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The effects of (Na + K)/Na molar ratio and kinetic studies on the rapid crystallization of a large pored titanium silicate, ETS-10 using cost efficient titanium oxysulfate, TiOSO$_4$ under stirring

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Abstract

A large pored variety of titanium silicate, ETS-10 was synthesized to investigate the effects of (Na + K)/Na molar ratio on the crystallization and phase purity using cost efficient titanium oxysulfate as the titanium source under stirring at 200 rpm and to calculate activation energy. The results showed that the (Na + K)/Na molar ratio significantly affects the crystallization and phase purity. In addition, regardless of silica and titanium sources, the morphology of ETS-10 synthesized under stirred condition is quite different from that synthesized under static condition showing a small spherical shape, and seems to be significantly affected by stirring. The composition with the shortest reaction time to reach the 100% crystallinity and purity for different silica and titanium source was chosen and applied to the kinetic study. All the experiments for kinetic study were carried out at 433, 453 and 473 K, respectively. The activation energies for three different stages, nucleation, transition and crystallization were calculated using the modified Avrami–Erofeev equation. The results of kinetic study also suggest that the effect of titanium source is more significant than that of silica source. As a comparison, the temperature dependency for titanium oxysulfate is less sensitive than for titanium sulfate except the lowest temperature (i.e., 433 K) studied in this study, suggesting that minimum temperature should be maintained to proceed the crystallization at reasonable rate for titanium oxysulfate. The modified Avrami–Erofeev equation to three different stages, nucleation, transition and crystallization for rapid crystallization seems to be excellent tool to predict the crystallization of ETS-10.
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1. Introduction

Recently, many research works have been focused on the synthesis of microporous titanium silicate having a unique framework. Especially, ETS-10 and ETS-4 have particular structure in comparison with classical zeotype family. ETS-10 and ETS-4, reported by Kuznicki [1,2], comprise corner-sharing SiO$_4$ tetrahedra and TiO$_6$ octahedra linked through bridging oxygen atoms and the pore system contains 12-membered ring. Two varieties of these materials include a small pored ETS-4, with a pore opening of 3.7 Å and a large pored sieve ETS-10 with a pore opening of 8 Å. ETS-10 exhibits good thermal stability up to 550 °C in air but ETS-4 has low thermal stability, because it contains structural water bound in chains along the channel system. This water is lost at temperature of 200 °C and the structure collapses [3]. A large pore variety, ETS-10 has received an abundance of attention due to its potential catalytic, adsorptive and ion-exchange properties.

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Since the first patent on the syntheses of these three-dimensional, microporous titanium silicates in 1989 were issued to Kuznicki [1], additional reports [4,5] on ETS-10 synthesis have appeared. However, the crystallization region of ETS-10 is quite limited to narrow compositional and pH zone. In addition, the impurities such as dense phase titanium silicate (AM-*n* materials [6]) are not only formed easily but are also thermally stable up to approximately 600 °C.

Valchev et al. [7,8] have reported the influence of different organic bases on the crystallization kinetics of ETS-10. Das et al. [9,10] have studied the influence of synthesis parameters such as temperature, concentration, organic templates and seeding on the kinetics of ETS-10 synthesis. Rocha et al. [11] have reported a comprehensive study of synthesis of ETS-10 using two of the most useful titanium sources, $TiCl_3$ and crystalline TiO_2 in form of anatase. Kim et al. [12,13] have reported the synthesis of pure ETS-10 within a short crystallization time in the absence of seeds under static condition and compositional and kinetic studies on the crystallization of ETS-10 in the presence of various organics. Yang et al. [14] have studied the synthesis of ETS-10 with TiF_4 and P25 as the titanium sources. Pavel et al. [15] examined the crystallization kinetics starting from gels containing tetraalkyl-ammonium bromides. Kim et al. [16] reported the effect of silica and titanium sources on the crystallization of ETS-4 under stirring condition. Recently, Ji et al. [17] reported the compositional study on the crystallization of ETS-10 using $Ti(SO_4)_2$ as the titanium source. As of now, however, there is no report on the crystallization of ETS-10 using more cost efficient titanium oxysulfate as the titanium source for the first time under stirring.

In this study, the effect of the $(Na + K)/Na$ molar ratio on the crystallization of ETS-10 using titanium oxysulfate with different silica sources along with titanium sulfate for comparison in the absence of seeds and organics under stirring condition will be presented. Kinetic studies based on optimized composition will also be presented.

