Effect of a Chelating Agent on The Synthesis of Zeolitic Materials from Waste Sandstone Cake using Alkali Fusion

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ABSTRACT

During quarrying, waste stone cake is discharged as industrial waste, and in Japan the amount of cake amounts annually to 50 millions tons. To promote waste recycling, we attempted to convert waste sandstone cake into zeolitic material using alkali fusion. However, calcium causes the synthesis of an undesirable zeolite by interfering in the synthesis of a high functional zeolite. As a means to inhibit this Ca-interference, we studied the effect of adding a chelating agent, EDTA (Ethylenediaminetetraacetic acid disodium dihydrate), on the synthesis of zeolitic material from sandstone cake using alkali fusion. Hydroxysodalite, zeolite-X and zeolite-P can be synthesized from sandstone cake using alkali fusion. With the addition of EDTA, calcium ions in solution were trapped by chelation, and the amount of zeolite-X and zeolite-P increased. A product with a high CEC, which has a high content of zeolite-X, can be obtained. The chelating agent can inhibit Ca-interference for zeolite synthesis by Ca-masking, and the product with high content of zeolite-X can be obtained from waste sandstone cake using alkali fusion.

Keywords: Zeolite synthesis, Waste sandstone cake, Alkali fusion, EDTA, Ca-masking

INTRODUCTION

Zeolites have attracted a great deal of attention from the chemical industry. Zeolites are a group of over 40 crystalline, hydrate alumino-silicate minerals with a structure based on a three-dimensional network of

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aluminum and silicon tetrahedra linked by sharing oxygen atoms. Due to specific pore sizes and large surface areas, zeolites have the potential for a wide range of applications such as molecular sieves, adsorbents, and catalysts [1]. Many researchers have reported the synthesis of various types of zeolites (zeolite-A, P, X and ZSM-5, etc.) from industrial waste (such as coal fly ash, paper sludge ash, municipal incinerated ash, and waste porcelain or perlite, which were mainly composed of SiO_2 and Al_2O_3 in amorphous phases [2 - 10]), via different hydrothermal activation methods, such as classic alkali activation [11], alkali fusion [12], two-stage synthesis [13], acid-leaching [14], and addition of silica sources [15, 16].

During quarrying, waste stone cake is discharged as an industrial waste. The annual amount of cake discharge is 50 millions tons per year in Japan. Although a part of the waste is used as artificial aggregate or in some minor applications, a large part of it is dumped in landfills. In recent years, however, it is becoming more difficult to dispose of stone cake due to the lack of available landfill sites. In Japan, furthermore, the Basic Law for Establishing a Recycling-Based Society and other laws to promote the effective use of resources are established, and improvement of recycling construction waste materials and by-products is required. Since stone cake is viewed as construction sludge, or waste, research and development has been conducted into its utilization in civil engineering as a foundation improvement or riverbed material [17, 18]. However, there have been no studies on its chemical conversion into functional materials.

One of the waste stone cakes, sandstone cake, is mainly composed of quartz, feldspar, and calcite, having a high SiO_2 and Al_2O_3 content. In our previous studies, no zeolite phases were synthesized from sandstone cake by the alkali hydrothermal method, while by the alkali fusion method, most of the sandstone cake can be converted into zeolitic materials, including zeolite-X [19]. By alkali fusion, most of the crystalline phases in the cake, which are difficult to dissolve into an alkali solution, could be converted into soluble phases, and transformed into zeolitic material with a high cation exchange capacity (CEC) [20]. This is a new way to convert stone cake into functional materials. However, the current product is a combination of the high value-added zeolite X and other low value-added zeolites, i.e. hydroxysodalite. Zeolite-X (faujasite type) is a high functional zeolite, and is one of the important targets in the zeolite synthesis from waste material. It can not only be used as cation exchanger and adsorbent, but also as molecular sieves and catalyst, and there are widespread applications in purification and separation of gases and organic components.

