Chapter 4. Synthesis of Silylated Nanozeolites in the Presence of Organic Phase: Two-Phase and Single Phase Methods

Gia-Thanh Vuong and Trong-On Do *

Department of Chemical Engineering, Laval University, Quebec G1K 7P4, Canada

Résumé

Deux méthodes de synthèse, l'une mono- l'autre biphasique ont été développées pour la préparation des nanozéolithes silylées. Dans ces méthodes, un solvant organique a été utilisé comme milieu de cristallisation de ces nanozéolithes. Pour illustrer ces deux méthodes, la zéolithe avec la structure MFI telle que silicalite-1 a été utilisée dans cette étude. Différentes techniques de caractérisation incluant XRD, MET, MEB, BET et RMN ont été utilisés pour caractériser les propriétés physico-chimiques de ces matériaux. Les résultats montrent que la méthode à phase unique produit (des nanocristaux uniformes) de silicalite-1, tandis que la méthode bi-phasique donne deux produits : nanozéolithe et microzéolithe dans la phase organique et la phase aqueuse respectivement. Cependant, la RMN indique que le caractère hydrophobe de ces silicalites-1 est conservé après calcination.

Abstract

Two synthesis methods: two-phase method and single-phase one, for the preparation of silylated nanozeolites were reported. In these methods an organic solvent was used as an effective medium for the crystallization of zeolites. To illustrate these two methods, silicalite-1 was selected in this study. Various techniques including XRD, TEM, SEM, BET and NMR techniques were used to monitor the physico-chemical properties of these synthesized materials. The results revealed that the single-phase method allows producing uniform/small nanosilicalite-1, whereas the two-phase one can bring two separate products: nanosized and microsized zeolite crystals in organic phase and in aqueous phase, respectively. Furthermore, the NMR results indicate that the hydrophobic surface character of these silicalite-1 samples can be obtained even after calcination.

Keywords: nanozelites, nanosilicalite-1, synthesis, organic medium, surface modification.

4.1. Introduction

Zeolites are crystalline aluminosilicate molecular sieves with uniform pores of molecular dimensions. They have been widely used as heterogeneous catalysts and adsorbents in the field of oil refining and in the petrochemical industry. Conventional zeolites with crystal sizes of several micrometers are synthesized under hydrothermal conditions. However, due to the pore size constraints (<15 Å), the unique catalytic properties of zeolites are limited to reactant molecules having kinetic diameters below 10 Å [1-3]. To overcome this limitation, there is an intensive research to either minimize the size of the zeolite crystals or to generate hierarchical zeolites containing a bimodal porosity, both micro-/mesopores [4-11] or micro-/macropores [12, 13]. The former strategy has led to the discovery of various types of zeolitic porous materials such as composite MFI/MCM-41 materials, UL-zeolites and MSU-S [4-11].

Nanozeolite with crystal sizes of less than 100 nm, has been receiving much of interest due to the fact that the reduction of zeolite crystal size from the micrometer to the nanometer scale leads to increase the external surface area and reduce diffusion path lengths [14, 15]. Furthermore, the reduction of crystal size to the nanometer scale results in substantial changes in the properties of materials, which have an impact on the performance of zeolites in traditional application areas such as catalysis and separation[16, 17]. Therefore, the synthesis of zeolite nanocrystals with small uniform diameter is highly desirable.

A number of synthesis methods has been reported, which allows the syntheses of nanozeolites with different structures, such as FAU, MFI, LTA and MOR [15, 18-20]. Synthesis methods are often carried out in the aqueous phase, and the key to the success was the use of so-called "clear gel solution" [15]. Another method, which is called confined space synthesis, has been developed for the preparation of nanosized zeolite crystals. The synthesis is conducted within an inert matrix such as porous carbon matrices [21-23], thermo-reversible polymer hydrogels, or microemulsions [24-29] which provides a steric hindered space for zeolite crystal growth. However, the external surface of the nanozeolites is generally hydrophilic and has high concentration of silanol groups that limit the catalytic

activity to the internal pore surface. Therefore, the synthesis of nanozeolites with hydrophobic external surface is highly interesting [30-32]. To achieve that, the nanozeolites have to undergo the post-synthesis treatment which often involves the silanization of the nanozeolite surfaces with organosilane agents [33-35].

Serrano et al. [36] have reported the use of organosilane as growth inhibitor. MFI and beta zeolites were synthesized in the aqueous medium, using phenylaminopropyl-trimethoxysilane (PHAPTMS). The synthesis is based on reducing the growth of zeolite crystals by silanization of the zeolitic seeds to hinder their further aggregation. However, as investigated by TEM analysis, the silylated MFI samples were prepared with a broad crystal size distribution in the range of 200–400 nm, which were formed by aggregation of ultra small units of 10 nm. Recently, we reported a new method, namely a single organic phase for the synthesis of controlled uniform size nanozeolites with the hydrophobic external surface. An organic solvent is used as the medium for crystallization instead of water. The zeolite precursors are functionalized with organic silane groups. They thus become hydrophobic and well dispersed in the organic solvent. Because the crystallization occurs in the organic phase and the zeolite precursors are protected by functional groups, catastrophic aggregation can be prevented hence resulting in small and uniform silylated nanozeolites with hydrophobic external surface [37]. Clear zeolite gel precursor was prepared using the method described in the literature [38, 39]. The as-made silylated nanozeolites are readily hydrophobic, hence, there is no need for the post-synthesis treatment. Therefore it can be suggested that organic solvent is an effective medium for the synthesis of nanozeolites.

The two-phase organic solvent/water synthesis is an appealing method which has been used in the synthesis of transition metal nanoparticles such as Pt, TiO_2, ZrO_2, CdS [40-47]. For the synthesis of TiO_2 nanocrystals, for example, a toluene solution containing titanium n-propoxide and oleic acid (OA) as a capping agent and an aqueous solution of tert-butylamine are mixed and heated. The formation of nanoparticles takes place at the toluene-water interface. The freshly formed nanoparticles capped with OA become hydrophobic and could be dispersed in toluene. They therefore stop growing and finally, monodisperse nanoparticles can be achieved [41-43]. The two phase synthesis can

be carried out with an appropriate choice of capping agents. These agents contain both hydrophilic groups at one end that can be bound to the nanoparticle surface and hydrophobic alkyl-chains at the other end [48].