2. Experimental

The reactants used in this study were sodium silicate solution (27% SiO_2, 14% NaOH, 59% H_2O, Aldrich) and Ludox AS-40 (Dupont Chem. Co.) as the silica sources, reagent grade NaOH pellet (Junsei Chem. Co.), 98% KF powder (BDH Laboratory) as the alkali sources, $Ti(SO_4)_2$ solution (10% TiO_2, 51% H_2SO_4, 39% H_2O, KEMIRA pigment), $TiOSO_4$ (81.3% $TiOSO_4$, 8.5% H_2SO_4, 10.2% H_2O, Tayca Co.) as the titanium sources, 2N/5N H_2SO_4 (95% H_2SO_4, Duksan Chem. Co.) as the ingredient of pH adjustment and deionized water. Especially, the crystallization of ETS-10 requires lower alkalinity than that of ETS-4 [1,18]. To investigate the effect of $(Na + K)/Na$ molar ratio on crystallization and phase purity of ETS-10, therefore, an optimum molar composition of initial reacting gel was chosen from the batch composition that

resulted in a highly pure phase ETS-10 from 2^3 factorial studies reported previously [12,18]. In this study, however, the optimum composition adopted from the previous result was slightly modified because of different reaction condition. To determine the optimum composition, the reaction was initially conducted at 200 °C (ETS-10) under stirring at 200 rpm until 100% crystallinity was obtained. To eliminate seed effects due to possible residual product from previous runs, teflon vessel was cleaned with hydrofluoric acid prior to each succeeding synthesis and a 10% NaOH solution was used at the hydrothermal condition of 150 °C for 1 h to clean the stirrer of pitch blade turbine, respectively.

2.1. Experimental procedures

2.1.1. Compositional study

The experimental works were carried out at 200 °C under stirring at 200 rpm for various reaction times using $TiO_2–5.5SiO_2–xNa_2O–yKF–zH_2O$ as a starting composition where x varied from 4.2 mol to 4.84 mol, y from 0.0 mol to 3.5 mol and z from 185 mol to 300 mol, respectively.

In all experiments, the initial reacting gel was prepared as follows. The predetermined amount of distilled water was added to the sodium silicate/Ludox AS-40 solution in Beaker I and rigorously stirred for 20 min. The predetermined amount of NaOH pellets and distilled water were added to beaker II and stirred for 20 min. Upon mixing these two beakers separately until homogeneous solutions were obtained, they were then mixed together and stirred for another 60 min. After that, the titanium sulfate/oxysulfate solution was drop wisely added to this solution and rigorously stirred for 20 min. Potassium fluoride powder dissolved in water was added to this mixture. Finally, the pH was measured and adjusted by sulfuric acid. All the experiments were focused on the crystallization of ETS-10 only, excluding the high pH range that preferably produces ETS-4 as previously reported [16]. The optimum pH of initial starting gel was chosen from the pH that resulted in a highly pure phase of ETS-10 from 2^3 factorial studies reported previously [12]. The final reaction mixture was then poured into a 300 ml teflon-lined autoclave and the reaction was carried out at 200 °C under stirring at 200 rpm. The sample was taken out of the reactor at intermediate time during the reaction until 100% crystallinity was achieved. The sample was then washed thoroughly and filtered until the pH of filtrate was 9.5 and dried overnight at 100 °C.

2.1.2. Kinetic study

Based on the results obtained, the composition that led to the shortest reaction time to reach 100% crystallinity and pure ETS-10 was chosen for kinetic study. The reaction was then conducted for various reaction times at 433, 453 and 473 K, respectively, following the same procedures as that of compositional study.

2.2. Characterization

X-ray powder diffraction analyses (Rigaku Model D/MAX III) using CuKα radiation were performed to identify the product phase and to calculate % crystallinity. The degree of crystallinity was calculated by comparing the areas below the peaks of 14.62, 3.60, 3.28 and 2.98 Å in d-spacing with them for the reference sample with the highest crystallinity obtained from the reaction. SEM (Jeol JSM 8380) identified the crystal size and morphology.

3. Results and discussion

As mentioned earlier, the optimum composition from previous report [12] was adopted and the results for the crystallization of ETS-10 using a new titanium source, titanium oxysulfate will be discussed as follows.

3.1. Compositional study: effects of (Na + K)/Na molar ratio

Based on the molar composition previously described, the experimental works were carried out at 200 °C for various reaction times to provide an optimum composition for kinetic study. As can be seen in Tables 1 and 2, two silica sources, sodium silicate and Ludox AS-40, and two titanium sources, titanium oxysulfate and titanium sulfate were used in the compositional study. As shown in Table 1, 17 experiments with different (Na + K)/Na molar ratios were conducted using sodium silicate and Ludox AS-40 as

Table 1
Summary of compositional study for optimization of ETS-10 synthesis using $TiOSO_4$ as the titanium source

