol. It was considered that the crystals *B* do not grow over the state *B* without water.

How much amount of water affected on the crystallization was considered by using [V] Method. The synthesis of sodalite crystals was carried out by addition of 0.6~6% water to 2-propanol. The excellent crystals were formed in 2-propanol solvent with addition of 1.2% water. The authors termed these crystals *A***. The crystals obtained from 2-propanol containing 1.8~6% water contained mixed crystals. Therfore, the crystals were termed *A**. From the results mentioned above, it was considered that in the perfect-non-aqueous solvent crystals *B* do not grow further without water.

On the other hand, D. M. Bibby et al. synthesized silica sodalite using ethylene glycol that tends to absorb many water molecules by hydrogen bond. So the presence of water in ethylene glycol was suspected. D. M. Bibby et al. did not deny clearly the presence of trace amounts of water in the reaction system[2]. Perhaps, it may be difficult to prevent perfectly the mixture of water from the reaction system.

When amount of water was controled precisely, the XRD patterns of products are shown in Fig.1. These are the results of sysnthesis using [Ⅲ] Method at constant aging time, 72hr. In the case of the addition of 1.2% water, the excellent crystals were formed.

At the amount of water was kept constant (1.2%), and the aging time was varied in the following, that is, 5, 25, 48, 60, 72, 120, 360 and 960hr. The representative case is shown in Fig.2. Sodalite crystals were observed after 72hr of aging time, but intermediate crystals or sodalite-like material had been produced before then. It was required to keep the aging time of 72hr for crystallization in this condition. The degree of crystallinity increased with aging time

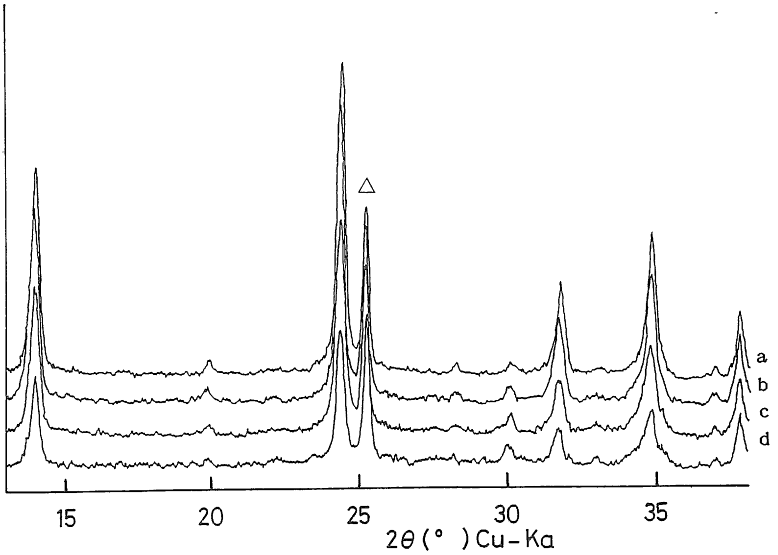

Fig.1 Changes of the XRD patterns with amount of water contained in solvent. a : 1.2%, b : 1.1%, c : 0.9%, d : 0.8%, Δ : Anatase (Internal standard)

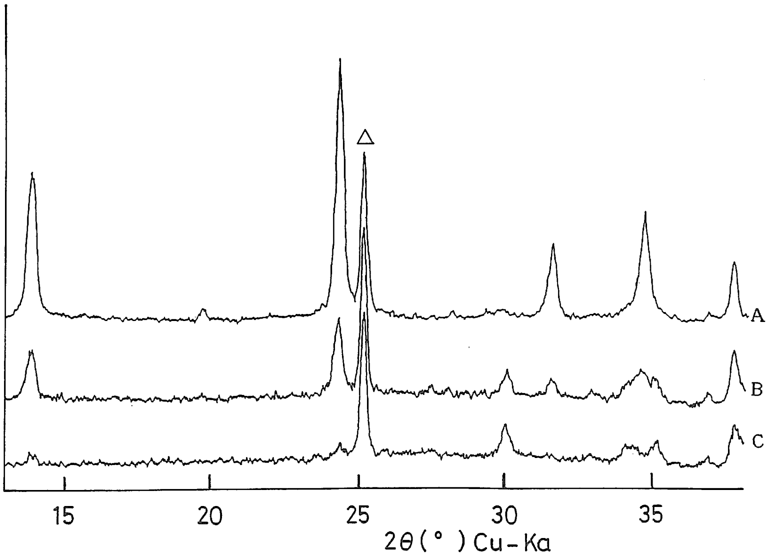

Fig.2 Changes of the XRD patterns with aging time at 80°C.
A : 72hr, B : 60hr, C : 5hr, Δ : Anatase (Internal standard)

