

## EFFECT OF AGING TIME TOWARD CRYSTALLINITY OF PRODUCTS IN SYNTHESIS OF MESOPOROUS SILICATES MCM-41

Suyanta<sup>1,2,\*</sup>, Narsito<sup>2</sup>, Endang Tri Wahyuni<sup>2</sup>, Triyono<sup>2</sup>, and Sutarno<sup>2</sup>

<sup>1</sup>Postgraduate Student of Chemistry Department, Faculty of Mathematic and Natural Sciences, Universitas Gadjah Mada

<sup>2</sup>Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Kotak Pos 21 Bls Yogyakarta, Indonesia 55281

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### ABSTRACT

Researches about the effects of aging time toward crystallinity of products in the synthesis of mesoporous silicates MCM-41 have been done. MCM-41 was synthesized by hydrothermal treatment to the mixture of sodium silicate, sodium hydroxide, cetyltrimethylammoniumbromide (CTMAB) and aquadest in the molar ratio of  $8\text{Na}_2\text{SiO}_3 : \text{CTMAB} : \text{NaOH} : 400\text{H}_2\text{O}$ . Hydrothermal treatment was carried out at  $110\text{ }^\circ\text{C}$  in a teflon-lined stainless steel autoclave heated in the oven, with variation of aging time, i.e.: 4, 8, 12, 16, 24, 36, 48, and 72 h respectively. The solid phase were filtered, then washed with deionised water, and dried in the oven at  $100\text{ }^\circ\text{C}$  for 2 h. The surfactant CTMAB was removed by calcinations at  $550\text{ }^\circ\text{C}$  for 10 h with heating rate  $2\text{ }^\circ\text{C}/\text{min}$ . The as-synthesized and calcined powders were characterized by using FTIR spectroscopy and X-ray diffraction method. The relative crystallinity of products was evaluated based on the intensity of  $d_{100}$  peaks. The best product was characterized by using  $\text{N}_2$  physisorption method in order to determine the specific surface area, mean pore diameter, lattice parameter, and pore walls thickness. It was concluded that the relative crystallinity of the products was sensitively influenced by the aging time. The highest relative crystallinity was achieved when used 36 h of aging time in hydrothermal treatment. In this optimum condition the product has  $946.607\text{ m}^2\text{g}^{-1}$  of specific surface area, 3.357 nm of mean pore diameter, 4.533 nm of lattice parameter, and 1.176 nm of pore walls thickness.

**Keywords:** MCM-41, crystallinity, aging time

### INTRODUCTION

The discovery of M41S family by scientists at the Mobil Co.[1-4] led to a great focusing of new possibilities of the mesoporous molecular sieves, with uniform pore sizes diameters ranging 2-10 nm, as adsorbents [5-6] and catalysts [7-8] for large species that did not enter conventional zeolite pores. These materials also have potential application as sensors [9-10], biomedicine [11-12], and optoelectronic devices [13] such as lasers, switches, transistors and information storage processes. The advantages of ordered silicate mesoporous materials for kinds of applications include a regular array of uniform pores, controllable pore size, and the ability to functionalize the surface for particular absorptions. Furthermore, MCM-41 has a rigid structure and so avoids the swelling problems encountered with some other materials. Silicates mesoporous materials have been prepared with specific surface areas of approximately  $1000\text{ m}^2\text{g}^{-1}$ . One member of this family, MCM-41, is reported as having a hexagonal array of uniform pores [1].

The crucial problem of MCM-41 material is its sensitivity to the boiling water, which can easily destroys its structure [14-15]. The material also showed

disintegration of its characteristic X-ray powder diffraction (XRD) pattern during experiments in aqueous solutions. The poor hydrothermal stability of the mesoporous structures at low temperature can be a serious limitation on applications of these materials. Based on viewpoints, the synthesis of mesoporous silicates which exhibits good hydrothermal stability is one of the most important requirements [16-17]. This is also essential to ensure successful post synthesis modification such as grafting and ion exchange, because such processes are generally carried out in aqueous solution.