Experiment no.	(Na + K)/Na	TiO_2	SiO_2	Na_2O	KF	H_2O	Remarks
Sodium silicate							
1	1.35	1	5.5	4.84	3.5	250	ETS-10
2	1.31	1	5.5	4.84	3.0	250	ETS-10
3	1.26	1	5.5	4.84	2.5	250	ETS-10 (excellent, 10 h)
4	1.21	1	5.5	4.84	2.0	250	ETS-10, AM-3
5	1.16	1	5.5	4.84	1.5	250	ETS-10, AM-3
Ludox AS-40							
6	1.31	1	5.5	4.84	3.0	220	ETS-10
7	1.36	1	5.5	4.2	3.0	220	ETS-10
8	1.26	1	5.5	4.84	2.5	220	ETS-10
9	1.30	1	5.5	4.2	2.5	220	ETS-10
10	1.26	1	5.5	4.84	2.5	250	ETS-10 (excellent, 10 h)
11	1.30	1	5.5	4.2	2.5	250	ETS-10
12	1.16	1	5.5	4.84	1.5	250	ETS-4, AM-1, ETS-10
13	1.18	1	5.5	4.2	1.5	250	AM-1, ETS-10
14	1.26	1	5.5	4.84	2.5	300	ETS-10 (excellent, 11 h)
15	1.30	1	5.5	4.2	2.5	300	ETS-10
16	1.16	1	5.5	4.84	1.5	300	AM-1
17	1.18	1	5.5	4.2	1.5	300	AM-1

Table 2
Summary of compositional study for optimization of ETS-10 synthesis using $Ti(SO_4)_2$ as the titanium source

Experiment no.	(Na + K)/Na	TiO_2	SiO_2	Na_2O	KF	H_2O	Remarks
Sodium silicate							
1	1.36	1	5.5	4.84	3.5	210	ETS-10, AM-3 (trace)
2	1.36	1	5.5	4.84	3.5	185	ETS-10, AM-3 (trace)
3	1.35	1	5.5	5.0	3.5	185	ETS-10, AM-3 (trace)
4	1.36	1	5.5	4.84	3.5	250	ETS-10
5	1.26	1	5.5	4.84	2.5	250	ETS-10 (excellent)
6	1.21	1	5.5	4.84	2.0	250	ETS-10, ETS-4, AM-3 (trace)
7	1.16	1	5.5	4.84	1.5	250	AM-3, unknown, ETS-10 (trace)
8	1.10	1	5.5	4.84	1.0	250	AM-3, unknown, ETS-10 (trace)
9	1.05	1	5.5	4.84	0.5	250	AM-3, unknown, ETS-10 (trace)
10	1.00	1	5.5	4.84	0	250	AM-3, unknown, ETS-10 (trace)
Ludox AS-40							
11	1.36	1	5.5	4.84	3.5	250	ETS-10, AM-3 (trace)
12	1.26	1	5.5	4.84	2.5	250	ETS-10 (excellent)
13	1.16	1	5.5	4.84	1.5	250	ETS-10, AM-1

the silica sources and titaniumoxysulfate as the titanium source. Based on TiO_2–$5.5SiO_2$–xNa_2O–yKF–zH_2O as a standard molar composition, the amount of KF was varied from 1.5 to 3.5 mol while the amount of Na_2O was varied from 4.2 to 4.84 mol. Kim et al. [16] reported that the effect of K^+ content on the crystallization of ETS-4 was not crucial but the effect of Na^+ content was very important. It is clearly seen, however, that the crystallization of ETS-10 would be quite different from that of ETS-4.

In the first set of experiment where sodium silicate was used as the silica source, the (Na + K)/Na ratio of 1.26 was chosen as the optimum composition regarding the reaction time, phase purity and crystallinity. In the second set of experiment where Ludox AS-40 was used as the silica source, a series of experiment was also conducted, based on the result from the previous case. Table 1 shows that a dense phase titanium silicate, AM-1 has been formed below 1.26 of (Na + K)/Na molar ratio. Like the previous case, therefore, the (Na + K)/Na molar ratio of 1.26 was also chosen as the optimum composition.

It is therefore concluded that regardless of silica source, the (Na + K)/Na ratio seems very critical and dense phase, AM-3 or AM-1 is likely to be formed below 2.1 of (Na + K)/Na ratio. In other words, the (Na + K)/Na molar ratio should be at least 2.6 to crystallize pure ETS-10 only.

Figs. 1 and 2 show the XRD patterns of the final product obtained from the optimum composition, TiO_2–$5.5SiO_2$–$4.84Na_2O$–xKF–$250H_2O$ using sodium silicate and Ludox AS-40 as the silica sources, and titanium oxysulfate as the titanium source, respectively. As can be seen in these figures, dense phase titanium silicates, AM-3 and AM-1 were formed when the K^+ contents were not sufficient. It is attributed to the fact that a smaller K^+ cation
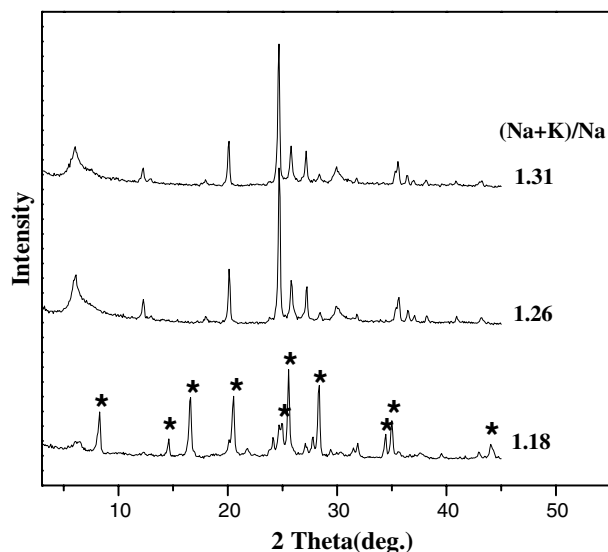