The prospect of applying this strategy for the synthesis of nanozeolites is attractive, it would be an effective approach for spatial isolation of zeolitic seeds from further growth and the size could be tuned via changing the capping agent content. However, the crystallization of zeolites is somewhat different and difficult as compared to the synthesis of transition metal nanoparticles. Care should be taken in choosing the appropriate capping agent and solvent for the synthesis of nanozeolites. One of the problems is that common capping agents such as oxalic acid, stearic acid are incapable of "capping" zeolitic seeds. In the synthesis of transition metal nanoparticles, these acids that contain donor group can attach to metal atoms by coordinate bonding. Thus, a transition metal of which the atom has an incomplete d shell is more likely to form the complex with the acids, compared to the main group Si and Al ions (e.g., no transition metal ions) in the structure of zeolites.

To overcome this problem, the synthesis strategy is based on hindering the growth of zeolite crystals by silanization of the zeolitic seeds using an organosilane. An aqueous clear solution containing zeolitic seeds was added in an organic solvent containing organosilane agent. As the organic solvent is insoluble in water, the organic phase stays on top of the aqueous phase. Since the zeolitic seeds are rich in silanol groups, they can react with the organosilane agents at the interface between the two phases. Because of the protecting organic groups, the functionalized zeolitic precursors become more hydrophobic and can diffuse into the organic phase.

In this paper, we report a two-phase method approach in which silylated nanosilicalite-1 was prepared in the presence of both organic and aqueous phases. Hexadecyltrimethoxysilane and toluene were used as silylating agent and organic solvent, respectively. These materials were characterized using XRD, TEM, BET and ^{29}Si MAS NMR techniques, and compared to those obtained by the single organic solvent phase method.

4.2. Experimental

4.2.1. Synthesis of silylated silicalite-1 using the two phase and single-phase methods

The synthesis of nanozeolites involves two steps: (i) In the fist step, clear zeolite gel solution was prepared according to the method described in the literature [38, 39]. (ii) The obtained clear gel solutions were then processed in different procedures depending on the method applied. The use of the same starting zeolite gel solution can provide the ease of comparison between these synthesis methods.

4.2.2. Two-phase method

The procedure is consisting of the following two steps (see Figure 4.1): (i) A clear zeolite gel solution was prepared with a molar gel composition of 2.68 SiO_2:1 TPAOH:168 H_2O. In a typical recipe, 14 g of tetrapropylammonium hydroxide (TPAOH) 20% in water was added to 7.8 g of tetraethoxysilane, $Si(OC_2H_5)_4$. The mixture was stirred vigorously for 24 h at room temperature. This clear solution was then heated at 80 °C for 12 h to speed up the formation of protozeolitic species (known as zeolite seeds). (ii) Typically, 21.8 g of clear zeolite gel solution was added with 93 g of a solution of toluene containing 1.22 wt% hexadecyltrimethoxysilane (note that the organosilane was in proportion of less than 10% mol with respect to the silica content in the gel). Since the solvent is insoluble in water, a two-phase system was obtained. The functionalization reaction was carried out batchwise in a glass reactor under stirring at 60 °C for 12 h and reflux. This two-phase mixture was transferred into a Teflon-lined stainless steel autoclave and then heated at 180 °C for 5 days. After crystallization, the two silicalite-1 products in organic phase (toluene) and aqueous phase were recovered separately by centrifugation and then washed with ethanol and water for several times. The products were then dried at 80 °C for 24 h and were denoted as OP (organic phase) and AP (aqueous phase) samples.
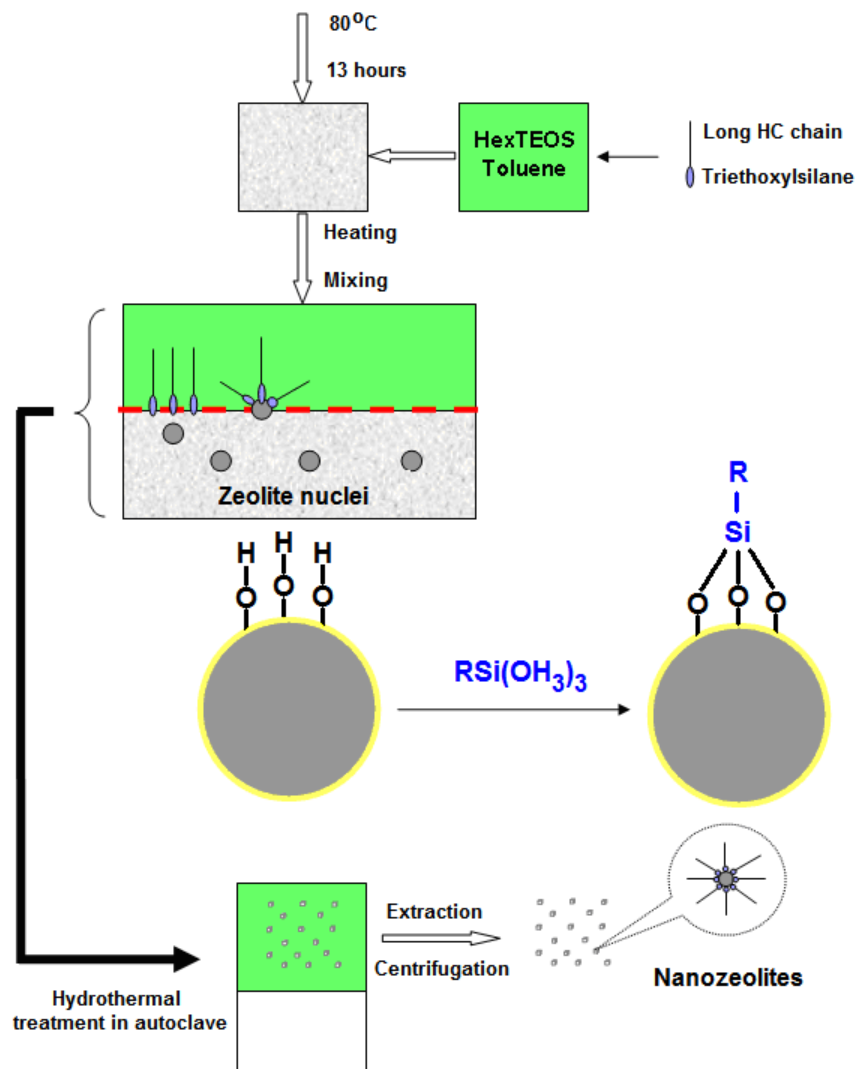
Figure 4.1. Schematic representation of the two-phase synthesis method.