One of the reasons for the production of low-value added zeolites is the high Ca/Si ratio in sandstone cake. The cake originates from sandstone sediment rock, and contains Ca in the form of calcite ($CaCO_3$). It is reported that ash with a high Ca content cannot be fully converted into the desirable zeolites, due to Ca-interference during the zeolite synthesis in the formation

of a desirable zeolite [21]. Reduction of the Ca-interference is an important issue in the production of desirable zeolitic material.

In this study, we applied Ca-masking with a chelating agent, EDTA, to reduce Ca-interference during synthesis in the formation of zeolitic material with a high CEC. EDTA is the most popular chelating agent, and is used as Ca-masking agent to decrease the hardness of water. We determined the effects of EDTA on zeolite synthesis from sandstone cake by alkali fusion.

MATERIALS AND METHODS
Raw material

Waste sandstone cake was obtained from one of the quarries in Kitakyushu, Fukuoka prefecture, Japan. Before the experiment, the cake was washed with distilled water and dried in an oven at 60 ^{o}C overnight. The particle diameter was 3 μm in average.

EDTA (Ethylenediaminetetraacetic acid disodium dihydrate) (Wako, G.R.) was used as chelating agent. The EDTA solution was adjusted from 0 - 1.0 M with addition of distilled water.

Synthesis of zeolitic material with EDTA addition

The zeolite synthesis was carried out as shown in Fig. 1. 10 g of cake was mixed with 16 g of NaOH powder, and grounded to obtain a homogenous mixture. This was subsequently heated in a nickel crucible in air at 600 ^{o}C for 1 h.

Waste sandstone cake

Mixed with NaOH powder
Heated at 600 ºC for 1 h

Fused material

Added to
the solution with EDTA (0-1 M)
Agitated for 24 h

Agitated material

Heated at 80 ºC for 8 h
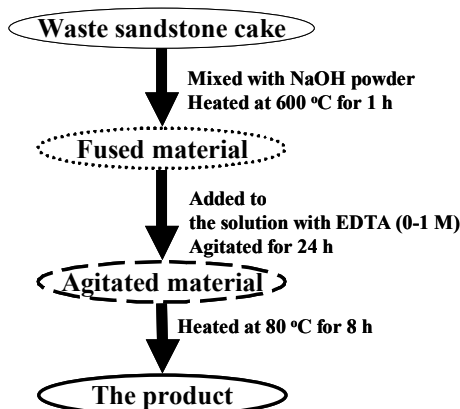
The product

Fig. 1. Flow chart of the experiments.

The resultant fused mixture was cooled to room temperature, and grounded again to obtain the fused material. 0.5 g of the fused material was added to 2 mL of distilled water with an EDTA concentration ranging from 0 – 1 M in a 10 mL tube made of polymethylpentene (TPX), followed by an aging process with vigorous agitation in a reciprocal shaker at room temperature, in order to obtain agitated material. After 24-h of agitation, the

agitated material was heated at 80 ^{o}C for 8 h with a water bath to synthesize zeolitic material. At the end of the process, the solid product was filtered, washed with distilled water, and dried in a drying oven at 60 ºC overnight. Characterization of the product and analysis of the filtrate were carried out to determine the effect of EDTA on zeolite synthesis from the cake using alkali fusion.

Characterization

Phase identification of the cake, agitated materials and products was carried by a X-ray powder diffractometer (XRD) (RIGAKU, XRD-DSC-XII) with graphite monochromatozed CuKα radiation (λ = 1.54178 Å), and information on morphology was obtained by scanning electron microscopy (SEM) (TOPCOM, SM-200) operated at 15 kV. Chemical composition of the sandstone cake was determined by X-ray fluorescent spectrometry (XRF, ZSX101e, Rigaku), and the concentrations of Si, Al, and Ca in the solution after synthesis were analyzed by inductively coupled plasma spectrometry (ICP) (SIMADZU, ICPS-7500). The CECs of the products were measured by the method reported by Wajima et al. [14]. The relative crystallinities of zeolites in the product were calculated by the method reported by Fernandes Machado and Malachini Miotto [22]. Hydroxysodalite and zeolite-P were prepared by the procedure as reported by Kato et al. [23], and commercial zeolite-X (Wako) were used as the standards.

