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Review

# Important synthesis parameters that affecting crystallization of zeolite T: A review.

Siti Z. Patuwan <sup>1</sup> and Sazmal E. Arshad <sup>2,\*</sup>

<sup>1</sup> Faculty of Science and Natural Resources, Universiti Malaysia Sabah, 88450 Kota Kinabalu, Sabah, Malaysia.; sitizubaidahpatuwan@gmail.com

<sup>2</sup> Faculty of Science and Natural Resources, Universiti Malaysia Sabah, 88450 Kota Kinabalu, Sabah, Malaysia; sazmal@ums.edu.my

\* Correspondence: sazmal@ums.edu.my

**Abstract:** Synthesis of zeolite T with a variety of desired characteristics necessitate extensive work in the formulation and practical experiments either by conventional hydrothermal methods or aided with different approaches and synthesis techniques such as secondary growth or microwave irradiation. The objectives of this review are to adduce the potential work in zeolite T (Offretite-Erionite) synthesis evaluating determining factors affecting synthesis and quality of the zeolite T crystals. Attention given to the extensive studies that interconnect with other significant findings.

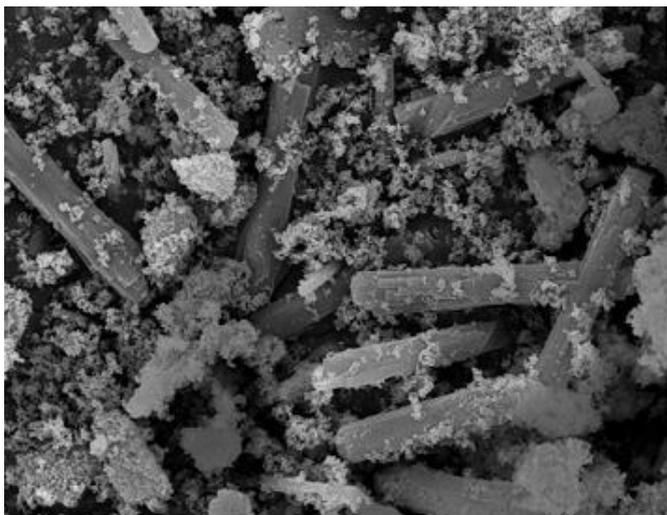
**Keywords:** zeolite T, offretite, erionite, hydrothermal, microwave, secondary growth

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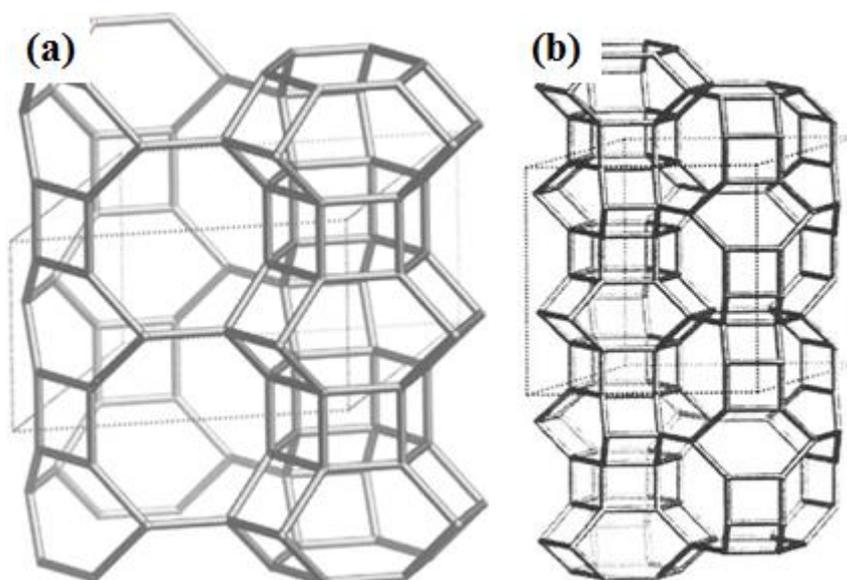
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## 1. Introduction

Zeolites are well known porous crystals systems existed in various size (nano-, micro-, etc) that had been widely used in different field of applications. It consists a uniform size of pores distribution [1] which also known as voids. Voids and cavities within the zeolite system that gives the unique properties to the zeolite. And this voids and cavities are controlled by the types of crystals that grow and intergrowth within the zeolite membrane. Introduced for the very first time by Bennet and Grad [2], nanoporous of zeolite T (rod-like shape as shown in figure 1) are identify to have an intergrowth frameworks lies within it which makes zeolite type T a very special species in zeolites family. The intergrowth systems are made up from chabazite group of hexagonal crystals of offretite (OFF) and erionite (ERI) (Figure 2). Interframing of these two entities had cause alteration in crystals arrangement of zeolite T which are AABAACAABAAC.. instead of AABAA-BAAB.. [3]. Despite of stacking within the zeolite system, these OFF-ERI had given characters to zeolite T in terms of thermal stability, mechanical and chemical stability [1] acid resistance, highly ion selectivity [4] which had made zeolite T as promising candidate in catalysis, molecular sieves, ion exchanger and other applications [5].



**Figure 1** Rod-like shape of zeolite T synthesized by [14].



**Figure 2** Framework of OFF [001] (a) and ERI [001] (b) (Flanigen *et al*, 1986)

Unlike others zeolite members, zeolite T possesses different voids size due to the intergrowth group of OFF and ERI. Offretite has 12-rings of channels that parallel to the c-axis and additional 8-rings of sub channels that normal to c-axis. The pore size for the 12-rings of channels are 0.67 nm x 0.68 nm while 0.36 nm x 0.49 nm are pore size for 8-ring sub channels. Alternately, erionite has only 8-ring channels which also parallel to c-axis with pore diameter of 0.36 nm x 0.51 nm [1]. Generally, the framework of OFF and ERI may be differ but they were closely related (Bennet & Grad, 1967 [3,7]) stated that ionic behavior of pure OFF and ERI are similar to the synthetic intergrowth OFF-ERI stacked in zeolite T and thus, it can be considered that intergrowth phases of zeolite T are homogenous mixtures of two pure components phases of OFF and ERI [3].

