

Crystallization of Zeolite X Type —Effects of Changes of Mother-Liquor Composition on Crystallization Process—

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The mechanism of zeolite crystallization has not been sufficiently elucidated. To clear the stability of chemical species in the solution of the reaction system, the composition and concentration of the solution were suddenly altered, and the variances of the solid phase were surveyed by XRD. That is, in the course of synthesis the condition of solution was stimulated by adding solution without a constituent. The chemical species such as secondary building units that may be incorporated with nucleus in the solution and the phase transition of crystals were considered.

1. Introduction

Zeolites are crystalline aluminosilicate with a three dimensional framework constituted of silica, alumina, alkali and water, have ion-exchange capacity and reversible dehydration without alternation of the structure. At the present time, the zeolite group includes more than 40 naturally occurring species¹⁾ and the number of the synthetic zeolite species exceeds much further than natural species.²⁾ This is owing not only to the interest of basic science but also to the industrial application.

Today the definition of zeolites is extended. They consist of only silicon³⁾ in the framework, aluminum and phosphorus⁴⁾ or transition element such as iron. Recently zeolites with the large 18-oxygen rings⁵⁾ was synthesized. The conventional definition of zeolites was remarkably altered in the point of chemical composition and structure.

As many zeolite crystals are formed under thermodynamic-metastable state,⁶⁾ from the standpoint of topology, many other zeolites with new structure are expected. On the synthesis of zeolites, not only inorganic bases but organic bases have been used. Recently, instead of water solvent, non-aqueous solvents system⁷⁾ has been attracted interest, and new development of aluminosilicate chemistry has been expected.

Although applications of zeolites for catalysis, adsorbents and non-phosphated detergents (builder) etc. in the field of resource and environmental problem are active and expected, the crystallization of crystals is still not sufficiently elucidated.⁸⁻¹⁰⁾ This is because the crystallization process contains the nucleation that is still not clear, and because the instrument of analysis for amorphous phase does not sufficiently exist. But recently, as some instruments, beginning with MASNMR,¹¹⁾ for structural and chemical analysis are appreciably developed, the crystallization process is further clear.

Now there are two representative hypotheses. The first mechanism is based on a

crystallization to occur in a solid phase.¹²⁻¹⁵⁾ During the aging of the solid phase, rearrangement of the aluminosilicate framework leads the amorphous gel to crystals. The other mechanism is based on a crystallization to occur in a liquid phase ; the constituents of zeolites are caused to be dissolved into a liquid phase. The authors^{20,21)} pointed out that the kinds of silica sources cause the difference of crystallization mechanism. As silicon is the elemental constituent of the zeolite framework, the sources of silicon influence enormously the mechanism of crystallization.

The method used by Ueda et al.²²⁾ was applied to this investigation, that is, the composition and concentration of liquid phase were altered suddenly at a fixed time, the variance of the products was surveyed by XRD. In this experiment, the secondary building units, that are precursor of crystals, and the stability of structure unit in the solution were considered. And the phase transition was considered, too.

2. Experimental

2.1 Starting materials

The sources of silica were tetraethoxysilane (Kanto Chemicals Co. Ltd.) distilled and silica sol (Snowtex C. S, Nissan Chemicals Co. Ltd.) diluted to double with distilled water. The source of alumina used was a sodium aluminate solution which had been synthesized from Al plate (99.99% Nakarai Chemicals Co. Ltd.) and sodium hydroxide solution. Sodium hydroxide solution ($5 \text{ mol} \cdot \text{dm}^{-3}$) was used as excess alkaline solution.

2.2 Method of preparation

The molar ratios of starting materials were decided in the region providing optimum conditions for synthesis of zeolite X using tetraethoxysilane. That is, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 8$, $\text{Na}_2\text{O}/\text{SiO}_2 = 6$, and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 50$, which corresponds to the formula $48\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2 \cdot 2400\text{H}_2\text{O}$.²³⁾

The fixed amount of starting materials was placed in the flask, and allowed to be stirred mechanically for 72hr, and it was heated in an air oven at 85°C for 24hr. Then the authors used this method. At the fixed time, in the course of synthesis, a solution was added to the reaction mixture and the compositions of the reactant were suddenly altered. In this way the authors tried to stimulate the chemical species in the mother liquor, and how much this stimulation influence the state of the product was considered. In this experiment, the additive solution was constituted of the starting composition, without sodium, aluminum or silicon component respectively.