RESULTS AND DISCUSSION
Waste sandstone cake and agitated material after alkali fusion

Table 1 shows the chemical compositions of sandstone cake, and Fig. 2 shows the mineralogical components of the cake. Sandstone cake is mainly composed of SiO_2 and Al_2O_3 in the form of silicate and aluminosilicate minerals, such as quartz, albite, muscovite, and clinochlore. It also contained a large amount of CO_2, thought to have originated in carbonate, mainly calcite.

Tab. 1. Chemical composition of waste sandstone cake

	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	CO_2	SO_3	P_2O_5	Total
Oxide (wt. %)	38.9	12.2	6.9	2.7	1.4	1.8	3.1	32.6	0.1	0.1	99.8

Fig. 3 shows the XRD patterns of material agitated in the solution with EDTA concentrations of (a) 0 M, (b) 0.1 M, (c) 0.25 M, and (d) 1 M. Without addition of EDTA, it was confirmed that all silicate minerals diminish to create amorphous materials, which is indicated by the broad peak of 20-40 ^{o}, and only calcite remained as crystalline phase in the

agitated material (Fig. 3 (a)). With increasing EDTA concentration in the solution, the peaks of calcite decrease and finally diminish in the solution with more than 0.25 M EDTA (Figs. 3 (b)-(d)).
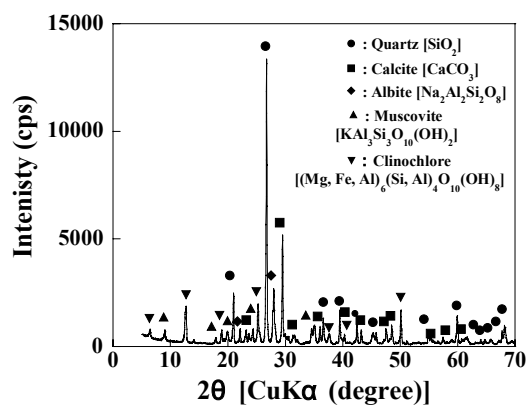

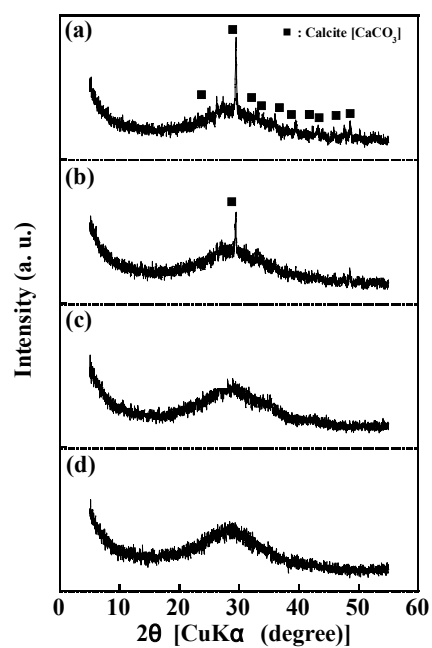Fig. 2. XRD patterns of waste sandstone cake.

Fig. 3. XRD patterns of materials agitated in the solution with EDTA concentrations of (a) 0 M, (b) 0.1 M, (c) 0.25 M and (d) 1 M.

