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Studies on the Mechanism of Zeolite X Crystallization. II. Effect of Silica Sources of Starting Materials on the Gas-phase Adsorption at Solid Phases

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The mechanism of zeolite X crystallization was studied by using two kinds of silica sources, tetraethyl orthosilicate and silica sol. The adsorption of benzene and cyclohexane was subjected to a measurement to clarify the distribution of cation Na^+ and the change in the pore structure and surface of solid phases with reaction progress. The relation between specific surface area and reaction time has been revealed by means of adsorption of nitrogen gas, benzene, and cyclohexane as follows: 1) In the early stage of reaction or in the amorphous solid state, $N_2 \approx C_6H_6 \approx C_6H_{12}$ for tetraethyl orthosilicate and $N_2 \approx C_6H_6 > C_6H_{12}$ for silica sol; 2) for crystals in the early stage, $N_2 > C_6H_{12} > C_6H_6$ for tetraethyl orthosilicate and $N_2 > C_6H_{12} \approx C_6H_6$ for silica sol; 3) for crystals in a sufficiently developed stage, $N_2 \gg C_6H_{12} > C_6H_6$ for tetraethyl orthosilicate and $N_2 \approx C_6H_6 > C_6H_{12}$ for silica sol. In the case of silica sol, the crystallization mechanism is based on inhomogeneous nucleation; a number of critical nuclei may be generated but their dimension is small. In the case of tetraethyl orthosilicate critical nuclei are fewer in number and larger in size than in the case of silica sol; the mechanism of crystallization is based on homogeneous nucleation.

Zeolites are aluminosilicate crystals which are easily formed from gels composed of silica, alumina, soda, and water. However, because of the complexity of aluminosilicate gel in structure and reaction, the process of zeolite crystallization has not yet been made clear.

Many investigations concerning zeolite crystallization have been done in recent years.[1—10] Two representative hypotheses exist as follows: One is a zeolite crystallization which occurs in the solid phase in such a way that crystals are formed through interaction between the solid and liquid phases of a gel. This is supported by Breck and Flanigen,[5] McNicol *et al.*,[11] and Aiello *et al.*[12] The other is a crystallization which occurs in the liquid phase in such a way that an amorphous precursor is formed from a reaction mixture and then caused its constituents to be dissolved in the liquid phase prior to crystallization. This has been supported by Kerr,[1] Ciric,[7] Culfaz and Sand,[2] and Cournoyer *et al.*[13]

Some additional investigations in support of the latter hypothesis have recently been reported by Ueda and Koizumi[10] and Kageyama *et al.*[9] They pointed out that the presence of the solid-gel phase is not always needed in the crystallization process of zeolite Y, because crystals are grown in homogeneous solution. But, in general, the presence of solid phases as transient intermediates has been observed in many systems for zeolite synthesis.

The present authors[14,15] have reported that sources of silica remarkably influence the crystallization process. In this study, we made measurements on the adsorption of benzene or cyclohexane vapor to clarify the distribution of cation Na^+ and the change in pore and surface with reaction progress, and made an inference on the change in solid phases by considering both the interaction between the cation and the π-electrons of benzene and the physical adsorption of cyclohexane.

Experimental

The preparation of specimens, the chemical analysis of solid phases, and the adsorption of nitrogen gas were conducted as described in previous papers.[14,15] The absorption of benzene or cyclohexane vapor was subjected to volumetric measurements at 25 °C. The pretreatment of specimens was carried out in such a sequence that specimens were placed in a bath thermostated at 110 °C for 24 h, heated at 300 °C for 2 h, and finally degassed under a reduced pressure of 1×10^{-4} mmHg (1 mmHg≈133.322 Pa) at 300 °C. The adsorbates, benzene and cyclohexane, were obtained by purifying commercial guaranteed reagents by distillation.

Results and Discussion

The change in the chemical composition of solid phases with reaction time is shown in Fig. 1. Figure 1 indicates analytical values obtained for the solid phases during the process of aging with mechanical stirring at room temperature for 6—72 h followed by standing in the bath thermostated at 85 °C for 74—96 h. As can be seen from Fig. 1, the change in the analytical values for the solid phases derived from silica sol is abrupt as compared with those derived from tetraethyl orthosilicate.