4.2.3. Single-phase method

The synthesis of silylated nanosilicalite-1 was carried out according to the procedure described in reference [37]. 10 g of clear gel solution containing zeolitic seeds was added to 500 ml of a solution of toluene containing n-butanol (30 wt%) and a proper amount of hexadecyltrimethoxysilane. An amount of n-butanol is introduced in the organic phase, which is expected to increase the miscibility of the organic phase toward the aqueous one, since n-butanol is miscible in hydrocarbon solvent, however it is moderately soluble in water. The mixture was heated in a glass reactor under stirring at 60 °C for 12 h and reflux. After 12 h of stirring, a mixture of only one clear liquid phase was observed.

This mixture was then transferred to a Teflon-lined stainless steel autoclave for further hydrothermal treatment at 180 °C for 5 days. After the crystallization, the crude solution of nanosilicalite-1 product was precipitated with ethanol and further isolated by centrifugation and then washed with ethanol for several times. The product was then dried at 80 °C for 24 h and is denoted as SOP sample.

4.2.4. Conventional method (synthesis of nanozeolites in aqueous medium)

The conventional synthesis of the zeolites in aqueous medium was carried out according to the procedure described in the literature [19, 38, 39]. After being filled with the same starting silicalite-1 gel solution for the single-phase and two-phase methods, the Teflon-lined stainless steel autoclave was completely sealed and heated in a convection oven at 150 °C for 3 days. The solid product was recovered by centrifugation, washed several times with distilled water, dried over night at 80 °C. The products synthesized using this conventional method, were denoted as reference or conventional silicalite-1 samples.

4.2.5. Characterization

The FTIR spectra were recorded using a Biorad FTS-60 spectrometer on sample wafers. Powder XRD patterns of the materials were recorded on a Philips X-ray diffractometer (PW 1010 generator and PW 1050 computer assisted goniometer) using nickel-filtered Cu Kα ($\lambda = 1.5406$ Å) radiation, 0.0258° step size and a 1 s step time.

The nitrogen adsorption/desorption measurements were carried out using an Omnisorp-100 automatic analyzer at -196 °C after degassing about 30 mg of calcined sample at 200 °C for at least 4 h under vacuum (10^{-4} to 10^{-5} torr). The specific surface area (S_{BET}) was determined from the linear part of the BET equation ($P/P_o = 0.05 - 0.15$). High-resolution TEM images were obtained on a JEOL 200 CX transmission electron microscope operated at 120 kV. The samples for TEM were prepared by dispersing the fine powders of the products in slurry in ethanol onto honeycomb carbon copper grids. However, for scanning electron microscope (SEM), JEOL JSM-840 scanning electron microscope operated at 15 kV was used. Solid-state ^{29}Si MAS NMR spectra were recorded at room temperature on a Bruker ASX 300 spectrometer.

4.3. Results and discussion

The synthesis of nanosilicalite-1 was selected to demonstrate the two phase method approach (Figure 4.1). Hexadecyltrimethoxysilane and toluene were used as silylating agent and organic solvent, respectively[29, 36]. After crystallization, the products were recovered and denoted as OP in the organic phase and AP in the aqueous phase. The mass ratio of the OP and AP products is about 6/4 in this work. For the single-phase method [37], the water/oil ratio was reduced significantly (see Figure 4.2). To obtain a mixture of only one clear liquid phase after stirring at 60 °C for 12 h, an appropriate amount of clear aqueous zeolite gel solution is added to a solution of toluene containing both n-butanol and hexadecyltrimethoxysilane (see Section 5.2 for details). The product is denoted as the SOP sample.

The physico-chemical properties of the calcined silylated nanozeolite and zeolite samples prepared from the same clear zeolite gel, using different methods: the two-phase, single-phase and conventional methods are summarized in Table 4.1.

Table 4.1. Physico-chemical properties of the calcined silylated nanozeolite and zeolite samples prepared from the same clear zeolite gel, using different methods: the two-phase, single-phase and conventional methods.

Sample	Preparation	S_{BET}(m²/g)	S_{EXT}(m²/g)	S_{MIC}(m²/g)	V_{MIC}(cm³/g)	R_{PORE}(nm)	Crystal size (nm)
OP nanosilicalite-1	Two-phase method*	520	105	415	0.150	–	30–50
AP silicalite-1	Two-phase method*	500	10	490	0.152	–	1500
SOP nanosilicalite-1	Single organic phase method	570	150	420	0.155	3.7	~20
Silicalite-1	Conventional method	510	15	495	0.160	–	~300