Fig. 2. XRD patterns showing the effect of KF content on the phase of solid product obtained from TiO_2–$5.5SiO_2$–$4.84Na_2O$–xKF–$250H_2O$ at 200 °C using Ludox AS-40 and titanium oxysulfate: (★) indicates AM-1 phase.

should be maintained at minimum level to accommodate the limited space around Ti^{2+} site.

For the comparison, a series of experiment were conducted using titanium sulfate as the titanium source and the results are summarized in Table 2. Unlike the previous case, the compositional range for titanium sulfate toward the formation of pure ETS-10 is quite restricted, compared to that for titanium oxysulfate as shown in Fig. 3; that is, dense phase, AM-3 or AM-1 is likely to be formed above or below 1.26 of (Na + K)/Na molar ratio. It is therefore concluded that cost efficient titanium oxysulfate would be an excellent alternative of other titanium sources regarding
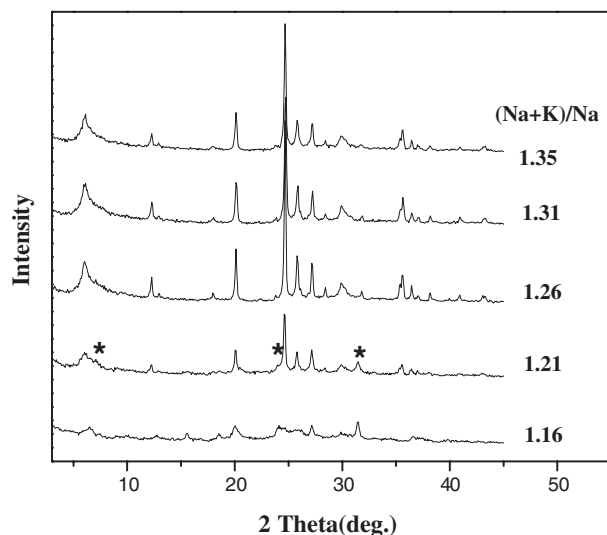

Fig. 1. XRD patterns showing the effect of KF content on the phase of solid product obtained from TiO_2–$5.5SiO_2$–$4.84Na_2O$–xKF–$250H_2O$ at 200 °C using sodium silicate and titanium oxysulfate: (★) indicates AM-3 phase.
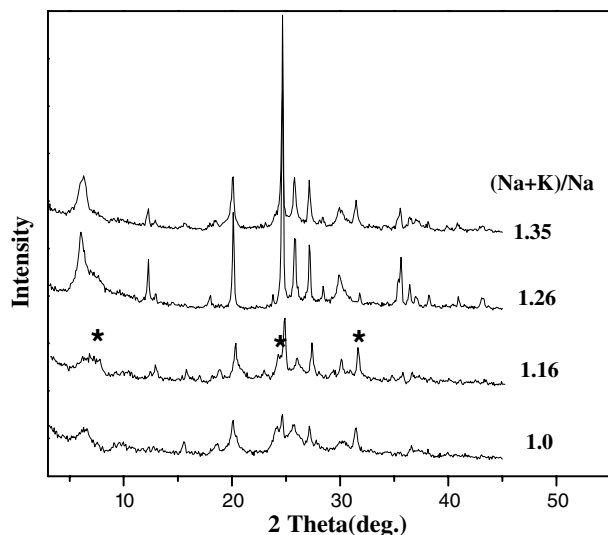
Fig. 3. XRD patterns showing the effect of KF content on the phase of solid product obtained from TiO_2–$5.5SiO_2$–$4.84Na_2O$–xKF–$250H_2O$ at 200 °C using sodium silicate and titanium sulfate: (★) indicates AM-3 phase.

phase purity of final product toward ETS-10, reaction time and cost.

