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微波场中 T 型分子筛的合成及晶化研究

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摘要:研究了微波场中 T 型分子筛的结晶过程。考察了微波加热体系中合成参数如合成时间、溶胶组成、反应压力和模板剂用量对分子筛晶化的影响。微波加热的主要优点是减少合成时间,无模板剂的溶胶在普通加热条件下的晶化时间需要 120 h,而在微波场中则仅需要 20~25 h。另一方面,由于微波的快速加热特性促进了稳定相钙十字沸石的生成,从而减小了次稳定相 T 型分子筛的结晶区间。在未添加模板剂条件时,100 ℃下微波水热合成 T 型分子筛的结晶区间为:$20 \leqslant n_{SiO_2}/n_{Al_2O_3} \leqslant 22$ 和 $0.31 \leqslant n_{M_2O}/n_{SiO_2} \leqslant 0.33$(其中 $M_2O=Na_2O+K_2O$, $n_{Na}/n_K=3$ 和 $n_{SiO_2}/n_{H_2O}=11.70$)。在普通加热和微波加热合成体系中,添加模板剂均能扩大结晶区间,同时还可以进一步减少合成时间。

关键词:T 型分子筛;微波加热;普通加热;水热合成;机理
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Synthesis and Crystallization of Zeolite T by Microwave Heating

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Abstract: The crystallization of Zeolite T under microwave-heating system was studied. The effects of synthesis parameters such as synthesis time, gel composition, reaction pressure and template on crystallization were investigated. The results show that the crystalline zeolite T is obtained in 20~25 h without template under the microwave hydrothermal treatment in contrast to more than 120 h by conventional heating method. The crystallization fields of the metastable phase of zeolite T is narrowed due to the favored formation of the stable phase of phillipsite by the fast heating of microwave irradiation. The formation fields of zeolite T without template under microwave hydrothermal synthesis are: $20 \leqslant n_{SiO_2}/n_{Al_2O_3} \leqslant 22$ and $0.31 \leqslant n_{M_2O}/n_{SiO_2} \leqslant 0.33$(where $M_2O=Na_2O+K_2O$, $n_{Na}/n_K=3$ and $n_{SiO_2}/n_{H_2O}=11.70$) at 100 ℃. The addition of template(tetramethylammonium(TMA) cation) will broaden the crystallization field of zeolite T and further reduce the synthesis time in both of the microwave-heating system and the conventional-heating system.

Key words: zeolite T; conventional heating; microwave heating; hydrothermal crystallization; mechanism

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Due to fast and instantaneous heating, microwave techniques have attracted growing attention for the rapid synthesis of zeolites. The technique can reduce the crystallization time and the final particle size compared with those obtained by conventional heating. Many zeolites such as zeolite LTA [1], MCM-41 [2], ZMS-5[3], $AlPO_4$-11[4] and zeolite β[5] were successfully synthesized within short time by microwave heating. Nano-sized and uniform NaY[6] and VSB-5[7] zeolites were also reported to grow under microwave irradiation; in contrast, those crystals obtained by conventional heating were of 1~10 micrometers in size. On the other hand, it was reported that the crystalline phase of the final product formed by microwave heating was different from those grew by conventional heating in the synthesis of some aluminophosphates[4,8]. According to Park et al.[4], $AlPO_4$-31 together with a metastable phase of $AlPO_4$-11 was obtained by conventional heating, whereas, the pure stable phase of $AlPO_4$-31 was gained under microwave irradiation with the same gel composition.