### 1.1. Hydrothermal conventional method

Hydrothermal treatment is most conventional and widely applied for synthesizing zeolite T and had been considered as earliest synthesis method which lead to high percentage (88% - 90%) product yields. It is a treatment that involve high temperature and

pressure in presence of water that acts as solvent, transferring pressure, mediator in reaction, changing physical and chemical properties of reagent or products and potential to be an accelerator in chemical reaction [8]. Hydrothermal synthesis technique usually conducted on mixture in sealed vessel where heat treatment are applied. This procedure were also labelled as an *in-situ* reaction which are strongly depending on temperature and time. Temperature needed to initiate the crystallization and time taken to complete the reaction are the most crucial parameters in conduction zeolization of T-type zeolite under hydrothermal technique [1]. Extensive research has been conducted in various ways to investigate various parameters upon hydrothermal treatment and most findings are considered successful as nano-sized crystals of zeolite T are manages to be synthesized. Hence, this method is easily to control during the synthesis phase and recently, thru hydrothermal, high purity and crystallinity of zeolite T with particles size of 150-200 nm were successfully synthesized by [9]. Yin *et al* (2013) proclaimed about 300 nm of zeolite T successfully synthesized based on additional parameters such as structure directing agent (SDA) and precipitate silica [10], while study by Sazmal *et al.*, 2018 had successfully obtained nanosized zeolite T crystals via SDA additions [11-12].

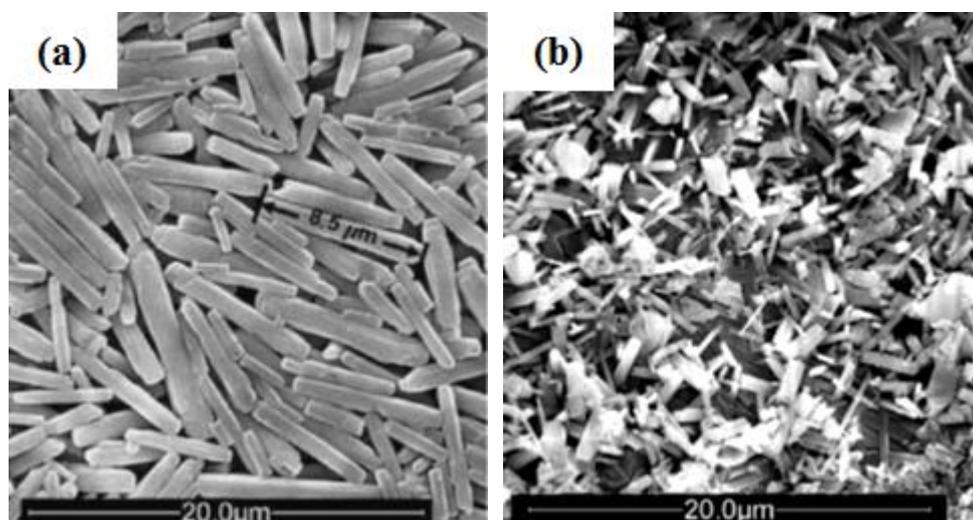
### 1.2 Microwave-assisted method

Synthesis of zeolite T using microwave-assisted is one of an alternative ways that can be used to be in-cooperate with hydrothermal technique. It has been widely applied in zeolite synthesis for a decade due to its capability in producing high purity product with less time consuming [13]. Yin *et al* (2015) able to developed zeolite T membrane at only 9 h crystallization time [14]. The modification of conventional method is to investigate the relation between synthesis product and time taken thru comparison of synthesis temperatures. Concept of microwave is based on frequency power density where hydrothermal treatment of the composite gel mixture in sealed vessels used when carried out prior to microwave irradiation.

Theoretical microwave irradiation mentioned by Park *et al* [15-16] stated that normal hydrogen (H) bonding of water were annihilated due to microwave irradiation causing ion oscillation and dipole rotation, and this produces isolated so-called active water molecules which responsible to the high rate of dissolving of the composition gel. Meanwhile, Carmona *et al* [15-16] proposed that coupling behavior of microwave with hydration of shell water molecules is efficient and yet favoring the coordination change of alumina octahedral layer to tetrahedral layer which is more reactive and essential in growing of zeolite materials.

Figure 3 (a) show the morphology of thin compact a&b-oriented zeolite T membranes that were prepared in a short time of 30 h under ~100 °C using secondary growth to enhance and complete the synthesis of rod-like zeolite T with 8.5 µm via hydrothermal conventional with microwave-assisted. Zhou *et al* (2009) reported that characteristic of loose and newly synthesized zeolite T crystals with only 2.5 µm are randomly loose distributed if the parameters designated thru hydrothermal only as shown in figure 3(b) [15]. Meanwhile, the distribution were enhanced as the microwave-irradiation was applied into the conventional parameters. Result from differing parameters has provided comparable results as high purity of zeolite T were formed without other zeolite phases

as impurities when microwave technique used for zeolization of T. Hence, microwave-assisted method surely enhance the crystallization and maximized the formation of crystallized zeolite T with economical time consumed [15-16].



**Figure 3** Crystals of zeolite T in 30 h, 373 K (a) 8.5  $\mu\text{m}$  long of rod-like shape, (b) loosely packed on surface of  $\alpha\text{-Al}_2\text{O}_3$  support tube [16].

### 1.3 Secondary growth / Dip-coating

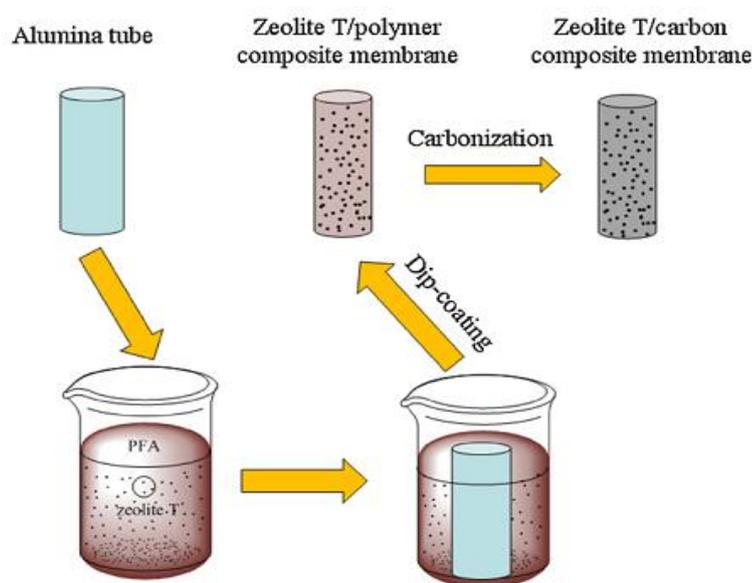
Extensive work has been carried in order to improve the synthesis method, performance of synthesis method and the performance of desired product [1,4,10,17-20]. Recent technique that had been widely applied are dip-coating as a secondary method. Secondary method is a combination of primary method in which synthesizing zeolite T following the optimum formulation and yet repeated twice by using supporter membrane (organic or inorganic) or allowing more zeolite crystals to growth within the first system in two or more different formulation of composition gel. Secondary growth always related with seeding zeolite crystals seed on the supports in the direct hydrothermal *in situ*-crystallization neither in a clear solution or an aqueous gel inside an autoclave at different temperature depending on the types of zeolite, 90 -100 °C for FAU or LTA while 180 °C for MFI type membranes [21].

