EFFECT OF K_2SO_4 TO THE PORE PROPERTIES OF PRODUCTS IN THE SYNTHESIS OF MESOPOROUS SILICATES MCM-41

PENGARUH K_2SO_4 TERHADAP KARAKTERISTIK PORI PRODUK DALAM SINTESIS SILIKAT MESOPORI MCM-41

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ABSTRACT

Researchs about the effects of K_2SO_4 to the pore properties of the products in the synthesis of mesoporous silicates MCM-41 has been done. MCM-41 was synthesized by hydrothermal treatment of the mixture containing : 9.31 of sodium silicate solution, 8.67 g of cetyltrimetylammoniumbromide (CTMAB) and 29 g of distilled water (molar ratio of 8 Na_2SiO_3 : CTMAB : NaOH : 400H_2O). The hydrothermal treatment was carried out at 100 ^oC in a teflon-lined stainless steel autoclave heated in the oven for 36 h. The solid phase was filtered, washed with distilled water, and dried in the oven at 100 ^oC for 2 h. The surfactant CTMAB was removed by calcinations at 550 ^oC for 10 h with heating rate of 2 ^oC/min. The as-synthesized MCM-41 was characterized by using FTIR spectroscopy and X-ray diffraction, while calcined-MCM-41 was characterized by using FTIR spectroscopy, X-ray diffraction; and N_2 physisorption methods. The same procedure was carried out, with the addition of 17.4 g of K_2SO_4 and 21.6 ml of distilled water to obstain the molar composition of the gel of: 8Na_2SiO_3 : CTMAB : NaOH: 400H_2O : 2 K_2SO_4. The results showed that the addition of K_2SO_4 increased the crystalinity. MCM-41 prepared with K_2SO_4 has a higher specific surface area of 972.812 m^2 g^{-1} compared to the MCM-41 prepared without K_2SO_4 (i.e., 946.607 m^2 g^{-1}), higher mean pore diameter of 3.714 nm compared to the MCM-41 prepared without K_2SO_4 (i.e. 3.357 nm), and thicker pore walls of 0.830 nm compared to the MCM-41 prepared without K_2SO_4 (i.e. 1.176 nm).

Key words : MCM-41, K_2SO_4, pore properties

ABSTRAK

Telah dilakukan penelitian pengaruh penambahan K_2SO_4 terhadap karakteristik pori produk dalam sintesis silikat mesopori MCM-41. Sintesis MCM-41 dilakukan dengan perlakuan hidrotermal atas campuran yang mengandung 9,31 g larutan natrium silikat, 8,67 g CTMAB dan 29 g akuades (komposisi molar 8Na_2SiO_3 : CTMAB : NaOH : 400H_2O). Perlakuan hidrotermal dilakukan dengan menempatkan sampel dalam *autoclave* kemudian dipanaskan dalam oven pada suhu 100 ^oC selama 36 jam. Sampel didinginkan di udara terbuka, kemudian fasa padat disaring, dicuci dengan akuades, dan dikeringkan dalam oven pada suhu 100 ^oC selama 2 jam. Penghilangan surfaktan dilakukan dengan kalsinasi pada temperatur 550 ^oC selama 10 jam dengan laju pemanasan 2 ^oC /menit. Sampel

sebelum kalsinasi dikarakterisasi dengan metode XRD dan FTIR, sedang sampel setelah kalsinasi dikarakterisasi dengan metode XRD, FTIR dan fisisorpsi N_2. Prosedur serupa dilakukan kembali dengan menambahkan 17,4 g dan 21,6 ml akuades untuk memperoleh komposisi molar $8Na_2SiO_3$: CTMAB : NaOH : $400H_2O$: $2K_2SO_4$. Hasil penelitian menunjukkan bahwa MCM-41 yang disintesis dengan penambahan K_2SO_4 memiliki kristalinitas yang lebih tinggi. Luas permukaannya 972,812 m^2 g^{-1}, lebih besar dibanding dengan yang disintesis tanpa K_2SO_4 (946,607 m^2g^{-1}) ; diameter pori reratanya 3,714 nm, lebih besar dibanding dengan yang disintesis tanpa K_2SO_4 (3,357 nm); sedang dinding porinya 0,830 nm, lebih tipis dibanding yang disintesis tanpa K_2SO_4 (1,176 nm).