*Product recovered in aqueous phase

The specific surface area, S_{BET} determined from the linear part of the BET equation ($P/P_0 = 0.05$–0.15). The mesopore size distribution calculated using the desorption branch of the N_2 adsorption/desorption isotherms and the Barrett–Joyner–Halenda (BJH) formula. The mesopore surface area (S_{EXT}) and mesopore volume (V_{BJH}) obtained from the pore size distribution curves. The micropore surface area (S_{MIC}) obtained as S_{BET}–S_{EXT} and the average mesopore radius, (R_{PORE}) calculated as $4V_{BJH}/S_{BJH}$[49].
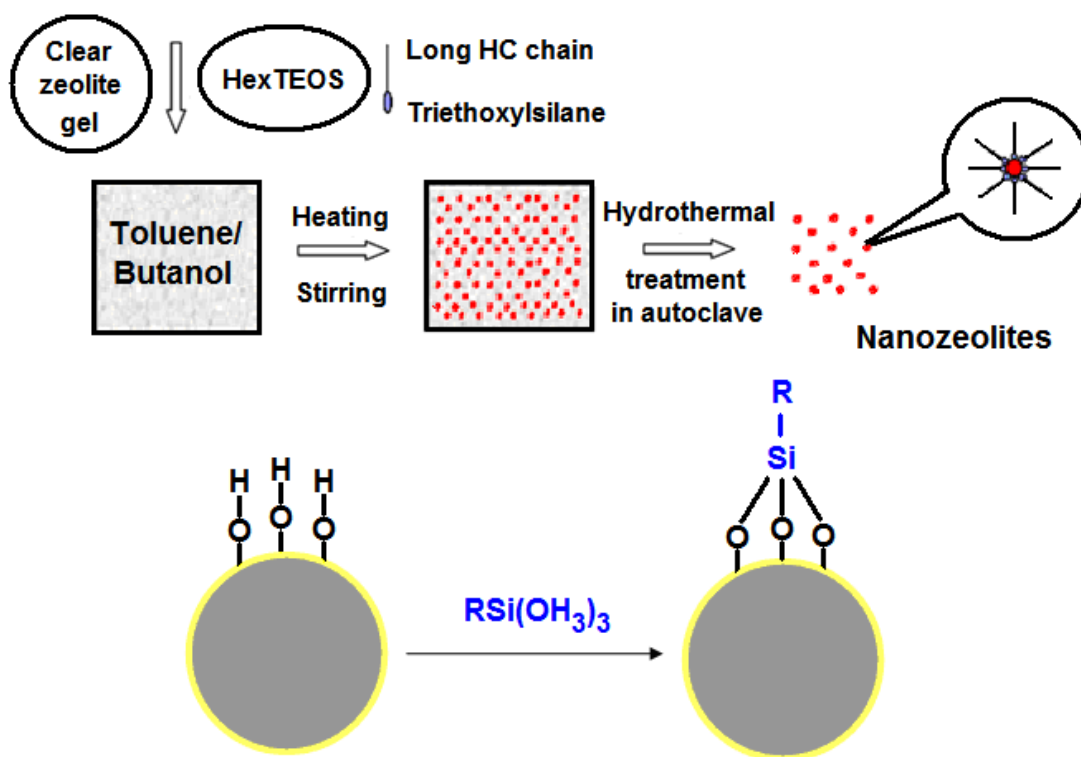
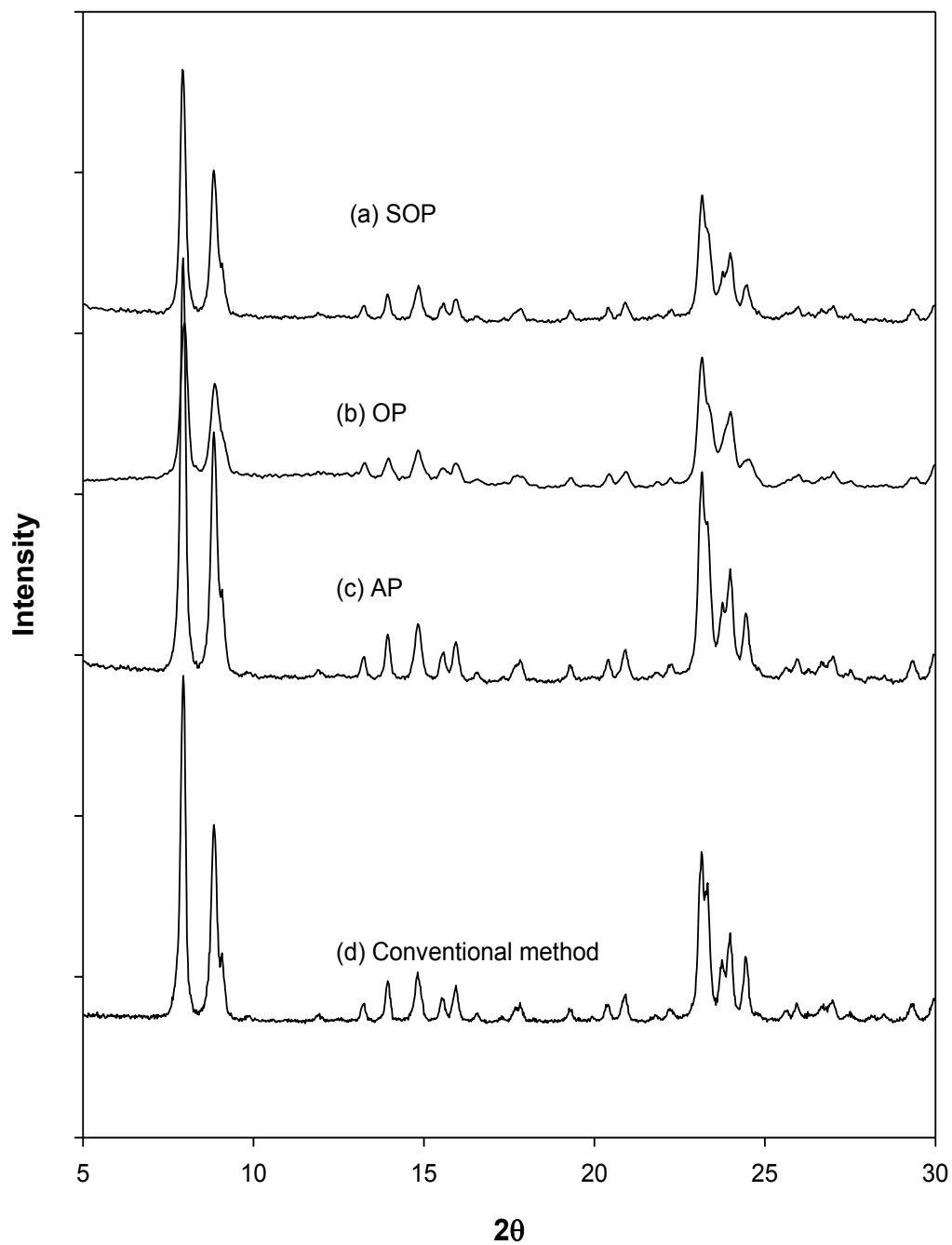**Figure 4.2.** Schematic representation of the single-phase synthesis method.

Figure 4.3. XRD patterns of the as-made silicalite-1 samples, (a) sample prepared using the conventional method in aqueous medium, (b) AP silicalite-1, (c) OP silicalite-1 using the two-phase method and (d) SOP silicalite-1 using single-phase method.