Zeolite T is an intergrowth-type zeolite of erionite and offretite. Erionite has an 8-ring channels normal to *c*-axis with the pore size of 0.36×0.51 nm. On the other hand, offretite has two dimensional channels with the pore size of 0.36×0.49 nm and 0.67×0.68 nm, respectively. Zeolite T and zeolite T membranes were important inorganic microporous materials and were widely applied in catalysis[9,10], absorption[11], and liquids separation[12,13] processes. To the best of our knowledge, the synthesis of zeolite T was only performed under conventional heating with or without template[14~20]. For the template-free synthesis, zeolite T was always grown at the narrow ranges of gel composition by a slow crystallization rate, and other zeolite phases such as zeolite L and phillipsite (PHI) were reported to grow easily together with it when the synthesis conditions were changed slightly [16, 18]. As for their phase stability, it increases in the order: L<T<PHI[19]. For the template-assisted synthesis, tetramethylammonium (TMA) cation was considered as the most effective template to greatly shorten the synthesis time, i.e. from 5 d to 2 d at 100 ℃[20], and to broaden the crystalline filed.

And no reports have been concerned with the synthesis of zeolite T by microwave heating in the absence of organic template, neither the discussion on the formation of a pure metastable zeolite phase under fast microwave irradiation. In a previous work[21], we have reported the fast synthesis of zeolite T by microwave heating using the tetramethylammonium hydroxide (TMAOH) as the template. Here we report the template-free synthesis of zeolite T by microwave heating and the crystallization of zeolite T under microwave irradiation.

1 Experimental

1.1 Hydrogel preparation

Experiments were performed in aluminosilicate gels with $n_{SiO_2}:n_{Al_2O_3}:n_{M_2O}:n_{H_2O}=1:0.055:0.31:11.7$ (where $M_2O=Na_2O+K_2O$ and $n_{Na}/n_K=3$) unless otherwise specified. Firstly, 4.22 g aluminum hydroxide (Wako, technique), 9.43 g sodium hydroxide (Tianjin Hengxin Chemical Co. Ltd., 96 wt%) and 5.38 g potassium hydroxide(Shanghai Qingxi Chemical Co. Ltd., 82%) were dissolved in 102.78 g deionized water, and then a clear solution was obtained after heated with stirring. The solution was cooled at room temperature for about half an hour, then if necessary, 0.2 ~6wt% TMAOH solution (Aldrich, 10wt%) was added. The alkali solution was mixed with 29.53 g precipitated silica (Degussa VN2, 98wt%), agitated vigorously to give a uniform hydrogel. Finally, the gel was aged in a vibrating bed at ambient temperature for 12 h.

1.2 Zeolite synthesis

The crystallization experiments under microwave irradiation were carried out using two techniques. For the technique of microwave hydrothermal synthesis (MH), a closed PTFE autoclave filled with the 100 mL hydrogel was placed in a microwave oven (NJL08-2, Jiequan Micro. Tech. Co.). The reaction temperature rose immediately to 100 ℃ within 2 min under maximum power of 700 W, and the set temperature was maintained automatically for 0~48 h. Microwave power was around 80 W when heat equilibrium was reached. For the technique of microwave heating under reflux condition (MR), an open quartz vessel (200 mL) with a water a condenser was used for the synthesis under atmospheric pressure and the operation procedure of mi-

crowave oven was similar to those experiments by MH technique. For comparison, the synthesis by conventional hydrothermal synthesis(CH) was also launched in the electric air oven using a closed PP bottle. At the end of all experiments, the solid products were recovered by filtration, washed with deionized water, and dried overnight at 110 ℃.

1.3 Characterization

XRD characterization was performed on a BRUKER, D8 ADVANCE X-ray diffractometer(Cu $K\alpha$ radiation, λ =0.154 18 nm), 40 kV of operation voltage, 120 mA of operation current, graphite monochromator, 5° ~50° of 2θ value range). The crystalline size and morphology were observed by scanning electron microscopy (SEM) (FEI, QUANTA 200, High Vacuum mode, 30 kV). BET surface areas and the mean pore size were estimated by the low temperature nitrogen adsorption tests (QUAUTA CHROM, CHEMBET-3000). The samples were fully dried at 300 ℃ for 4 h before the measurement.

