Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 32 (2012) 198 – 204

Procedia Engineering

www.elsevier.com/locate/procedia

I-SEEC2011

Fast Crystallization of SUZ-4 Zeolite with Hydrothermal Synthesis: Part I Temperature and Time Effect

P. Vongvoradit and P. Worathanakul*

Department of Chemical engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok, 10800, Thailand

Elsevier use only: Received 30 September 2011; Revised 10 November 2011; Accepted 25 November 2011.

Abstract

SUZ-4 zeolites were synthesized by hydrothermal technique under autogenous pressure with SiO_2:Al_2O_3 ratio of 21.22 using silica-sol and tetraethlyammonium hydroxide as a silica source and a template, respectively. Effect of temperature with 150, 165, and 180°C and crystallization time with 24, 18, and 12 h were studied to obtain the suitable conditions at crystallization. SUZ-4 zeolite synthesis using short time compared to the conventional method was successful synthesized. The synthesized SUZ-4 zeolites were characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), BET-N_2 adsorption, and X-ray fluorescence (XRF). The results show that SUZ-4 zeolite was obtained from rapid crystallization having a narrow pore size distribution and needle-shaped crystals. Highly crystallined SUZ-4 depended on enhanced temperature and time of crystallization conditions.

Keywords: SUZ-4 zeolite; hydrothermal synthesis; needle-shaped; fast crystallization

1. Introduction

Zeolite is a crystalline aluminosilicate with a three-dimensional framework structure that forms uniformly sized pores of molecular dimensions. As the pores preferentially adsorb molecules, they act as sieves on a molecular scale. Thus, zeolites are a subset of molecular sieves consisting of robust, crystalline silica(SiO_2) frameworks. At some places, the framework Al^{3+} has replaced Si^{4+} and it carries a negative charge [2]. SUZ-4 is a new synthetic aluminosilicate patented by the British Petroleum Company. The proposed framework topology of SUZ-4 consists of five-, six-, eight-, and ten-membered rings having pore openings 4.6 and 5.2 Å [6]. Zeolite SUZ-4 was prepared by a hydrothermal

* Corresponding author. Tel.: +66 29132500x8242; fax: +66 25870024.
E-mail address: patcharinw@kmutnb.ac.th.

doi:10.1016/j.proeng.2012.01.1257

crystallization from a different gel composition, crystallization was carried out at 150-180°C under autogenous pressure for 2-4 days [3, 4, 7]. It is clear that after 4 days at 150°C, a highly crystalline sample is obtained and the crystal system type is orthorhombic and its growth is to be small needle shaped particle [3].

In the past three decades, efforts directly relate to synthetic aluminosilicate zeolites are generally in area of high silica (Si/Al > 5) or pure silica molecular sieves [18]. In general, the crystallization temperature (100-200°C) is higher than that required for the synthesis of hydrated zeolite. Aljali-metal ions, in addition to the organic materials, are usually use to control the pH and promote the crystallization of high silica zeolite[12]. Low (Si/Al ≤ 2) and intermediate (2 ≤ Si/Al ≤ 5) silica zeolites are used as ion exchangers and found use as adsorbents for applications such as air separation [12]. Many researchers have focused on modified zeolites synthesis through reduced period of time i.e. highly crystalline ZSM-5 were synthesized in 4-6 h under high pressures [14-16]. J. Sun, et al. reported that the fast crystallization of MFI zeolites of silicate-1 and ZSM-5 with enhanced silica condensation in presence of CO2-in-water microemulsions [16]. The highly crystalline SZM-5 is synthesized in very short time under high temperatures and high pressures [14]. Microwave heating reduces the waiting time for the beginning of crystallization of phillipsite[17]. For SUZ-4 zeolite, it was first discovered using the organic templates of tetraethylammonium hydroxide ($(C_2H_5)_4NOH$, TEAOH) and quinuclidine. Zeolite SUZ-4 was successfully synthesized with TEAOH under a vigorous stirring condition. Crystal morphology of SUZ-4 was controlled by adjustment of water concentrations [5], and later it was successfully synthesized in the presence of *N,N,N,N,N,N*-hexaethylpentane diammonium bromide (Et_6-diquat-5) [5,6,8], and reported to give SUZ-4 with higher Si/Al ratios than TEAOH. The ^{1}H-^{13C} CP MAS NMR, Raman spectra of Et_6-diquat-5 ions encapsulated SUZ-4 zeolite and molecular modelling studies were presented and conformation of guest molecule and the geometry of the host structure are oobserved for the medium-pore SUZ-4 zeolite, revealing the existence of organic structure directing effect [8, 10]. However, the temperature and time effect in systematic have not been found in SUZ-4 zeolite.

