

Splicing growth of zeolite 4A in hydrothermal system^①

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[Abstract] The morphology evolution of zeolite 4A in hydrothermal system was studied via XRD, TEM and electron diffractometry. A phenomenon of aggregation of nanocrystals of zeolite 4A exists in the crystallization process, and microcrystals are derived from nanocrystal aggregating directly. The splicing growth model of zeolite 4A is described as: 1) an induction period which exists at the beginning of crystallization, 2) followed by many nanometer crystals initiating immediately, and 3) the nanocrystals congregated as slices and spliced with each other to form a larger crystal.

[Key words] splicing growth, zeolite, aggregating growth, crystal growth, nanocrystal, hydrothermal synthesis

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1 INTRODUCTION

Molecular sieves of crystalline zeolite are well known in world of art and now comprise over 250 species of both naturally occurring and synthetic compositions. Zeolite is an aluminosilicate with a framework formed from the AlO_4 and the SiO_4 tetrahedral joined by the oxygen atoms. It is characterized by having pore openings of uniform dimensions, significant capacity, and capability of reversibly desorbing an adsorbed phase which is dispersed through the internal voids of the crystal without displacing any atoms which comprise the permanent crystal structure^[1]. Furthermore, the nanozeolites or the super-fine powders of zeolites appear to have better properties for ion-exchange and catalysis than the larger scaled zeolites do. The properties are the result of more specific surface area and the openness of the zeolite structure and its holes system. Compared with other materials, the complexity of the zeolite crystal structure involves more challenges for preparing nanocrystal powder. Although zeolites with diameter less than 100 nm have been synthesized hydrothermally^[2-5], the morphological evolution or application was not reported yet. In contrast, large crystal zeolites herein having a mass mean diameter of at least two micrometers^[6, 7] are many times desirable in the hydrocarbon conversion processes and have less specific outer crystal surface area which reduce the amount of reactions at the surface. Furthermore, large crystal zeolite with longer diffusion path lengths can be used to modify catalytic reactions. Therefore controlling the crystal size is necessary to meet different applications.

With its excellent properties of adsorption, desiccation and catalysis for calcium ion exchange, and its con-

venient preparation, zeolite 4A has been used in many applications since it was first synthesized^[1]. Although there are many reports regarding its crystallization conditions, crystallinity, properties and applications^[2, 4, 8], no special report of the morphological evolution of zeolite 4A has been made. The mechanism of zeolite 4A remains obscure between two mechanisms: solid phase transformation and liquid state transformation. It is known that aggregation of crystals or particles often takes place during the synthesis process^[2, 9], and the aggregation affects the morphology of the crystal and the size distribution of the nanoparticles. In addition aggregation has a close relationship with the zeolite crystal size. Therefore, the morphological evolution and the crystal aggregation must be examined more thoroughly.

This article focuses the morphological evolution of nanocrystal to micrometer particles of zeolite 4A via hydrothermal synthesis. The growth mechanism of crystal aggregation is studied and the model of splicing growth of zeolite crystals is presented.

2 EXPERIMENTAL

The following materials were used: $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, (GPR grade, Jinshan Co., Shanghai), NaOH (GPR grade, Hongxing Co., Shanghai), and $\text{Al}(\text{OH})_3$ (GPR grade Hongxing Co., Shanghai) with distilled water. The composition of reactant mixture for synthesis of zeolite 4A chosen for this study was $3\text{Na}_2\text{O} + \text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 180\text{H}_2\text{O}$.

Each batch was made in an one liter polypropylene bottle. Batch 1 was prepared by dissolving NaOH in distilled water, and batch 2 was prepared by dissolving Al

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(OH)₃ into NaOH solution to form sodium aluminosilicate solution. Each batch was placed into different glass flasks. The batch 1 was stirred vigorously at room temperature while the solution of batch 2 was steadily dripped into batch 1 and a gel phase for synthesis of zeolite 4A immediately was formed. The gel mixture was continuously stirred for 1 h so the mixture changed into a homogenous phase before the crystallization reaction was conducted.