Kata kunci : MCM-41, K_2SO_4 , karakteristik pori

1. INTRODUCTION

In 1992, a novel family of ordered silicate mesoporous molecular sieves, designated as M41S was discovered by researchers at Mobil R & D Corporation (Kresge *et al*., 1992 ; Beck and Vartuli, 1996). Since then, numerous studies on their synthesis, characterization and application have been reported (Zhao *et al*., 1996 ; Selvam *et al*., 2001). The most important member among these materials is MCM-41 which possesses an ordered structure with uniform mesopores arranged into a hexagonal, honeycomb-like lattice (Kresge *et al*., 1992). The synthesis starts with the formation of organic micellar species in an aqueous solution, followed by the polycondensation of an inorganic matrix, and ends with the removal of the organic template (Zhao *et al*., 2002). Interaction between the organic surfactant and the inorganic matrix is dictated by the synthesis reagents and the preparation conditions is a controlling factor in influencing the physical and chemical properties of the synthesized mesoporous materials (Biz *et al*., 1998 ; Kimura, 2005).

The uniqueness of MCM-41 mesoporous materials are the pore size uniform and tunable in the range between 1.6-10 nm. This innovative discovery has greatly expanded the area of microporous molecular sieves (zeolites) into the mesopore range and has created new opportunities beyond catalysis (Schüth, 2001). Also, the ordered mesoporous materials have been found as promising materials in optics and electronics, as nano size template, and as adsorbents for heavy metals (Schüth, 2001), adsorbents for gases and liquid (Ho *et al*., 2993), biomolecular immobilization (Diaz and Balkus, 1996) and separation (Grun, 1996).

Addition of electrolytes in the synthesis of mesoporous silicate can improve the properties of the materials, especially the stability of the materials by developing the interface properties (Leontidis, 2002). Stucky and Dougall (1990) reported that in the synthesis of mesoporous silicates SBA-15, the addition of inorganic highly charged salts such as K_2SO_4, can increase the interaction of silicate species with hydrophilic head groups of nonionic block copolymers. This strong interaction of head groups with the silicate species results in long-range ordered domain of silica-surfactant mesostructures, finally the long-range order favors the formation of mesoporous single crystals. Briefly, it was found that in the synthesis of SBA-15 used a non ionic triblock copolymer as a surfactant in acidic media, addition of K_2SO_4 stimulates the formation of single crystal materials instead of amorphous materials.

In this paper we report the effect of K_2SO_4 to the pore properties of products in the synthesis of mesoporous silicates MCM-41 synthesized using cetyltrimetylamonium cation as a surfactant in alkaline condition. The results showed that the addition of K_2SO_4 increased the crystalinity, specific surface area and mean pore diameter, but decreased the pore wall thickness.

2. EXPERIMENTAL

Starting Materials

The materials used for the preparation of the mesoporous MCM-41 silicates are: cetyltrimethylammoniumbromide (CTMAB, E. Merck), sulfuric acid (H_2SO_4, E. Merck), sodium silicate solution (27 wt % SiO_2, 8 % wt Na_2O, 65 % H_2O, E. Merck), sodium hydroxide (NaOH; E. Merck), K_2SO_4 (E. Merck), and distilled water produced by Laboratory of Analytical Chemistry Gadjah Mada University Yogyakarta Indonesia.