The origins of the poor stability of MCM-41 are their thin pore walls of ca. 0.5 nm which are also amorphous [1]. Amorphous frameworks of the mesoporous materials are believed to be easily attacked by hydrolysis, compared with completely cross-linked aluminosilicates frameworks in zeolites. The hydrolysis seems to result in the structure disintegration through opening of Si-O-Si linkage in the structure [15]. Furthermore, Mori et al. [16] reported that the surface crystallinity of the sample plays a pivotal role in protecting the sample against attack by water.

\* Corresponding author. Tel/Fax : +62-85729639243  
Email address : suyantakimiaugm@yahoo.co.id

In the synthesis of MCM-41, the surfactant molecules interact with silicates polyanions leads under finite conditions to the formation of supramolecular particles which are condensed from solution and form a mesostructured mesophase arranged according to the laws of a liquid crystal medium. After hydrothermal treatment in autoclave and subsequent calcinations in air for removing of organic template, a mesostructured porous material is formed [17]. During the hydrothermal treatment, cross-linking of polyanions in a wall which is the lengthiest process occurs [17], therefore the authors estimated that the aging time of hydrothermal treatment influenced the crystallinity of pore walls.

From such viewpoints, here the authors report the effects of aging time toward crystallinity of product in the synthesis of mesoporous silicates MCM-41. We concluded that the highest relative crystallinity was achieved when the gel was aged for 36 h. In this optimum condition the product has  $0.794 \text{ cm}^3\text{g}^{-1}$  of pore volume,  $946.607 \text{ m}^2\text{g}^{-1}$  of surface area,  $3.714 \text{ nm}$  of pore diameter and  $1.176 \text{ nm}$  of pore walls thickness.

## EXPERIMENTAL SECTION

### Materials

The following materials were used for the preparation of the mesoporous silicates MCM-41: cetyltrimethylammonium bromide (CTAB; Aldrich),  $\text{H}_2\text{SO}_4$  (E. Merck), sodium silicate (27 wt %  $\text{SiO}_2$ , 8% wt  $\text{Na}_2\text{O}$ , Aldrich), sodium hydroxide (E. Merck), and distilled water (Lab. of analytical Chemistry of Universitas Gadjah Mada).

### Instrumentation

The equipments used in this research included chemical laboratory glassware, 3X Shimadzu X-ray diffractometer (XRD) with  $\text{Cu-K}\alpha$  radiation, and PC-8201 Shimadzu Fourier Transform Infra Red (FTIR) Spectrometer which are available at Universitas Gadjah Mada, and NOVA Ver. 2.00 sorptiometer which is available at State Islamic University Yogyakarta.

### Procedure

#### Synthesis of MCM-41

MCM-41 was synthesized 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  $\text{H}_2\text{SO}_4$  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

$8\text{Na}_2\text{SiO}_3$  : CTMAB : NaOH:  $400\text{H}_2\text{O}$ . The silica-surfactant gel found was aged at  $110^\circ\text{C}$  in a teflon-lined stainless steel autoclave for 4 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 open air at  $90^\circ\text{C}$ . Surfactant was removed by calcining the as-synthesized product at  $550^\circ\text{C}$  for 10 h with heating rate of  $2^\circ/\text{min}$ . In order to investigate the effect of aging time, the same procedure was carried out, with variation of aging time, i.e.: 8, 12, 16, 24, 36, 48, and 72 h.

### Characterization

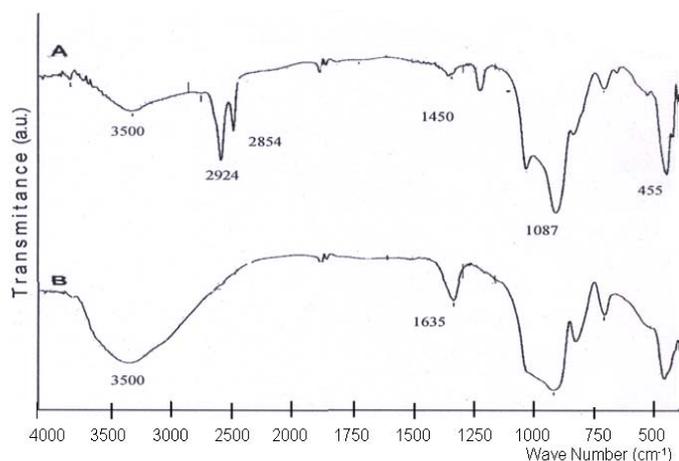
Characterization of the powder phases and determination of the phase purities in the calcined MCM-41 samples were carried out by XRD (Shimadzu XD-3H) using nickel-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ). The samples were scanned from  $1$  to  $10^\circ$  ( $2\theta$ ), where  $\theta$  is the angle of incidence of the X-ray beam to the plane. The lattice parameters ( $a_0$ ) were 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 lattice parameter ( $a_0$ ).