The crystallization of zeolite 4A was conducted in a hydrothermal condition. The hydrothermal reaction was conducted in a three-necked bottle with the middle neck joined to a condenser, a switched-mode thermometer and mercury thermometer positioned in the two other necks. The three-necked bottle was placed into a constant temperature water bath. Hydrothermal crystallization was performed at 343 K, 353 K, 358 K and 363 K for dif-

ferent times.

Samples were taken out by a certain crystallization duration and the samples were washed and filtrated to pH < 9.5, and alcohol absolute (A. R, Lianshi chemical co., Shanghai) was used in the final wash which allowed for easy drying. The samples were dried at 383 K for 5 h. All samples were examined by X-ray diffractometry (XRD, Cu K α , Bruker powder diffractometer, Germany) and by transmission electron microscopy (H800, in Central South University).

3 RESULTS

3.1 Morphology evolution of zeolite 4A

The micrographs of the samples synthesized at 363 K for 40, 60, 80, 100, 180 and 240 min respectively are shown in Fig. 1. The evolution of the

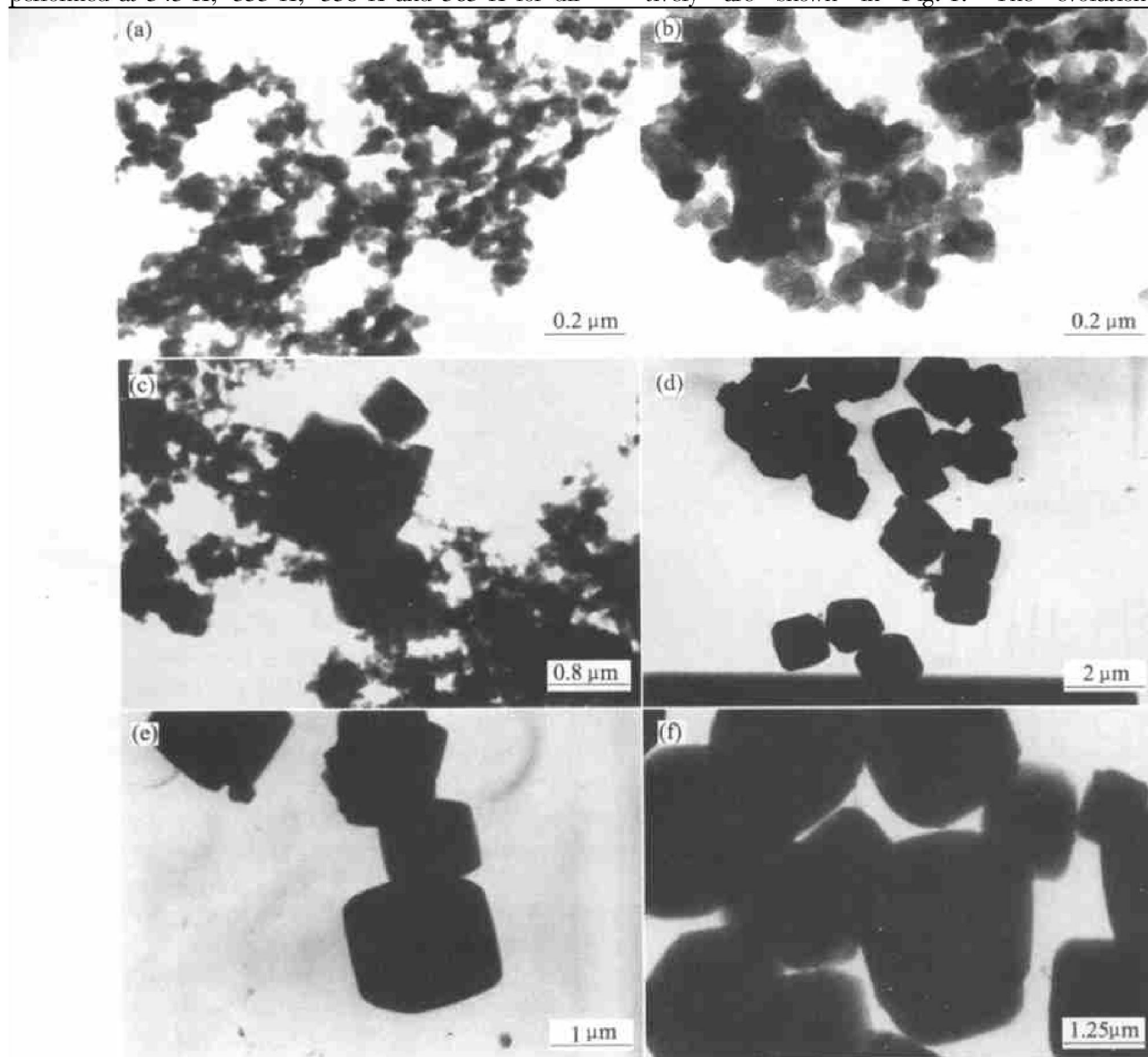


Fig. 1 TEM morphologies of zeolite 4A synthesized at 363 K for different times (a) —40 min; (b) —60 min; (c) —80 min; (d) —100 min; (e) —180 min; (f) —240 min

crystal appearance was clearly observed. A large number of gel particles appear in Fig. 1(a), and the range of particle size is 20~ 50 nm. Fig. 1(b) shows some irregular larger particles. Many aggregations of particles (similar to Figs. 1(a) and (b)) are