2 Results and discussion

2.1 As-synthesized zeolite T samples

The properties of zeolite T samples under different synthesis condition by microwave heating are listed in Table 1. The fine zeolite T crystals with the mean particle size of 0.2 μm could be crystallized in the gel with 0.56wt% TMAOH as the template(n_{TMA_2O}/n_{SiO_2}=0.1) after a microwave-hydrothermal treatment of 20 h at 85 ℃. The crystal had the largest BET surface area of 530 $m^2 \cdot g^{-1}$ but the poorest crystallinity than the other three samples. Zeolite T particles with high crystallinity were fast prepared in the gel containing 0.1wt% TMAOH(n_{TMA_2O}/n_{SiO_2}=0.018) within 8 h by MH technique at 100 ℃. The crystal had a large BET surface area of 500 $m^2 \cdot g^{-1}$ and mean particle size of 0.6 μm. The MR technique in the template-free gel could obtain zeolite T crystal after 25 h. In addition to the longer synthesis time, the BET surface area of the sample was lower than that by template-assisted MH technique. Specially, the template-free MH technique gained zeolite phase of phillipsite other than zeolite T with the same gel composition, but obtained pure zeolite T with the modified gel composition of $n_{SiO_2}:n_{Al_2O_3}:n_{M_2O}:n_{H_2O}$=1:0.045:0.31:11.70. It has been observed that the minimum synthesis time for the presence of zeolite T crystal depends on the synthesis conditions including techniques and the template. The minimum time required decreases in the order: template-free MR>template-free MH >template-assisted MH. As far as the mean pore size are concerned, sample A and B synthesized in the presence of template are larger than sample C and D obtained from the template-free gels. However, the mean pore sizes of the four samples are less than that of pure offretite with a large 12-ring channel (0.67×0.68 nm), which shows that stack faults of intergrowth erionite-offretite (zeolite T) effectively block the large 12-ring channel in offretite, especially in the case of sample C and D synthesized in the absence of template.

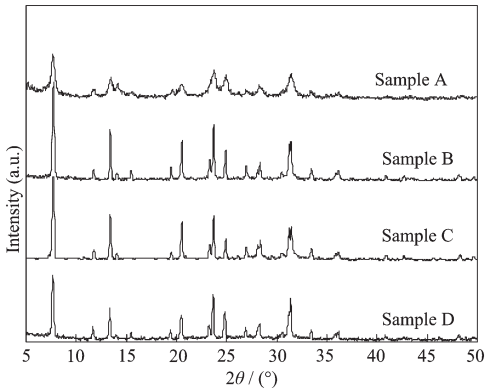
Table 1 Synthesis conditions and the properties of synthesized zeolite T samples by microwave heating

Sample	Conditions				Results			
	$n_{SiO_2}:n_{Al_2O_3}:n_{M_2O}:n_{H_2O}:n_{TMAOH}$	Technique	Temp. / ℃	Time / h	Degree of crystallinity / %	BET surface area / ($m^2 \cdot g^{-1}$)	Mean particle size / μm	Mean pore size / nm
A	1:0.055:0.31:11.70:0.10	MH	85	20	65	530	0.2	0.47
B	1:0.055:0.31:11.70:0.018	MH	100	8	100	500	0.6	0.46
C	1:0.055:0.31:11.70:0	MR	100	25	85	280	1.5	0.41
D	1:0.045:0.31:11.70:0	MH	100	20	78	230	2.5	0.39

Fig.1 shows XRD patterns of zeolite T samples obtained under the four different synthesis conditions. The four samples are with characteristic peaks of zeolite T (see peaks at 2θ=7.7°, 13.3° and 20.4° in their XRD patterns)[22]. Sample B with the highest crystallinity is selected as the norm for normalization. As a result, the degree of relative crystallinity of sample A, C and D is 65%, 85% and 78%, respectively.