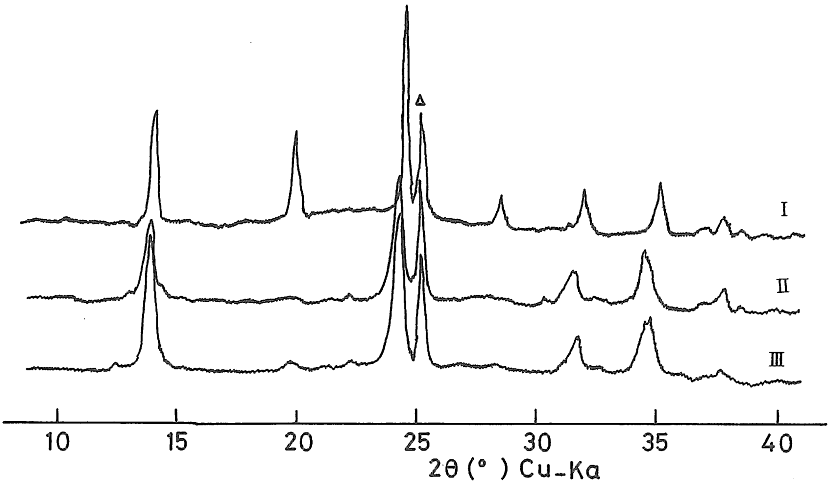

Fig.3 The XRD patterns of sodalite crystals.
I : Silica sodalite obtained from Bibby et al. 's method.
II : Sodalite crystals obtained from 2-propanol.
III : Sodalite crystals obtained from 2-propanol containing 1.2% water.
Δ : Anatase (Internal standard)

but on the contrary the crystallinity decreased and phase transition was observed beyond the aging time 960hr.

Sodalite crystals were prepared by D. M. Bibby et al. 's methods, [Ⅶ] Method, and [Ⅷ] Method. Sodalite crystals were produced in 2-propanol for the first time. Each method was considered to be perfect-non-aqueous system.

The XRD patterns of sodalite crystals prepared from [Ⅴ], [Ⅶ] and [Ⅷ] Methods are shown in Fig.3. The crystals obtained from [Ⅶ] Method were silica sodalite, so the diffraction angle (2θ) was higher than others. Silica sodalite is consisted of only silicon and oxygen2), so the lattice constant is shorter than others. But diffraction angle of sodalite crystals obtained from [Ⅴ] and [Ⅷ] Method were nearly same.

IR spectra are shown in Fig.4. The absorption bands of silica sodalite slightly shifted to higher wave number compared with others. This is responsible for the silica-rich structure.

Much attention has been paied to the solvent itself in the synthesis in the non-aqueous solvent. D. M. Bibby et al. used fumed silica as a source of silica. As fumed silica is very fine

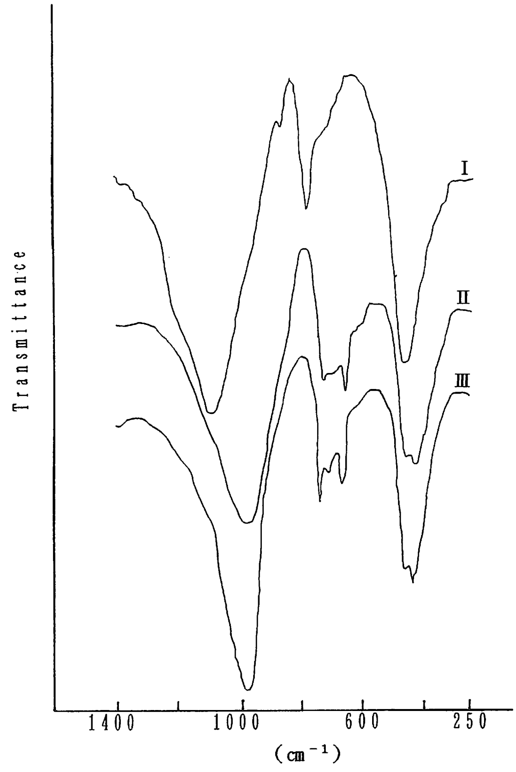

Fig.4 IR sprctra of sodalite crystals

Ⅰ : Silica sodalite obtained from Bibby et al. 's method.