80

Fig. 4 shows the Si, Al, and Ca concentrations in the solution with various EDTA concentrations after agitation. Under all conditions, the Al concentration is zero. Without addition of EDTA, the Si concentration in the solution is 10000 mg/L, and Ca concentration is zero. With addition of EDTA above 0.25 M, Si and Ca concentrations reach 13000 mg/L and 2500 mg/L, respectively.
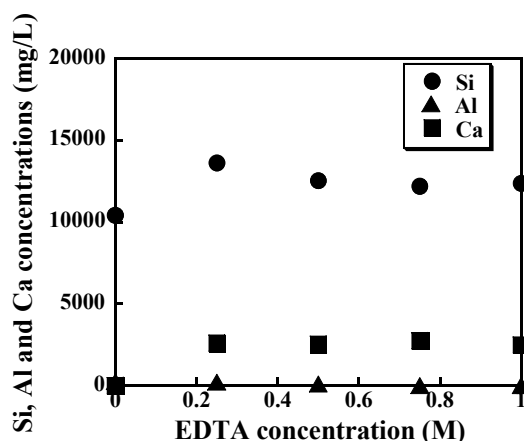

Fig. 4. Si, Al and Ca concentrations in the solution with various EDTA concentrations after agitation.

From these results, it is deduced that most Ca content was extracted from the solid into the solution due to capture by EDTA in concentrations above 0.25 M. The Si content in the solution increases due to a decrease in the amount of reactions between Si and Ca to precipitate as amorphous gel.

Effect of EDTA on zeolite synthesis

Fig. 5 shows the relative crystallinities of zeolite phases in the product synthesized in the solution with various EDTA concentrations. Hydroxysodalite, zeolite-X, and zeolite-P were synthesized from the cake in the solution with EDTA ranging from 0 to 1 M. The relative crystalinity of hydroxysodalite, zeolite-X, and zeolite-P are almost the same in the product synthesized in the solution without EDTA. With addition of EDTA, the crystalinity of hydroxysodalite in the product is almost constant, but those of zeolite-X and zeolite-P range around a concentration of 0.5 M EDTA. By increasing the EDTA concentration to 0.5 M, the crystalinity of zeolite-X becomes the highest in the mixture, and is twice as high as that without EDTA, while that of zeolite-P is lower than that without EDTA. By increasing the EDTA concentration above 0.5 M, the crystalinity of zeolite-P becomes highest, and that of zeolite-X decreases to be the same as that of hydroxysodalite.
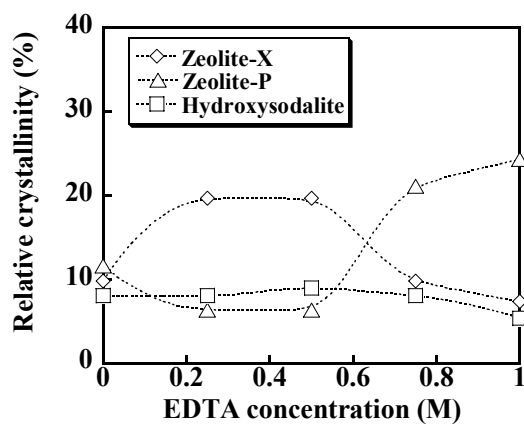
81

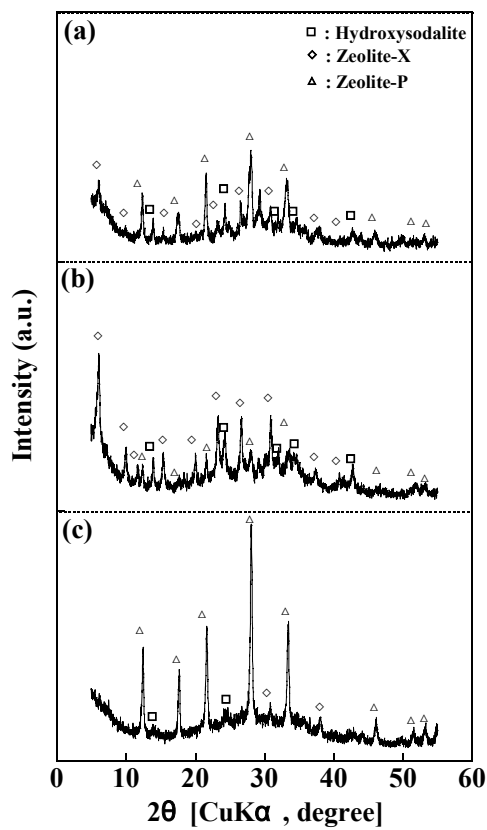Fig. 5. Crystalinities of zeolite phases in the product synthesized in the solution with various EDTA concentrations.