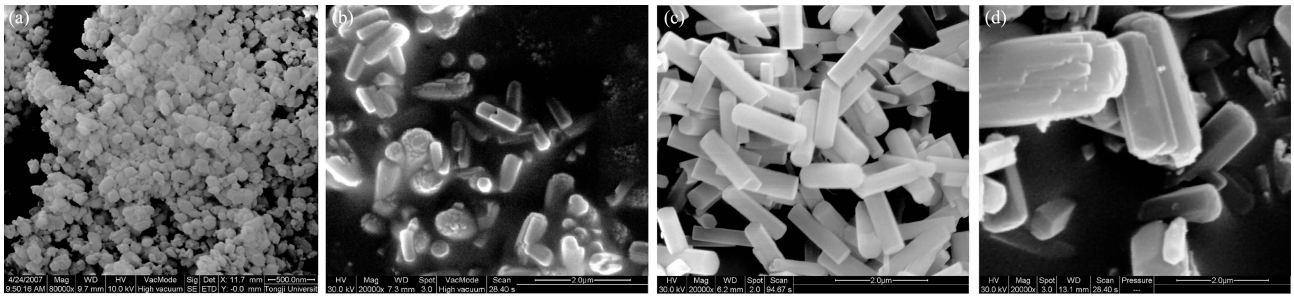
Fig.2 shows the morphology of zeolite T crystals synthesized by template-assisted MH, template-free MR

and MH techniques. The zeolite T crystals crystallized from the gel with relatively high template concentration at 85 ℃ by MH(sample A) show the spherical morphology with a smaller particle size of 0.2 μm. The mean crystal size of sample B obtained by template-assisted MH technique at 100 ℃ is estimated to be 0.2×0.6 μm with a column shape. The crystals gained by template-free MR (sample C) and template-free MH (sample D) techniques also have the column shape with relatively large particle size of 0.5×1.5 μm and 1×2.5 μm, respectively.



(a) sample A, (b) sample B, (c) sample C, and (d) sample D

Fig.1　XRD patterns of zeolite T samples



(a) sample A, (b) sample B, (c) sample C, and (d) sample D

Fig.2　SEM images of zeolite T samples

Crystal size and distribution are greatly dependent on the number of nuclei and the growth rate of crystal, which are influenced by some synthesis parameters such as synthesis temperature, time, pressure, template, heating method and so on. To obtain small crystals with a narrow particle size distribution, the emphasis should be on the simultaneous release of the gel nuclei and the interrupted growth of the crystals once released[1]. Those crystals (sample A and B) obtained in the presence of template have smaller particle sizes with narrower distribution compared with those (sample C and D) gained without template(shown in Fig.3). The great effect of the template on the particle size and distribution would be contributed to its strong arrangement the nutrients to nuclei in a short period and fast release of nuclei, and the afterward slow growth rate of crystal because of the low density of nutrients. Synthesis temperature was reported as another important effect on particle size and distribution of zeolite NaA crystal[1]. The energy of nucleation(about 15 kJ·mol^{-1}) is much less than the energy of crystal growth(about 60 kJ·mol^{-1}). Hence, lower temperature favors nucleation, in contract that crystal

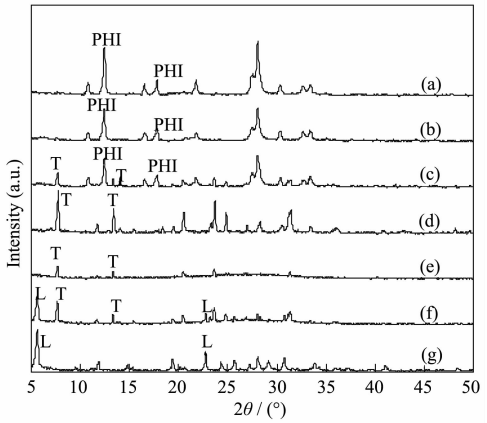


Fig.3　XRD patterns of zeolites prepared by template-free MH in the gels with $n_{SiO_2}/n_{Al_2O_3}$ and n_{M_2O}/n_{SiO_2} ratio of (a) 15, 0.31; (b) 18, 0.31; (c) 20, 0.31; (d) 22, 0.31; (e) 25, 0.31; (f) 22, 0.33; (g) 22, 0.36, respectively

growth surpasses nucleation at relatively higher temperature. In our cases, both template and relatively low temperature benefit the nucleation of zeolite T, and result in the smallest crystal particles with mean size of 200 nm(sample A).

