

SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS ALUMINOSILICATES AI-MCM-41 AND INVESTIGATION OF ITS THERMAL, HYDROTHERMAL AND ACIDITY STABILITY

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ABSTRACT

The synthesis and characterization of mesoporous aluminosilicates AI-MCM-41 and the investigation of its thermal, hydrothermal and acidity stability have been done. AI-MCM-41 were synthesized by hydrothermal method to the mixture of sodium silicate as Si source, aluminium hydroxide as Al source, sodium hydroxide as a solvent, and cetyltrimethylammoniumbromide (CTAB) as structure directing agent. The reaction were carried out in alkaline condition (pH = 10.2) at 383 K for about 24 h, followed by calcination at 723 K for about 10 h. The synthesized crystals were characterized using FTIR spectroscopy, X-ray diffraction and N₂ fisisorption methods. The result showed that AI-MCM-41 sample with hexagonal structure was formed, it has a good in thermal and acid stability, but the structure disintegrated in an alkaline solution (pH = 10) and in boiled water.

Keywords: synthesis, characterization, AI-MCM-41, stability

INTRODUCTION

A wide range of liquid-phase industrial reactions rely on the use of minerals acids (such as: H₂SO₄, HF, H₃PO₄, HNO₃, etc.) as a catalyst. The use of minerals acids, however, needs an aqueous quenching and a neutralization steps to remove the acid in the final isolation of product, resulting in enormous quantities of hazardous waste. This fact is driving the industry toward the implementation of innovative "clean technology" including the use of alternative heterogeneously catalyzed processes [1].

Zeolites are widely used as heterogeneous catalysts within the petrochemical industry; unfortunately the use of zeolites is restricted by their small pore sizes of around < 8 Å, which makes them unsuitable for reactions involving bulky substrates. The discovery of the M41S family of mesoporous molecular sieves (MCM-41, MCM-48 and MCM-50) offering pore sizes in the range 20–100 Å which opens up new possibilities for liquid-phase acid catalysis [1].

MCM-41 is a commonly used as mesoporous material [2]. It is usually synthesized by a templating mechanism. Through phase separation, a continuous network surrounding template molecules is formed first. Then, by combustion and/or extraction, the template is removed, leaving the empty space inside the network material as mesopores [3]. MCM-41 having well-defined structure symmetry are featured with tuneable pore diameters, high surface areas, and large pore volumes, enabling themselves to be promising candidates used in

catalysis, separation, adsorption, sensing, nanostructure templating, and immobilization of biomolecules [4].

Purely siliceous Si-MCM-41 which is composed of [SiO₄] tetrahedrons as building blocks does not possess acidity [5]. The incorporation of different elements within the silica framework of MCM-41 has been implemented in order to increase the acidity, ion exchange capacity and specific catalytic activity of the mesoporous silica molecular sieves [6]. Incorporation of Al into the mesoporous structure led aluminosilicates AI-MCM-41, in which some of [SiO₄] tetrahedrons are replaced by [AlO₄] tetrahedrons, resulting in a negative framework charge. This negative charge inside the structure is compensated by counter ions (such as H⁺), generated the Brønstead-acidity [5].

The synthesis and characterization of Al incorporated mesoporous materials has been studied [7]. It is well known that the preparation of Al-containing mesostructures consists of two main methods. One is direct incorporation of Al into the framework via homogeneous self-assembly and condensation procedures, another is post-synthetic treatment of pre-existing silica mesostructures with various aluminating agents.

The scope of the current work was to investigate the hydrothermal synthesis of AI-MCM-41 via homogeneous self-assembly and condensation procedures, characterize the product, and investigate the thermal, hydrothermal and acid stability.

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EXPERIMENTAL SECTION

Materials

The following materials were used for the preparation of the mesoporous aluminosilicates Al-MCM-41: cetyltrimethylammonium bromide (CTAB; Aldrich), H₂SO₄ (E. Merck), sodium silicate (27 wt % SiO₂, 8% wt Na₂O, Aldrich), sodium hydroxide (E. Merck), aluminium hydroxide (E. Merck) and distilled water (Lab. of analytical Chemistry Universitas Gadjah Mada).