observed and a few crystals of zeolite 4A are observed in Fig. 1(c). The crystals in Fig. 1(c) have a diameter of 0.5~ 1 μm and a cubic geometrical shape similar to standard zeolite 4A. Almost all crystals of zeolite 4A appear with perfect crystallographic shapes in Fig. 1(d). Some of the nanocrystal adhere to the surface of the microcrystals of zeolite 4A. The diameters of the microcrystals and nanocrystals are 1~ 2 μm and 50~ 100 nm, respectively. The crystal growth step between both microcrystal and nanocrystal is 50~ 100 nm, which was similar to step height observed by others^[10, 11]. With increasing crystallization time, the surface of crystal of zeolite 4A becomes smooth and the crystalline size increases to 2 μm , as seen in Figs. 1(e) and (f).

The XRD patterns of the samples are shown in Fig. 2. It is learned that sample 1 (synthesized for 40 min) is amorphous, and samples 2~ 5 (synthesized for 60, 80, 100 and 240 min, respectively) have crystalline phase. The crystallinity of samples increases with increasing reaction time. In particular the crystallinity and crystal size curves of Fig. 3 corresponding to samples 2 and 3 have a precipitous rise in the time range of 60~ 90 min. A key point of this article is the intrinsic nature of the phenomena of the very fast crystallinity and large increase in crystal size of zeolite 4A between 60 min and 100 min, as seen in Figs. 1(b)~ (d).

Sample 3 in Fig. 1 is transition between the amorphous and the crystalline phases. More details of the crystal growth of sample 3 are observed in