Synthesis of MCM-41

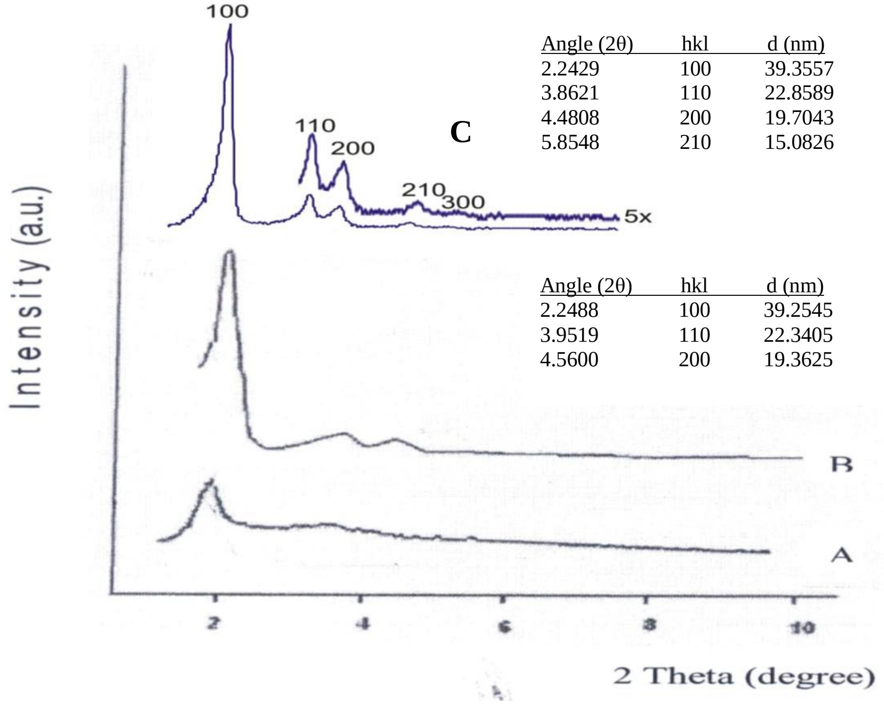
The MCM-41 was synthesised by hydrothermal method as follows. CTMAB (8.67 g) and 29 g of distilled water were mixed and stirred for 30 min. There after 9.31 g of sodium silicate solution was added dropped wise to the surfactant solution under vigorous stirring. After stirring for 30 min. a small amount of 1 M H_2SO_4 was added to the above mixture to reduce the pH to 10.2 and stirred for 1 h. The mol composition of the resulting gel was $8Na_2SiO_3$: CTMAB : NaOH: $400H_2O$. The gel was then transfered into 150 cm^3 teflon-lined stainless steel autoclave and heated at 383 K for 36 h. After cooling at the room temperature, the resulting solid product was recovered by filtration on a Buchner funnel, washed with distilled water, and dried in the air at 363 K. Surfactant was removed by calcining the as-synthesized product at 823 K for 10 h with heating rate of 2^o/min. The products were characterized by various techniques including XRD, FTIR, and N_2 physisorption. In order to investigate the effects of K_2SO_4, the same procedure was carried out, with the addition of 17.4 g of K_2SO_4 to obtain the mol composition of the gel $8Na_2SiO_3$: CTMAB : NaOH: $400H_2O$: $2K_2SO_4$. The addition of K_2SO_4 into the gel was done before hydrothermal treatment.

Characterization

Characterization of the crystalline phases and determination of the phase purities in the as-synthesized and calcined MCM-41 samples were carried out by XRD (Shimadzu XD-3H) using nickel-filtered Cu K_α radiation (λ=1.5406 Å). The samples were scanned from 1 to 10^o (2θ), where θ is the angle of incidence of the X-ray beam to the plane. The latice parameters (a_0) was calculated by formula : $a_0 = 2d_{100}/\sqrt{3}$, where d_{100} is the interplanar spacing corresponding to the (100) Bragg reflection. Infra-red spectra were recorded with a Shimadzu-8201 PC FTIR Spectrometer from KBr Pellets (0.005 g sample with 0.1 g KBr). The specific surface area and pore diameter of calcined-MCM-41 were analyzed using a NOVA Ver. 2.2 sorptiometer, by apply the conventional Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) equations. The pore wall thickness was calculated by subtracting the pore diameter from the latice parameter (a_0).

3. RESULTS AND DISCUSSION

X-ray Difractogram



Angle (2θ)	hkl	d (nm)
2.2429	100	39.3557
3.8621	110	22.8589
4.4808	200	19.7043
5.8548	210	15.0826

Angle (2θ)	hkl	d (nm)
2.2488	100	39.2545
3.9519	110	22.3405
4.5600	200	19.3625

Fig. 1 XRD powder patterns of : (A) as-synthesized MCM-41 prepared without K_2SO_4 (B) calcined-MCM-41 prepared without K_2SO_4 and (C) calcined-MCM-41 prepared with K_2SO_4

Fig. 1 shows the XRD patterns of as-synthesized MCM-41 prepared without K_2SO_4, calcined-MCM-41 prepared without K_2SO_4, and calcined-MCM-41 prepared with K_2SO_4 The calcined-MCM-41 prepared without K_2SO_4 (Fig.1B) exhibits a strong (100) reflection which correspond to Bragg spacings of 39.2545, and two weak (110 and 200) reflections which correspond to Bragg spacings of 22.3405 and 19.3625 nm respectively. The presence of those peaks indicates that the material possess a long range order in hexagonal symmetry. Upon calcination in the air at 823 K for 10 h with heating rate 2^o/min, the intensity of the XRD peaks increased by about 2.7 times compared to the as-synthesized MCM-41 (Fig. 1A). These results reflect that the degree of ordering was dramatically improved by surfactant removal. In addition, after calcination 2θ of the peak shifts to a higher value, indicating contraction of the lattice. Contraction of the lattice is caused by the removal of template and subsequent condensation of silanol (Si-OH) groups.