Instrumentation

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

Procedure

Synthesis of Al-MCM-41

The Al-MCM-41 was synthesized by direct incorporation of Al into the framework via homogeneous self-assembly and condensation procedures according to Bordoloi et al. [7] with some modification, as follows: (i) 8.67 g of CTAB 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 with vigorous stirring. After stirring for 30 min the mixture of 0.114 g of aluminium hydroxide, 0.0585 g of NaOH and 2 g of distilled water was added to the first mixture and the resulting gel was stirred for 15 min. The solution of 0.6 g of conc. H₂SO₄ in 2.5 g of water was then added to the mixture in order to reduce the pH become to ± 10.2 . The gel was then transferred into 150 cm³ Teflon-lined stainless steel autoclave and heated at 383 K for 24 h. After cooling into the room temperature, the solid phase was recovered by filtration on a Buchner funnel, washed with distilled water, and dried in air at 363 K. Surfactant was removed by calcining the as-synthesized Al-MCM-41 at 813 K for 10 h with the heating rate of 2 deg/min.

Characterization

Characterization of the as-synthesized and calcined Al-MCM-41 samples was carried out by XRD (Shimadzu XD-3H) using nickel-filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). 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 pore properties of

calcined Al-MCM-41 were analyzed using a NOVA Ver. 2.00 sorptometer.

Investigation of the thermal, hydrothermal and acidity stability

In order to investigate the thermal stability of calcined Al-MCM-41, 1 g of sample was heated at 473 K for 6 h, and then the crystallinity was measured by using X-ray diffraction method based on the intensity of d₁₀₀ plane. Those procedures were repeated at 673 K. In order to investigate the hydrothermal stability of calcined Al-MCM-41, 1 g of sample was reflux in 50 mL of boiled water for 4 h. After cooling at the room temperature, the solid phase was recovered by filtration on a Buchner funnel, washed with distilled water, and immediately dried in the oven at 383 K for 2 h. Then the crystallinity was measured by using X-ray diffraction method based on the intensity of d₁₀₀ plane. In the study of acidity stability, 1 g of Al-MCM-41 was added into 50 mL of HCl solution having pH of 1, then stirred for 2 h. The solid phase was recovered by filtration on a Buchner funnel, washed with distilled water, and dried in the air at room temperature. The crystallinity was monitored by using X-ray diffraction method, based on the intensity of d₁₀₀ plane. Those procedures were repeated at pH of 6 and 10 respectively.

RESULT AND DISCUSSION

Characterization

Fig. 1(A) showed the XRD powder patterns of as-synthesized Al-MCM-41 samples. The structure of the as-synthesized Al-MCM-41 material was confirmed by observing a typical peak with a very prominent (100) reflection at low angle ($2\theta = 2-3^\circ$).

The presence of this peak indicates that the material possesses a long range order in hexagonal symmetry [8-9]. According to Fig. 1(B), upon calcinations at 813 K for 10 h with the heating rate of 2 deg/min, the intensity of the XRD peaks increased by about 3 times, in addition there are some other weak peaks at more higher angle ($2\theta = 3-6^\circ$). These results reflect that the degree of ordering was dramatically improved by removal of surfactant. It is important to note the shift of the reflection maximum in the patterns of these two samples. The as-synthesized Al-MCM-41 has a spacing of 37 Å, which upon calcinations decreased to 35.2 Å. This decreasing in the d spacing value is due to the contraction of the pore structure, which is taking place during the process of calcinations. No apparent peaks at a high angle of 30-50° were observed (not shown here) indicating that no separate phase of aluminium oxide was formed during the synthesis and calcinations processes.