In order to investigate the effect of (Na + K)/Na molar ratio on the morphology, several samples with different (Na + K)/Na molar ratio were chosen and the SEM images were taken. Fig. 4 is the SEM images of products obtained from 1.26 of (Na + K)/Na molar ratio using sodium silicate and Ludox AS-40 as the silica sources and titanium oxysulfate as the titanium source. As can be seen in this figure, the morphology of pure ETS-10 shows a small spherical shape with crystal size of 200–300 nm, which is quite different from the previous ones obtained from static condition [12]. Recently, Kim et al. [16] reported that the reaction condition such as stirring would have a significant effect on the crystal growth mechanism of ETS-4. Fig. 4(a) and (b) clearly show that pure ETS-10 only was formed at 1.26 of (Na + K)/Na molar ratio and the morphologies are almost similar regardless of silica source. As discussed in XRD analysis, the (Na + K)/Na molar ratio below 1.26 led to the formation of dense phase titanium silicate such as AM-1 or AM-3, suggesting the importance of (Na + K)/Na molar ratio. Fig. 5 also shows the
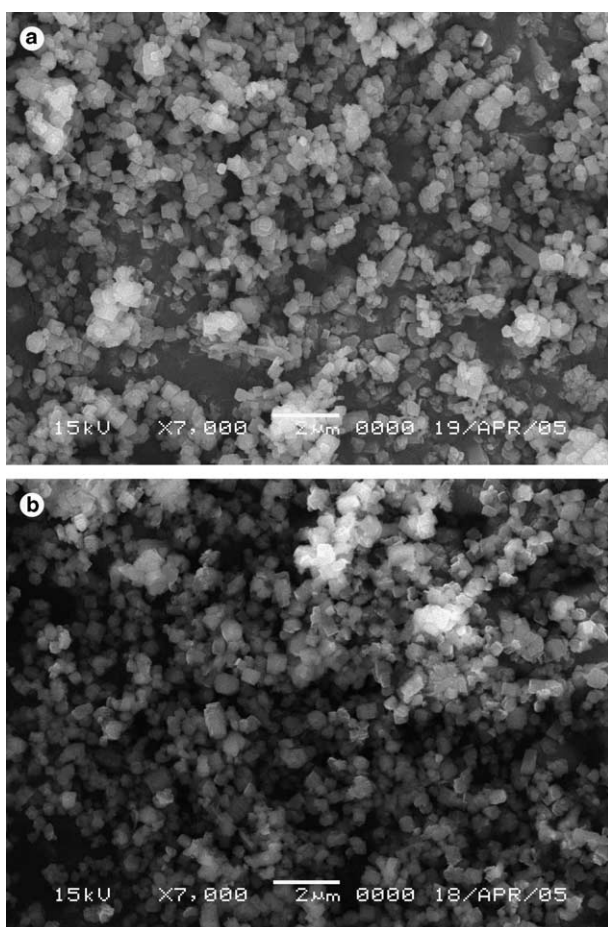

Fig. 5. SEM images of solid products obtained from the (Na + K)/Na molar ratio of 1.26 using titanium sulfate as titanium source: (a) sodium silicate as the silica source and (b) Ludox AS-40 as the silica source.
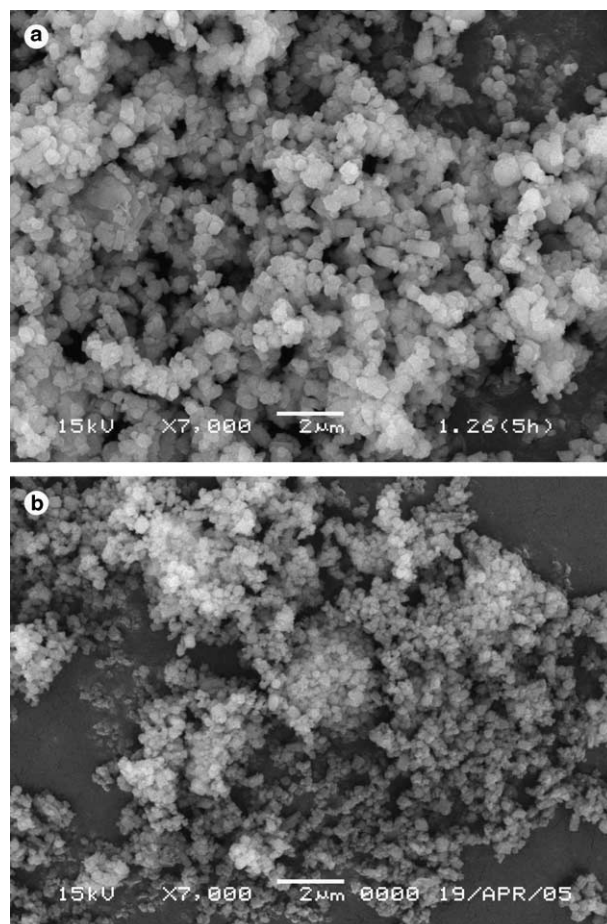

Fig. 4. SEM images of solid products obtained from the (Na + K)/Na molar ratio of 1.26 using titanium oxysulfate as titanium source: (a) sodium silicate as the silica source and (b) Ludox AS-40 as the silica source.

morphologies of the final products obtained from sodium silicate and Ludox AS-40 with titanium sulfate as the titanium source. It is interesting to notice that in case of using titanium sulfate as the titanium source, the effect of silica source on the morphology seems to be more significant than the previous case. As can be seen in Fig. 5(a) and (b), the size of ETS-10 obtained from Ludox AS-40 is much smaller than that obtained from sodium silicate. Unlike the previous case, in case of using sodium silicate as the silica source, other types of dense phases, AM-1 and ETS-4 other than AM-3 have been formed for the (Na + K)/Na molar ratio below 1.26.