2.2　Effects of $n_{SiO_2}/n_{Al_2O_3}$ and $n_{Na_2O+K_2O}/n_{SiO_2}$ ratio

Fig.3 compares the gel composition and the corre-

sponding zeolite product prepared by template-free MH technique. The $n_{SiO_2}/n_{Al_2O_3}$ and n_{M_2O}/n_{SiO_2} ratios are varied from 15 to 25 and from 0.28 to 0.36, respectively. Crystallization is performed at 100 ℃ for 20 h for all reactions. Phillipsite is formed in the $n_{SiO_2}/n_{Al_2O_3}$ ratio range of 15 to 18. And the mixture of zeolite T and phillipsite is gained using the gel with $n_{SiO_2}/n_{Al_2O_3}$ ratio of 20. Only when $n_{SiO_2}/n_{Al_2O_3}$ ratio is adjusted to a narrow zone($n_{SiO_2}/n_{Al_2O_3}$=22), could pure zeolite T be obtained. The amorphous phase appears instead of zeolite phase with the $n_{SiO_2}/n_{Al_2O_3}$ ratio of 25. The crystalline product could not be gained when n_{M_2O}/n_{SiO_2} ratio is less than 0.28 under our preparation condition. Zeolite T could be crystallized in the gel with n_{M_2O}/n_{SiO_2} ratio of 0.31 to 0.33. Zeolite L, which crystallizes together with zeolite T in the gel with relatively high n_{M_2O}/n_{SiO_2} ratio of 0.33, is crystallized well when n_{M_2O}/n_{SiO_2} ratio is up to 0.36.

Zeolite T was reported to be formed in the narrow range of $n_{SiO_2}/n_{Al_2O_3}$ and n_{M_2O}/n_{SiO_2} ratios[14,18,20]. Cichocki [18] has reported the crystallization field of zeolite T: $24 \leqslant n_{SiO_2}/n_{Al_2O_3} \leqslant 29$, $0.34 \leqslant n_{M_2O}/n_{SiO_2} \leqslant 0.41$ and $n_{Na}/n_K=3$ at 100 ℃ using a steel autoclave by conventional heating, but phillipsite appears in the product when the $n_{SiO_2}/n_{Al_2O_3}$ ratio is reduced from 24 to 10 and zeolite L is formed in the gel with relatively high n_{M_2O}/n_{SiO_2} ratio. Similar to that by conventional heating, the results in our present work show that the gels with relatively high $n_{SiO_2}/n_{Al_2O_3}$ ratio and low n_{M_2O}/n_{SiO_2} ratio may also be suitable to the crystallization of zeolite T by microwave heating.

2.3 Effect of synthesis time

Fig.4 reveals the relative crystallinity of the product as a function of synthesis time using template-free MH technique with the gel composition of $n_{SiO_2}:n_{Al_2O_3}:n_{M_2O}:n_{H_2O}=1:0.055:0.31:11.70$ (where $M_2O=Na_2O+K_2O$ and $n_{Na}/n_K=3$). The areas of the diffraction peaks(related to the degree of crystallinity) generally increase with the synthesis time. Amorphous phase is confirmed as the main phase in the products when the synthesis time lasts for 0, 5 and 10 h, respectively. Zeolite T with the degree of relative crystallinity about 30% is detected by