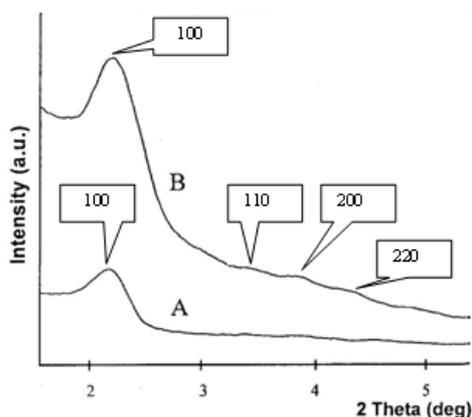


Fig 1. XRD powder patterns of: (A) as-synthesized and (B) calcined Al-MCM-41

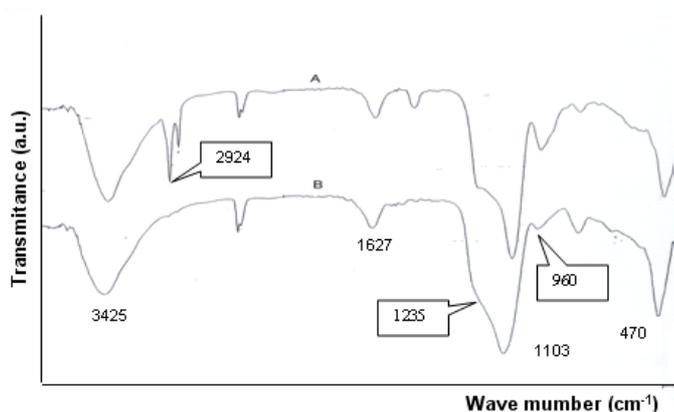


Fig 2. FTIR spectra of (A) as-synthesized and (B) calcined Al-MCM-41

Infrared spectroscopy was used extensively for characterization of the aluminosilicate. Fig. 2 showed the FTIR spectra of as-synthesized and calcined Al-MCM-41 in the wave number region of 400-4000 cm^{-1} . The as-synthesized Al-MCM-41 sample exhibits absorption bands around 2924 and 2854 cm^{-1} . According to Flanigen et al. [10], those peaks were corresponding to *n*-C-H and *d*-C-H stretching vibration of surfactant molecules. The broad bands around 3425 cm^{-1} may be attributed to the silanols at the surface and adsorbed water molecules, while deformational vibrations of adsorbed molecules cause the adsorption bands at around 1627 cm^{-1} . Based on the spectra of calcined Al-MCM-41 samples, there are bands at 1103 cm^{-1} and shoulder at about 1235 cm^{-1} which are assigned to the asymmetric Si-O-T (T= Si or Al) stretching vibration. The band at about 964 cm^{-1} is associated with symmetric Si-O-M (M = H or Al) stretching and the band around 470 cm^{-1} is assigned to a SiO_4 bending mode. The stretching vibration of silanol group took place at 964 cm^{-1} .

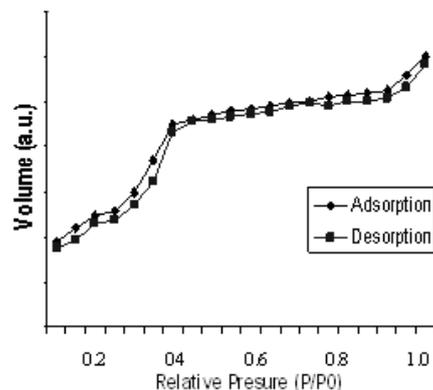


Fig 3. Nitrogen adsorption-desorption isotherms of calcined Al-MCM-41

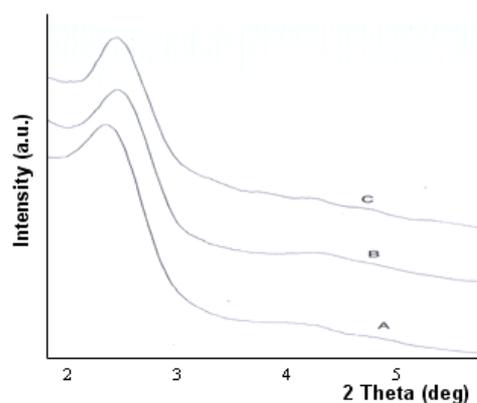


Fig 4. The effects of heating to the crystallinity of Al-MCM-41: (A) original sample, (B) heated sample at 473 K for 6 h, (C) heated sample at 673 K for 6 h

Nitrogen adsorption isotherms of Al-MCM-41 are presented in Fig. 3 at $P/P_0 = 0.30$, the accessible pores are totally filled with adsorbate and the isotherm reaches a plateau that remains fairly invariant as P/P_0 approaches 0.38-0.84. The nitrogen sorption isotherms showed that the Al-MCM-41 structure was of type IV; typically observed in mesoporous materials [11]. The total mesopore volume was calculated from the amount of vapor adsorbed at $P/P_0 = 0.20$; assuming that Al-MCM-41 was then filled with condensed liquid nitrogen in the normal liquid state. Adsorption at low pressure ($P/P_0 < 0.20$) is accounted for by monolayer-multilayer adsorption of N_2 on the wall of mesopores. The Fig. 3 showed a sharp step capillary condensation in mesopores region (P/P_0) = 0.22 - 0.38, suggesting a narrow pore distribution.