Yeo *et al* (2014) reported various zeolite membranes on porous support in different form structure has been developed for over the past two decades and yet fewer information regarding zeolite T membrane [22]. Generally, typical porous tube that usually implanted in synthesizing zeolite T using the secondary method. Meanwhile, [5] prepared zeolite T membrane on mullite tubes via hydrothermal using molar composition of 20  $\text{SiO}_2$  :  $\text{Al}_2\text{O}_3$  : 5.2  $\text{Na}_2\text{O}$  : 1.8  $\text{K}_2\text{O}$  : 280  $\text{H}_2\text{O}$  for about 101°C (378 K) in 10-40 h. By using simple dip-coating method, uniform and continuous layer of T-type zeolite membrane were able to developed on the surface of mulite tubes. Additional of more variances into composition gel or secondary growth will alter the performance properties of zeolite T membrane tube.

In addition, [10] had illustrated the schematic diagram (figure 4) of dip-coating method in preparing zeolite-T/carbon composite membrane. They synthesized zeolite T

using composition gel of 18.2 SiO<sub>2</sub> : 1 Al<sub>2</sub>O<sub>3</sub> : 4.2 Na<sub>2</sub>O : 1.5 K<sub>2</sub>O : 1.82 TMAOH : 212.7 H<sub>2</sub>O and the mixture is sealed in the stainless steel autoclave for hydrothermal synthesis ( 373 K / 100 °C, 48 h). The coating gel were prepared via ultrasonic treatment (2 h) by mixing the removed T-zeolite crystals with 40% of polyfurfuryl alcohol (PFA) and 60 % acetone. In order to prepare zeolite T/carbon composite, alumina porous tube were dip into the prepared coating gel for 60 s followed with carbonization phase.

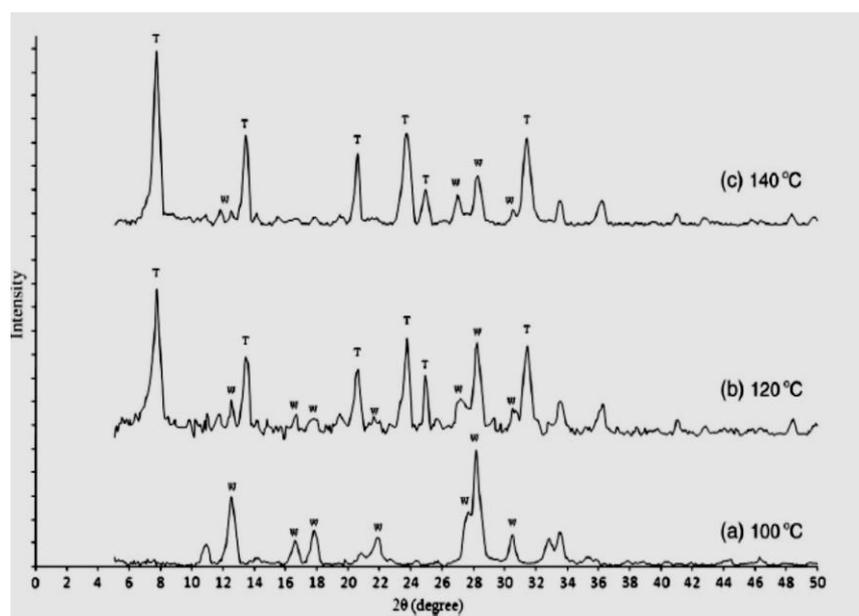
Instead of porous mullite and  $\alpha$ -alumina tube used as supporter, other material such as YSZ hollow fibres [23] or crosslinked with glutaraldehyde (Veerapur *et al*, 2008) also can be used. Wang *et al* (2014) proclaimed that the high quality of zeolite T membranes prepared on thin yttria-stabilized zirconia YSZ hollow fibres substrates via hydrothermal with temperature 100 °C for only 40 h. Zeolite T with composition mixtures of 1SiO<sub>2</sub> : 0.10 Al<sub>2</sub>O<sub>3</sub> : 0.23 Na<sub>2</sub>O : 0.08 K<sub>2</sub>O : 15.2 H<sub>2</sub>O : 0.012 TMAOH secondarily grew on the outer surface of hollow fibres by three different methods namely dip-coating, rubbing and vacuum-coating [23].