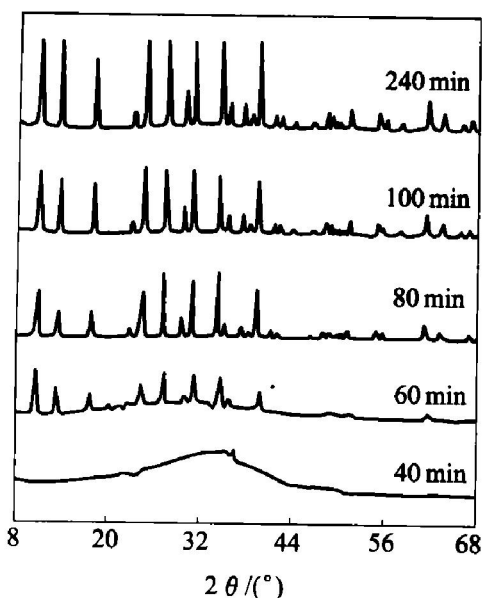


Fig. 2 XRD patterns of zeolite 4A synthesized at 363 K for different times

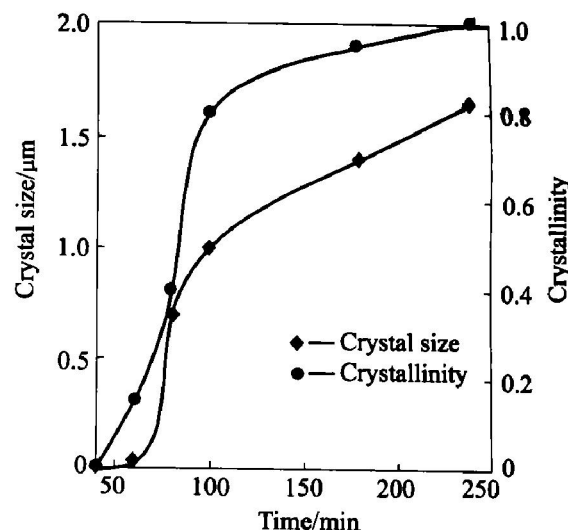


Fig. 3 Relationship of crystal size and crystallinity with crystallization time of zeolite 4A synthesized at 363 K

Fig. 4. Fig. 4(a) shows that many microcrystal of zeolite 4A formed with a very rough surface composed of nanoparticles. In Fig. 4(a), some nearly round aggregates are clearly observed and marked "P1". Because of imperfect aggregation, some cavity (marked as "P2") exist in a crystal of zeolite 4A, as shown in Fig. 4(b). An imperfect crystal and an aggregate (marked "P4") appear simultaneously in Fig. 4(d). The shape of the aggregate is similar to the crystal, which confirms that the crystal is formed from aggregation like the one in Fig. 4(d). A perfect crystal appears in Fig. 4(c) and is marked "P3".

Electron diffraction analysis was used to determine the phase or structure of the aggregate and crystals. The pattern of electron diffraction is shown in Fig. 5. The patterns of samples 1 and 2 herein are the samples 1 and 2 in Fig. 1 which are amorphous and polycrystalline, respectively. The patterns (c) and (d) relate to the crystals in "P4" in Fig. 4(d) and in "P3" in Fig. 4(c), respectively. The pattern in Fig. 5(c) contains both imperfect diffraction spots and obscure diffraction rings, and the pattern in Fig. 5(d) has only the perfect diffraction spots of zeolite 4A. It was obvious that the crystal growth of zeolite 4A experienced the process of "coalescent growth" from nano- to microcrystals in a very short time (about 20 min).

3.2 Morphology of zeolite 4A synthesized at different temperatures

The micrographs of zeolite 4A synthesized under different temperatures are shown in Fig. 6. Samples T1, T2, T3, T4, and T5 were synthesized at 333 K, 343 K, 348 K, 353 K and 358 K respectively for 2 h using the same system and composition. Sample T6 was synthesized at 348 K by