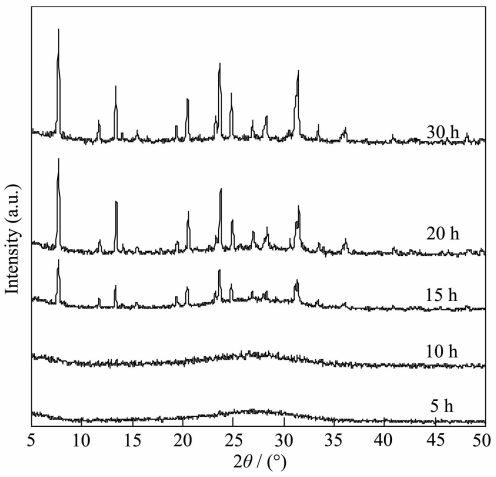


Fig.4 XRD patterns of zeolite T obtained by template-free MH technique for different synthesis time

XRD when the reaction has lasted for 15 h. And its crystallinity increases fast along with the synthesis time from 15 to 20 h. When the synthesis time is prolonged to 30 h, there is not any other crystalline phase in the final product. It shows that the formation and crystallinity of zeolite T are strongly related to the synthesis time.

2.4 Effect of reaction pressure

In the hydrothermal synthesis, high reaction pressure could normally lead to a rapid crystallization rate of zeolites [23]. The experiences under atmospheric pressure by MR technique and autogenic pressure (about 2×10^5 Pa) by MH technique at 100 ℃ are compared. As mentioned above, the reaction under atmospheric pressure at boiling point(about 100 ℃) results in zeolite T phase after 30 h, but a more stable phase phillipsite could be obtained under autogenic pressures at 100 ℃ for 20 h. The necessary synthesis time under autogenic pressure(about 2×10^5 Pa) is less than that under atmospheric pressure. Those results show that the reaction pressure has an important effect on the synthesis of zeolite T by microwave heating. However, according to Cichocki[18], zeolite T could be gained under open (atmospheric pressure) and closed systems (autogenic pressure) using the same gels by conventional heating. The mechanism of reaction pressure on the crystallization of zeolites is still not clear. The possible explanation is that the higher reaction pressure together with the microwave irradia-

tion accelerates the crystallization rate, promoting the formation of a stable phase of phillipsite. But in conventional-heating system, the effect of autogenic pressure is not enough to induce the formation of the stable phase.

2.5 Effect of template

The organics containing nitrogen such as TMAOH and cholinchloride are selected as template for the synthesis of zeolite T in various publications [15~17]. Fig.5 shows the XRD patterns of crystalline products synthesized with various amounts of TMAOH from 0 to 0.1wt% by MH technique at 100 ℃. The phillipsite phase is gained from the template-free gel. And then, mixtures of zeolite T as main phase and phillipsite as minimum phase are obtained when 0.02wt% TMAOH is added to the gel. Finally, the pure zeolite T could crystallize in the gel containing 0.1wt% TMAOH within shorter synthesis time of 8 h. Meanwhile, the addition of the template broadens the crystallization fields of zeolite T. For example, the ranges of $n_{SiO_2}/n_{Al_2O_3}$ and n_{M_2O}/n_{SiO_2} ratios are determined to be from 18 to 22 and from 0.31 to 0.36, respectively, when 0.1wt% TMAOH is used.

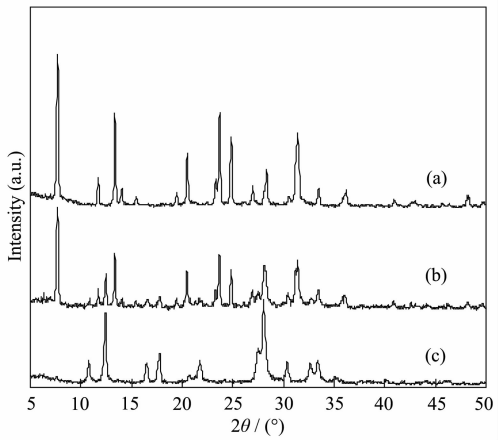


Fig.5 XRD patterns of crystalline products synthesized under different amounts of template and synthesis time by MH technique: (a) 0.1wt%, 8 h; (b) 0.02wt%, 20 h; (c) 0wt%, 20 h