Ⅱ : Sodalite crystals obtained from 2-propanol.

Ⅲ : Sodalite crystals obtained from 2-propanol containing 1.2% water.

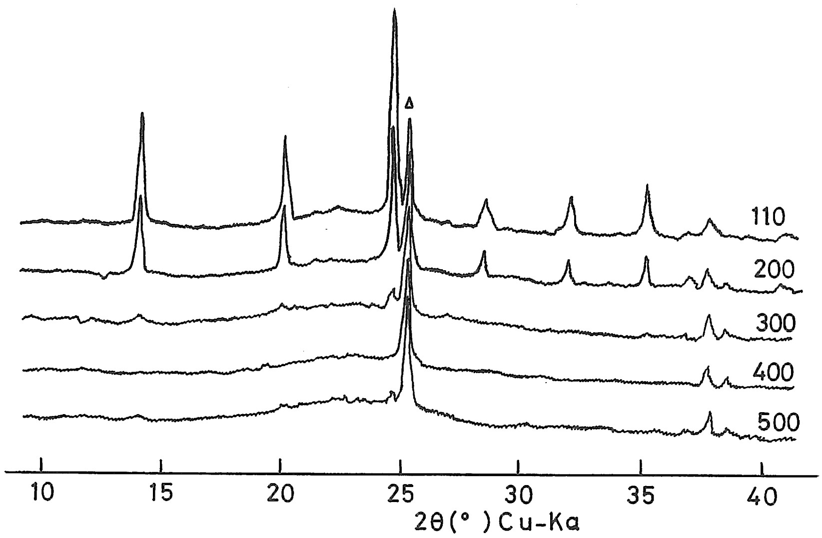

Fig.5 Changes of the crystallinity with heating temperature of fumed silica in the [Ⅶ] Method.
Figures denote the heating temperature (°C).
Δ : Anatase (Internal standard)

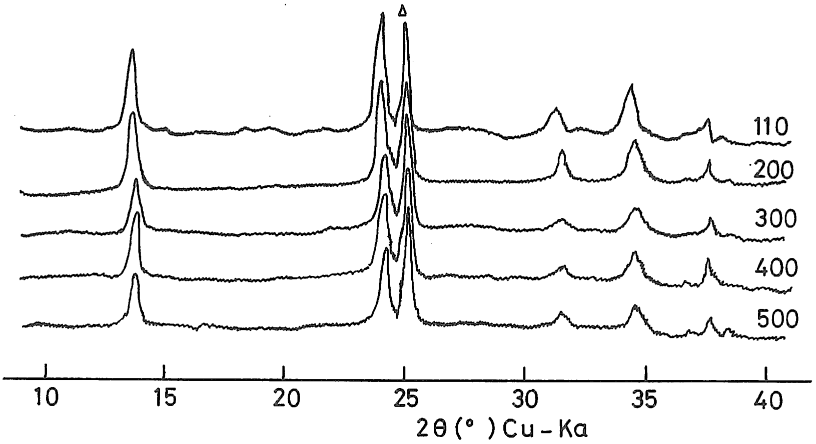

Fig.6 Changes of the crystallinity with heating temperature of fumed silica in the [Ⅷ] Method.
Figures denote the heating temperature (°C).
Δ : Anatase (Internal standard)

powder, it has a large surface area. So Si-OH and chemical water may exist on the surface and may affect on the crystallization mechanism.

In the [Ⅶ] Method, the variances of XRD patterns with heating of silica source are shown in Fig.5. The crystals derived from fumed silica heated at 300°C revealed considerably low crystallinity, nearly state of crystals *B*. This suggets that the presence of water is very important in the synthesis of zeolites. But in the synthesis of Bibby et al. and other workers, how much attention have been paied to the presence of water included in the starting materials is obscure. The authors carried out the same experiment in the 2-propanol system as mentioned above. The results are shown in Fig.6. Figure 6 shows that sodalite crystals were formed in spite of fumed silica heated at 500°C, the results differed greatly from the ones of Bibby et al. This is because this system contains aluminum in the solution, so the crystals tend to be crystallized.

3.2 Characterization of crystals

Adsorption isotherms of nitrogen gas are shown in Fig.7. In this figure, silica sodalite and sodalite crystals obtained from 2-propanol containing 1.2% water are only shown. Other specimens revealed nearly same isotherms. Sodalite crystals adsorbed little nitrogen gas. They consist of 4-and 6-oxygen rings only, so they have not the window that makes nitrogen gas penetrate into a pore[11]. Especially silica sodalite adsorbed little nitrogen gas compared with other crystals. The adsorption isotherms of oxygen gas were measured, too. The tendency of isotherms was nearly same as nitrogen gas.