The solid phases derived fom tetraethyl orthosilicate contain all constituents uniformly throughout the

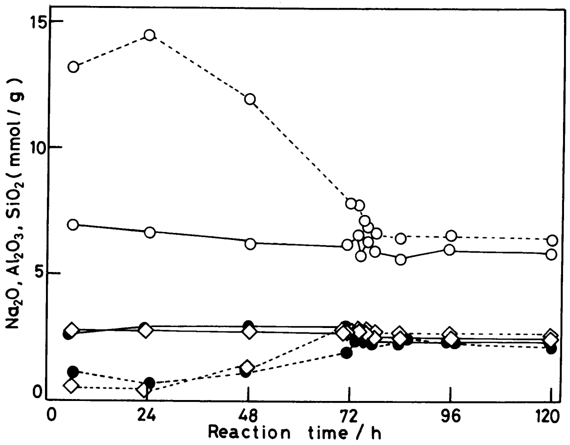

Fig. 1. Relation between reaction time and component concentrations in the solid phase.
——: Si $(OC_2H_5)_4$, ------: silica sol, ○: SiO_2, ◇: Al_2O_3, ●: Na_2O.

course of reaction. For example, the SiO_2/Al_2O_3 molar ratios of the solid phases obtained at 24, 72, and 96 h are 32.7, 2.89, and 2.60 in the case of silica sol in contrast to 2.34, 2.40, and 2.44 in the case of tetraethyl orthosilicate; thus the constituent concentration of the solid phases in the latter case changes little as compared with that in the former case.

Adsorption isotherms with benzene and cyclohexane vapors on the solid phases derived from tetraethyl orthosilicate are shown in Figs. 2 and 3, respectively. The adsorption isotherms in each figure are classified into three groups. The solid phases (24E–75E, where the figure denotes the reaction time and the symbol E indicates that the solid phase concerned has been obtained from tetraethyl orthosilicate) obtained in the early stage of reaction were amorphous and capable of adsorbing the vapors only in small quantities. The amount adsorbed increased greatly with the progress of crystallization.

The crystals obtained in the early stage (76E) and a sufficiently developed stage (84E–96E) gave the same adsorbed quantities at a relative pressure of 0.5 for benzene and at 0.25 for cyclohexane. Above these relative pressures, the former crystal caused no increased adsorption, whereas the latter ones resulted in adsorption in large quantities. This different behavior sug-

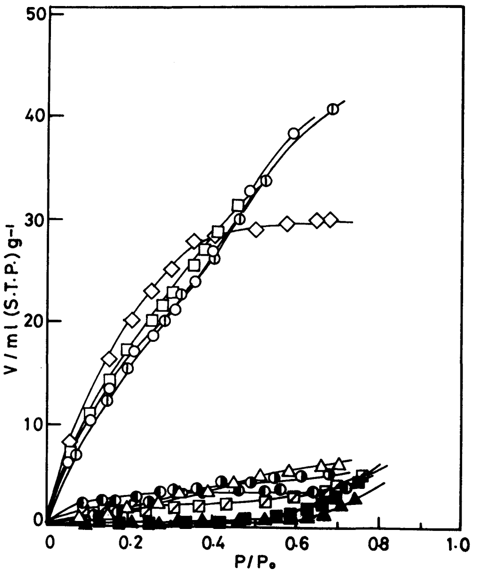

Fig. 2. Adsorption isotherms of benzene vapor on the solid phases derived from tetraethyl orthosilicate at 25 °C.
○: 96E, ⦶: 84E, □: 78E, ◇: 76E, ⧄: 75E, △: 74E, ◐: 72E, ◑: 48E, ■: 24E, ▲: 6E.