## RESULT AND DISCUSSION

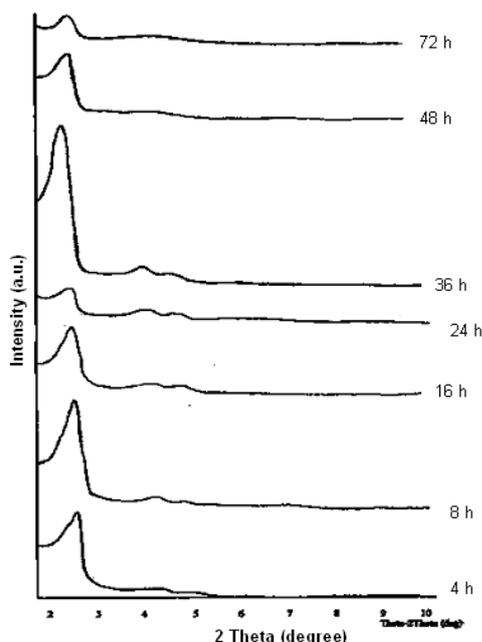
### Characterization with FTIR Method

Fig. 1 shows the FTIR spectra of as-synthesized and calcined MCM-41 in the wave number region of  $400\text{-}4000 \text{ cm}^{-1}$ . Both of spectra exhibit sharp bands around  $1080 \text{ cm}^{-1}$  and  $1226 \text{ cm}^{-1}$  of wave number which characteristic for vibration of symmetric and asymmetric stretching O-Si-O bridge respectively [18]. These bridges are the part of silicates polymer formed in the hydrothermal treatment [17]. A broad absorption band in the hydroxyl region between  $3000$  and  $3700 \text{ cm}^{-1}$  with a maximum in the range of  $3450\text{-}3500 \text{ cm}^{-1}$  was observed in both cases. This band associated with stretching vibration of Si-O-H group in the framework perturbed by physically adsorbed water molecules [18]. Do to emerge of a lot of Si-O-H groups after calcinations; the intensity of those absorption bands was significantly increased.

The weak band at  $956\text{-}970 \text{ cm}^{-1}$  of wave number assigned the stretching of Si-O<sup>-</sup> group, while the strong



**Fig 1.** FTIR Spectra of as-synthesized (A) and calcined (B) MCM-41



**Fig 2.** Diffractogram of MCM-41 synthesized with several of aging time

band at  $450\text{ cm}^{-1}$  related to bending vibration of Si-O group [19]. An absorption bands at  $2924$  and  $2854\text{ cm}^{-1}$  assigned asymmetric and symmetric stretching vibration of  $-\text{CH}_2-$ , respectively; whereas absorption around  $1481\text{ cm}^{-1}$  attributed scissoring vibration of  $-\text{CH}_2-$  as well as asymmetric bending vibration of  $\text{CH}_3-\text{N}^+$ . Those various C-H vibrations due to the presence of the organic surfactant molecules appeared in the as-synthesized sample disappeared after the removal of the surfactant. This case attributed to the perfectly combustion of surfactant in the calcinations treatment.