**Figure 4** Schematic diagram of dip-coating method in preparing zeolite T/carbon composite [10].

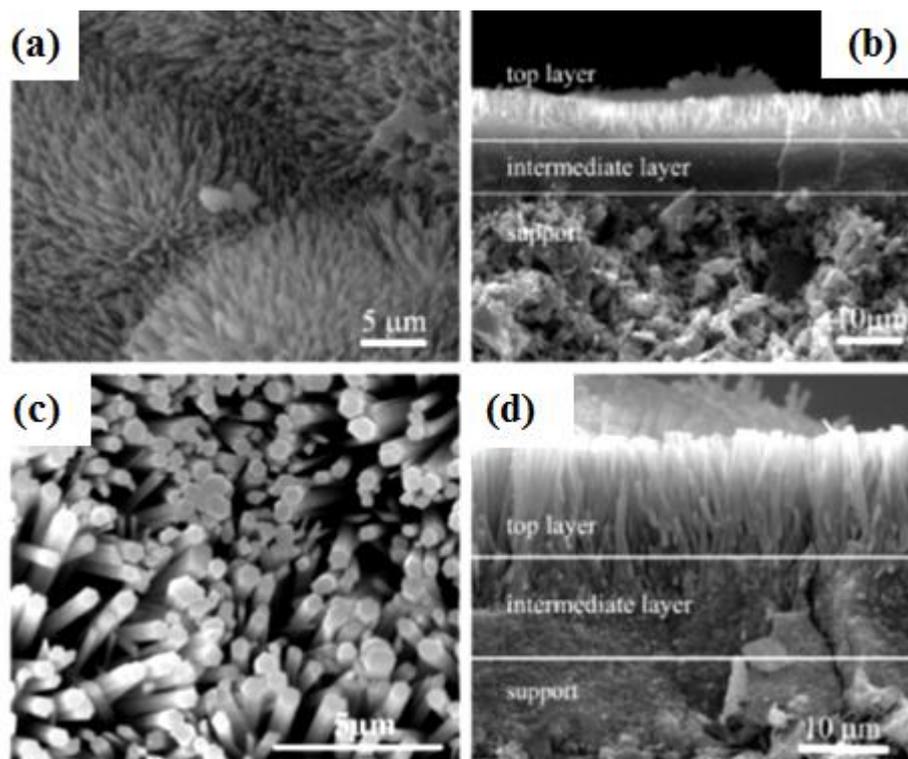
Despite the frequent usage of porous tube in secondary growth, zeolite T also can be prepared on  $\alpha$ -alumina disc compact as reported by Yeo *et al*, (2014). Hybrid membrane of zeolite T with ZIF-8 dispersed uniformly at  $\alpha$ -alumina support involving hydrothermal with ultrasonic bath treatment [22]. The purpose of ultrasonic bath is to remove the loose particles from polished disc support. Milky viscous mixture of zeolite T was prepared in composition gel ratio of 1 SiO<sub>2</sub>: 0.04 Al<sub>2</sub>O<sub>3</sub>: 0.26 Na<sub>2</sub>O: 0.009 K<sub>2</sub>O: 14 H<sub>2</sub>O and undergo hydrothermal crystallization at 110 °C in Teflon-lined autoclave. However, the seeding of zeolite T on ZIF-8 membrane supported  $\alpha$ -alumina disc were facing disturbance due to formation and evolution of zeolite T phase at larger duration, where at 30 h and 55 h, zeolite W and zeolite L were produced respectively. Strong peak of zeolite T

can only be synthesized at crystallization time of 45 h while other time variables resulting to different species of zeolite co-existed such as zeolite L and W respectively. Figure 5 shows the co-existing of different zeolite phase under same preparation condition exceptional to time had justified the findings reported by Mirfendereski & Mohammadi (2011). The only difference between these two literatures are time taken for formation and evolution phase occurred, Mirfendereski & Mohammadi reported formation of zeolite W at 24 – 240 h, zeolite L at 24 – 168 h while zeolite T at 120 – 216 h, compared to the work of Yeo *et al.*



**Figure 5** XRD spectrum showing formation of zeolite w and zeolite T based on temperatures [1].

In fact, the alteration in zeolite T synthesis using secondary growth had boost and enhance the properties and performance of free-standing of zeolite T.  $\text{CO}_2/\text{CH}_4$  selectivity increase from 68 to 182 [22], good stability for dehydration of a propanol solution [23] and good hydrothermal stability [6]. In addition, Zhou *et al* 2013 had develop zeolite T on the membrane of mullite tube as the surface and cross-section of the sample's morphologies shown in figure 6.



**Figure 6** SEM for zeolite T membrane at 373 K (100°C), 35 h for (a) and (b), 423 K (150°C) for 20 h for (c) and (d) [6].

## 2. Factors affecting crystallization of zeolite T

Zeolite T can be prepared by using various ways either using independent chemicals, or aided with a support for seeding. The only matter in synthesizing zeolite T are during the crystallization phase which determines the effectiveness of the methods in preparation requirements. Cichocki *et al* (1997) had successfully carried out hydrothermal synthesis based on the formulation parameters with regards to the chemical composition [24]. Meanwhile, either hydrothermally synthesis or aided with microwave irradiation, crystal formation of zeolite T are affected by several main factors which have been reported. From past and recent literatures, several cases involving crystals behavior upon several factors namely  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, alkalinity ( $n(\text{OH}^-)/n(\text{SiO}_2)$ ), water ratio, synthesis temperature and crystallization time, and addition of structure directing agents (SDA) while according to Zhou *et al* (2009) pressure is not directly involved in zeolite T synthesis [25]. This review summarizes the factors that affect zeolite T's growth.

### 2.1. Effects of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio

Silicate and aluminate sources are the crucial components in zeolite mixtures system. It is proven that the value ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  will affect the crystallization behavior of zeolite T. Based on the literature Cejka *et al* (2007) and Rad *et al*, (2012), high-silica zeolites are possible to be prepared from a mixture made up from a high Si/Al ratio under weak alkaline activation. Thus, the percentage yield of zeolite T can be maximized by increasing the molar ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  in the system. In addition, Rad *et al* (2012) concluded that high purity of zeolite T synthesized without any templates was achieved at 20 and 25 of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio with the presence of silica sources in 0.71 alkalinity [2]. Different literatures have different

optimum condition regarding the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio due to the presence of others reagents such as silica sources, structure directing agents and also types of alumino-silicate that were used.

Usually, the effects of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio were determined on the crystallization behavior that has been applied by [1-2], while some other literatures used properties behavior of zeolite T to determine the effectiveness of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. [26] figured that  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio strongly influenced the behavior of synthesized zeolite T in terms of its performance in pervaporation (PV). Varied the amount of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  from 50 to 2000 (0.0005 – 0.020 in ratio), the permeation efficiency increased as the ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  slightly increased but only until it reached 66.7 (0.015) which considered as optimum ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$ . Pervaporation flux increased up to 0.015  $\text{SiO}_2/\text{Al}_2\text{O}_3$  while gradually fall as the amount supplemented.

Hence, ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  not only affect the crystallization behavior but also the application performances of the synthesized zeolite T.