Fig. 6. XRD patterns of the typical product synthesized in the solution with EDTA concentrations of (a) 0 M, (b) 0.5 M, and (c) 1 M.

82

Fig. 6 shows XRD patterns of typical products synthesized in the solution with EDTA concentrations ranging from (a) 0 M, (b) 0.5 M, and (c) 1 M. Without addition of EDTA, the mixture of hydroxysodalite, zeolite-X, and zeolite-P was synthesized from the cake (Fig. 6 (a)). In the case of a concentration of 0.5 M EDTA, zeolite phases in the product are the same, and the main phase in the mixture becomes zeolite-X (Fig. 6 (b)). In the case of 1 M EDTA concentration, zeolite-P was the main phase in the product (Fig. 6 (c)).

Fig. 7 shows SEM photographs of the product synthesized in the solution with EDTA concentrations of (a) 0 M, (b) 0.5 M, and (c) 1 M. Each product was different morphology. In the case of (a), a mixture of hydroxysodalite, zeolite-X, and zeolite-P was observed. Hydroxysodalite ($Na_6Al_6Si_6O_{24} \cdot 8H_2O$) is a member of the sodalite group, and its structure comprises a framework of 4- and 6- membered rings of SiO_4 and AlO_4 tetrahedra. In the case of (b) and (c), zeolite-X ($Na_{22}Si_{26}Al_{22}O_{96} \cdot 55H_2O$) and zeolite-P ($Na_6Si_{10}Al_6O_{32} \cdot 12H_2O$) were the main zeolitic phases in the product, respectively. Zeolite-X crystallizes in a typical octahedral form, and is a member of faujasite group. Its structural framework consists of 4- and 8- membered rings. Zeolite-P is a member of gismondine group, and its structural framework is built of 4- and 8- membered rings. Note that the order of Si /Al ratios in the zeolite structure is hydroxysodalite (1:1) < zeolite-X (13:11) < zeolite-P (5:3).
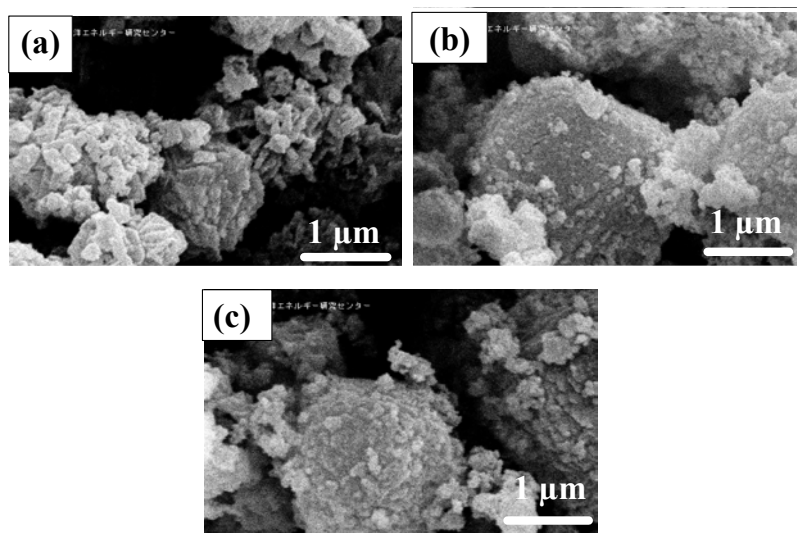

Fig. 7. SEM photographs of the typical product synthesized in the solution with EDTA concentrations of (a) 0 M, (b) 0.5 M, and (c) 1 M.