3.2. Kinetic study

In order to investigate the effect of silica and titanium sources on the crystallization under stirred condition, ETS-10 was synthesized at three different temperatures, 433, 453 and 473 K, respectively, using the optimum composition chosen from the compositional study.

It has been realized that the nucleation has a significant effect on the crystallization of zeolite [19], suggesting that factors other than the crystallization of zeolites may affect

the induction time. Den Ouden and Thompson [19] reported that some pre-crystallization such as hydrolysis and condensation, and heating rate may affect the induction time, leading to quite different prediction of nucleation rates and thus the kinetics of zeolite crystallization. Valtchev and Mintova [20] introduced a transition period to separate nucleation and crystallization more clearly, choosing an arbitrary point that corresponds to 15% in crystallinity as the upper limit of a transition period for the crystallization curves obtained at different temperatures. It was claimed, however, that the application of arbitrarily chosen values to the upper limit of transition period on the crystallization curve may seem to be valid for slow and moderate crystallization but not for rapid crystallization. More recently, Kim et al. [14,16,21] reported the kinetic studies for the rapid crystallization of ETS-10 under static condition, ETS-4 and ZSM-5 under stirred condition where the upper limit of transition stage was obtained by fitting modified Avrami–Erofeev equation. The crystallization curves of the synthesis of ETS-10 using various silica and titanium sources under stirring are shown in Figs. 6–9.

In this study, the activation energy for nucleation stage was calculated from the temperature dependence of nucleation rate in Eq. (1).

$$\ln(1/t_0) = \ln A_{n1} - E_{n1}/RT \tag{1}$$

where t_0 is an induction time, A_{n1} is a pre-exponential factor, and E_{n1} is activation energy for nucleation stage.

Fitting the crystallization curves by modified Avrami–Erofeev equation (2), the rate of crystallization for transition period, V_{n2}, was obtained by $d\alpha/dt$, the first derivative of Eq. (2) at t_{tr}. The procedure to determine t_{tr}, the time
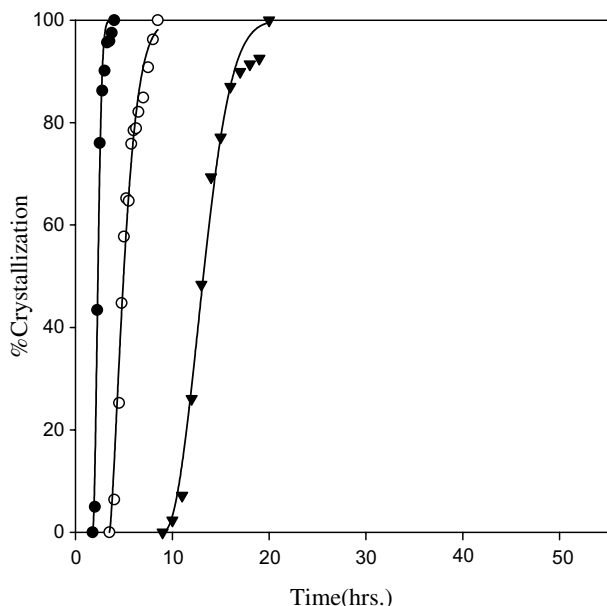

Fig. 6. Crystallization curves for ETS-10 obtained from $1.0TiO_2$–$5.5SiO_2$–$4.84Na_2O$–$2.5KF$–$250H_2O$ using sodium silicate and titanium sulfate as silica and titanium sources, respectively: (▼) 433 K, (○) 453 K and (●) 473 K.
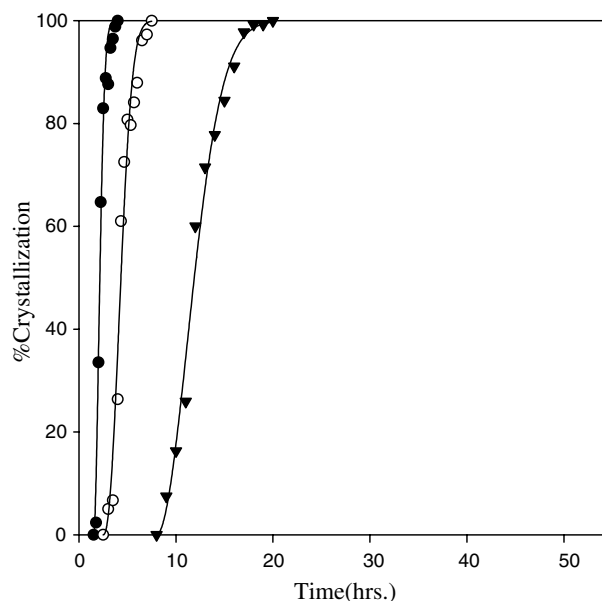