In this work, fast crystallization of SUZ-4 zeolite was studied to determine the optimum condition for time reduction. Different crystallization time and temperature were prepared in order to obtain the desired SUZ-4 zeolite. The SUZ-4 zeolites were analyzed using X-ray powder diffraction, BET N_2-adsorption and, Scaning electron microscopy.

2. Materials and methods

2.1 Materials

The materials used to synthesize SUZ-4 zeolite are as follows. Aluminum powder (93.0% Al, HiMedia) was used as the aluminum source, silica sol (LUDOX AS-40 colloidal silica, 40 wt.% SiO_2 in water, Aldrich) was used as the silica source, tetraethylammonium hydroxide (TEAOH, 35% in water, Aldrich) was used as the template, and potassium hydroxide (85% KOH pellet, Carlo Erba) was the K^+ source.

2.2 SUZ-4 synthesis

SUZ-4 zeolite was synthesized by hydrothermal technique carried out in an autoclave stainless steel reactor(Amar DAS 2.0, Amar Equipments, India). In a typical synthesis of gel for one of our batches is described here as an example. 2.53 g KOH was dissolved in 20.02 g of distilled water. 0.28 g of Al powder was then added and stirring continued until the Al was completely dissolved. A solution of 15.01 g of LUDOX, 5.19 g of TEAOH aqueous solution, and 9.97 g of distilled water stirred for 2 hours and added to the aluminum solution and stirred for 3 hours. The final mixture with the molar composition of

$21.22SiO_2:Al_2O_3:7.9KOH:2.6TEAOH:498.6H_2O$ was transferred to the reactor and crystallized for 24 hours at 150°C under stirring 250 rpm. The solid product was filtered, washed with distilled water, dried at 120°C for 2 h, and calcined in air at 550°C for 4 h. Similar experiments were performed varying crystallized time and temperature.

2.3 Material characterization

- *X-ray powder diffraction (XRD)*
  The crystal structure of synthesized SUZ-4 zeolites were determined using X-ray powder diffraction (Phillips PW 1830/40) with Cu-K_α1 radiation (λ = 1.5406 Å), generator tension 40 kV and generator current 30 mV, and scanning in the range of 5-70° (2θ) with a rate of 0.01° /min.
- *X-ray fluorescence spectroscopy (XRF)*
  Chemical analysis was determine using fluorescence. Quantitative analysis of the silica content was performed without any preparatory work.
- *Scanning electron microscopy (SEM)*
  The crystal morphology and size of the obtained zeolites were determined via scanning electron microscopy (JEOL JSM-6301F, and JEOL JSM-5800LV). The sample was coated with a thin layer of gold using a sputter coater (Edwareds Laboratories, Milpitas, CA).
- *BET N_2-adsorption/desorption isotherm*
  Specific surface area (SSA), adsorption/desorption isotherms, pore size and pore size distribution (PSD) of the prepared samples were determined using BET-N_2 adsorption (Quantachrome, Autosorb®-1-C) with micropore analysis (74 points N_2 adsorption/desorption).

3. Results and discussion

For these experiments, crystallization ratio of $SiO_2:Al_2O_3$ = 21.22 was a high purity SUZ-4 zeolite can be achieved and offer to the chemical composition of the mixture is very sensitive for SUZ-4 synthesis [11].

3.1 Effects of temperature

The effect of reaction temperature was examined using the experimental conditions, the crystallization temperature was studied with 3 conditions for 150°C, 165°C, and 180°C under autogenous pressure for only one day crystallization time compared to the our previous study. Under stirring at 250 rpm of the autoclave. Synthesized SUZ-4 zeolites were indicated the ratio of Si:Al at 5.5-5.8 using X-ray fluores cence spectroscopy (XRF)

Fig. 1 shown XRD patterns with different temperatures for 24 hours crystallization, using the temperature 150°C still gave some impurities of FER. The structure of ferrierite(FER) is well-known, and its two-dimensional pore system consists of ten-membered ring channels interconnected with eight-membered ring channels. Both the ten- and eight-membered ring channels in ferrierite are elliptical in shape with dimensions of 4.2 × 5.4 Å and 3.5 × 4.8 Å, respectively, which are very similar to those in SUZ-4 [7]. Good sample of synthesized SUZ-4 zeolite for 24 hours crystallization time can be produced from 165°C and 180°C under our experiment conditions [11, 12].