The results of adsorption of water, methanol, benzene, cyclohexane and pyridine vapor on silica sodalite and sodalite crystals obtained from 2-propanol are shown in Table 2. Silica sodalite adsorbed smaller amounts of each vapor than sodalite obtained from 2-propanol. The latter crystal is aluminosilicate, so it contains sodium and aluminum in the framework. Therefore this crystal interact strongly with each vapor molecule compared with silica sodalite. As the size of molecules increased, the amount adsorbed decreased on the each crystal. The order of amount adsorbed decreased nearly, water > methanol > benzene > cyclohexane > pyridine. Comparing silica sodalite and sodalite crystals obtained from 2-propanol, they adsorbed nearly equal amount of cyclohexane, but the former adsorbed benzene molecule

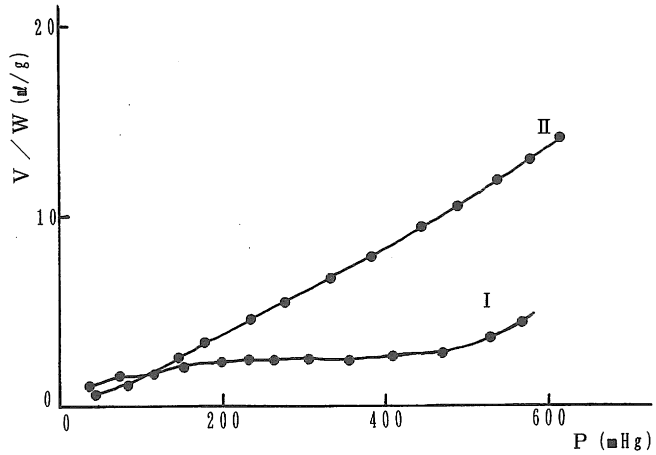

Fig.7 Adsorption isotherm of nitrogen gas.
I : Silica sodalite obtained from Bibby et al. 's method.
II : Sodalite crystals obtained from 2-propanol containing 1.2% water.

nearly a half amount of the latter, and adsorbed pyridine molecules nearly two third of the latter respectively. These molecules are considered to have same molecular size. Therefore, this cause is considered that silica sodalite does not consist of sodium and aluminum, so the surface can not interact with π electron of benzene and lonepair of electrons of pyridine.

The heat of immersion of silica sodalite and sodalite crystals obtained from 2-propanol were 2.12 cal/g and 15.6 cal/g respectively. The value of the former was considerably smaller than the latter. The smaller value of former is caused by the few constituents of aluminum and sodium in the framework of crystals. That is, silica sodalite is hydrophobic crystal. Relation between the degree of crystallinity and the heat of immersion of sodalite crystals obtained from 2-propanol containing 1.2% water is shown in Fig.8. As the degree of crystallinity increased, the heat of immersion decreased. This is because the size of crystals becomes larger with degree of crystallinity. In Fig.3. the degree of crystallinity was evaluated by comparing the XRD intensity of the samples and TiO_2 (Anatase) as a internal standard.

In water solvent, zeolite *A* type could be synthesized using the same mol ratio of the starting materials of sodalite crystals. The heat of immersion of zeolite *A* with water is shown in Fig.9. In this case, the heat of immersion increased with the degree of crystallinity. This tendency is opposite to that of sodalite crystals. This is because zeolite *A* crystals consist of 8-oxygen rings that make water molecule penetrate fully, so the heat of immersion increased with the degree of crystallinity. On the other hand, sodalite ctystals obtained from 2-propanol containing 1.2% water can not adsorb fully water.

DTA-TGA were carried out on sodalite crystals. Silica sodalite revealed exothermic peak that may be responsible for combustion of solvent at 440 and 600°C. This suggests two different