The authors chose three points for addition of the solution.

- 1) At early stage of reaction (after 24hr of the beginning of the reaction)
- 2) After sufficient aging in the room temperature (after 72hr of the beginning of the reaction)
- 3) Just before crystallization (after 75hr of the beginning of the reaction for tetraethoxysilane and 74hr for silica sol)

The sampling was initiated after 96hr of the beginning of the reaction, when the excellent

Table 1 Chemical Composition of Mother Liquor

Additional solution	Mother liquor
	Initial solution
	48 Na ₂ O · Al ₂ O ₃ · 8 SiO ₂ · 2400 H ₂ O
	Solution after addition
2 Na ₂ O · Al ₂ O ₃ · 8 SiO ₂ · 2400 H ₂ O	25 Na ₂ O · Al ₂ O ₃ · 8 SiO ₂ · 2400 H ₂ O
48 Na ₂ O · Al ₂ O ₃ · 2400 H ₂ O	48 Na ₂ O · Al ₂ O ₃ · 4 SiO ₂ · 2400 H ₂ O
48 Na ₂ O · 8 SiO ₂ · 2400 H ₂ O	96 Na ₂ O · Al ₂ O ₃ · 16 SiO ₂ · 4800 H ₂ O

crystals were obtained. The chemical composition of the initial reaction and the composition after adding the additive solution are shown in Table 1.

2.3 Identification of products

After a fixed time, the solid phase was filtered off and washed with distilled water until the pH of washing reached 10.5 and then dried at 110°C for 24hr.

Products were identified by XRD using a Toshiba ADG301 (CuK α , Ni filter, 30 Kv, 20 mA, G.M. detector). The crystallinity was determined by XRD method with LMS 13X as reference.

3. Results and Discussion

3.1 In the case of tetraethoxysilane

3.1.1 Without addition

The results of crystal phases obtained from the solution without altering the composition of the reactant, aging for 96-264hr, are shown in Fig.1. From the early work of the authors, it was clear that zeolite X of high crystallinity was produced after 96hr of the beginning of the reaction.²³ Elongation of the reaction time over 264hr, gradually led a lowering of crystallinity of zeolite X.

After about 144hr of aging time, phillipsite Pc and Pt²⁴) began to grow, at 264hr, the crystal Pt predominated over zeolite X crystals. That is, zeolite X began to be transformed to phillipsite that was more thermodynamic stable.

In this reaction system, because many silicon species that were not incorporated with framework existed in the solution, it was supposed P type that tended to be crystallized in silica-rich solution was formed. As can be seen from Fig. 1, the growth of Pt significantly exceeded Pc crystals. It was suggested Pt crystals were thermodynamic stable compared with Pc crystals in this condition.

3.1.2 Addition of the solution without sodium

The crystal phases produced from the solution using the addition without sodium after 24hr, 72hr and 75hr of the beginning of the reaction are shown in Fig.2. The solid phase was considerably low crystallinity or amorphous phase after 96hr of the beginning of reaction. That is the time when the excellent crystals are produced in no addition system. The additive solution was added during aging the reactant at the room temperature and the crystals revealed particularly low crystallinity.

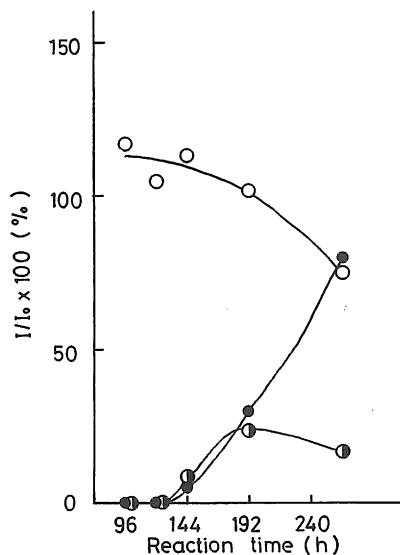


Fig.1 Relation between crystalline products and reaction time in the case of non-addition
 Silica source : tetraethoxysilane
 I_0 : Intensity of (111) peak of LMS 13X
 I : Intensity of main peak of product
 ○ : X type, ● : Pt, ◐ : Pc

In the case of addition at 75hr, the nucleation had been developed until then, the crystals revealed the highest crystallinity among the three crystals. But in this system, afterwards the crystals rapidly grew up, so the influence of the concentration of sodium on the reaction rate of crystallization was revealed.