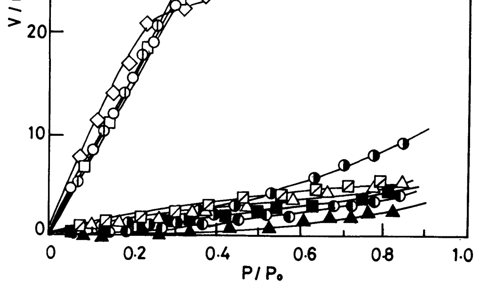

Fig. 3. Adsorption isotherms of cyclohexane vapor on the solid phases derived from tetraethyl orthosilicate at 25 °C.
○: 96E, ⦶: 84E, □: 78E, ◇: 76E, ⧄: 75E, △: 74E, ◐: 72E, ◑: 48E, ■: 24E, ▲: 6E.

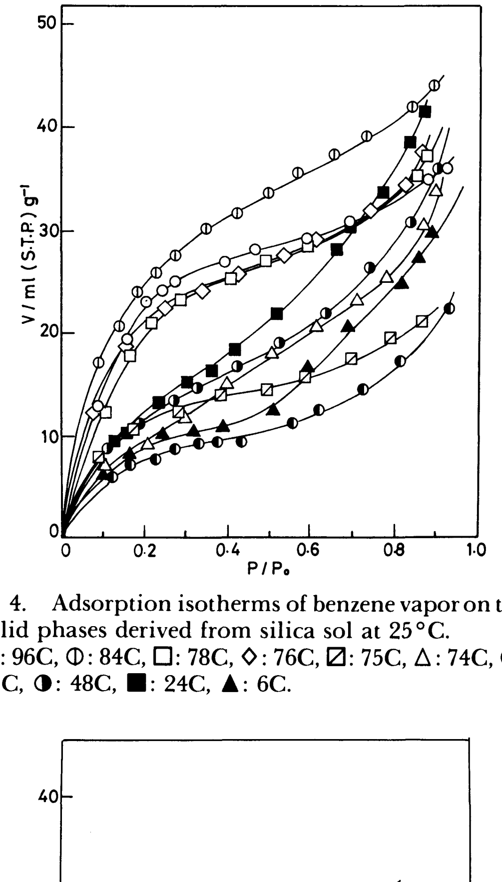

Fig. 4. Adsorption isotherms of benzene vapor on the solid phases derived from silica sol at 25 °C.
○: 96C, ⦶: 84C, □: 78C, ◇: 76C, ⧄: 75C, △: 74C, ◐: 72C, ◑: 48C, ■: 24C, ▲: 6C.

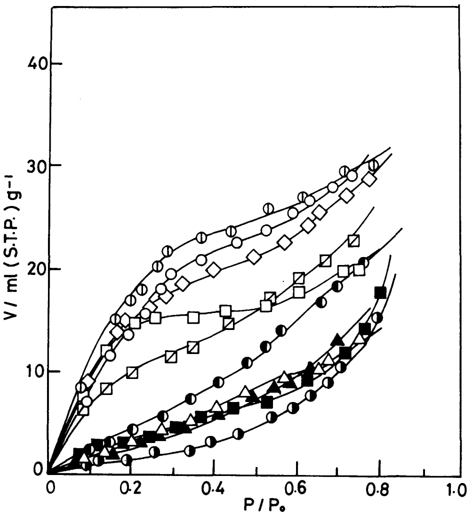

Fig. 5. Adsorption isotherms of cyclohexane vapor on the solid phases derived from silica sol at 25 °C.
○: 96C, ⦶: 84C, □: 78C, ◇: 76C, ⧄: 75C, △: 74C, ◐: 72C, ◑: 48C, ■: 24C, ▲: 6C.

gests a difference in the developments of pore structure of the crystals.

The adsorption isotherms of benzene and cyclohexane on the solid phases derived from silica sol are shown in Figs. 4 and 5, respectively. The adsorption isotherms in each figure may be classified into three groups in the same way as in the case of tetraethyl orthosilicate. The solid phases in the early stage (6C–74C, where the figure denotes the reaction time and the symbol C indicates that the solid phase concerned has been derived from silica sol) adsorbed fairly large quantities of benzene and cyclohexane, as compared with the case of tetraethyl orthosilicate. In addition, the amount adsorbed increased steeply with increasing relative pressure. These features are consistent with the results obtained from a nitrogen-gas adsorption, that is, the measured quantities depend primarily on the particle size distribution of the amorphous solid phases.[15]

In Figs. 4 and 5, the crystal in the early stage (75C) and those in a sufficiently developed stage (78C–96C) exhibit somewhat similar patterns of isotherms, although the latter adsorb the adsorbates in larger quantities than the former. As mentioned in the case of tetraethyl orthosilicate, this difference is due primarily to the difference in pore-structure development.