Figure 4.3 shows the X-ray powder pattern of the as-made silylated SOP sample using the single-phase method, and as-made silylated OP and AP samples using the two

phase method. Sample prepared by the conventional method in aqueous medium from the same clear zeolite gel solution without organosilane was used as a reference (d). The XRD patterns of these samples are identical to that of the reference sample, indicating the MFI structure of the samples. This also suggests that the presence of organosilane in the synthesis mixture did not affect the formation of the desired structure. However, for the SOP sample prepared using the single-phase method and the OP sample, there is a clear broadening of the reflections, which is attributed to small crystals. In addition, no significant peak at $2\theta = 20–30°$ which is characteristic of amorphous phase was observed suggesting a relatively high crystallinity of the silylated samples.

The crystal size of these samples was also investigated by scanning and transmission electron microscope (SEM and TEM) techniques. The SEM micrographs of the as-made silylated OP and AP silicalite-1 samples (e.g., the products in organic phase and aqueous phase, respectively) are shown in Figure 4.4. The crystal size of the OP silicalite-1 sample was uniform, ranging from 30 to 50 nm. In contrast, large crystals of 5μm were observed for the AP silicalite-1 sample. A difference in crystal size between the two samples suggests the effect of media for crystallization on crystal size of the product. Further, for the as-made silylated SOP silicalite-1 sample, a representative TEM micrograph is also shown in Figure 4.5 and exhibits very uniform nanocrystal sizes with mostly spherical and cubic shaped particles. The particle size is about 21 nm. Owing to the organosilane being grafted on the zeolite precursors, the nanoparticles remain well dispersed in the organic medium and are protected from drastic aggregation during crystallization.
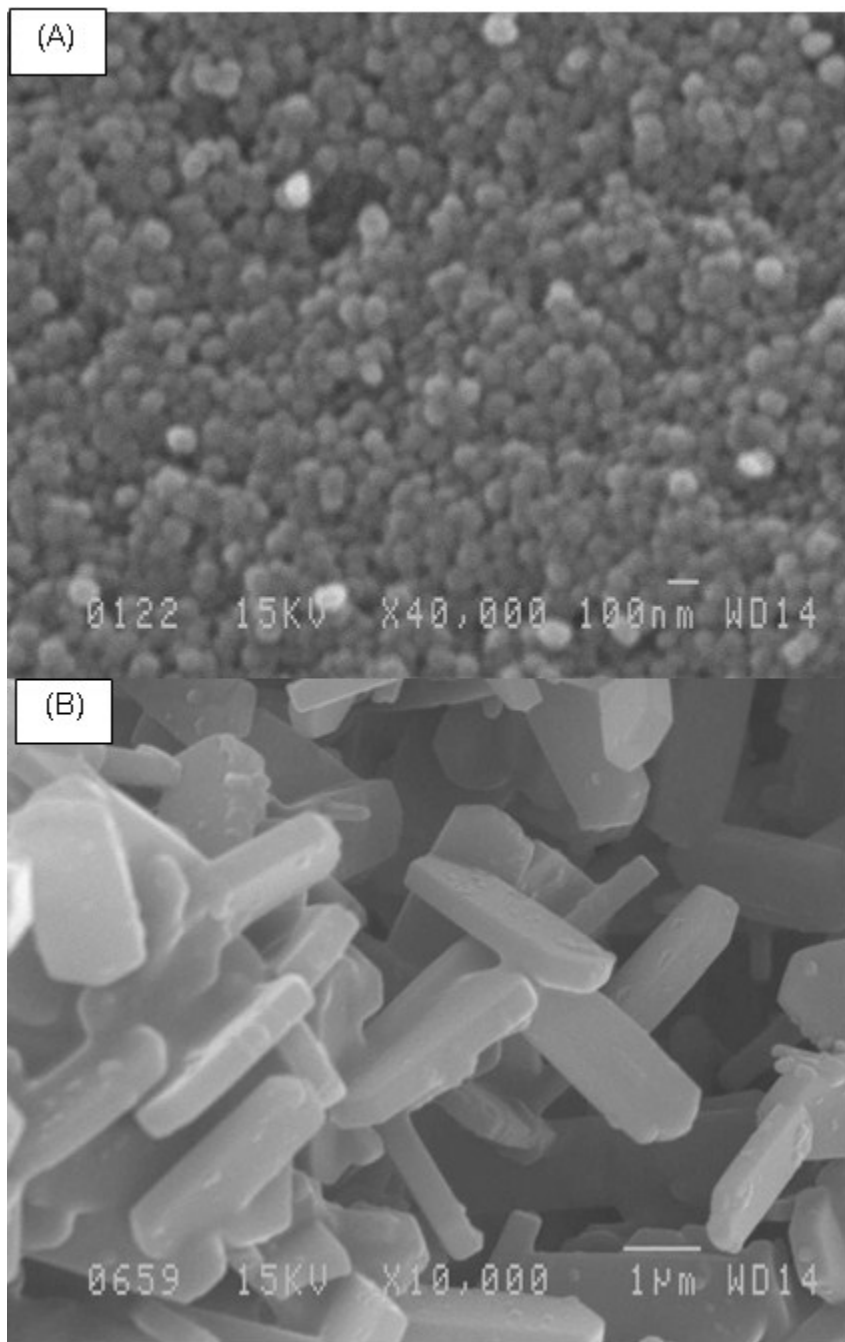
Figure 4.4. SEM micrographs of the as-made samples, (A) silylated OP silicalite-1 and (B) silylated AP silicalite-1.
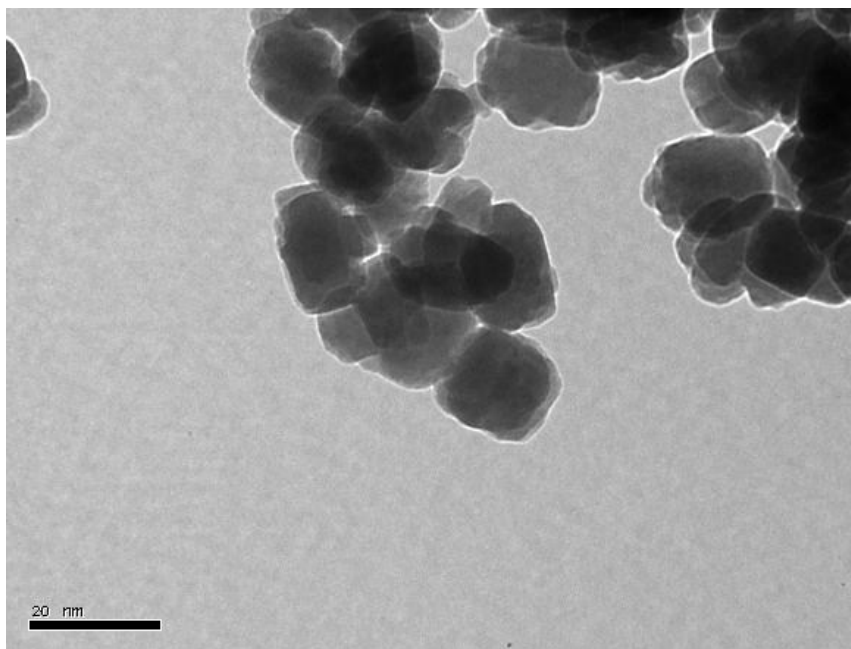
Figure 4.5. TEM micrograph of the as-made SOP nanosilicalite-1 sample prepared using the single-phase method.