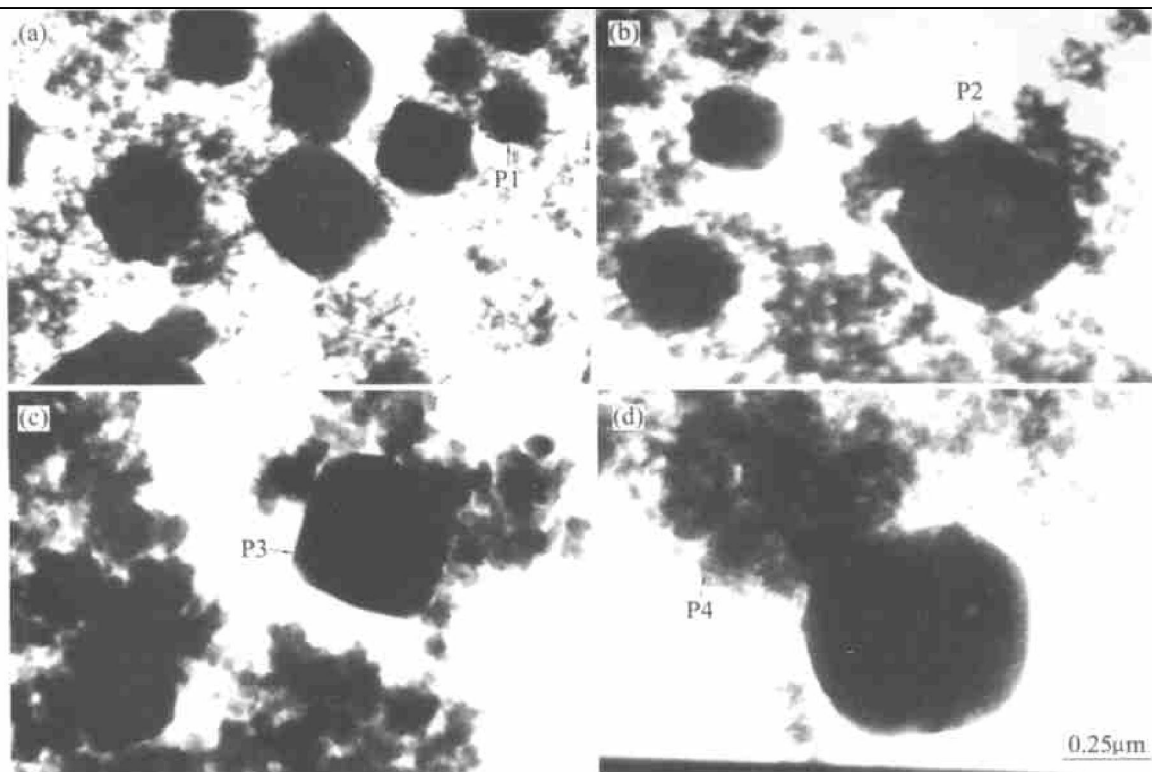


Fig. 4 TEM morphologies of zeolite 4A synthesized at 363 K for 80 min
(P1 and P4 —Aggregation of nanoparticles; P2 —Cavity in aggregation of microcrystal; P3 —Perfect microcrystal)