### The Effect of Aging Time toward Crystallinity of Product

The effect of aging time toward crystallinity of MCM-41 was examined by analyze the diffractogram pattern of sample as presented in Fig. 2. It is seen that all of diffractogram display the main peak at  $2-3^\circ$  of  $2\theta$  which can be indexed according to the plane of  $d_{100}$  hexagonal lattice, assigned the ordered mesoporous phase's characteristic of mesostructured MCM-41 type materials. In addition, there are other weak peaks at  $4-7^\circ$  of  $2\theta$ , according to the planes of  $d_{110}$ ,  $d_{200}$ ,  $d_{210}$  respectively. The main peak at  $2-3^\circ$  of  $2\theta$  assigned the hexagonal structure of MCM-41, while the other weak peaks at  $4-7^\circ$  of  $2\theta$  attributed the highly ordered of the structure [1,20].

The intensity of  $d_{100}$  peak of sample in this research is sensitively influenced by the aging time. As shown in Fig. 2, at aging time lower than 8 h, the intensity becomes higher as the aging time increases. At aging time 8-24 h, the intensity becomes lower as the aging time increases. At aging time 24-36 h, the intensity becomes higher as the aging time increases, and then the intensity decreases again at aging time  $> 36$  h. The relative crystallinity of the sample can be measured based on the relative intensity of  $d_{100}$  peak [16] as presented quantitatively in Table 1.

The increase of crystallinity occurred when the aging time was added from 4 h (51.02 of relative crystallinity) becomes 8 h (75.72 of relative crystallinity). On the contrary, the crystallinity of product decreased when the aging time was added becomes 12 h (51.08 of relative crystallinity) as well as 24 h (26.35 of relative crystallinity). But, the increase of crystallinity occurred again when the gel was aged for 36 h. It seems 36 h is the optimal of aging time, because the crystallinity of product precisely decreased when the gel was aged for 48 as well as 72 h. When the gel was aged for 36 h, the highly ordered structure of MCM-41 materials was found. This case was assigned by emerge of high intensity of main peaks ( $d_{100}$ ) as well as two weak peaks ( $d_{110}$  and  $d_{200}$ ). The high intensity of diffractogram peak indicated that there are many identical crystalline plane formed.

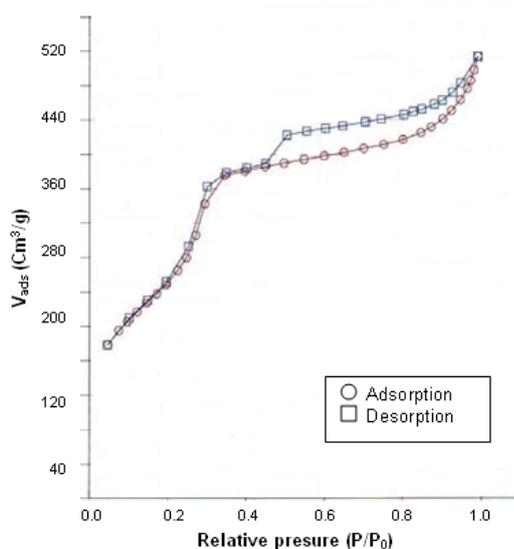
The plane of  $d_{100}$  has actually been formed when the gel was aged for 4 h, this fact was assigned by emerge of peak at  $2-3^\circ$  of  $2\theta$ . When the gel was aged for 8 h, intensity of those peak increases indicated the formation of more  $d_{100}$  plane. This case related to the more ordered hexagonal arrangement due to more completed condensation of silicate and cationic micelles. Nevertheless, increasing aging time furthermore becomes 24 h caused the adverse effect on intensity of  $d_{100}$  peak. It seems, the siloxane (Si-O-Si) groups formed in the previously process can

**Table 1** The influence of aging time toward the interplanar spacing, lattice parameter and relative crystallinity

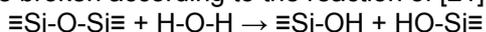
Aging time (h)	Interplanar spacing, $d_{100}$ (Å)	Lattice parameter, $a_0^*$ (Å)	Total Intensity (Count)	Relative crystallinity** (%)
4	36.00	41.57	1696	51.02
8	36.04	41.61	2517	75.72
12	35.83	41.37	1698	51.08
24	36.07	41.65	876	26.35
36	39.25	45.33	3324	100
48	37.36	43.13	1328	39.95
72	36.48	42.12	762	22.92