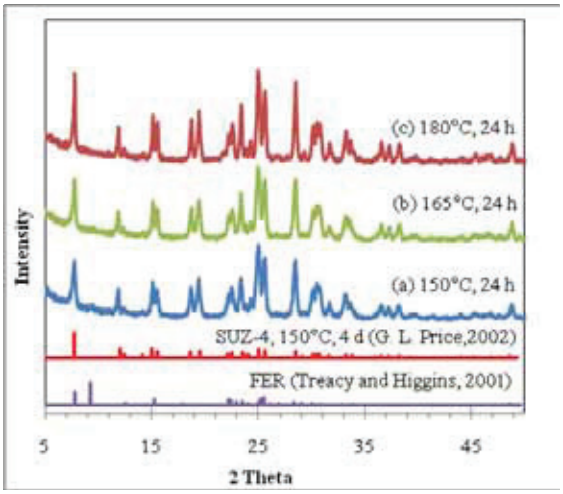

Fig. 1. XRD patterns of zeolite SUZ-4 prepared at 24 hours with different temperature (a) 150°C (b) 165°C and (c) 180°C

The formation of SUZ-4 can be confirmed by SEM images prepared using TEAOH template for 24 hours under autogeneous pressure with different crystallization temperature are shown in Fig. 2. The crystals can be characterized are needled shape. The image clearly shows that larger needled-shape crystals were attained from samples with a higher temperature.

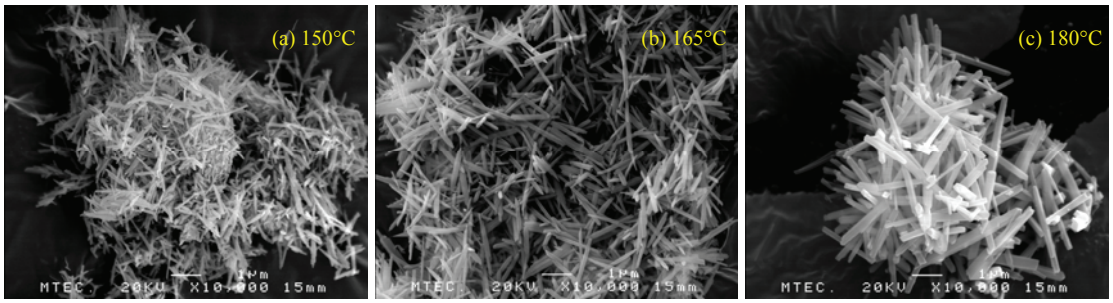

Fig. 2. SEM images of zeolite SUZ-4 crystals prepared at 24 hours with different temperature (a) 150°C (0.0652±0.01 μm dia.× 0.6452±0.16 μm long) (b) 165°C (0.1654± 0.01μm dia.× 1.6761± 0.25μm long) (c) 180°C (0.0628±0. 03μm dia.× 1.1421±0.50 μm long)

Table 1. BET surface area and pore volume of synthesized zeolites with different temperature for 24 h crystallization

Temp. (°C)	BET surface area[2] (m^2/g)	External surface area[1] (m^2/g)	Micropore area[1] (m^2/g)	Micropore volume[1] (cm^3/g)	Total pore volume[2] (cm^3/g)	Pore diameter[3] (Å)
150	446.2	308.3	138	0.0889	0.6407	5.6±0.10
165	366.4	223.3	143.1	0.0902	0.462	5.9±0.10
180	330.7	182	148.7	0.0908	0.2578	5.3±0.10

[1]t-plot micropore analysis method
[2]MP micropore analysis method at P/P_0 close to unity
[3]SF micropore analysis method

In addition, specific surface area, pore volume and pore diameter with different temperatures were characterized by BET N_2-adsorption/desorption isotherms as shown in Table 1. The results of crystallization at 150°C under autogenous pressure for only one day exhibits a high surface area of 446.2 m^2/g and large total pore volume of 0.6407 cm^3/g. The sample from our previous study for 150°C with 4 days crystallization has shown 440.4 m^2/g [11].