## 2.2 Effects of alkalinity

Zeolite T are typically and mostly synthesized under activation of basic medium which usually made up from mineralizer components of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . The alkalinity will strongly influence the level of crystallinity and stability of the zeolites structures. It is also effecting the performance of zeolite T in its applications. Generally, when the medium in high alkalinity at about 0.71 [2], it will accelerate the nucleation of zeolite T crystals and shorten the crystallization time because, at high pH,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  tend loose and dissolved by releasing their  $\text{OH}^-$ , and this will accelerate the reaction between aluminate and silicate ions while the degree of silicate anions polymerization decrease [17, 27].

However, at higher alkalinity beyond 0.71 [2], synthesized crystals of T-zeolite tends to re-dissolve again and also create low density of product which will affect the performance properties of zeolite T [17]. This is due to the characteristic of aluminosilicate layers tend to aggregates and forming another phase because of high alkalinity ( $\geq 0.82$ ) surroundings [28]. The theory are proven when literature reported by [2] that relative alkalinity had strong impact in crystallization of zeolite T. Resulting from their analyzed samples, relative crystallinity of zeolite T are reduced as the relative alkalinity increase because under high alkalinity, the condition has given favorable gel for the formation of competitive phase of zeolite L. Therefore, synthesis of T-type zeolite must in low optimum alkalinity (0.71) conditions though the theory of higher alkalinity will enhance the solubility of Si and Al and speed up crystallization of zeolites. This is because at higher alkalinity, crystallization of zeolite increase but only at time range of 24 h to 168 h before the desired product re-dissolved and undergo evolution phase to forms impurities phases. In table 1 listed the formulation used in study conducted by [2] while the evolution phase of zeolite T crystals along with the morphologies for each sample shown in figure 7 (a) and (b).

**Table 1** Formulations of zeolite T samples conducted by [2].

Sample	$\eta$ RM	$\alpha$	Silica sources	Relative crystallinity	Product phase
S1	20	0.82	Silica acid	0	L + W
S2	20	0.71	Silica acid	69	T + L
S3	25	0.71	Colloidal silica	80	T + L
S4	25	0.71	Colloidal silica	100	T
S5	25	0.82	Colloidal silica	54	T + L
S6	20	0.82	Colloidal silica	26	T + L
S7	20	0.71	Colloidal silica	82	T
S8	25	0.82	Silica acid	35	T + L

$\eta$ RM :  $SiO_2/Al_2O_3$  ratio,  $\alpha$ : relative alkalinity Source : [2]

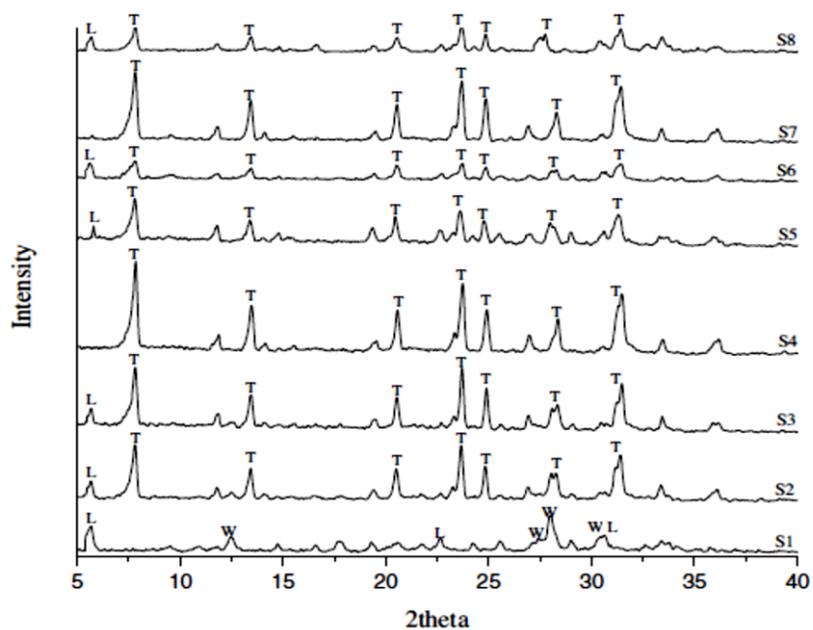
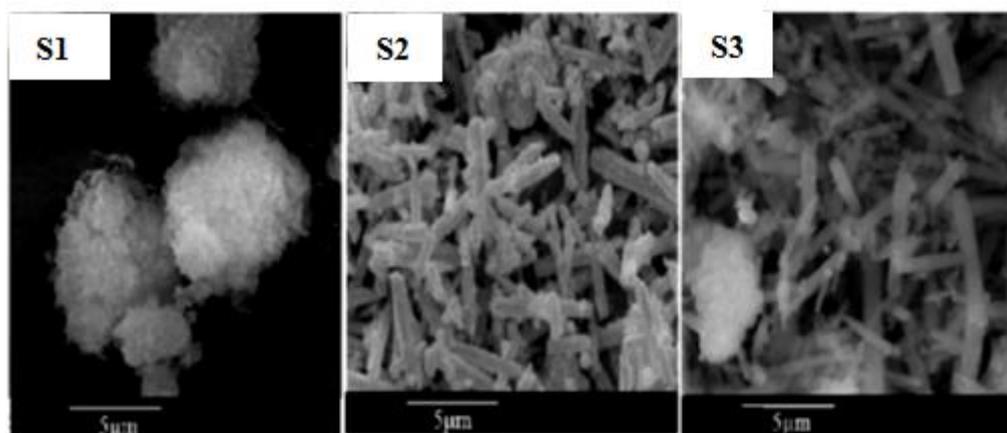
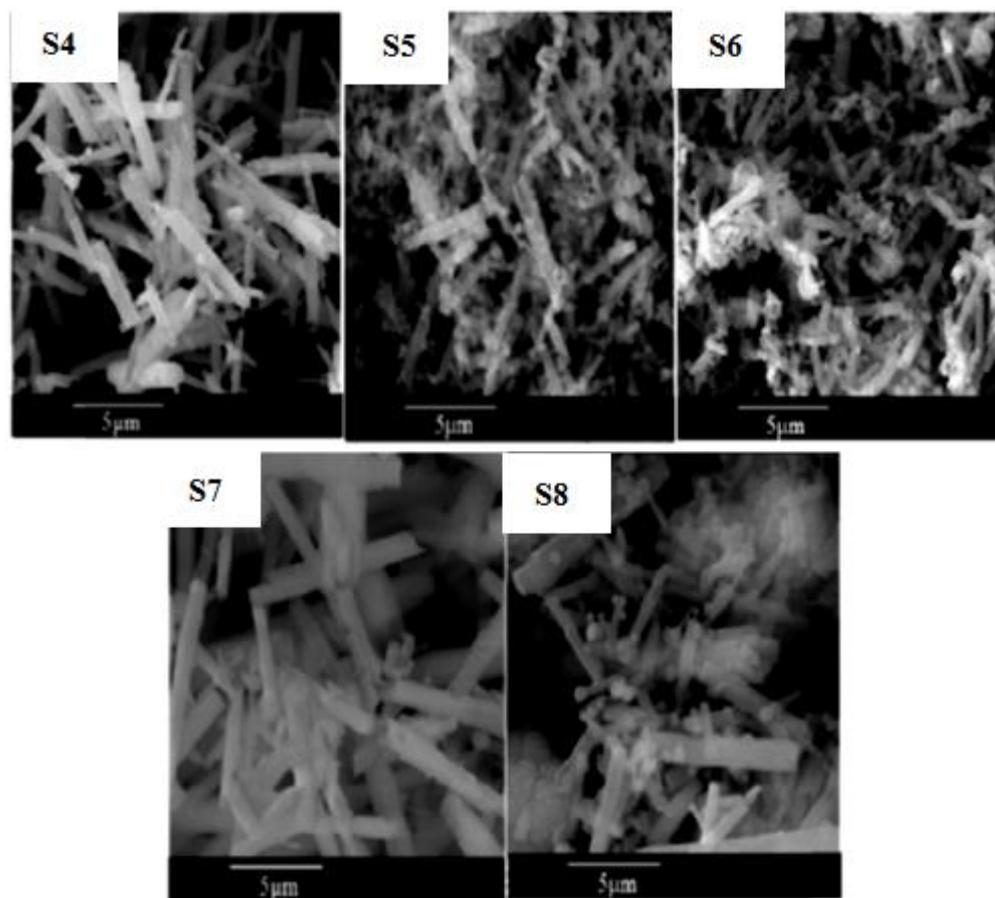