\*)  $a_0 = 2d_{100}/\sqrt{3}$ 

\*\*) compared to the sample which has highest of crystallinity

**Fig 3.** Nitrogen adsorption-desorption isotherms of MCM-41 prepared with 36 h of hydrothermal duration

stimulate the formation of hydrogen bonding with water molecules. Finally, those siloxane groups were hydrolyzed and a part of the well-organized hexagonal structure broken according to the reaction of [21]:



After the depolymerization, the hydrolyzed silicates seems turn to interact with remain rode micell, leads the formation of hexagonal liquid crystalline phase. This interpretation was based on the high intensity of  $d_{100}$  peak when hydrothermal treatment was carried out for 36 h. In addition, the  $d_{100}$  peak is now significantly shifted to the lower of  $2\theta$ ; this is an indication of the increasing of pore diameter [14]. If aging time >36 h, however, the crystallinity of product was poor, matched with the low intensity of  $d_{100}$  peak. It means that the longer hydrothermal treatment leads to the flaw of liquid crystal structure. This was agreed with the low hydrothermal stability of MCM-41 as reported by other previous researchers [15].

Diffraction peaks of the sample synthesized with 36 h of aging time in this research exhibits three peaks which can be indexed as 100, 110, and 200 plane

respectively ; and 45.33 Å of lattice parameter,  $a_0$  (calculated by formula :  $a_0 = 2d_{100}/\sqrt{3}$ ). It was in good agreement with MCM-41 diffractogram reported by some previous researchers. The diffractogram of MCM-41 publicized by Kresge et al. [1] displayed 4 peaks with 100, 110, 200, and 210 of Miller Index and 40 Å of lattice parameter. Whereas Beck et al. [20] reported MCM-41 diffractogram with 100, 110, 200, and 210 of Miller Index and 45 Å of lattice parameter.

### Nitrogen Physisorption

Fig. 3 shows the nitrogen adsorption-desorption isotherms of sample prepared with 36 h of aging time. According to IUPAC classification, type IV isotherms are obtained for this material. The pore filling (by capillary condensation) for that sample is restricted to a narrow range of  $P/P_0 = 0.3-0.4$ , which is a typical feature for mesoporous MCM-41 materials [1].

This isotherm exhibits three stages; the first stage was a linear part going through the origin, which was caused by monolayer absorption of  $\text{N}_2$  on the walls of the mesopores ( $P/P_0 < 0.25$ ). The second stage was at higher pressures, which the absorption in mesopores leads to multilayer formation until condensation takes place, giving a sharp increase in absorption volume. According to Zhao et al. [22] and Selvam et al. [23], 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 absorption continues on the external surface. The third stage in the absorption isotherm was an almost horizontal part after the relative pressure  $P/P_0$  of  $\pm 0.38$ , due to multi layer absorption on the outer surface of the particles [1-2]. The total mesopore volume was calculated from the amount of vapor adsorbed at  $P/P_0 = 0.38$ ; assuming that MCM-41 were then filled with condensed liquid nitrogen in the normal liquid state.

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. [24] 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 [25].

The pore properties of the sample prepared with 36 h of aging time is as bellow: 946.607 m<sup>2</sup>/g of specific surface area ( $S_{\text{BET}}$ ), 3.357 nm of mean pore diameter ( $d_{\text{mp}}$ ), 4.533 nm of lattice parameter ( $a_0$ ), and 1.176 nm of pore walls thickness ( $W_i$ ). The specific surface area was determined from the linear section of the BET plot. The mean pore diameter was calculated from the N<sub>2</sub> absorption data, using the BJH (Barrett-Joyner-Halenda) method. The wall thickness was calculated by subtracting the pore diameter from the lattice parameter ( $a_0$ ).

## CONCLUSION

The crystallinity of MCM-41 produced in this research is sensitively influenced by the aging time. The highest relative crystallinity was achieved when hydrothermal treatment carried out for 36 h. In this optimum condition the product has 0.794 cm<sup>3</sup>g<sup>-1</sup> of pore volume, 946.607 m<sup>2</sup>g<sup>-1</sup> of surface area, 3.714 nm of pore diameter and 1.176 nm of pore walls thickness.

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