Two stages, the amorphous primary units of SiO_4 and AlO_4 forming the secondary building units of zeolite framework and the arrangement of the secondary building units regularly to the crystalline unit cell, are considered to be the key steps of zeolites synthesis. The framework of zeolite T is composed of single/double 6-ring[24], but phillipsite has the secondary building unit of double 4-ring[25]. Under the specific synthesis condition, the template effect of TMA cation is considered to initiate selectively the amorphous phase of primary building units such as SiO_4 and AlO_4 to form the secondary building unit of single/double 6-ring, then to arrange those secondary building units (as nuclei) to crystalline unit cell, finally to bear the zeolite T crystal other than phillipsite. While adding a very little amount of template(e.g. 0.02wt%), the inductive effect of the template appears to be not strong enough to avoid the formation of phillipsite. When the template increases to a certain value (e.g. 0.1wt%), pure zeolite T phase will be obtained within short time due to its strong inductive effect on the gel arrangement.

Furthermore, the knowledge of the framework structure of TMA-zeolite T could support our statement. According to Lillerud et al.[16], the TMA cation exits not only in hexagonal and dodecagonal prisms along c-axis but also in the gmelinite cage and supercage along a-axis of zeolite T framework, and its existence in the internal space of the gmelinite cage is probably important to the stability of zeolite T framework. The existence of TMA cation in hexagonal prism implies that TMA cation plays the role of the template during the initial stage: the amorphous primary units of SiO_4 and AlO_4 forming the secondary building units of single/double 6-ring. Furthermore, the TMA cation could accelerate the regular arrangement of the secondary building units to crystalline unit cell on the basis of the fact that the TMA cation exists in the gmelinite cage and supercage. Deduced from the framework of TMA-zeolite T[16], it is reasonable that the template shows strong inductive effect during the formations of both secondary building units and crystalline unit cell.

In both CH and MH systems, we consider that the inductive procedure of the template is similar. The fact of short synthesis time of 8 h by MH technique compared with that of 48 h by CH technique in the presence of 0.1wt% TMAOH, would be contributed to the combinative effects of microwave and the template based on our previous work[21].

2.6 Comparison of MH and CH techniques

Fig.6 compares the crystallization curves of zeolite T by MH and CH techniques in the absence of the template. All experiments were carried out using the gel with molar composition of $n_{SiO_2}:n_{Al_2O_3}:n_{M_2O}:n_{H_2O}=1:0.045:0.31:11.70$ in an autoclave at 100 ℃. It is observed clearly that the induction period by MH technique is about 15 h, which is much shorter than that by CH technique. On the other hand, the growth rate of crystals by MH technique is faster. In general, the MH technique leads to crystallization rate by 5~6 times.

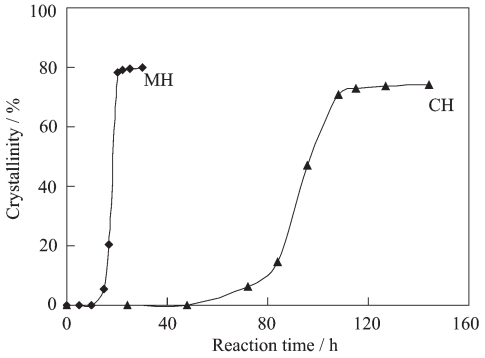


Fig.6 Crystallization curves of zeolite T synthesized by MH and CH with gel composition of $n_{SiO_2}:n_{Al_2O_3}:n_{M_2O}:n_{H_2O}=1:0.045:0.31:11.70$ at 100 ℃

Table 2 compares the template-free synthesis of zeolite T by MH and CH under different gel compositions. As discussed above, zeolite T is suitable to be crystallized in the fields: $20\leqslant n_{SiO_2}/n_{Al_2O_3}\leqslant 22$ and $0.31\leqslant n_{M_2O}/n_{SiO_2}\leqslant 0.33$ by MH. Whereas, the CH technique could gain zeolite T in the considered composition fields of the gels: $15\leqslant n_{SiO_2}:n_{Al_2O_3}\leqslant 25$ and $0.31\leqslant n_{M_2O}/n_{SiO_2}\leqslant 0.36$.