In the case of addition at 24hr chabazite crystals were formed. This is because silicon and aluminum were newly supplied to the reaction system by the addition of the solution without sodium, and $\text{SiO}_2/\text{Al}_2\text{O}_3$ mol ratio increased and $\text{Na}_2\text{O}/\text{SiO}_2$ mol ratio decreased relatively, so this composition of solution was supposed to produce chabazite crystals. But in the case 72hr and 75hr, no chabazite crystals were formed.

This may be because chabazite takes a long aging time for crystallization. In this system, in the same manner as no addition systems zeolite X crystals degenerated into the crystals of lower crystallinity with the aging time, Pt and Pc crystals grew, and then Pt crystals exceeded Pc.

3.1.3 Addition of the solution without silicon

The crystal phases produced from the solution using the additon without silicon after 24hr, 72hr and 75hr of the beginning of reaction are shown in Fig.3. In this case, as the concentrations of aluminum and sodium increased relatively, the formation of sodalite crystals was observed at every case.

In the case of 24hr, the formation of zeolite A was observed too. But when additive

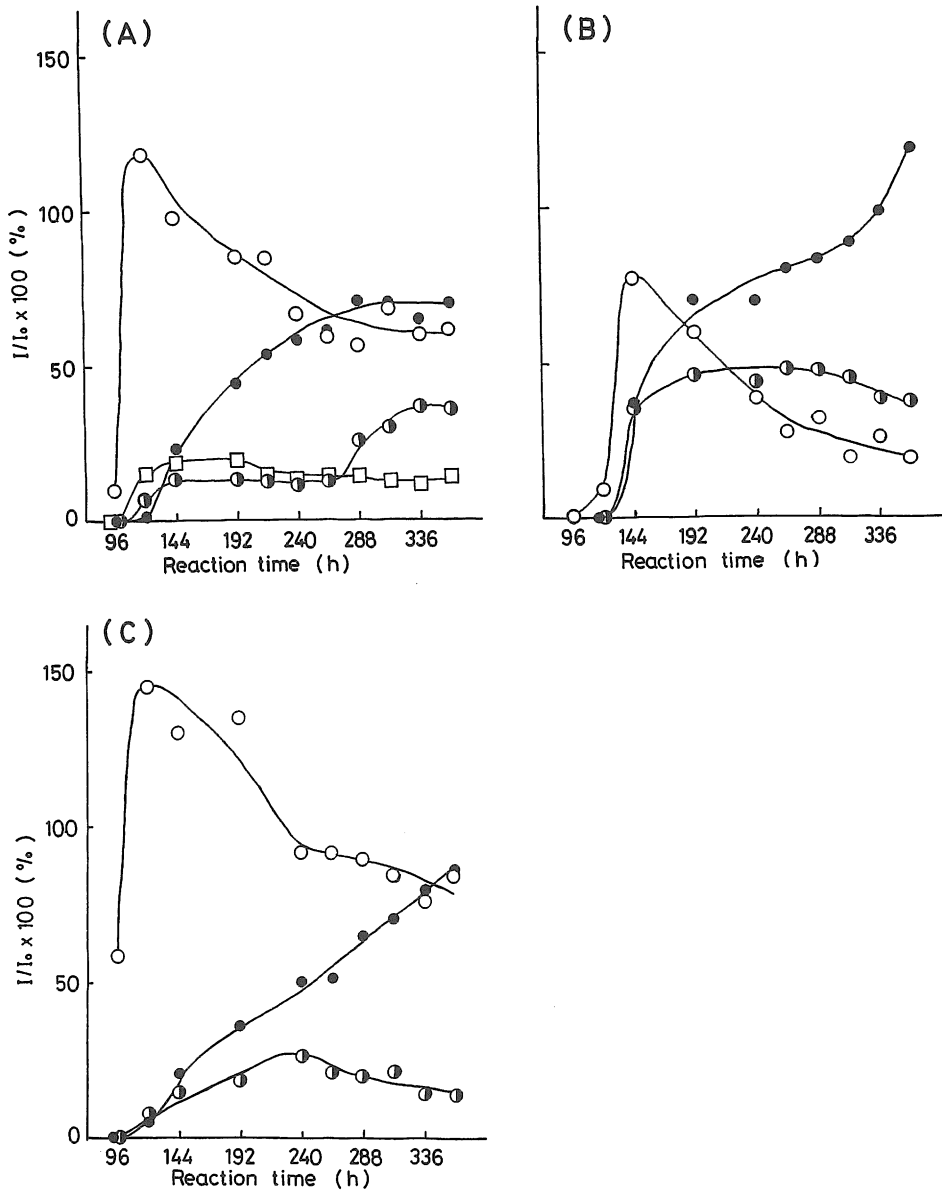


Fig.2 Relation between crystalline products and reaction time in the case of addition of solution without sodium

(A) : 24hr, (B) : 72hr, (C) : 75hr

Silica source : tetraethoxysilane

I_0 : Intensity of (111) peak of LMS 13X

I : Intensity of main peak of product

○ : X type, ● : Pt, ◐ : Pc, □ : chabazite

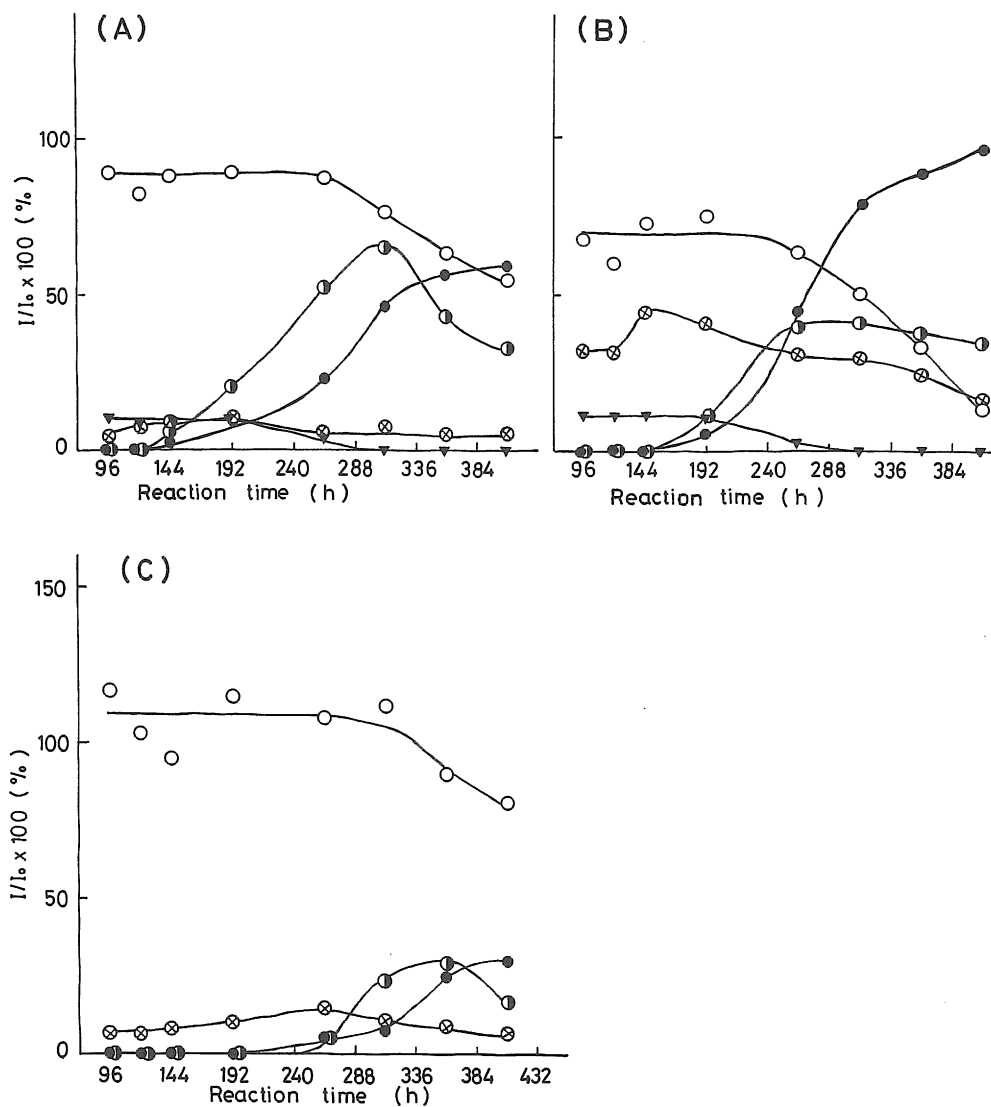


Fig.3 Relation between crystalline products and reaction time in the case of addition of solution without silicon