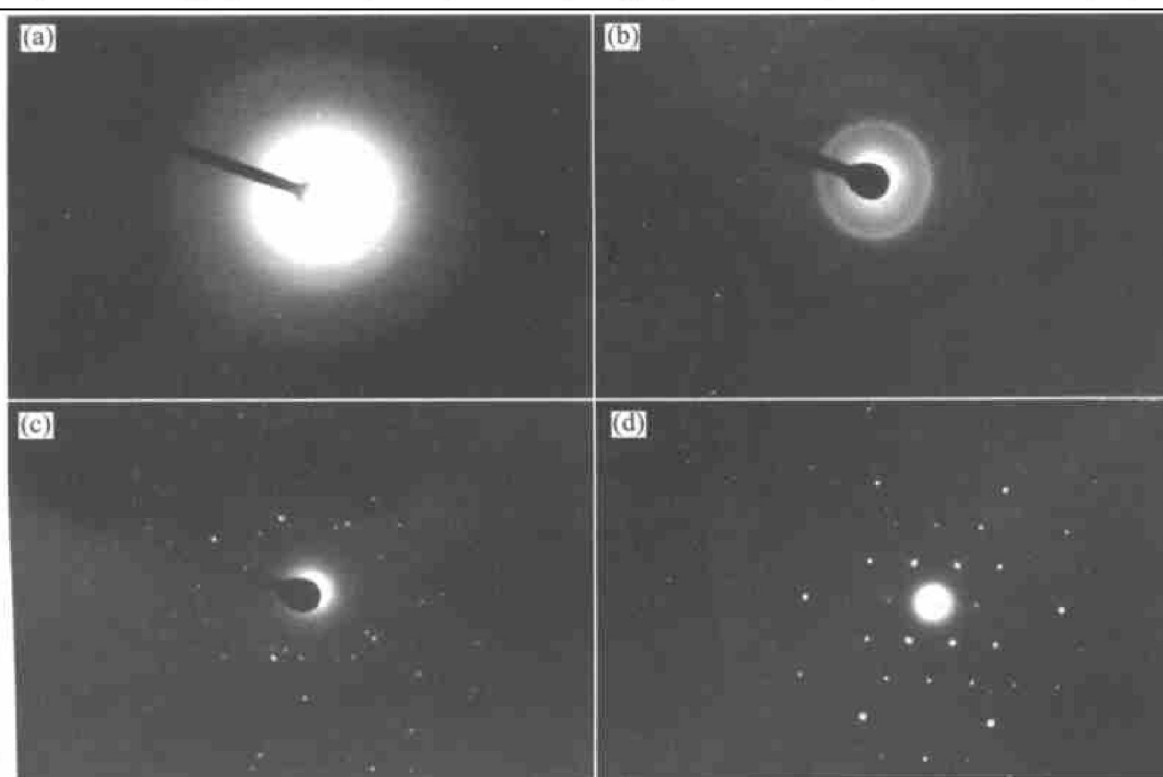


Fig. 5 Electron diffraction patterns of samples
(a) —Observed in Fig. 1(a); (b) —Observed in Fig. 1(b); (c) —Crystal P4 in Fig. 4; (d) —Crystal P3 in Fig. 4

stirring for 2 h. The aggregation of nanoparticles also existed in the process of crystallization, particularly in samples T2 and T3, which contained some cavity inside the zeolite crystals and had nonperfect surface or the accumulation of nanoparticles on the surface of microcrystals.

Some cubic nanocrystals also attached to the surfaces of microcrystals of zeolite 4A. The standard appearance of zeolite 4A indicated that the crystallization of T4 was completed. The temperature difference between T2