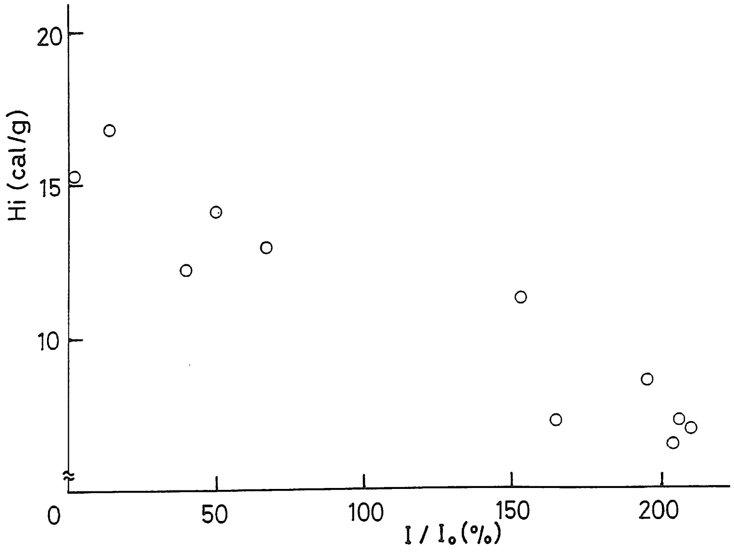

Fig.8 Relation between the crystallinity and the heat of immersion of sodalite crystals obtained from 2-propanol containing 1.2% water.

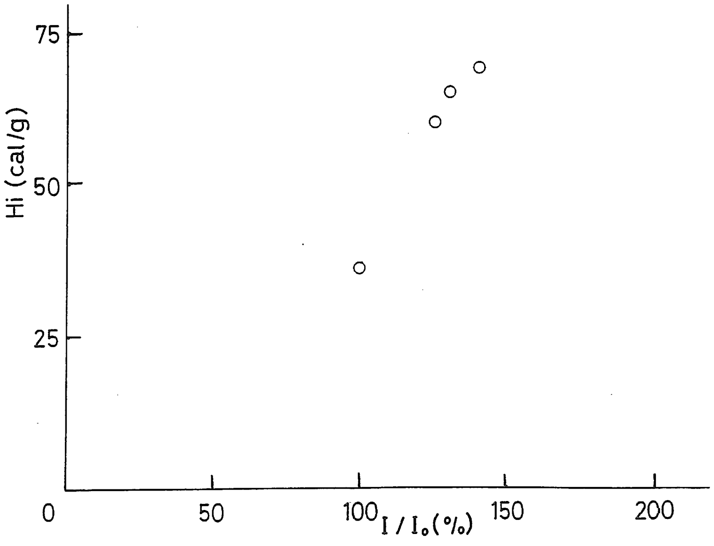

Fig.9 Relation between the crystallinity and the heat of immersion of zeolite *A*.

states of solvent in the crystals. This crystal revealed the phase transition to unknown material at around 900°C. Sodalite crystals obtained from 2-propanol revealed the loss in weight until 300°C, and the exothermic peak that is responsible for phase transition to nepheline at arround 800°C. Sodalite crystals obtained from 2-propanol containing 1.2% water revealed nearly the same behavior. But this crystal revealed the phase transition to nepheline at around 900°C.

4. Conclusion

The synthesis of zeolites was carried out using tetraethoxysilane, aluminum triisopropoxide and sodium hydroxide in non-aqueous solvent such as methanol, xylene and 2-propanol. Crystals did not grow beyond the state *B* termed the precursor of sodalite crystals. The excellent crystals of sodalite were formed in 2-propanol containing 1.2% water. It became apparent that trace amounts of water influences significantly the crystallization of zeolites in organic solvent.

Excellent sodalite crystals were obtained using fumed silica, aluminum triisopropoxide and sodium hydroxide in 2-propanol for the first time. On the other hand, silica sodalite crystals were prepared in ethylene glycol, that is, using the Bibby et al. 's method.

XRD revealed that silica sodalite is silica-rich crystal and the lattice constant is shorter than others. The absorption bands of IR spectra shifted to higher wave number compared with others. In D. M. Bibby et al. 's method, they used fumed silica as a silica source. When fumed silica was heated at 300°C for 1hr, the crystals did not grow sufficiently.

The surface property of silica sodalite was unique compared with other crystals containing aluminum and sodium. Silica sodalite adsorbed a little benzene and cyclohexane vapor and nitrogen gas. The heat of immersion of silica sodalite with water was lower compared with other crystals obtained from 2-propanol. Therefore, the surface property of silica sodalite is hydrophobic. Sodalite crystals obtained from 2-propanol have the nearly same property as others.

In the synthesis of zeolite crystals in non-aqueous solvent, trace amounts of water must be noted and excluded from the reaction system. Futrher details of surface properties of sodalite crystals obtained from ethylene glycol, 2-propanol and 2-pronanol containing 1.2% water will be reported with other properties.

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