The calcined-MCM-41 prepared with K_2SO_4 (Fig.1C) exhibits a sharp and strong (100) reflection which correspond to Bragg spacings of 39.3557, and four weak (110, 200, 220 and 300) reflections which correspond to Bragg spacings of 22.8589, 19.7043, 15.0826 and 13.3643_nm respectively. These are the indicative of well-defined on crystalinity (structure orderliness) of the material. This results agree with the experiment carried out by Stucky and Dougall (1990) who found that addition of K_2SO_4 in the case of SBA-15 synthesis stimulates the formation of single crystal materials instead of amorphous materials. This congruity indicated that addition of K_2SO_4 increased crystalinity in the synthesis of both MCM-41 and SBA-15 even used different surfactant type and media condition. In the case of SBA-15, Stucky and Dougall (1990) used non ionic triblock copolymer surfactants in acidic media, while in the case of MCM-41 the authors used cetyltrimetylamonium ion as surfactant in alkaline condition (pH=10.2). Stucky and Dougall (1990) stated that the addition of K_2SO_4 increased the interaction of silicate species with hydrophilic head groups of surfactants and the strong interaction of head groups with the silicate species resulting long-range ordered domain of silica-surfactant mesostructures. Finally, the long-range order favors the formation of mesoporous single crystals.

It also should be noted that the peaks pattern of MCM-41 prepared with K_2SO_4 (2θ□ = 2.2429, 3.8621 and 4.4808) shift to the lower angle compared to MCM-41 prepared without K_2SO_4 (2θ□ = 2.2488, 3.9519, and 4.5600), indicated that addition of K_2SO_4 in the synthesis of MCM-41 increased the pore size of product. This phenomenon can be explained by using the effects of anion on the solubility of surfactant. The effects of anion on the solubility of surfactant are separated into two categories known as the Hofmeister effect. The anions can be divided into two categories according to their effects on the solubility of both proteins and surfactants

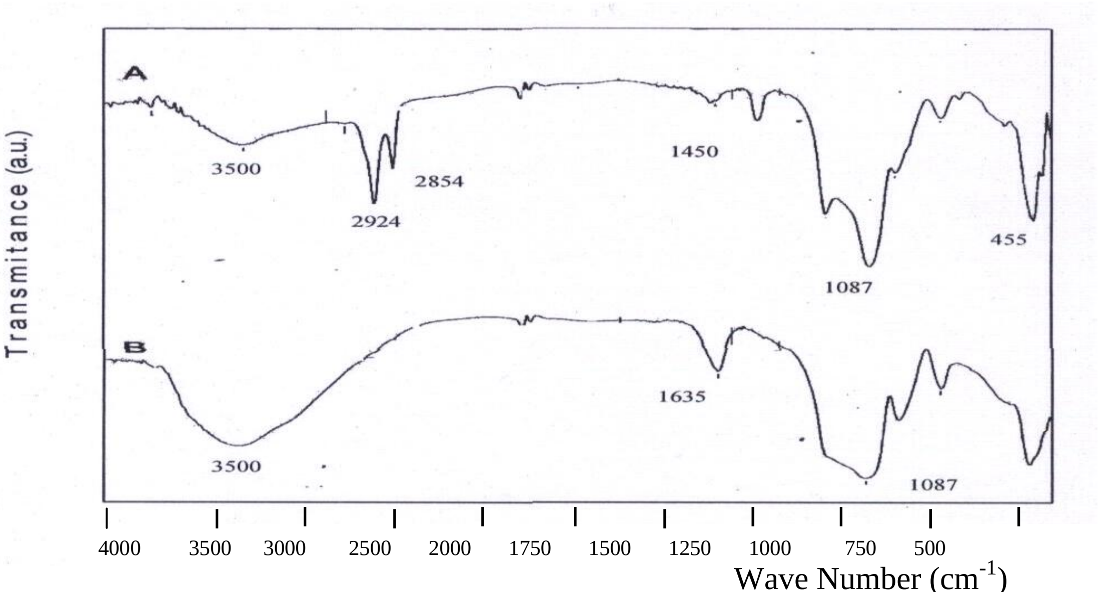


Fig. 2 FTIR spectra of MCM-41 prepared without K_2SO_4 :as-synthesized (A) and calcined (B)