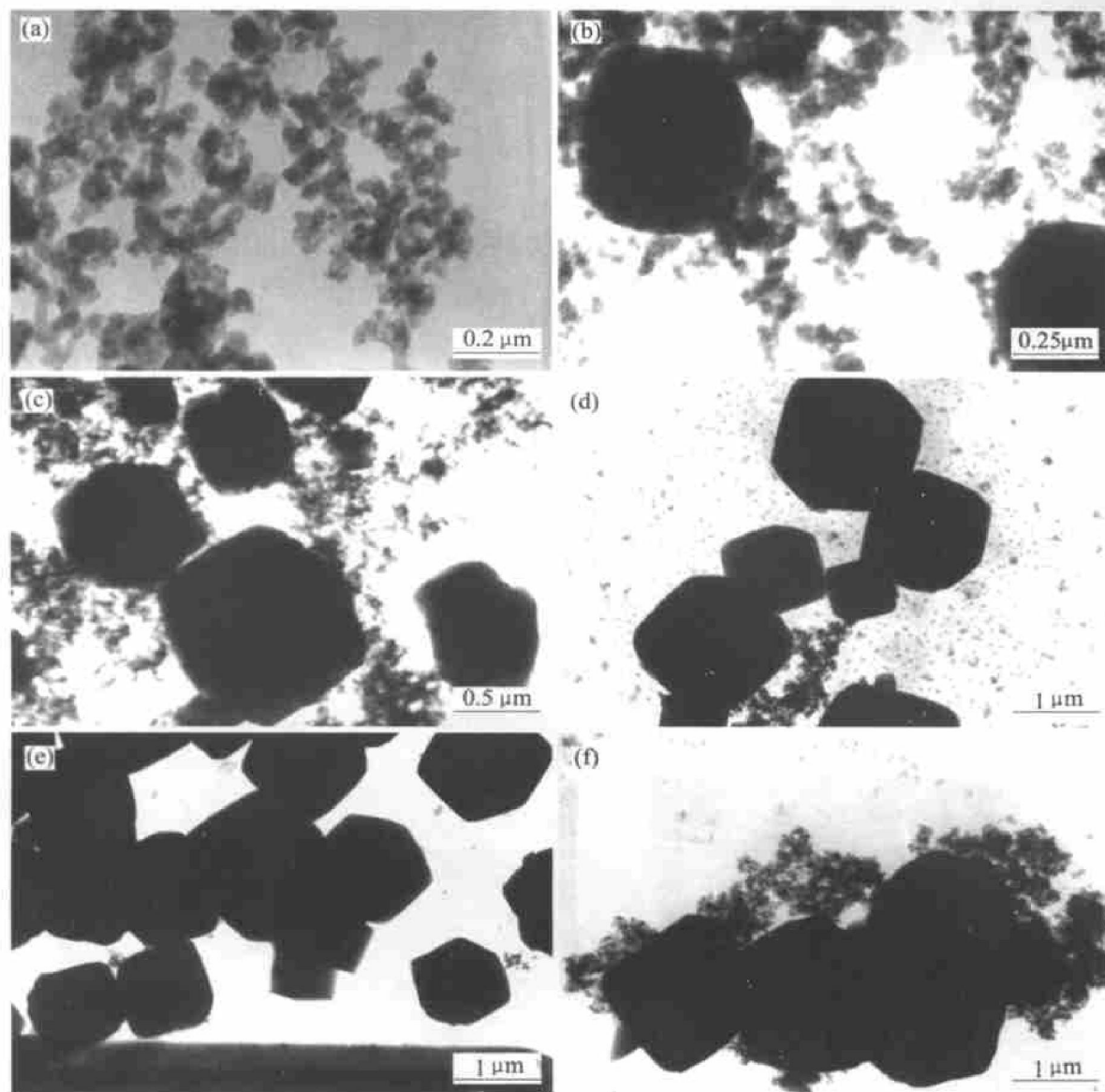


Fig. 6 TEM morphologies of zeolite 4A synthesized at different temperatures for 2 h
 (a) -333 K (T1); (b) -343 K (T2); (c) -348 K (T3); (d) -353 K (T4); (e) -358 K (T5); (f) -348 K (T6)
 ((a) ~ (e) —Without stirring; (f) —With stirring)

and T4 was only 10 K. So it could be concluded that the crystal growth of zeolite 4A by splicing growth was too fast to control the crystal size. The crystal size was larger in sample T6 than the other samples due to the aggregation prompted by stirring.

4 MODEL OF SPLICING GROWTH

According to our observation the splicing growth was actually involved in the process of the crystal growth of zeolite 4A. This splicing growth has a very dominant role and is important to understand the model of the crystal growth process and in turn to control the synthesis of the crystals. The Kossel Model^[12] considered the crystal as a very ideal one with smooth surface and having an obvious borderline between the crystalline surface and the environmental phases. Sunagawa^[13] considered that the crystal is imperfect and has not a smooth surface but have a permanent spiral or trapezoidal step in crystal

surface which grow continuously along the crystal surface. These models proposed that the crystal size increased linearly, which was very different from the coalesce growth observed in our study.

In this experiment, a large crystal (1 μm) of zeolite 4A was grown from an aggregation of a large number of nanocrystals or nanoparticles, which had very rough surfaces. There were many accumulations of nanocrystals attached to the surface of the microcrystal (as shown in Fig. 4). The interior and the surface of the microcrystal were examined by electron diffractometry. The result showed that the electron diffraction pattern of the interior appeared as perfect diffraction spot and the pattern of the surface layer appeared as several rings similar to the patterns shown in Fig. 5 (d) and sample 2. However, the crystallization time from nano- to microcrystal was too short to observe. Therefore, the microcrystal was not derived from spiral growth. The unpublished results of our

research on zeolite 4A and some works^[14, 15] showed that the size of large crystal has a linear growth in hydrothermal system. We considered that the nanocrystal and the smaller slice could be the slices of the large crystal structure piece of zeolite 4A. The slice size was always in the range of one angstrom to scores of nanometer.