(A) : 24hr, (B) : 72hr, (C) : 75hr

Silica source : tetraethoxysilane

I_0 : Intensity of (111) peak of LMS 13X

I : Intensity of main peak of product

\circ : X type, \bullet : Pt, \ominus : Pc, \otimes : sodalite, \blacktriangledown : A type

solution was added at 75hr, no zeolite A crystals were formed. This suggests that zeolite A crystals have higher-order structure, so the longer aging time is required for crystallization compared with sodalite crystals. It became apparent that zeolite X, A and sodalite crystals that have same secondary building units and sodalite units were transformed into Pt and Pc crystals that are more thermodynamic stable with the aging time.

The crystallization of zeolite X continued stably for considerably long time. This may be owing to the supply of sodium and aluminum to the system. That is, these elements further reacted with silicon that existed in the solution, and new nuclei were formed. This suggested that under this condition, there are many nuclei that tend to grow zeolite X in the solution. Therefore formation of Pt and Pc crystals was restricted.

3.1.4 Addition of the solution without aluminum

The crystal phases produced from the solution using the addition without aluminum after 24hr, 72hr and 75hr of the beginning of the reaction are shown in Fig.4.

In the case of 72hr and 75hr, zeolite X revealed the high crystallinity different from others. This may be because aluminum in the solution was already consumed in the early stage, and because it was difficult to form the new nucleus of low silica zeolites by addition of the solution without aluminum. It was proved that at early stage of the reaction, addition of the solution without aluminum to this system increased relatively the concentration of silicon and sodium, and the crystallization of phillipsite and the transformation of zeolite X to phillipsite were accelerated.

3.2 In the case of silica sol

3.2.1 Without addition

The results of crystal phase obtained from the solution without altering the composition of the reactant for 96-264hr, are shown in Fig.5.

The various kinds of crystals were formed quite differently from tetraethoxysilane used as a silica source. These crystals may be produced from the aluminosilicate polymers comprised of various forms of silicate derived from silica sol. In this system, zeolite X and sodalite crystals were transformed to Pc, Pt and analcime. These are more thermodynamic stable, and are not changed during the reaction time.

3.2.2 Addition of the solution without sodium

The results of crystal phases obtained from the addition of the solution without sodium after 24hr, 72hr and 74hr of the beginning of the reaction are shown in Fig.6. All the phases contained zeolite X crystals with the almost same crystallinity, and the formation of analcime crystals was depressed with the time of addition. In the case of 24hr of the beginning of the reaction, as the secondary building units were unstable, the addition of the solution without sodium changed the solution into silica rich and transferred the region of zeolite X to the region of analcime.

In the case of 72hr and 74hr, as the nucleus of zeolite X crystals had been formed, if stimulation was added to the mother liquor, the nuclei of other zeolite species could not be formed. That is, nucleus of zeolite X was comparatively stable at this stage, and the crystals of the degradation or the change were not brought about with the addition of solution.