It is well known that water phase which is used as a crystallization medium, plays a role of transporting monomers to the surface of zeolite crystals and large crystal sizes were obtained. However, using an organic solvent instead of water, the zeolite precursors are functionalized with organic silane groups. They thus become hydrophobic and highly dispersed in the organic phase. Because of the crystallization occurs in the organic phase with a limited water amount, catastrophic aggregation can be prevented. As a result, small and uniform nanozeolites were observed for the OP silicalite-1 and SOP silicalite-1 samples. Figure 4.6 also shows the FTIR spectra of the samples prepared using the conventional and single-phase methods (the calcined SOP sample). The FTIR peak positions are identical to those of the MFI structure. In particular, the band at 550 cm^{-1} is assigned to the asymmetric stretching mode of the five-membered ring present in ZSM-5 which is an indication of the MFI structure. Splitting of this lattice-sensitive band into a doublet has been observed in nanophase silicalite-1 [39]. The FTIR spectrum of the SOP silicalite-1 sample prepared using the single-phase method in Figure 4.6 shows the doublet band at 561/547 cm^{-1} which indicates the formation of nanocrystals.

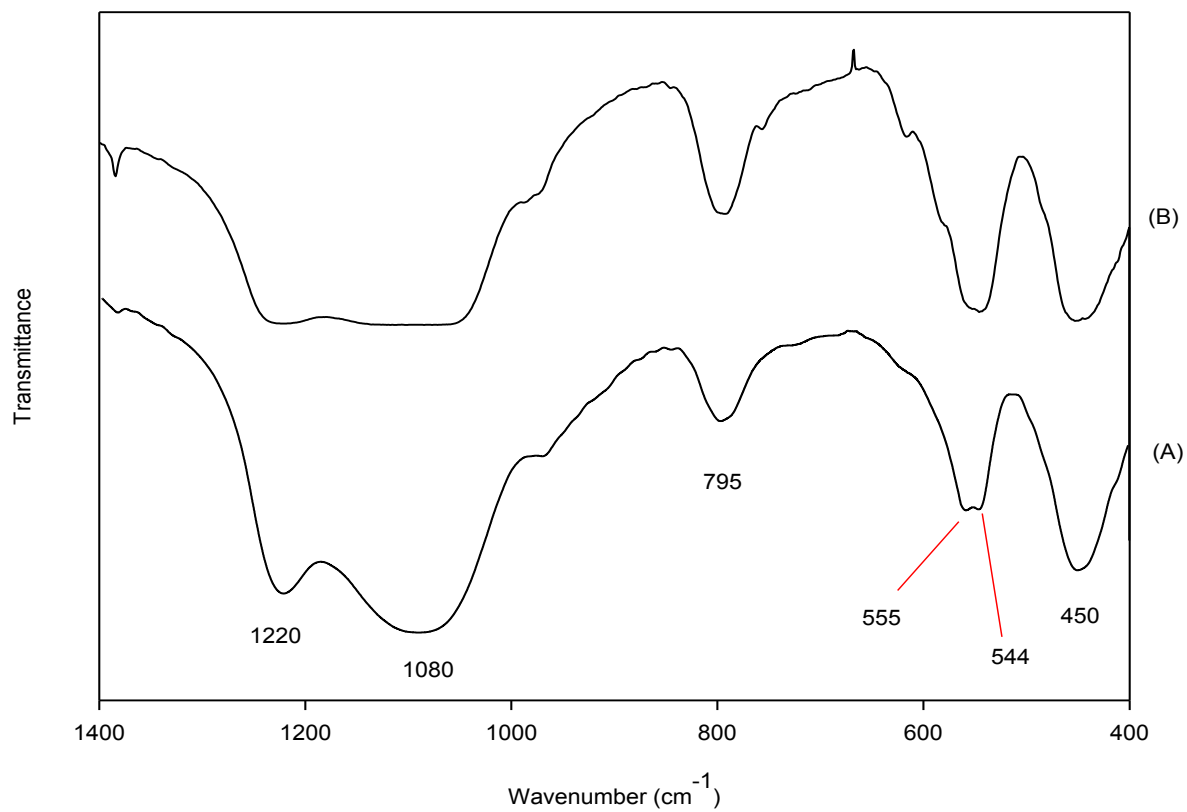**Figure 4.6.** FTIR spectra of the silicalite-1 samples prepared using the single-phase method (A) and the conventional method (B).
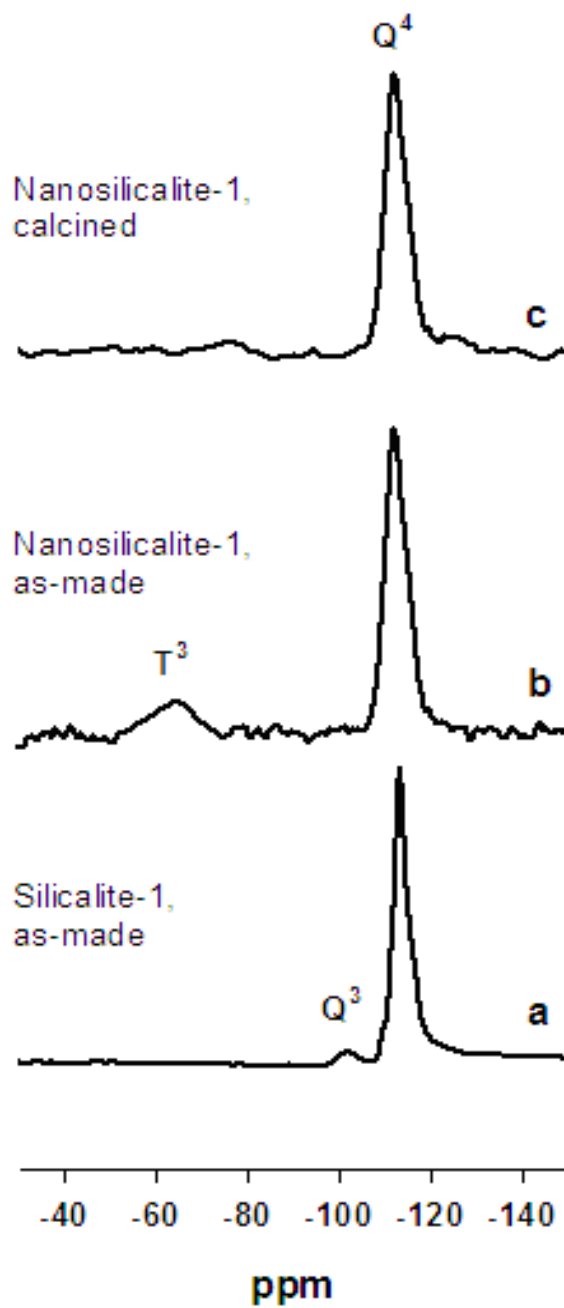
Figure 4.7 ^{29}Si MAS NMR spectra of the silicalite-1 samples prepared from the same zeolite gel solution using (a) the conventional method in aqueous medium without organosilane, (b) as-made SOP nanosilicalite-1 using single-phase method in organic solvent and (c) calcined SOP nanosilicalite-1.