The stability of Al-MCM-41

Fig. 4 illustrated the effects of heating temperature in the air for 6 h on the structure of Al-MCM-41. The original calcined sample, the heated sample

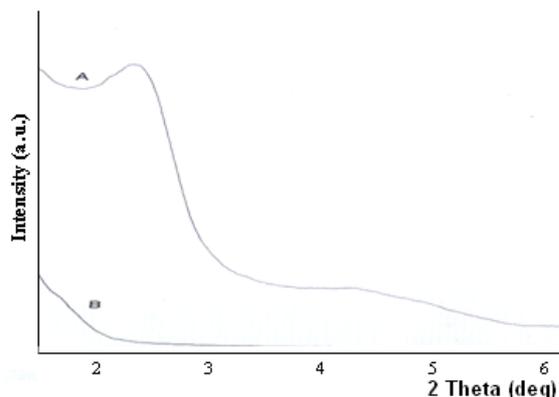


Fig 5. The effects of hydrothermal in the boiled water to the crystallinity of Al-MCM-41: (A) original sample, (B) heated sample in the boiled water for 4 h

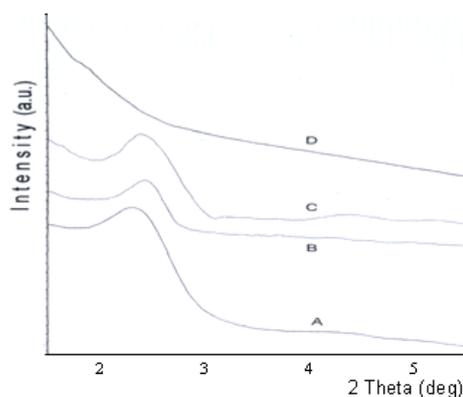
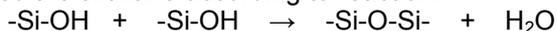


Fig 6. The effects of solution pH to the crystallinity of Al-MCM-41: (A) original sample, (B) after treatment with solution having pH of 1, (C) after treatment with solution having pH of 6, (D) after treatment with solution having pH of 10

at 473 K and the heated sample at 673 K for 6 h were presented in Fig. of 4(A), 4(B) and 4(C) respectively.

All of diffractogram in Fig. 4 are very similar, indicating that the structure of AlMCM-41 was maintained during the heating. The slight increasing in the peak intensity of d_{100} plane for the heated sample at 673 K may be caused by condensation of silanol groups formed the siloxane according to reaction:



The thermal stability of Al-MCM-41 was consistent with the experiment done by amount of researchers in the case of pure silica Si-MCM-41. Chen et al. [12] reported that Si-MCM-41 could be heated to 1123 K before structural collapsed began. Kim et al. [13] showed that the powder X-ray diffraction pattern and BET surface area were not affected significantly by heating to 1170 K in air and O_2 containing water vapor up to 2.3 kPa. More recently, Kim and Ryoo [14] reported that the mesoporous structure constructed with a pure silica

framework was stable in 100% steam flow under atmospheric pressure at 700 K.

Fig. 5 illustrated the effects of heating in the boiled water to the structure of Al-MCM-41. The diffractogram of original calcined Al-MCM-41 was very different compared to the sample heated in the boiled water for 4 h, indicating the disintegration of the Al-MCM-41 structure. It means that the sample has a poor in hydrothermal stability. Disintegration of the Al-MCM-41 structure may be caused by the hydrolysis of silicate framework according to the reaction:



The poor hydrothermal stability of Al-MCM-41 was consistent with the experiment done by Ryoo and Jun [15] in the case of Si-MCM-41, who reported that the Si-MCM-41 structure prepared from three different procedures lost after heating in boiled water for 12 h.

Fig. 6 illustrated the effects of pH on the structure of Al-MCM-41. The Fig. 6 showed that AlMCM-41 structure was stable in the acidic aqueous solutions (pH of 1 – 6) at room temperature for 2 h; in the alkaline condition (pH of 10), however, the structure disintegration occurred seriously. This behavior could be understood based on the acid properties of silanol groups. In the acidic conditions, protonation will be occurred without damaged the linkage on the silanol groups, but in the alkaline conditions the silanol groups seemed were hydrolyzed.

CONCLUSION

Mesoporous aluminosilicate Al-MCM-41 sample with ordered hexagonal structure had been prepared hydrothermally using CTAB surfactant as the template. The materials exhibit good in thermal and acidity stability, but its structure disintegrated in the alkaline solution at room temperature and in boiled water.

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