Table 2 Comparative synthesis by MH and CH under different gel compositions

Experiment	$n_{SiO_2}:n_{Al_2O_3}:n_{M_2O}:n_{H_2O}$	MH		CH	
		Time / h	Product phase	Time / h	Product phase
1	1:0.067:0.31:11.70	20	PHI	120	T+(PHI)[a]
2	1:0.055:0.31:11.70	20	PHI	120	T
3	1:0.050:0.31:11.70	20	PHI+T	120	T
4	1:0.045:0.31:11.70	20	T	120	T
5	1:0.040:0.31:11.70	20	Am[b]+(T)	120	T+Am
6	1:0.045:0.33:11.70	20	L+(T)	120	T
7	1:0.040:0.33:11.70	20	T+(L)	120	T
8	1:0.045:0.36:11.70	20	L	120	T+(L)

Note: [a] ( )=minority phases; [b] Am=Amorphous phase

From the combined results of Fig.6 and Table 2, it can be concluded that the microwave irradiation increases the crystallization rate but narrows the formation field of a metastable phase of zeolite T. These effects are doom to be resulted from fast dissolution of gel and high heating rate of microwave irradiation[4]. In MH system microwave irradiation destroys the hydrogen bridges between the water molecules by ion oscillation and water dipole rotation to result in isolated active water[4,26]. The lone pairs and OH groups of the active water molecules have a higher potential to dissolve the gel than normal water. The high supersaturation of the gel together with high heating rate of induction heating could increase surely the crystallization rate. On the other hand, according to Ostwald rule: more stable phases appear as the speed of crystallization increases, higher crystallization rate under microwave irradiation benefits more stable phase of phillipsite other than zeolite T.

Fortunately, zeolite T crystal has its different secondary building units and n_{Si}/n_{Al} in the framework compared with phillipsite. Therefore, it is possible under microwave irradiation to find a certain gel composition field even under template-free condition, in which the secondary building units of single and double 6-rings is favorable to be formed, furthermore zeolite T crystal is grew, even if the fast heating of microwave does not benefit the formation of the metastable phase of zeolite T.

The arguments above suggest that the formation of a metastable zeolite phase under microwave irradiation is difficult, but probably by the way of the adjustment of

the reaction condition or template addition. In general, the addition of organic template is a more effective way to crystallize a metastable phase in the microwave-heating system due to its strong inductive and/or template effects on the formation of zeolite frameworks.

3 Conclusions

Zeolite T could be synthesized without the template by microwave heating in a short time under optimized synthesis conditions. The synthesis time is reduced by 80% compared with that obtained by conventional heating. The crystals obtained by template-free MH have similar crystallinity, morphology and particle size to those synthesized by conventional heating. On the other hand, the crystallization fields of metastable phase zeolite T are narrowed under microwave irradiation due to its fast and homogenous heating. The crystallization fields of zeolite T under microwave hydrothermal synthesis without template are: $20 \leqslant n_{SiO_2}/n_{Al_2O_3} \leqslant 22$ and $0.31 \leqslant n_{M_2O}/n_{SiO_2} \leqslant 0.33$ (where $n_{Na}/n_K=3$ and $n_{SiO_2}/n_{H_2O}=11.70$) at 100 ℃.

TMA cation as the template in microwave-heating system could broaden the crystallization field of zeolite T and further reduce the synthesis time as well as in conventional-heating system. Because the TMA cation is confirmed to exist in small hexagonal prism and large gmelinite cage and supercage, the template seems to take effect on the two key stages: the formation of secondary building unit and that of crystal, and by this way, the formation of zeolite T crystal could become faster and easier.

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