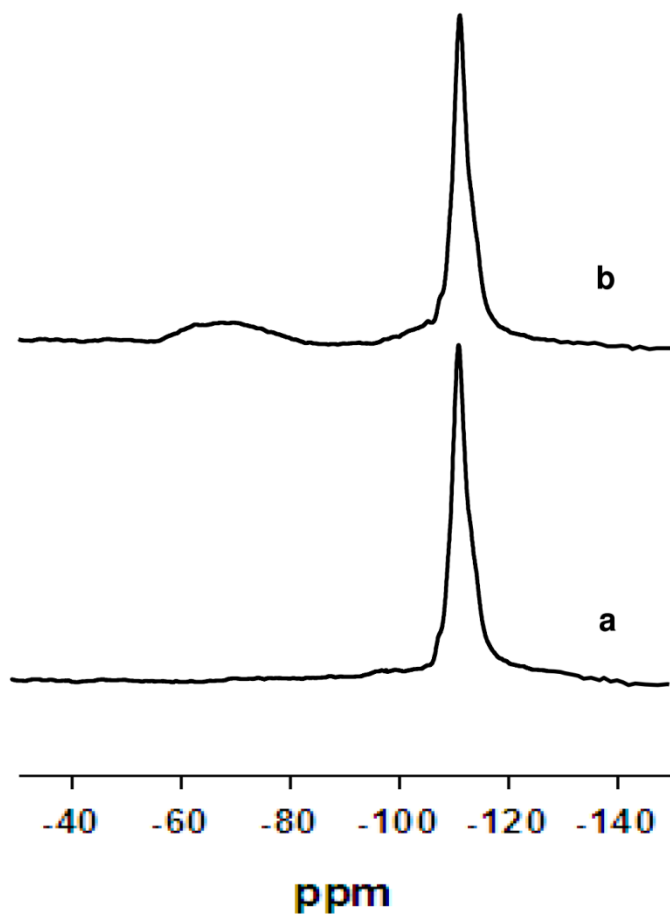
Figure 4.8 ^{29}Si MAS NMR spectra of the as-made silicalite-1 samples prepared from the same zeolite gel solution using the two-phase method: (a) as-made AP nanosilicalite-1 and (b) as-made OP nanosilicalite-1.

The ^{29}Si MAS NMR spectra of the as-made silicalite-1 samples prepared using different methods from the same zeolite gel solution were investigated (Figure 4.7 and Figure 4.8). The NMR spectrum of the as-made silicalite-1 sample prepared using the conventional method, in the absent of organosilane, shows a main resonance at approximately −110 ppm and a weak resonance peak at approximately −100 ppm which are attributed to Si(OSi)$_4$, Q^4 and Si(OSi)$_3$OH, Q^3 species, respectively (Figure 4.7a). However, for the as-made SOP silicalite-1 sample, only one resonance peak at approximately −110 ppm attributable to Q^4 species was observed, an additional intense peak at −65 ppm assigned to R-C-Si-(OSi)$_3$ species is present [33]. This additional peak is the result from the reaction between the silicon in the organosilane and the silanol groups of zeolite nuclei

110

during the crystallization. This NMR broad peak at 50–70 ppm could be contributed to T^2 and T^3 which correspond to two and three OH groups consumed by one organosilane molecule. The calcined sample also shows essentially a single resonance peak Q^4 at approximately −110 ppm (Figure 4.7b and c). It clearly indicates that the silanol groups which disappear in the chemical interaction with the organosilane do not reappear upon calcination. This could be due to two or three OH groups on the nanoparticle surface consumed by one organosilane molecule. As a result, only one resonance Q^4 of this sample, even after calcination, suggests its hydrophobic surface character.