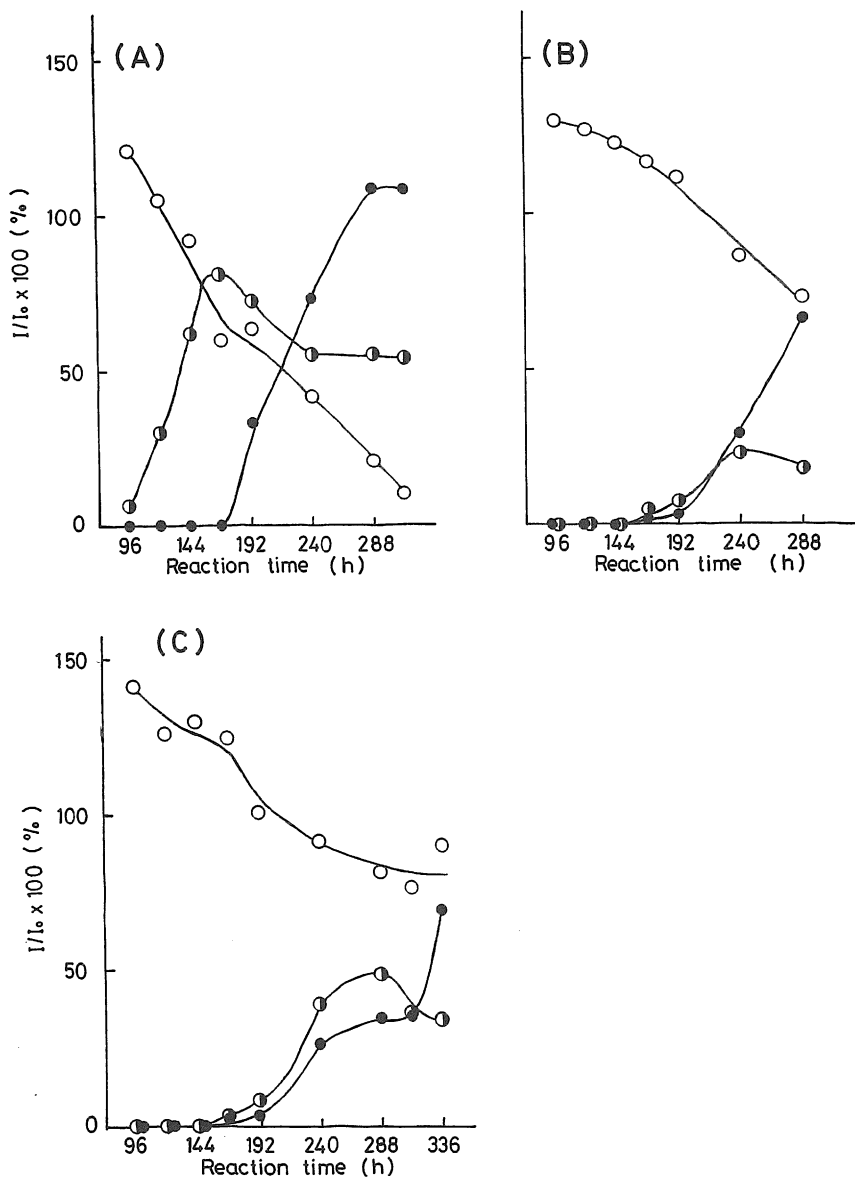


Fig.4 Relation between crystalline products and reaction time in the case of addition of solution without aluminum

(A) : 24hr, (B) : 72hr, (C) : 75hr

Silica source : tetraethoxysilane

I_0 : Intensity of (111) peak of LMS 13X

I : Intensity of main peak of product

○ : X type, ● : Pt, ◐ : Pc

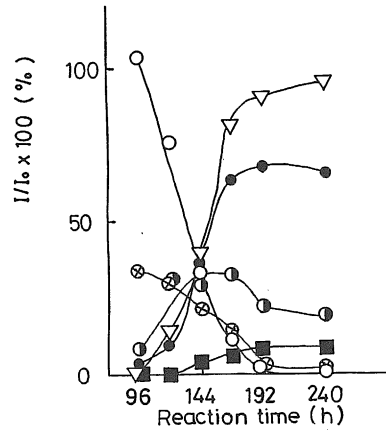


Fig. 5 Relation between crystalline products and reaction time in the case of non-addition
 Silica source : silica sol
 I_0 : Intensity of (111) peak of LMS 13X
 I : Intensity of main peak of product
 ○ : X type, ● : Pt, ● : Pc, ⊗ : sodalite, ▽ : analcime, ■ : unknown