By applying the BET method[16] to the adsorption isotherms, the monolayer capacity, V_m, for benzene or cyclohexane was calculated except the case of amorphous states (6E–48E). In this case (6E–48E), the BET method could not apply to the isotherms, because these solid phases adsorbed the vapors in too small a quantity. The monolayer capacity, specific surface area, and the constant C are listed in Table 1. The specific surface areas evaluated from the nitrogen-gas isotherms are tabulated in the same table.

For the calculation of the specific surface area for solid phases from the monolayer capacity, we used the molecular dimensions of $7.4\,(l)\times 6.7\,(b)$ for benzene and of $7.2\,(l)\times 6.4\,(b)$ for cyclohexane,[17,18] where the symbols (l) and (b) denote the length and breadth for the molecular dimensions in Å, respectively. We assumed that the molecules adsorbed are oriented nearly flat to the solid surface.[19–21]

In Table 1, the specific surface areas of the amorphous phases derived from tetraethyl orthosilicate are nearly equal for both the benzene and cyclohexane adsorptions. In addition, they are consistent with those as evaluated from the nitrogen adsorption. Therefore, the surface of the solid phases may be taken to be covered with these adsorbates in the same manner. In contrast, the crystal phases adsorb cyclohexane more than benzene. This different behavior suggests that the adsorption depends mainly on the molecular dimensions rather than the effect of the interaction between the cations and the π-electrons of benzene.

As seen from a comparison of data of the crystals formed in the early stage and those in a sufficiently developed stage, the specific surface area slightly decreases with reaction time. This seems due to the change in the particle size distribution with the development of crystal phase. The surface area as evaluated by the nitrogen-gas adsorption does not show any of the tendency mentioned above, because the degree of development of micro pores has a strong effect on the specific surface area, as compared with the change in the outer specific surface area. This agrees with the fact that the outer area of zeolite crystals is only about 1% of the total surface area.[22]

TABLE 1. MONOLAYEER CAPACITY, SPECIFIC SURFACE AREA, AND CONSTANT C OF SOLID PHASES

Specimen	V_m mmol g^{-1}	S_s m^2 g^{-1}	$C^{a)}$	$S_s^{b)}$ m^2 g^{-1}
Benzene				
96E	0.850	254	8.4	717
84E	0.844	252	8.3	746
78E	0.900	268	8.4	708
76E	0.976	291	11	457
75E	0.0546	16	13	19
74E	0.0609	18	13	4
72E	0.100	29	10	7
48E	—	—	—	3
24E	—	—	—	4
6E	—	—	—	4
Cyclohexane				
96E	1.17	325	3.4	
84E	1.34	371	2.9	
78E	1.50	416	2.4	
76E	1.31	363	3.4	
75E	0.107	30	5.9	
74E	0.0736	20	5.9	
72E	0.0378	1	12	
48E	—	—	—	
24E	—	—	—	
6E	—	—	—	
Benzene				
96C	1.13	337	7.7	324
84C	1.09	325	14	366
78C	0.940	281	7.7	257
76C	1.05	313	9.9	251
75C	0.399	119	39	141
74C	0.393	117	17	107
72C	0.296	88	54	112
48C	0.548	164	10	159
24C	0.621	185	5.6	174
6C	0.367	110	31	123
Cyclohexane				
96C	0.879	244	5.3	
84C	0.923	256	7.8	
78C	0.800	222	7.7	
76C	0.585	162	72	
75C	0.392	109	30	
74C	0.235	65	3.8	
72C	0.363	101	2.9	
48C	0.0708	19	34	
24C	0.154	43	19	
6C	0.215	60	4	

a) Evaluated by using the BET equation. b) Evaluated by means of nitrogen adsortion.