The narrow pore size distribution of SUZ-4 crystals was shown in Fig. 3.

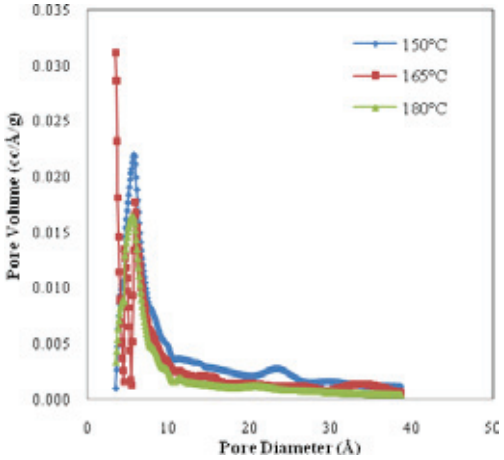

Fig. 3. Pore size distribution (SF method) of SUZ-4 zeolite prepared at 24 hours with different temperature

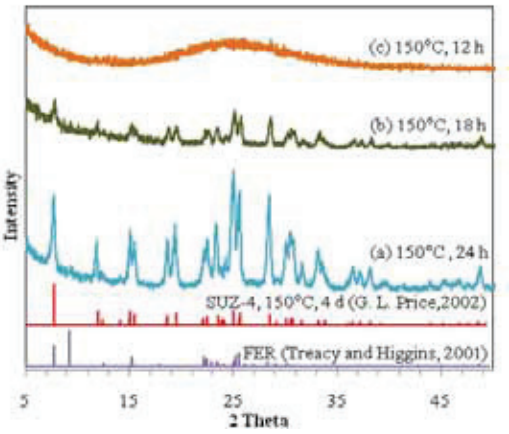

Fig. 4. XRD patterns of zeolite SUZ-4 prepared at 150°C with different crystallization time

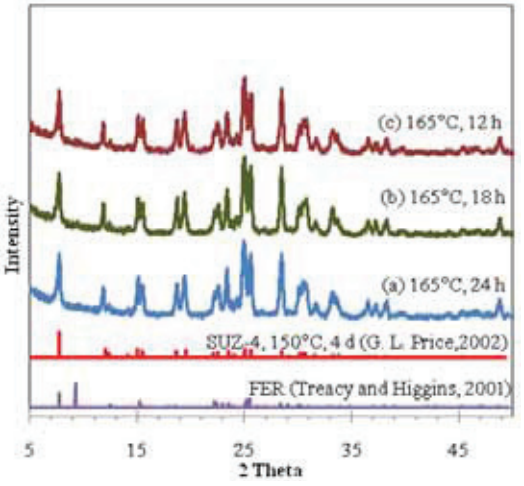

Fig. 5. XRD patterns of zeolite SUZ-4 prepared at 165°C with different crystallization time

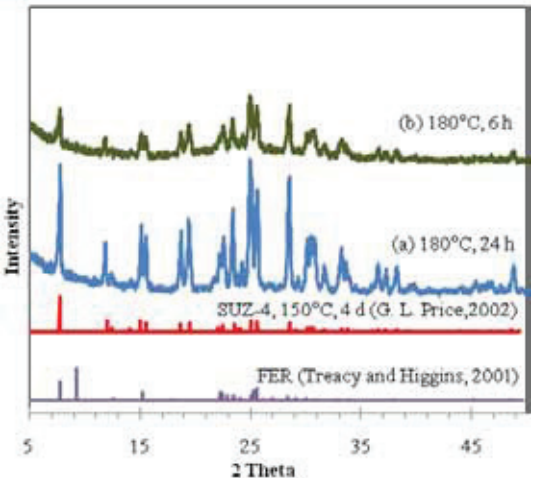

Fig. 6. XRD patterns of zeolite SUZ-4 prepared at 180°C with different crystallization time

3.2 Effects of crystallization time

Under the conditions employed in the experiments here, crystallization time was decreased continuously with 24, 18, 12 hours at 150°C under autogenous pressure. XRD patterns of SUZ-4 zeolite were shown in Fig. 4. The obtained zeolites with 18 hours crystallization time still gave SUZ-4 zeolite as

the position of peak for 24 hours but intensity peak was decreased. While crystallization time was decreased to 12 hours, amorphous of the sample was found.