Fig. 7. Crystallization curves for ETS-10 obtained from $1.0TiO_2$–$5.5SiO_2$–$4.8Na_2O$–$2.5KF$–$250H_2O$ using Ludox AS-40 and titanium sulfate as silica and titanium sources, respectively: (▼) 433 K, (○) 453 K and (●) 473 K.
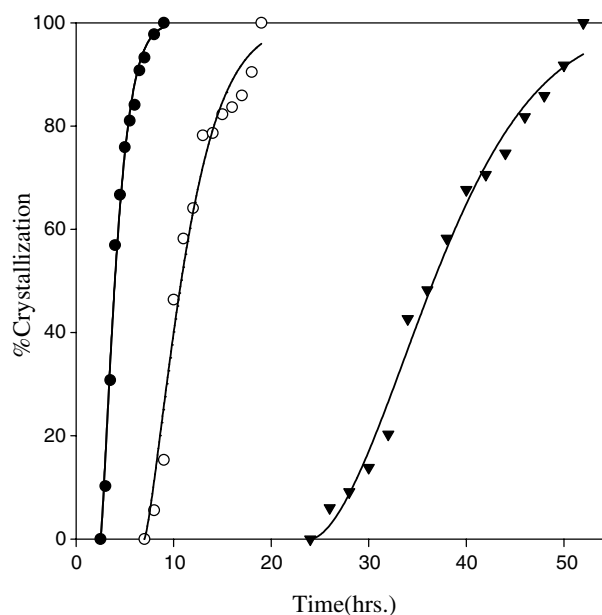

Fig. 8. Crystallization curves for ETS-10 obtained from $1.0TiO_2$–$5.5SiO_2$–$4.84Na_2O$–$2.5KF$–$250H_2O$ using sodium silicate and titanium oxysulfate as silica and titanium sources, respectively: (▼) 433 K, (○) 453 K and (●) 473 K.

corresponding to the upper limit of transition period can be found in elsewhere [13,22].

$$\alpha = 1 - \exp[-k(t - t_0)^n] \tag{2}$$

where α is a crystallinity, k, combined constant, and n, empirical constant exponent.

Finally, the rate of crystallization, V_c was determined from the inflection point of the crystallization stage, which
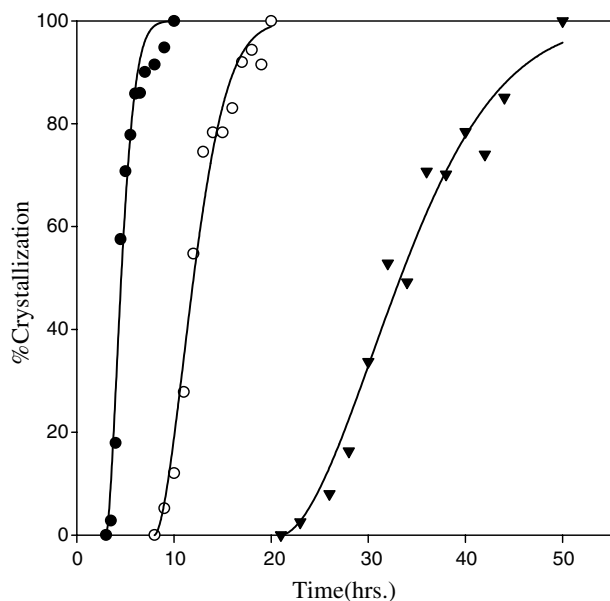
Fig. 9. Crystallization curves for ETS-10 obtained from $1.0TiO_2$–$5.5SiO_2$–$4.84Na_2O$–$2.5KF$–$250H_2O$ using Ludox AS-40 and titanium oxysulfate as silica and titanium sources, respectively: (▼) 433 K, (○) 453 K and (●) 473 K.

corresponds to the steepest slope on crystallization curve. The inflection point was determined by the rearrangement

of the first derivative of Eq. (2) in terms of n, k and α. The activation energies for transition and crystallization stages were then calculated from Arrhenius equation. The modified Avrami–Erofeev parameters, activation energies and pre-exponential factors are summarized in Tables 3 and 4. As can be seen in these tables, regardless of silica sources, $Ti(SO_4)_2$ gives shorter induction time than $TiOSO_4$. Comparing the activation energies for two titanium sources, quite different trends were observed. Although titanium sulfate is more strict type of source regarding the formation of ETS-10, the activation energy for nucleation stage is quite low compared to those of titanium oxysulfate as the titanium source, indicating that titanium sulfate is more suitable in nucleation than titanium oxysulfate. Although the magnitude of activation energy provides only relative comparison, in case of using titanium sulfate, the activation energies through three stages, that is, nucleation, transition and crystallization are smaller. This result means that $Ti(SO_4)_2$ indicates a higher reactivity than $TiOSO_4$ as long as a right composition is adopted.