On the other hand, the solid phases derived from silica sol give larger specific surface areas by the benzene adsorption than by the cyclohexane adsorption. The degree of the difference in this case is somewhat smaller than that in the case of tetraethyl orthosilicate. But the amorphous phases (6C–74C) adsorb benzene in larger quantities than cyclohexane. Consequently, the interaction between adsorbates and cations has a somewhat stronger effect than the molecular dimensions. This suggests that, as previously mentioned,[14,15] the crystal phase derived from silica sol includes an amorphous substance, and that the micro structure of crystals is not yet be developed sufficiently. Therefore, the large specific surface areas evaluated with benzene depend mainly on the amorphous substance included in crystals. This indicates that the surface of the solid phase can be covered with benzene, but that there is a portion on the surface that cannot be sufficiently covered with cyclohexane. On the whole, the amorphous phases prepared from silica sol give larger specific surface areas than those derived from tetraethyl orthosilicate. This depends on the interaction between adsorbates and cations in addition to the difference in the particle size distribution.

No regularity of constant *C* is found in the case of silica sol, in contrast to the case of tetraethyl orthosilicate. As previously pointed out,[14,15] the surface of the solid phase derived from tetraethyl orthosilicate is supposed to be made up of aluminosilicate with chemical and structural orderliness. On the contrary, the surface of the solid phase derived from silica sol is influenced by complex factors such as the heterogeneity of surface, the wide distribution of particle sizes, the presence of foreign substances, and the interaction between hydroxyl groups and adsorbate.

The relation between the monolayer capacity obtained with benzene, V_m, and the cation concentration is shown in Fig. 6. The monolayer capacity of the amorphous solid phases (72E–75E) derived from tetraethyl orthosilicate changes little with increase in cation concentration. But the monolayer capacity of the crystals in the early stage (76E) and those in a sufficiently developed stage (78E–96E) changes considerably in a steeply linear relationship with cation concentration.

In the case of the amorphous solid phases (6C–72C), the monolayer capacity somewhat decreases with change in cation concentration, and the crystal phases (75C–96C) exhibit an approximately linear relationship between the monolayer capacity and cation concentration. This result suggests that the interaction of π-electrons of benzene is stronger with cations existing in cavities of crystals than with those on the surface of solid phases.

The monolayer capacity obtained with cyclohexane shows none of such a relationship as that with benzene does. This result indicates the existence of a strong interaction between π-electrons of benzene and cations on the solid surface. It has been suggested that benzene is associated with a similarly strong interaction, whereas cyclohexane with some weak interaction.[23]

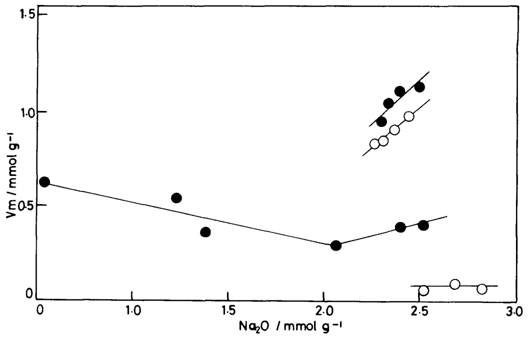

Fig. 6. Relation between monolayer capacity, V_m, and cation (Na_2O) concentration. —○—: $Si(OC_2H_5)_4$, —●—: silica sol.

On the basis of these results and discussions, the change in pores and channels of the solid phases and the mechanism of the crystallization of zeolite X are to be considered.

The schematic representation of the channel and pore formation is given in Fig. 7. The amorphous solid phases derived from tetraethyl orthosilicate are of the same chemical composition as the crystal phase, and therefore, Na^+ ions are contained in the solid phase in large quantities. These solids adsorb benzene and cyclohexane in rather small quantities.