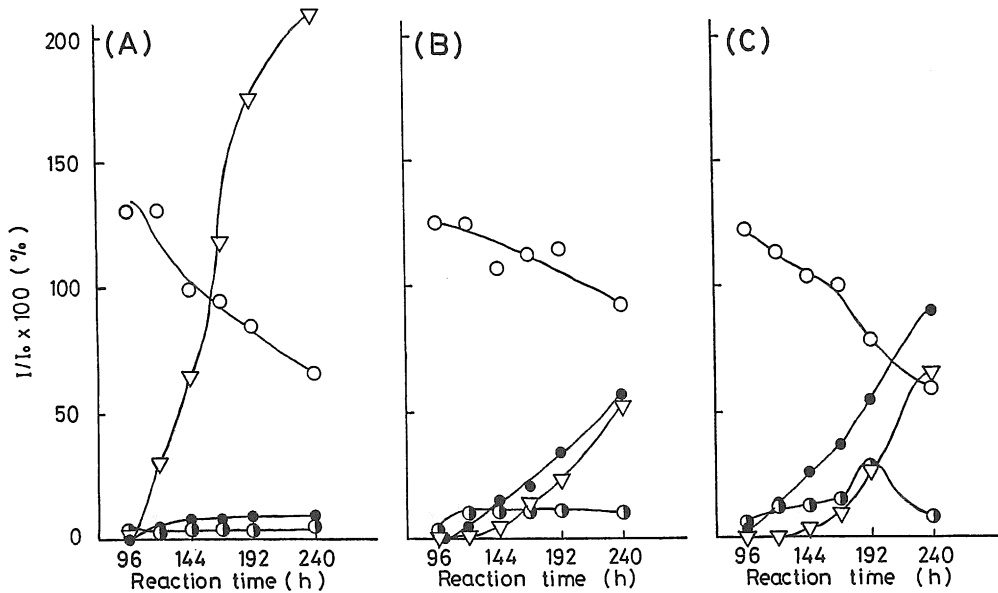


Fig. 6 Relation between crystalline products and reaction time in the case of addition of solution without sodium
 (A) : 24hr, (B) : 72hr, (C) : 74hr
 Silica source : silica sol
 I_0 : Intensity of (111) peak of LMS 13X
 I : Intensity of main peak of product
 ○ : X type, ● : Pt, ● : Pc, ▽ : analcime

With the reaction time, the crystallinity of zeolite X fell and Pt, Pc and analcime crystals grew in a similar manner as tetraethoxysilane. The crystallinity of Pt crystals exceeded Pc crystals with the reaction time. Analcime crystals grew accompanying Pt crystals.

3.2.3 Addition of the solution without silicon

Results of crystal phases obtained from addition of the solution without silicon are shown in Fig.7. In the case of 24hr, sodalite crystals formed predominately. Adding the solution without silicon to the system, the concentrations of aluminium and sodium increased relatively, so the condition favored sodalite crystallization. But when the addition of the solution to the system was late, the formation of sodalite crystals was depressed.

3.2.4 Addition of the solution without aluminum

The results of crystals obtained from the solution using the addition without aluminum are shown in Fig.8.

All the case, zeolite X was produced with the almost same crystallinity. When the addition of the additive solution was late, the formation of analcime crystals was depressed. In the case of 72hr and 75hr, the phase transition of zeolite X crystals to Pc and of Pc crystals to Pt were apparent.

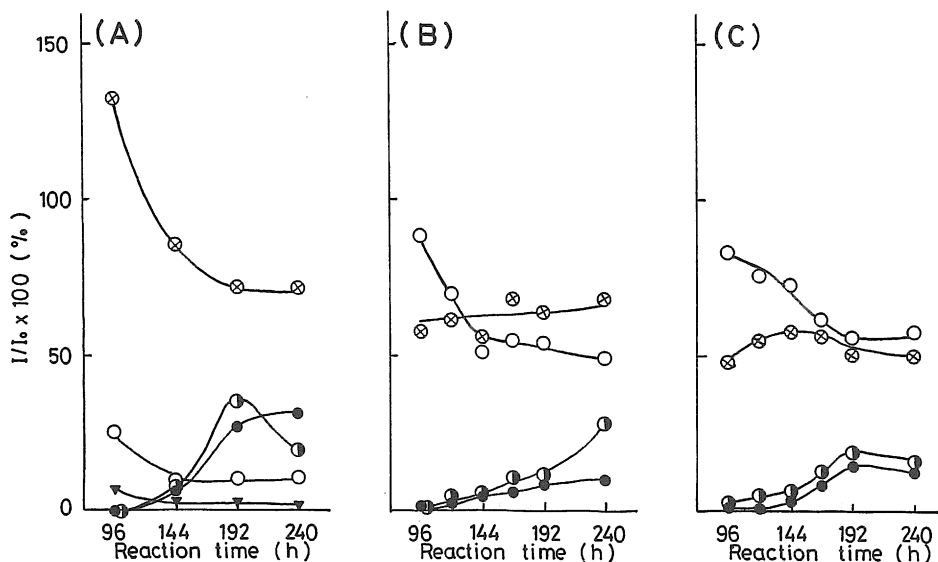


Fig.7 Relation between crystalline products and reaction time in the case of addition of solution without silicon