Furthermore, the as-made OP and AP silicalite-1 samples exhibit also only one NMR peak at approximately −110 ppm characteristic of Q^4 along with a NMR broad peak at 50–70 ppm attributed to T^2 and T^3 for the OP sample and a very weak peak for the AP sample (Figure 4.8). This also suggests the silanization on the external surface of silicalite-1, which acts to heal defect sites (e.g., silanol groups) on the zeolite surface. Thus, it can be concluded that the presence of only one resonance Q^4 even after calcination of the silylated silicalite-1 samples suggests their hydrophobic surface character.
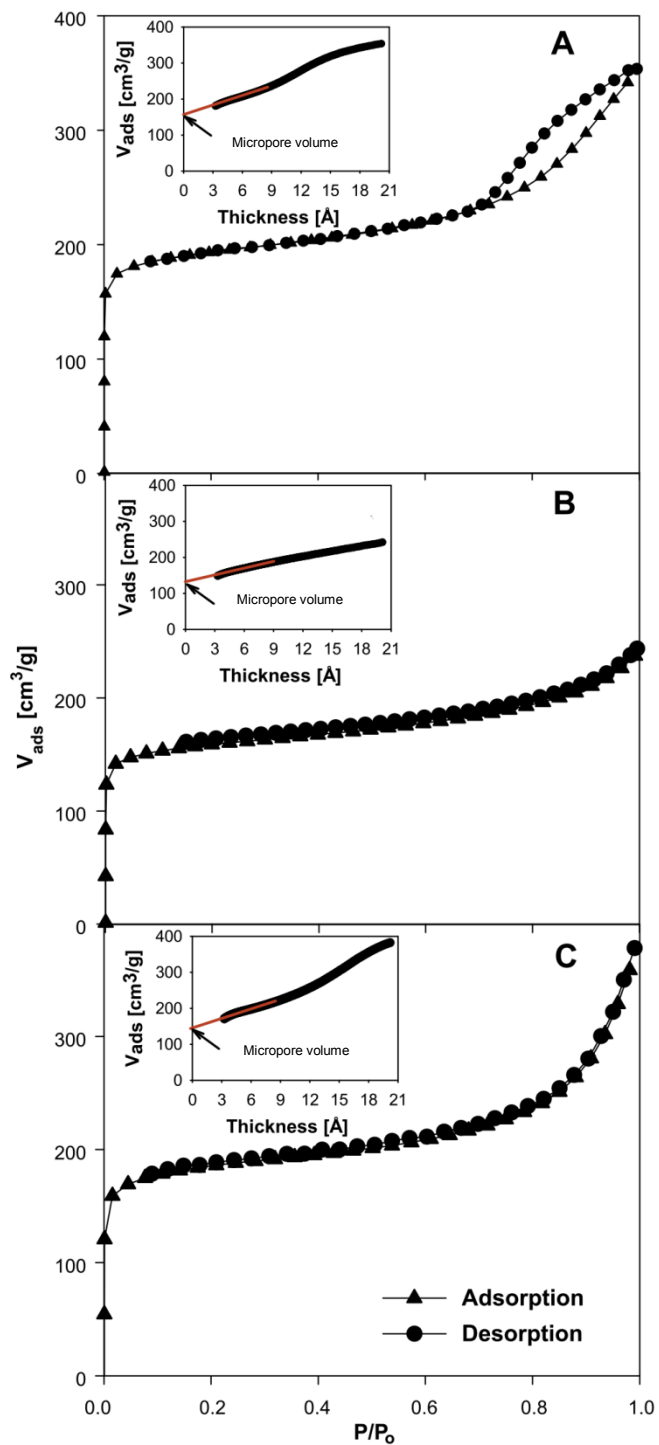
Figure 4.9. Nitrogen adsorption/desorption isotherms of the calcined samples: (A) SOP silicalite-1, (B) OP silicalite-1 and (C) AP silicalite-1 (inset: t-plot curve).

Figure 4.9 shows the N2 adsorption/desorption isotherms and the BJH pore radius distribution of the calcined SOP nanosilicalite-1 and OP nanosilicalite-1 samples. At low relative P/P_o pressure, a steep rise in uptake, followed by a flat curve, corresponds to filling

of micropores with nitrogen. An inflection at higher pressures (e.g., in P/P_o range from 0.7 to 0.9) and a hysteresis loop for the OP nanosilicalite-1 sample are characteristic of capillary condensation and are related to the range of mesopores due to the interparticles. For the AP silicalite-1 sample, mesopores were not observed (see Figure 4.9B) owing to its large particle size. However, for the SOP nanosilicalite-1 sample no hysteresis loop is present; even its particle size is smaller than that of the OP sample. This can be explained by uncompacted nanoparticles of this sample [49]. The specific surface areas are 570 and 520 m^2/g, and the external surface areas based on t-plot calculation are 150 and 106 m^2/g for the SOP nanosilicalite-1 and OP nanosilicalite-1 samples, respectively. However, for the AP silicalite-1 sample with large crystal size, the external surface area is very low, only 10 m^2/g (Table 4.1). The high external surface values indicate the small crystal size of the sample.

Indeed, silanol groups on silicalite-1 are mainly located on the external surface and therefore the quantity of silanol sites is related to the zeolite crystal size. Due to the bulky size of hexadecyltrimethoxysilane, only the silanol groups on the external surface of zeolite crystals are accessible for the silanization. Hence the high external surface of nanozeolites provides silanol sites which are available for the chemical functionalization. The order of the external surface areas and of the amount of silanol sites reacted with organic silane groups based on the NMR peak intensity at −65 ppm was found to be: SOP silicalite-1 > OP silicalite-1 > AP silicalite-1. In contrast, the order of crystal size is: AP silicalite-1 > OP silicalite-1 > SOP silicalite-1. Furthermore, as seen the NMR results, the silylated silicalite-1 sample synthesized by these methods exhibit a hydrophobic character, even after calcination.

4.4. Conclusion

In conclusion, we have demonstrated two methods in the presence of organic medium for the synthesis of nanozeolites with hydrophobic external surface. Depending on the method of synthesis, different crystal sizes can be synthesized: Uniform and small nanozeolites using the single-phase method, however, using the two phase method, large nanosized and microsized zeolite crystals in organic phase and in aqueous phase, respectively. We believe that these methodologies can be applied to the synthesis of other

types of nanozeolites. Detailed studies of the sorption behavior and catalytic properties of this class of nanozeolites are underway.

Acknowledgments