Figure 7 (a) XRD spectrum for sample S1- S2 [2].





**Figure 7 (b)** SEM morphologies for sample S1-S2 [2].

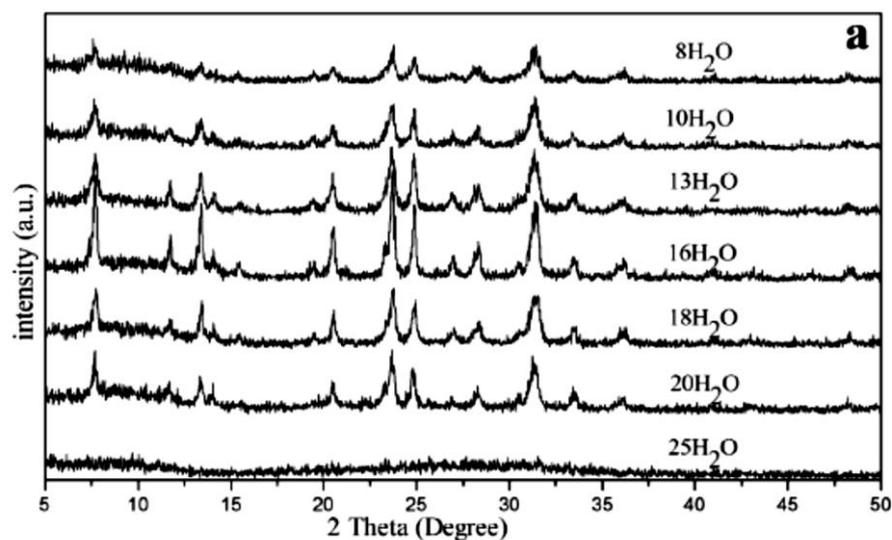
Thus, synthesis of zeolite T must be in between of high alkalinity of 0.71 [1-2] held only at optimum crystallization time (24 h – 168 h) to allow the growth inclination.

### 2.3. Effects of pH and water ratio

Water component added into the zeolite T system are calculated and specifically present in an adequate amount as the alkalinity of the medium are depending on the amount of water added. Zeolite formation greatly affected by the pH values range (0.71- 0.82) which correspond to the values of water precursors of the solutions [14]. Thus, pH of the alkaline medium can be vary by altering the amount of water in mole of 8 – 16 [14] fused in. When amount of water inside the system is decrease, it initiate the mineralizer from  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  to release  $\text{OH}^-$  and this will cause the pH increase and also the alkalinity [14]. As the synthetic medium is high alkalinity, the size of zeolite T particles are decrease because the size aggregation of zeolite T can be obtained in smaller size as water component is decrease [29]. Moreover, water content inside the mixture will decrease the degree of  $\text{OH}^-$  concentration and this will lead to decreasing of monotonic of zeolite growth and crystallinity [30].

Unfortunately, crystallization of zeolite T will stunt if the relative amount of water low at less than 14  $\text{H}_2\text{O}$  as the chemical reaction of the synthetic mixture's reagent are incomplete. This is due to the function of water in the system as ion transporter which also known as cavities. However, the addition of excessive amount of water that as needed in the system will diminished the zeolite T crystals into an amorphous system

[14]. Kuperman *et al* (1993) reported that water is an important factor in synthesis of zeolite T as it required small amount of water and utterly controlled [7]. Thus, excessive amount of water inside the synthetic solution will cause poorest selectivity of zeolite T crystals intergrowth layer. Meanwhile, in figure 8 shows the XRD analysis and for samples synthesized at water mole 25 with no zeolite crystals form and indicates the amorphous phase evolved [14]. Therefore, only an adequate mole amount of water, 14 – 16 H<sub>2</sub>O, are needed in performing the optimum crystallization of zeolite T as the water control the pH ranges (Veerapur *et al*, 2008 [2,14]).