Fig. 8 shows the CEC of products synthesized in the solution at various EDTA concentrations. By increasing the EDTA concentration to 0.25 M, the CEC of the product increases to be constant at 2.1 mmol/g, which is higher than that of commercial natural zeolite (1.85 mmol/g) [9], but above 0.5 M EDTA concentration, the CEC of the product decreases. The point at which CEC starts to decrease is the same as that for the main zeolitic phase in the product. The calculated CECs of zeolite-X and zeolite-P, based on theoretical formulae, are 7.80 mmol/g and 4.58 mmol/g, respectively; hydroxysodalite has the lowest CEC (< 1.0 mmol/g) in the zeolite group. Therefore, the product with the highest CEC can be obtained in a solution with 0.25- 0.5 M EDTA, which is mainly composed of zeolite-X.
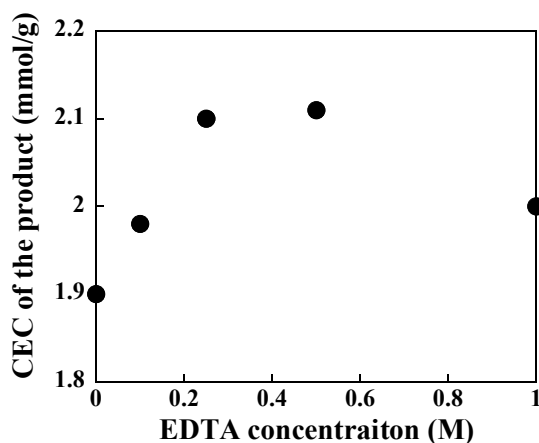

Fig. 8. CEC of the product synthesized in the solution with various EDTA concentrations.

Fig. 9 shows the Si, Al and Ca concentrations in the solution with various EDTA concentrations after synthesis. In all conditions, the Al concentration is zero. The Ca concentration in the solution after zeolite synthesis is almost same as that before synthesis, as shown in Fig. 4. It is considered that Ca-masking preserved in the solution during zeolite synthesis. The Si concentration in the solution after synthesis is lower than that before synthesis, due to the consumption of Si in solution for the synthesis of zeolite crystals. By increasing EDTA concentrations to 0.25 M, the Si concentration increases, and then becomes a constant (saturated); above 0.5 M EDTA, the Si concentration decreases. In the case of concentrations lower than 0.25 M EDTA, un-masked Ca remains in the solution before synthesis. Therefore, reactive Ca consumes Si in the solution during synthesis. In the case of concentrations higher than 0.5M EDTA, the main zeolitic phase in the product changes from zeolite-X to zeolite-P. The

order of the Si: Al ratio for zeolite crystal is zeolite-P (5:3) > zeolite-X (13:11). Therefore, the consumption of the Si content in solution increases during the zeolite synthesis; the Si concentration in solution after zeolite synthesis decreases.
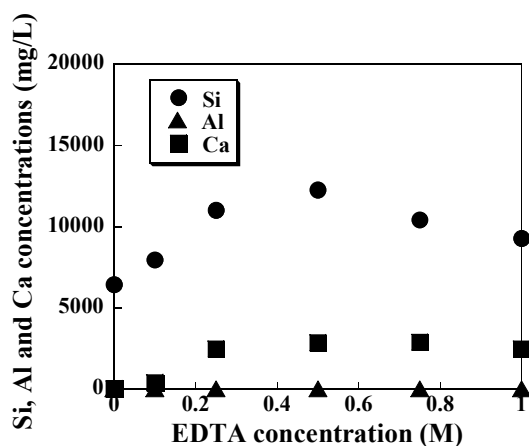

Fig. 9. Si, Al and Ca concentrations in the solution with various EDTA
concentrations after synthesis.