Moreover, XRD patterns of SUZ-4 zeolite prepared at 165°C and 180°C with different characterization time were shown in Fig. 5 and Fig. 6, respectively. In each crystallization temperature, it was found that using decreased time still gave SUZ-4 zeolite peaks as for 24 hours but its intensity decreased. At 180°C temperature, SUZ-4 can be obtained for only short period time of 8 hours only (Fig. 6).

However, the formation of SUZ-4 synthesized under the same condition for 18 hours with 150°C under autogeneous pressure have been shown in details of characterization from lowest temperature on this study. The crystals can be characterized are needled shape (Fig. 7).

Subsequently, specific surface area, pore volume and pore diameter with different temperature were characterized by BET N_2-adsorption/desorption isotherms as shown higher specific surface area of 452.5 m^2/g and large total pore volume of 0.7408 cm^3/g than using 24 hours crystallization time. The sample from our previous study for 150°C with 4 days crystallization shown 440.4 m^2/g [11].

The pore size distribution was shown in Fig. 8 and found that SUZ-4 crystals were obtained narrow pore size distribution with 5.6±0.10 Å.

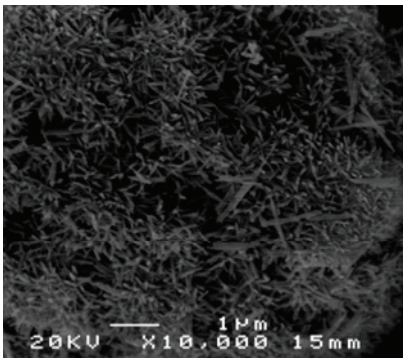

Fig. 7. SEM images of zeolite SUZ-4 crystals prepared at 18 h with 150°C (0.0687±0.01 μm dia.× 0.3787±0.06 μm long)

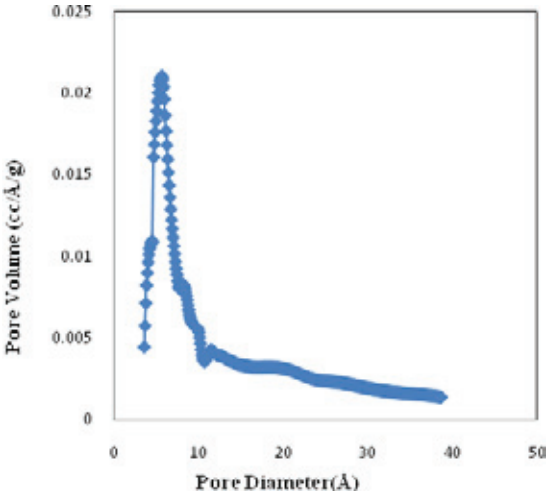

Fig. 8. Pore size distribution (SF method) of SUZ-4 zeolite prepared at 18 hours with 150°C

4. Conclusion

SUZ-4 zeolites have been successfully synthesized under different conditions. The effect of crystallization temperature and time affected on XRD intensity peaks. With TEAOH as a structure directing agent, a good sample from a gel mixture of SiO_2/Al_2O_3 = 21.22 under autogenous pressure using the stainless steel autoclave at a holding temperature 150-180°C for fast synthesis process (24-6 hours) were suitable. The synthesized pure SUZ-4 zeolite can be achieved at high temperature with less crystallization time. However, the optimum condition should be further researched for other parameters and using this zeolite as a catalyst for NO_x reduction.

Acknowledgements

The authors gratefully acknowledge the financial support of Thailand Research Fund (TRF) under grant number MRG5280110. We also acknowledge the grant for new researcher 2011 (Patcharin Worathanakul) from the Science and Technology Research Institute King Mongkut's University of Technology North Bangkok (STRI, KMUTNB), Graduate school and Department of Chemical Engineering King Mongkut's University of Technology North Bangkok. We also acknowledge the grant for Patcharin Worathanakul from National Nanotechnology Center. Renewable Product and Energy Technology Center (STRI, KMUTNB).