**Figure 8** XRD spectrum of zeolite T's samples synthesized at different mole of water [14].

#### 2.4. Effects of synthesis temperature and crystallization time

Generally, temperature and time have high crucial impact upon T-type zeolites during crystallization. Though synthesizing zeolite T aided with different nucleation agents, the crystals phase are capable to develop defects of other zeolite phases and species if the composition gel exposed in insufficient or excessive temperature or omitted inappropriate crystallization time. Meanwhile, [1] studied the effect of crystallization temperature time in synthesizing zeolite T and has parsing the Ostwald's theory that under same synthesizing condition, zeolite T can coexist with other species which literally developed either depending on time and temperature variations. Table 2 has the summary of the findings of their study.

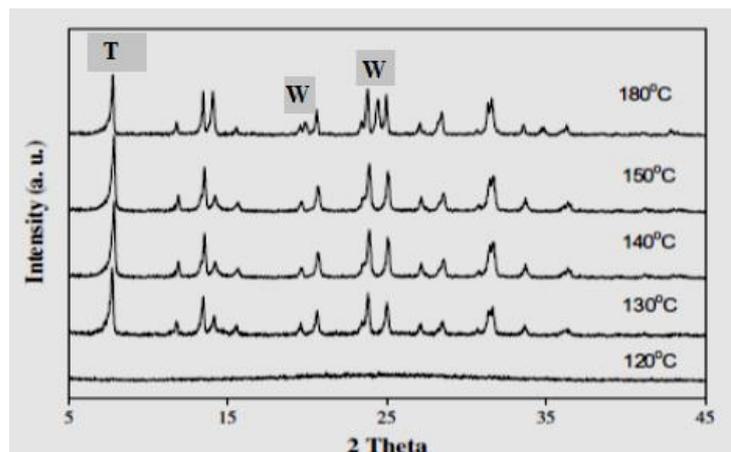
**Table 2** Summary of evolution phases in synthesis zeolite T hydrothermally

Sample	Crystallization parameters		Obtained product (s), Zeolite type
	Temperature (°C)	Time (h)	
1	100	120	Majority : W

2	100	168	Majority : T
3	100	216	Majority : T, minor : W
4	120	120	Majority : T
5	120	168	Majority : T
6	120	216	Majority : W , minor : L
7	140	120	Majority : W, minor : L
8	140	168	Majority : L, minor : T, W
9	140	216	Majority : L
Source : [1]			

Zeolite T can be developed at low ambient temperature as 100 °C if

only it is conducted at 168 to 216 hours and its disappear at high ambient temperature of 120 °C and beyond. [9] describing the behavior of zeolite T in different parameters unexceptionally crystallization temperature and time. Based on the sample synthesized by [9], zeolite T synthesized at 120 °C in time of 144 h has no crystalline phase while as the temperature increased up to 150 °C, zeolite T peaks are subdued but increased steadily as the temperature applied at 180 °C but at 180 °C, zeolite T developed together with zeolite W (2T = 19.8 and 24.3). However, zeolite T with high purity had been synthesized by lowering the temperature at 130 °C optimally to develop only zeolite T at 144 h and restricting the formation of others phases (Figure 9). Additionally, Jiang *et al* did mentioned that crystallization time does not significantly effects the crystallinity of zeolite T without SEM morphologies and conclude 120 h as the minimum time needed to developed zeolite T via hydrothermal method. Moreover, according to literature reported by [25], whereas the zeolite T were synthesized in different methods namely conventional refluxing heating (CR), conventional hydrothermal heating (CH), microwave refluxing heating (MR) and microwave hydrothermal heating (MH). They managed to shows significant of crystallization time on zeolite T in constant temperature and pressure as summarized in table 3 whereas PHI defined on zeolite phillipsite.



**Figure 9** XRD analysis for zeolite T samples synthesized at different temperature for 144 h with formulation  $1\text{SiO}_2 : 0.025\text{Al}_2\text{O}_3 : 0.15\text{Na}_2\text{O} : 0.15\text{K}_2\text{O} : 14\text{H}_2\text{O} : 0.06\text{TMAOH}$ , where T and W indicates peaks of zeolite T and W respectively [9].

**Table 3** Summary of experimental conditions in synthesizing zeolite T

Experiment	Technique	Time (h)	Product phase (XRD)
1	CR, T = 100 °C, P = 1 atm	48	Amorphous
2		72	Amorphous
3		96	T + amorphous
4		120	T
5		168	T
6	MR, T = 100 °C, P = 1 atm	5	Amorphous
7		10	Amorphous
8		20	Amorphous + T
9		30	T
10		48	T
11	CH, T = 100 °C, P = 1 atm	48	Amorphous
12		72	Amorphous + T
13		96	T
14		120	T
15		168	T
16	MH, T = 100 °C, P = 1 atm	5	Amorphous
17		10	Amorphous
18		15	Amorphous + PHI
19		20	PHI
20		30	PHI

Source : [25]