(Hofmeister, 1888). Anions such as SO_4^{2-} and HPO_4^{2-} that decrease the solubility of the surfactants are known as "salting-out" and the others anions such as I^- and ClO_4^- that increase the solubility of the surfactants are known as "salting-in". The salting out effect of the anions decreases as the following (Hofmeister,1888) : $SO_4^{2-} > HPO_4^{2-} > CrO_4^{2-} > CO_3^{2-} > Cl^- > Br^- > NO_3^- > I^- > ClO_4^{2-} > SCN^-$. The salting-out anions generally have high charge and low polarizability. In the solution, they bound their hydration water strongly and they do not interact with other ions directly but via the coordinated water molecules. The decrease of surfactant solubility in water caused the thinner wallpore and larger pore. In this case the salting-out anions may be have alike function with organic molecules such as mesytilene (1,2,3 trimethyl benzene) that can be used to enlarge the pore size of mesoporous silicates MCM-41.

FTIR Spectra

Fig. 2 and Fig. 3 shows the FTIR spectra of MCM-41 prepared without and with K_2SO_4 respectively before and after calcination in the wavenumber region of 400-4000 cm^{-1}. No significant difference was observed in the structure of MCM-41 prepare [illegible] thout and with addition of K_2SO_4.

The as-synthesized MCM-41 sample on both figures shows well defined bands at about 2924 and 2854 cm^{-1} corresponding to *n*-C-H and *d*-C-H stretching vibration of surfactant molecules (Flanigen *et al*., 1971). The broad bands arround 3500 cm^{-1} attributted to the silanols at the surface and adsorbed water molecules, while deformational vibrations of adsorbed molecules cause the absorption bands at arround 1635 cm^{-1}. Based on the spectrum of calcined samples, there is an intense band at 1087 cm^{-1} which is assigned to the asymmetric Si-O-Si stretching vibration. The band at arround 964 cm^{-1} is associated with symmetric Si-O-H stretching vibration and the band at arround 455 cm^{-1} is assigned to a SiO_4 bending mode. For as-synthesized MCM-41 sample, a similar vibration band with low intensities are observed. The band at 717 cm^{-1} is associated with vibrations by the organic template (Flanigen *et al*., 1971). Those bands indicated that the Si-MCM-41 was successfully synthesized.

Nitrogen fisisorption.

Nitrogen adsorption-desorption isotherms of MCM-41 prepared without and with K_2SO_4 are presented in Fig. 4. According to IUPAC classification, the MCM-41 isotherms are classified as type IV, typically observed in mesoporous materials (Kresge *et al*., 1992). Both isotherms exhibit three stages; the first stage was a linear part going through the origin, which was caused by monolayer adsorption of N_2 on the walls of the mesopores ($P/P_0 < 0.25$). The second stage was at higher pressures, which the adsorption in mesopores leads to multilayer

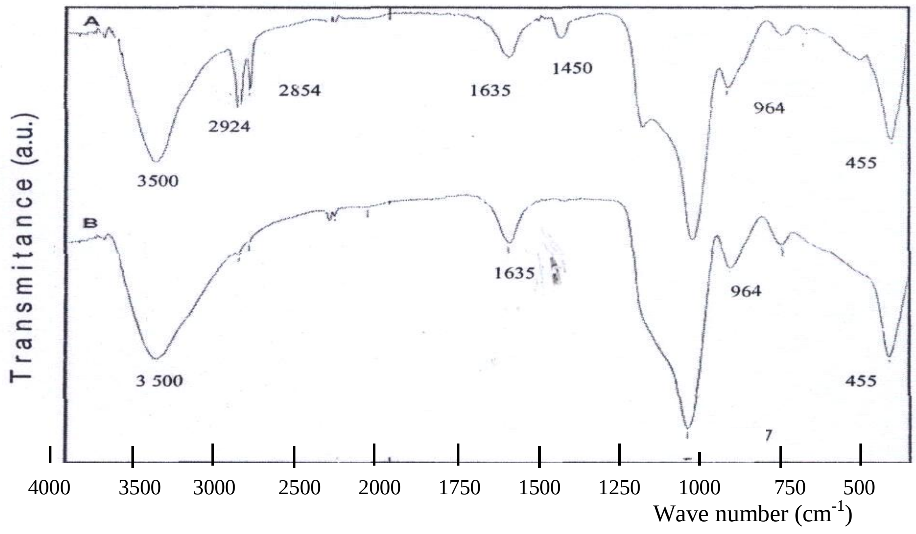


Fig. 3 FTIR spectra of MCM-41 prepared with K_2SO_4 addition
(A) as-synthesized and (B) calcined