References

[1] M.A. Asensi, M.A. Camblor, A. Martinez. Zeolite SUZ-4: Reproducible synthesis, physicochemical characterization and catalytic evaluation for the skeletalisomerization of n-butenes. *Micropor. Mesopor. Mater.* 1999;**28**:427-436.
[2] H.V. Bekkum, E.M Flanigen, P.A. Jacobs, J.C. Jansen. *Introduction to zeolite science and practice*. 2nd ed. Amsterdam: Elsevier Science; 2001.
[3] A.C. Gujar, G.L. Price. Synthesis of SUZ-4 in the K^+/TEA^+ system. *Micropor. Mesopor. Mater.* 2002;**54**:201-205.
[4] S. Jiang, Y.K. Hwang, S.H. Jhung, J.S. Chang, J.S. Hwang. Zeolite SUZ-4 as selctive dehydration catalyst for methanol conversion to dimethy ether. *Chemistry Letters* 2004;**33**:1048-1049.
[5] D.K. Kim, Y.H. Kim, Y.K. Hwang, J.S. Chang, S.E. Park. Effect of synthesis conditions on physicochemical properties of zeolite SUZ-4. *Journal of the Korean Chemical Society* 2004;**48**:623-628.
[6] S.L. Lawton, J.M. Bennett, J.L. Schlenker, M.K. Rubin. Synthesis and proposed framework topology of zeolite SUZ-4. *J. Chem. Soc., Chem. Commun.* 1993;**11**:894–896.
[7] D.B. Lukyanov, V.L. Zholobenko, J. Dwyer, S.A.I. Barri, W.J. Smith. On the Structural, Acidic and Catalytic Properties of Zeolites SUZ-4. *J. Phys. Chem. B* 1999;**103**:197-202.
[8] W.C. Paik, C.H. Shin, J.M. Lee, B.J. Ahn, S.B. Hong. Host-guest interactions in P1, SUZ-4, and ZSM-57 zeolites containing N,N,N,N',N',N' hexaethylpentanediammonium ion as a guest molecule. *J. Phys. Chem. B* 2001;**105**:9994-10000.
[9] M.M.J. Treacy, J.B. Higgins. *Collection of Simulated XRD Powder Patterns for Zeolites*. fourth rev ed. Amsterdam: Elsevier Science; 2001.
[10] P. Worathanakul, P. Kongkachuichay. New SUZ-4 Zeolite Membrane from Sol-Gel Technique. *World Academy of Science, Engineering and Technology* 2008;**47**:90-94.
[11] P. Worathanakul, D. Trisuwan, A. Phatruk, P. Kongkachuichay. Effect of sol-gel synthesis parameters and Cu loading on the physicochemical properties of a new SUZ-4 zeolite. *Colloids and Surfaces A: Physicochem. Eng. Aspects*. 2011;**377**:187-194.
[12] P. Worathanakul. *Novel synthesis of nanostructured materials: SiO_2-TiO_2, SiO_2-Al_2O_3 and SUZ-4 zeolite for environmental applications*. Ph.D.Thesis, Chemical Engineering, Kasetsart University; 2008.
[13] V.L. Zholobenko, D.B. Lukyanov, J. Dwyer. Ferrierite and SUZ-4 Zeolite: Characterization of Acid Sites. *J. Phys. Chem. B* 1998;**102**:2715-2721.
[14] S.J. Kulkarni, P. Srinivasu, N. Narender, K.V. Raghavan. Fast and efficient synthesis of ZSM-5 under high pressure. *Catalysis Communications* 2002;**3**:113-117.
[15] M. Chareonpanich, T. Namto, P. Kongkachuichay, J. Limtrakul. Synthesis of ZSM-5 zeolite from lignite fly ash and rice husk ash. *Fuel Processing Technology* 2004;**85**:1623-1634.
[16] J. Sun, C. Wang, L. Wang, L. Liang, X. Liu, L. Chen, F.S. Xiao. Synthesis of MFI zeolites with improved crystallization rate and mesoporosity in the presence of CO2-in-water emulsions. *Catalysis Today* 2010;**158**:273-278.
[17] K. Fukui, K. Arai, K. Kanayama,H. Yoshida. Phillipsite synthesis from fly ash prepared by hydrothermal treatment with microwave heating. *Advanced Powder Technol.* 2006;**17**:369-382.
[18] X. Bu, P. Feng. Crystalline microporous and open framework materials. *The Chemistry of Nanostructured Materials***.** In Yang, P World Scientific: New Jersey; 2003, pp. 1-37.