In summary, we propose the following mechanism for EDTA addition, as shown in Fig. 10. Zeolite synthesis consists of three reactions; dissolution, gelation, and crystallization. During zeolite synthesis from cake using alkali fusion, the agitation process mainly consist of dissolution and gelation, and subsequently the heating process promotes the crystallization process. Without addition of EDTA during the agitation process, the Si, Al, and Ca content in the fused material dissolve into the solution, precipitate as Si-Al-Ca gel in the solid, and the unreacted Si content remains in the liquid. In the heating process, the Si-Al-Ca gel in the solid reacts with Si in the liquid to be converted into zeolite phases. However, the Ca content in the gel interferes with the crystallization of zeolite-X and zeolite-P. Therefore, the product has a low zeolite-X and zeolite-P content. With addition of EDTA, the Si, Al, and Ca content in the fused material dissolved into the solution, and the Ca content was captured by EDTA, and Si-Al gel precipitated to remain with unreacted Si content in the liquid phase. In the heating process, the Si-Al gel reacts with Si in the liquid phase to be converted into zeolite phases. The interference of Ca content was inhibited by Ca-masking with EDTA, and a high content of Si-Al gel with high Si/Al ratio can be converted into zeolite-X and zeolite-P. Zeolite-X is a metastable phase, and can be easily transformed into zeolite-P by a long reaction time or high alkali condition. It may be assumed that zeolite-P is synthesized in

85

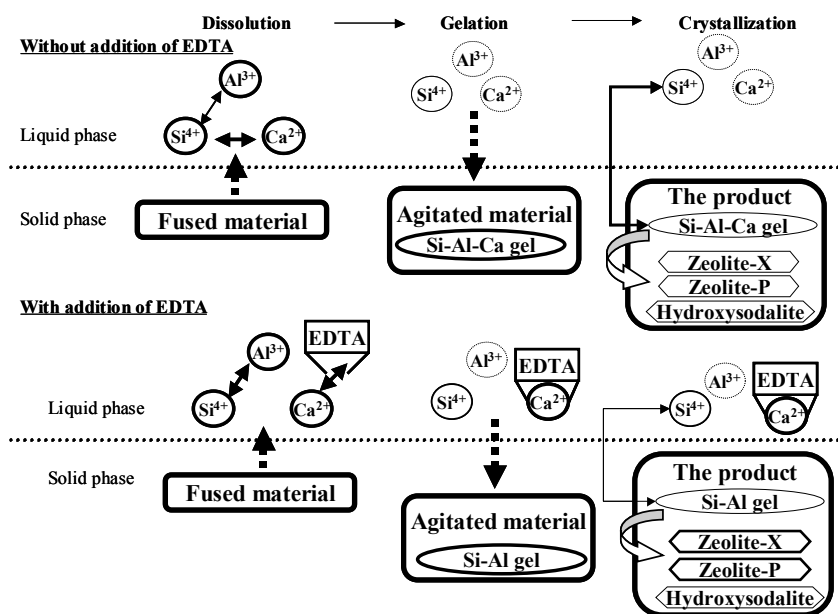the solution with concentrations over 0.5 M EDTA due to the increase of sodium content with the addition of EDTA.

Fig. 10. Proposed mechanisms for zeolitic reaction with addition of EDTA.

CONCLUSIONS

We applied Ca-masking with EDTA to synthesize highly functional zeolitic material from waste sandstone cake using alkali fusion. The following conclusions can be drawn from the results:

(1) EDTA can extract Ca into solution, and inhibit Ca-interference during zeolite synthesis by Ca-masking.

(2) Hydroxysodalite, zeolite-X, and zeolite-P can be synthesized from sandstone cake using alkali fusion, and the main zeolite phase can be adjusted by the addition of EDTA.

(3) A product with a high CEC, which is high content of zeolite-X, can be obtained.

Therefore, a chelating agent can inhibit the Ca-interference in the zeolite synthesis by Ca-masking, and a product with a high content of zeolite-X can be obtained from waste sandstone cake using alkali fusion.

86

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