formation until condensation takes place, giving a sharp increase in adsorption volume. According to Zhao *et al*. (1996) and Selvam *et al*. (2001), the P/P_0 value at which the inflection starts (at ca. $P/P_0 = 0.25$) is attributed to the commencement of pore filling from which the pore diameter can be roughly estimated. The sharpness in this step indicates the uniformity of the pore size distribution. As the mesopores are filled, the adsorption continues on the external surface. The third stage in the adsorption isotherm was an almost horizontal part after the relative pressure P/P_0 of ± 0.38, due to multi layer adsorption on the outer surface of the particles (Zhao *et al*., 1996 ; Selvam *et al*., 2001). The total mesopore volume was calculated from the amount of vapour adsorbed at $P/P_0 = 0.38$; assuming that MCM-41 were then filled with condensed liquid nitrogen in the normal liquid state.

In the case of MCM-41 synthesized without K_2SO_4, the hysteresis loop is observed at relative pressure P/P_0 of > 0.42. It is consistent with type H3 hysteresis and is characteristic of capillary condensation between lamellar particles or in solids containing slit-shaped mesopores. According to Gusev *et al*.(1996) there are two possible explanations: condensation of the nitrogen (a) in interparticle spaces and/or (b) in residual lamellar mesostructures which occur during the templating mechanism which forms the hexagonal structure. The absence of hysteresis loops in the capillary condensation range is an indication that the material possesses pores in a lower mesopore range (Mohammed, 2005).

According to Gregg and Sing (1984), nitrogen desorption on most adsorbents does not show capillary hysteresis at relative pressures below 0.41, which is believed to be determined by nitrogen's properties. In the case of MCM-41 synthesized with K_2SO_4, however, hysteresis in the region of 0.2-0.3 P/P_0 is detected. Gusev *et al.*(1996) stated that hysteresis in the region of 0.2-0.3 P/P_0 may be indicative of some change in size and/or shape of the pore structure. The hysteresis loop at lower pressure can be accounted for by a phase transformation within these pores. At pressures above 0.42 there is a second hysteresis loop for MCM-41 synthesized with K_2SO_4. A bidisperse adsorbent structure can be inferred from such an adsorption isotherm.

The pore properties of the sample prepared without and with the addition of K_2SO_4 were presented in Table 1.

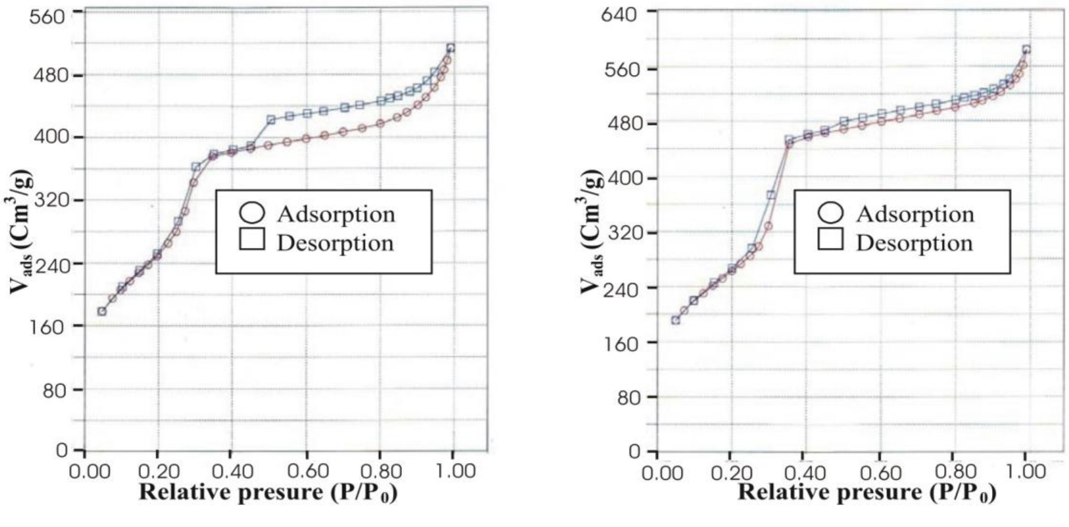


Fig. 4 Nitrogen adsorption-desorption isotherms of MCM-41: (A) prepared without K_2SO and (B) prepared with K_2SO_4