In case of using $Ti(SO_4)_2$ as the titanium source, Figs. 6 and 7 show that the crystallization have been proceeded faster in case of Ludox AS-40 than of sodium silicate. Table 3 also clearly shows that the crystallization rate (V_c) for sodium silicate is more sensitive to temperature

Table 3
Modified Avrami–Erofeev parameters for ETS-10 syntheses

Silica and titanium sources	Temperature (K)	t_0 (h)	n	k (h^{-1})	V_{tr} (h^{-1})	α_{tr} (%)	V_c (h^{-1})	α_c (%)
$Ti(SO_4)_2$								
Sodium silicate	433	9.0	2.13	0.03	0.10	6.6	0.18	41.2
	453	3.5	1.43	0.40	0.25	2.6	0.39	25.8
	473	1.7	2.04	2.22	0.70	6.2	1.29	40.0
Ludox AS-40	433	8.0	1.92	0.05	0.10	5.6	0.18	38.0
	453	2.5	2.28	0.18	0.23	7.1	0.44	42.9
	473	1.5	1.95	1.60	0.60	5.7	1.07	38.5
$TiOSO_4$								
Sodium silicate	433	24	1.76	0.01	0.03	4.7	0.05	35.0
	453	7.0	1.33	0.12	0.10	1.9	0.15	21.8
	473	2.5	1.31	0.42	0.25	1.7	0.38	20.9
Ludox AS-40	433	21	1.77	0.01	0.03	4.8	0.05	35.3
	453	8.0	1.71	0.06	0.09	4.5	0.16	34.0
	473	3.0	1.64	0.33	0.23	4.1	0.39	32.4

Table 4
Activation energies and pre-exponential factors for nucleation, transition and crystallization stages in ETS-10 syntheses

Silica and titanium sources	E_{n1} (kJ/mol)	$\ln A_{n1}$	E_{n2} (kJ/mol)	$\ln A_{n2}$	E_c (kJ/mol)	$\ln A_c$	$\sum E_a$ (kJ/mol)	$\sum \ln A$
$Ti(SO_4)_2$								
Sodium silicate	69.8	17.2	84.4	21.1	83.6	21.4	237.8	59.7
Ludox AS-40	71.6	17.9	76.3	18.9	76.6	19.5	224.5	56.3
$TiOSO_4$								
Sodium silicate	96.3	23.6	92.1	22.1	84.9	20.6	273.8	66.3
Ludox AS-40	82.8	19.9	86.8	20.6	85.4	20.8	255.0	61.4

than for Ludox AS-40. Table 4 clearly shows that the larger activation energy for sodium silicate have been observed than for Ludox AS-40. It is concluded that Ludox AS-40 is more reactive than sodium silicate and the crystallization using sodium silicate as the silica source is higher temperature favored. In case of using titanium oxysulfate as the titanium source, a similar result to the previous case was obtained.

4. Conclusions

Through this study, several conclusions have been drawn and may be summarized as follows. The effects of the $(Na + K)/Na$ molar ratio on the crystallization and phase purity are critical. As the $(Na + K)/Na$ molar ratio decreases to lower than 1.26, pure ETS-10 is hardly formed but a dense phase titanium silicate, AM-1 or AM-3 is a main product. In addition, when $(Na + K)/Na$ molar ratio is 1.26, pure ETS-10 is formed. It might be ascribed to the fact that ETS-10 is formed when Na^+ and K^+ cation coexist with definite molar ratio. Besides, regardless of silica and titanium sources, the morphology and crystal size of ETS-10 are quite different from that synthesized under static condition showing a small spherical shape and seems to be significantly affected by stirring.

The kinetic study clearly shows that the effect of titanium source is more significant than that of silica source. When $Ti(SO_4)_2$ was used as the titanium source, the temperature dependency on the crystallization such as k and V_c for sodium silicate was observed to be more significant than for Ludox AS-40, suggesting a higher temperature favored for sodium silicate. It was observed, however, in case of titanium oxysulfate, that temperature dependencies on the crystallization for sodium silicate and Ludox AS-40 were similar. Finally, it is interesting to notice that the crystallization rate (V_c) for titanium oxysulfate is substantially slow compared to them for titanium sulfate and its temperature dependency is less sensitive than of titanium sulfate except the lowest temperature (i.e., 433 K) due to its low reactivity as discussed in activation energy. It suggests that minimum temperature should be maintained to proceed the crystallization at reasonable rate.

It is finally concluded that cost efficient titanium oxysulfate, one-tenth in cost as much as that of titanium sulfate would be promising alternative titanium source regarding cost and phase purity of final product.

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