(A) : 24hr, (B) : 72hr, (C) : 74hr

Silica source : silica sol

I_0 : Intensity of (111) peak of LMS 13X

I : Intensity of main peak of product

○ : X type, ● : Pt, ● (with dot) : Pc, ⊗ : sodalite, ▼ : A type

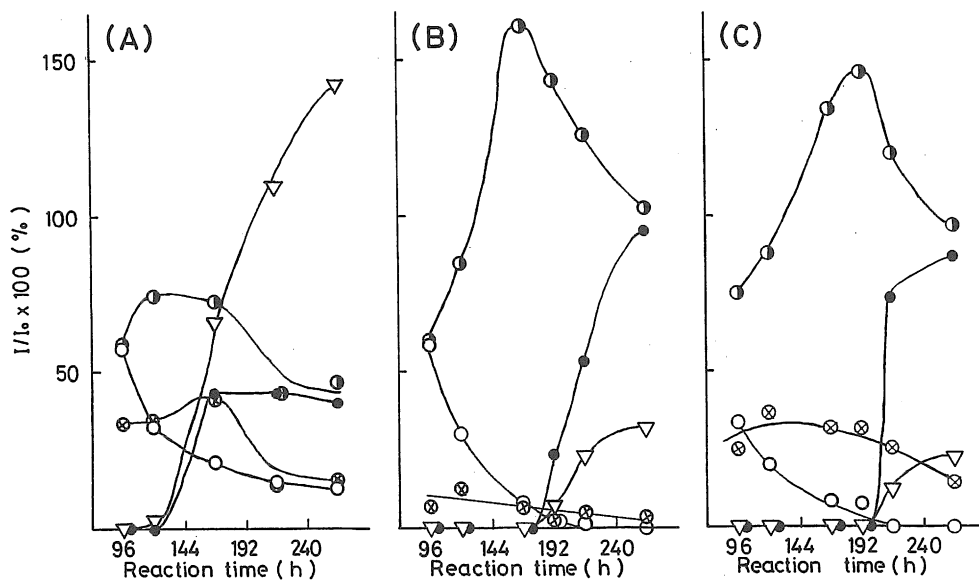


Fig.8 Relation between crystalline products and reaction time in the case of addition of solution without aluminum

(A) : 24hr, (B) : 72hr, (C) : 74hr

Silica source : silica sol

I_0 : Intensity of (111) peak of LMS 13X

I : Intensity of main peak of product

○ : X type, ● : Pt, ● : Pc, ⊗ : sodalite, ▼ : analcime

4. Summary

In the case of tetraethoxysilane as a silica source, zeolite X was the state of thermodynamic metastable, and transformed to more stable phase, phillipsite.

The changes of composition at the stage of 72hr after the beginning of the reaction most strongly influenced on the crystals. In this case, zeolite X crystals revealed a low crystallinity and the mixed crystals had a higher crystallinity. At this time, the system was strongly influenced by the stimulation. Therefore it was suggested that the rearrangement of the secondary building units proceeded and this crystal structure was formed at this time.

On the other hand, in the case of silica sol, the system of reaction was most strongly influenced at 24hr after the beginning of the reaction. This was suggested from the results that the mixed crystals were formed remarkably in the solution. It became apparent that the kinetic mechanism of zeolite crystals was different in the case of tetraethoxysilane and silica sol as a silica source.

Using silica sol as a silica source, the reaction system included the complex chemical species. This was suggested from the fact that the reaction system derived from silica sol produced various kinds of crystals. The dispersed colloidal silica was suddenly coagulated and

was dissolved gradually in the solution and formed silicic polymer, and aluminosilicate ions were formed. These aluminosilicate ions effected decisively on the crystals formed.

In this investigation, the compositions of the real synthetic solution were altered at the crystallization process, the effects of the solution were observed. And then the authors considered the crystallization process of zeolite X.

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