The amorphous solid phases derived from silica sol contain Na^+ ions in small quantities but adsorb benzene more than the solid phases derived from tetraethyl orthosilicate; they adsorb benzene more than cyclohexane. In addition, taking into account the different particle size distribution and the relative specific surface areas $N_2 \approx C_6H_6 \approx C_6H_{12}$ for tetraethyl orthosiicate and $N_2 \approx C_6H_6 > C_6H_{12}$ for silica sol, we have given schematic representations of the surfaces of the amorphous solid states derived from silica sol and tetraethyl orthosilicate in A-1 and B-1, respectively. In the case of tetraethyl orthosilicate, the cations in the solid phase exist in a similar state as in the crystal phase or ordered aluminosilicate, whereas in the case of silica sol, a small quantity of cations are widely distributed on the

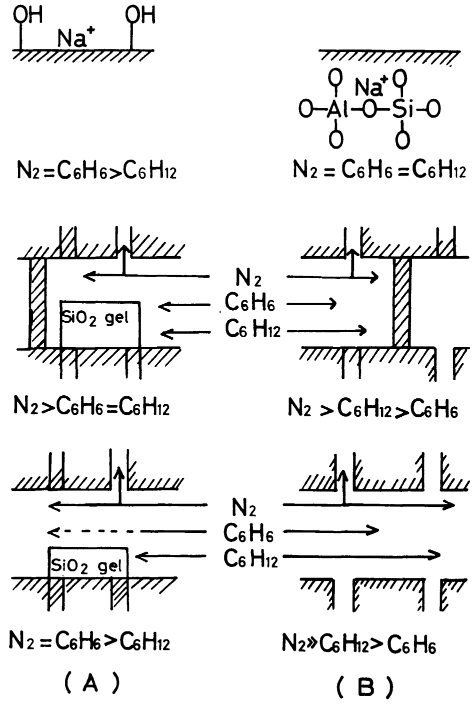

Fig. 7. Schematic diagram of channel and pore formations with reaction time. (A) and (B) are the solid phases derived from silica sol and tetraethyl orthosilicate respectively.

1) At early stage (amorphous), 2) crystals at early stage, 3) crystals at sufficiently developed stage.

outer surface of the solid phase. Furthermore, there seem to exist no less than the hydroxyl groups on the heterogeneous surface of the solid phase.[15]

The crystal phase derived from silica sol in the early stage give the order of specific surface areas: $N_2 > C_6H_{12} \approx C_6H_6$. This order suggests that the channels and pores characteristic of the zeolite structure have already been formed but not yet so much developed as to be able to adsorb benzene and cyclohexane in large quantities. This is due to a contamination of silicic polymers in the channel and pore structures, as previouly pointed out.[14,15]

The crystals derived from tetraethyl orthosilicate give the order of specific surface areas: $N_2 \gg C_6H_{12} > C_6H_6$. This differece in specific surface area is due to the molecular dimensions. The crystal phases derived from tetraethyl orthosilicate may be supposed not to be contaminated with amorphous substances such as a silicic polymer which will not be incorporated in the aluminosilicate framework; thus, these solid phases are capable of adsorbing nitrogen gas and cyclohexane in larger quantities than can be expected from the degree of crystallinity. This crystal phase adsorbs nitrogen gas and cyclohexane in fairly larger quantities than benzene. Therefore, the crystals in the early stage may be considered to have had their structure developed to a considerable extent with respect to channel and pore.

The crystals derived from tetraethyl orthosilicate in a sufficiently developed stage give the order of specific surface areas: $N_2 \gg C_6H_{12} > C_6H_6$. An increase in crystallinity is accompanied by development of the internal structure of crystals. On the whole, channels and pores, which can adsorb nitrogen gas but not appreciably benzene or cyclohexane, have been formed considerably in the crystal phase. This is in accord with the abrupt increase in the specific surface areas, evaluated by the nitrogen adsorption, from 460 for 76E to 720 m^2/g for 96E.

The crystals derived from silica sol in a developed stage give the order of specific surface areas: $N_2 \approx C_6H_6 > C_6H_{12}$. The channels and pores have fairly been developed. But the existene of amorphous substances in the crystal phase prevents cyclohexane to a higher degree from being adsorbed than nitrogen gas and benzene vapor. Because of the interaction between π-electrons of benzene and surface hydroxyl groups or cations distributed on the outer surface, benzene is adsorbed in larger quantities than cyclohexane. These considerations are in conformity with experimental results on IR spectra, chemical analyses, and crystallinity previously described.[14,15]

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