The models of Chernov^[16] and Temkin^[17] considered that the crystal growth layer was composed of monatomic layers or a polyatomic layer. Atoms, unit cell, or slice always settled in torsional position of crystal steps, and the step height was extremely smaller than that of the crystal. According to these models, crystal grew up by the step developing laterally, the layer thickness was in the size of mono-atom or polyatom, namely, in the range of an angstrom. These models can not explain the phenomenon that nanocrystals having similar size spliced with each other to form a large crystal and have not proposed the nanocrystal or nanopiece as slice of crystal growth. Pyda et al^[18] researched the hydrothermal crystallization of ZrO_2 and reported that each crystallite was composed of several smaller ones. Pyda et al^[18] suggested that the sticking of the elementary units in an ordered manner was the plausible mechanism of elongated particle growth in the basic environments. Nishizawa et al^[19, 20] observed small isometric cubic crystallites arranged in a highly oriented manner in a NaOH solution prior to the appearance of the elongated monoclinic crystallites. The evidence given by Pyda et al^[18] and Nishizawa et al^[19, 20] is similar to the phenomenon observed on our research and also is the evidence of splicing growth proposed in this article.

In fact other papers^[10, 11] reported that crystal step height was often in the range of several hundreds nanometers, which implied that a nanocrystal or nanoparticle could be the unit of crystal growth. Shi et al^[21] reported that coalescent growth existed in the crystallization process of BaTiO_3 , which was named as the second kind of coalescent growth differentiated from coalescent growth proposed by Chernov^[22]. Chernov considered coalescent growth as a process in which a crystal grows up through smaller particles dissolving. The splicing growth was not observed in low saturation system for zeolite 4A as the second kind coalescence growth when microcrystals were already formed and dominant. According to the study result of Shi et al^[21], a slice could be the negative polyhedron or lattice cell and its aggregation in a different dimension. The slice size was different in different systems or conditions and ranged from atomic (angstrom) to nanometer dimensions. In general, the nanometer crystal or particles were called slice of microcrystal in the research well-founded. The crystal growth model of zeolite 4A in this paper is described as an induction period existing at the beginning of crystallization, followed by the immediate initiation of a lot of

nanometer crystals^[2], then the nanocrystals congregated as slices and spliced with each other to form a larger crystal. At this stage, the system had a high saturation and the number of nanocrystals was enormous. In addition, high reaction activity existed on the surface of nanocrystals, therefore created the possibility of splicing growth. It was not like Frank model in which nanocrystal settled in torsional position of crystal steps. In our model, many nanocrystals congregated around the center to evolve into a large crystal. In the research this process of crystal growth observed was called splicing growth to be differentiated from coalescent growth of Chernov model. A schematic of splicing growth is shown in Fig. 7.

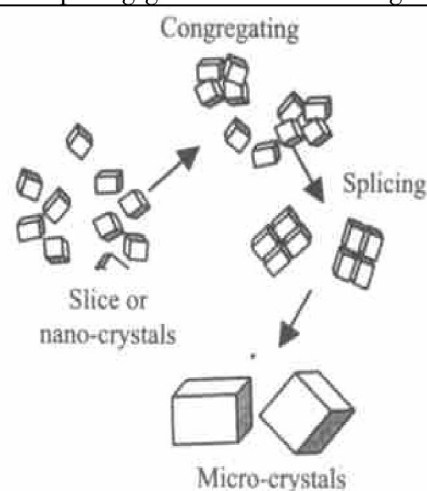


Fig. 7 Schematic of splicing growth of zeolite 4A observed in Figs. 1 and 4

5 CONCLUSIONS

1) A phenomenon of aggregation of nanocrystals exist in the crystallization process of zeolite 4A, and the microcrystals are derived from nanocrystals aggregating directly.

2) The splicing growth of zeolite 4A is described as follows. A large number of nanometer crystals initiate immediately after an induction period, and the nanocrystals congregate as slices and splice with each other to form microcrystals. The model proposes an explanation of the mechanism and new steps for controlling the crystal size.

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