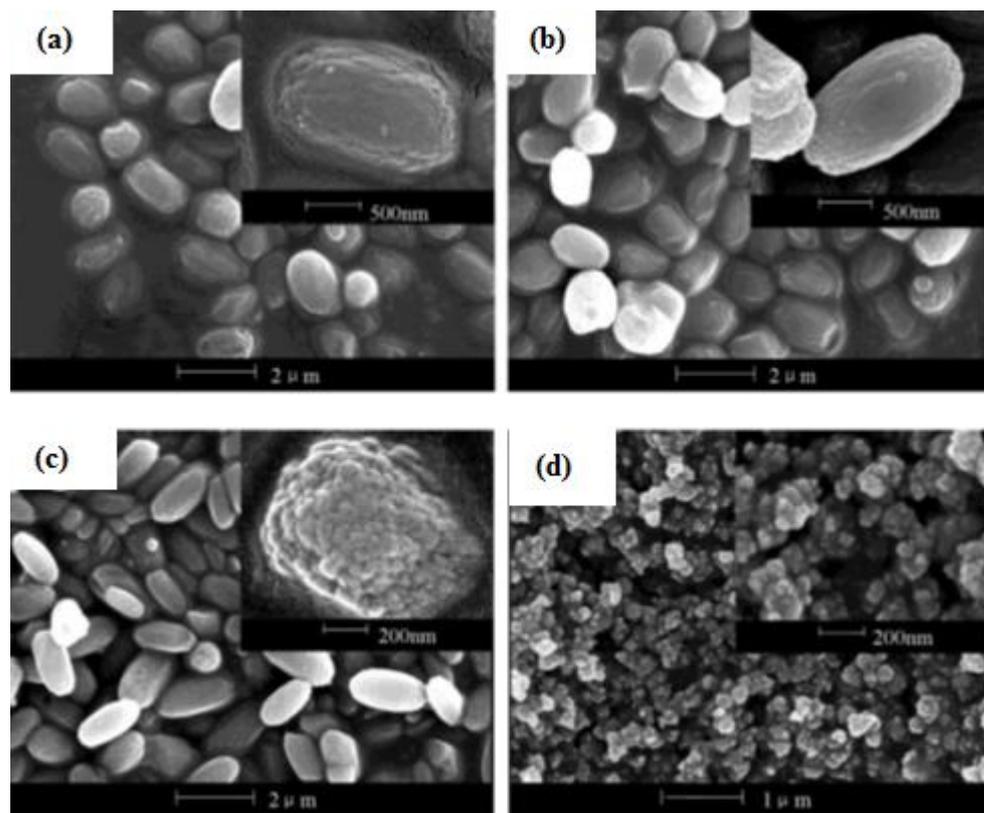
### 2.5. Effects of the addition of SDA

Structure directing agents (SDA) are substance that implant into the composition gel in synthesizing any desired zeolite to act as a template base and it will be dismissed right

after the crystallization phases. There were different types of SDA namely tetramethylammonium hydroxide (TMAOH), TMPBr<sub>2</sub>, tetraethylammonium hydroxide (TEAOH) and few more others. The presence of SDA in synthesis system carry significant role as it determined the impeccability of product crystals. Moreover, SDA can accelerate the nucleation and crystallization. For example of TMAOH, hydroxide anion within it will provide the necessary alkalinity and facilitates the formation of anionic silicates, thus, it expedited the rate of dissolution of silicate and aluminate [9,14,28]. Additionally [9] reported that by providing abundant amount of SDA will create high supersaturation condition and steric stabilization of proto-nuclei, which are the critical factors in formation of zeolite nanoparticles without aggregation [28]. Determination of the exact amount of SDA needed in synthesizing zeolite especially ERI-type zeolite is crucial because erionite (ERI) intergrowth crystals will not be formed effectively if the system contains large amount of cation [9,11-12]

In order to determine the effect of SDA upon crystallization behavior of T-type zeolite, different amount of TMAOH has been added into the mixture system of 1 SiO<sub>2</sub>: 0.025 Al<sub>2</sub>O<sub>3</sub>: 0.15 Na<sub>2</sub>O: 0.15 K<sub>2</sub>O:  $x$  TMAOH : 14 H<sub>2</sub>O, ( $x = 0, 0.01, 0.02, 0.04, 0.06, 0.1$ ) resulting that under zero SDA, no crystalline phase are formed up to 192 h. Aided with XRD spectrum analysis, addition of SDA for temperature of 120 °C demanded 0.06 of TMAOH to synthesis zeolite T with particle size of 500 – 700 nm, as it shows the maximum intensity peak ( $2\theta = 7.7^\circ$ ) and decreased as more TMAOH added.

Study conducted by [14] had justified the literatures reported by [9] in the effect of different ratio of TMAOH added into the composition gel of 1 SiO<sub>2</sub>: 0.055 Al<sub>2</sub>O<sub>3</sub>: 0.23 Na<sub>2</sub>O: 0.008 K<sub>2</sub>O:  $x$  TMAOH : 14 H<sub>2</sub>O, whereas  $x$  (0, 0.05, 0.10, 0.15 and 0.22). They found that synthesized zeolite T without TMAOH template took 192 h to developed 5 μm length in 373 K (100 °C) while at 0.05 TMAOH, pure zeolite T start to developed as early as 48 h and up to 0.15, 1-2 μm rod-like crystals of zeolite T were obtained as pictured on figure 10. However, at 0.22 TMAOH, rod-like shape crystals deforming into irregular small particles and they confirmed that zeolite T with crystals in nano-sized can be prepared in 0.22 TMAOH. Therefore by the varied additions of TMAOH amount into the synthesis gel can prepare zeolite T aggregates of size range from 2 μm to 200 nm. Though addition of SDA is proven to enhance the crystallization but it is crucial that alkaline cation content in the system at low level in order to prevent the aggregation of the negatively charged of aluminosilicate subcolloidal particles [28].



**Figure 10** SEM images of zeolite T at 373 K (100 °C) at different amount of TMAOH (a) 0.05 (b) 0.10m (c) 0.15 and (d) 0.22 [14].

The concept of participation of SDA in zeolite T crystallization are due to offretite/erionite type zeolite favor's condition, which are normally developed in presence of tetramethylammonium ion or NCOTs, nitrogen-containing organic templates namely benzyltrimethylammonium (BTMA) cations, 1,4-diazabicyclo-2,2,2-octane (DABCO) cations (Sand, 1978; [7]). Despite the synthesis of offretite/erionite tend to developed under proper NCOT present, NCOTs are specifically high cost and consumed high temperature to remove the templates which normally will affect the structure of synthesized zeolite crystals. Hence, NCOTs had been avoided in crystallization of zeolite crystals [7].

Therefore, for the past decade, TMAOH is the only favor SDA parameters in developing offretite/erionite zeolites – zeolite T. TMAOH had been actively involved in templating the crystallization of zeolite T while potential of other available SDAs remain unfold.

### 3. Conclusions

The synthesis parameters revealing the strongest factors influenced the zeolite T formation. Demands in synthesizing of zeolite T rose effectively with some precaution consideration toward the parameters and formulations. As T-type zeolite can be synthesized in various Si/Al sources such as using amorphous metakaolin or mulite from kaolinite or using independent chemicals or aided with nano or micro sized tube as a supporter. Via hydrothermal synthesis, zeolite T can be obtained at temperature and time as low as 120 °C in 168 h without any alteration in silica sources, meanwhile the time factor needed that can be altered by providing more source of nucleation (silica sources). However,

with aided of microwave irradiation, crystallization only consumed time at lower than hydrothermal conventional method. It is noted that, zeolite T can only be formed at optimum formulation depending on the technique and alkalinity. Zeolite T does not favor high alkaline medium but developed excellently in presence of SDA. Meanwhile, under certain condition, zeolite T can developed and coexist together with other zeolite phases as impurities and this system do affect the performance of zeolite T. Therefore, some consideration must be taken extensively prior to synthesis of zeolite T.

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