Table 1 The pore properties of the sample

Sample	Specific surface area, S_{BET}, (m^2/g)	Mean pore diameter, d_{mp} (nm)	Latice parameter, a_o (nm)	Pore walls thickness, W_t (nm)
MCM-41 prepared without K_2SO_4	946.607	3.357	4.533	1.176
MCM-41 prepared with K_2SO_4	972.812	3.714	4.544	0.830

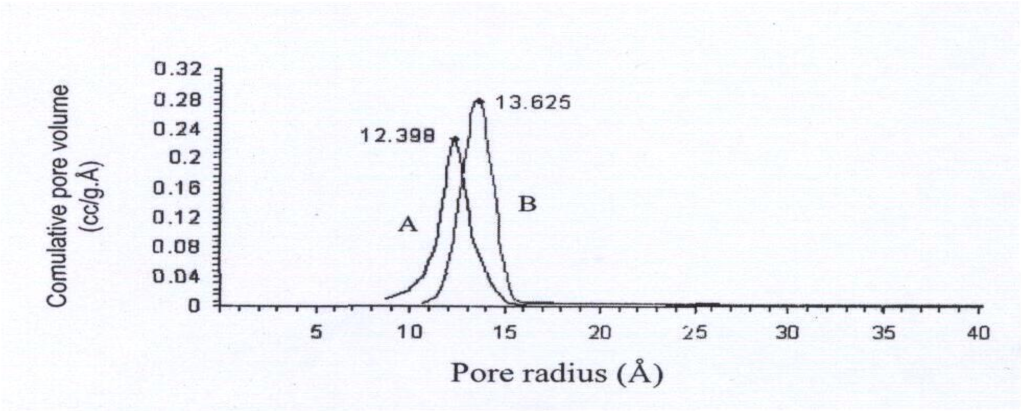


Fig. 5 Pore size distribution of MCM-41 prepared without K_2SO_4 (A) and with K_2SO_4 (B)

The specific surface area (S_{BET}) was determined from the linear section of the BET plot. The mean pore diameter (d_{mp}) was calculated from the N_2 adsorption data, using the BJH (Barrett-Joyner-Halenda) method. The latice parameters (a_0) was calculated by formula : $a_0 = 2d_{100}/\sqrt{3}$, here d_{100} is the interplanar spacing corresponding to the (100) Bragg reflection. The wall thickness (W_t) is calculated by substracting the pore diameter from the latice parameter (a_0). Accorrding to Table 1, the addition of K_2SO_4 in the synthesis of MCM-41 increased the specific surface area, mean pore diameter, and latice parameter ; but decreased the wall thickness.

The pore homogenity was investigated by calculation of pore distribution using BJH (Barrett-Joyner-Halenda) method, presented in the Fig. 5. It can be seen that both curves have a sharp peak. This indicated that both samples has a good homogenity in pore size. The sample prepared without K_2SO_4 has a maximum pore size about 1.2398 nm, while that of with K_2SO_4 about 1.3625 nm. The difference between average pore radius and maximum of pore size by the BJH model caused by the existence of large pore in the small quantity. This contributes to the increasing of average pore radius

4. CONCLUSIONS

Mesoporous silicate MCM-41 samples with ordered hexagonal structure have been prepared hydrothermally using CTMAB surfactant as the template with and without the addition of K_2SO_4. The addition of K_2SO_4 increased the crystalinity. The MCM-41 prepared with K_2SO_4 has a higher specific BET surface area of 972.812 m^2 g^{-1} compared to the MCM-41 prepared without K_2SO_4 (i.e., 946.607 m^2 g^{-1}), higher mean pore diameter of 3.714 nm compared to the MCM-41 prepared without K_2SO_4 (i.e., 3.357 nm), and thinner pore walls of 0.830 nm compared to the MCM-41 prepared without K_2SO_4 (i.e. 1.176 nm).

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