Utilization of Diatomite as Silica Source for the Synthesis of Ordered Mesoporous Silica Materials

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Abstract

Mesoporous silica is an important material which has wide range of industrial applications. Currently, it is produced from precursors that are costly. This paper presents the preparation of mesoporous silica MCM-41 materials using diatomite as inexpensive silica source and quaternary ammonium salt as structure directing agent by sol-gel method. The obtained samples were characterized by x-ray powder diffraction, N_2 physisorption, field emission scanning electron microscopy and transmission electron microscopy. The results indicated that as-synthesized MCM-41 possessed well-ordered hexagonal structure, monodispersed spheres particle, high surface area and pore volumes. MCM-41 was also produced from pure silica source for comparison. The results obtained in this work demonstrated the feasibility of diatomite as a potential source of silica and could significantly reduce the cost to preparation MCM-41 mesoporous materials.

Keywords: Diatomite; Mesoporous silica; MCM-41; Synthesis;

1. Introduction

Mesoporous silica is a mesoporous form of silica and it is recently developed in nanotechnology. These materials present the diameter of the pore in the range of 2 – 50 nm. More importantly, it consists of Silicon oxide (SiO_2) arrangement in a well-defined symmetrical geometry. Currently, there are various forms of mesoporous silica and play an important roles in a modern science technology due to its unique properties. One of the most investigated material is M41S family especially MCM-41(Beck et al., 1992; Kresge, Leonowicz, Roth, VartUli, & Beck, 1992). MCM-41 possess a variety of attractive properties including highly ordered pore systems with pore diameter between 2 and 10 nm. , 2-D hexagonal structure with high surface area (>1000 m^2/g), large pore volume and good thermal stability. These characteristic make MCM-41 to be a promising option for use as catalyst, catalyst support, adsorbent and guest-host chemistry(Gaydhankar, Taralkar, Jha, Joshi, & Kumar, 2005; Mokhonoana, 2005).

Several synthesis routes have been developed to obtain these materials. Sol-gel technique has been widely used as a simple method that offers a low temperature for synthesizing. The process is based on the hydrolysis and condensation reaction of organometallic compounds in alcoholic solutions(Singh et al., 2014). In the sol-gel process, there are 3 main compositions including starting inorganic materials (e.g. Tetramethyl orthosilicate (TMOS), Tetraethyl orthosilicate (TEOS), etc.), structure directing agent (Cetyltrimethyl ammonium bromine (CTAB), Sodium dodecyl sulfonate (SDS), Pluronic P123, etc.), and solvent (e.g. ethanol or water). However, from the practical viewpoint of the preparation of these materials, the cost of desired material produced strongly depends on the cost of silica source used. In recent years, a lot of companies have been devoted to reducing the cost of preparation by using natural raw materials or industrial solid wastes which contain high silica content(Misrana, Singha, Beguma, & Yarmob, 2007).

Diatomite or diatomaceous earth is a sedimentary rock composing the fossilized skeleton remains of diatoms and typically found in the muck of wetlands or lakes. The diatomite particles show a porous structure approximately 80-90% void, light-weight, large specific surface area and thermal stability(A.Q.Selim, A.A.El-Midany, & S.S.Ibrahim, 2010; Elden, Morsy, & Bakr, 2010). Additionally, they can be used as alternative silica source for the production of mesoporous materials because of its price and high silica content. So, this study will focus on the use of diatomite as alternative silica source for mesoporous silica MCM-41 synthesis by sol-gel method. The obtained samples were characterized by x-ray powder diffraction, N_2 physisorption, field emission scanning electron microscopy and transmission electron microscopy.

2. Experiments

2.1 Materials

As the staring materials for synthesis of the mesoporous silica, Diatomite was obtained from Maetha District of the Lampang province, Thailand. The chemical composition are shown in Table 1. The as-received diatomite was dried at 373 K overnight and gently ground to pass through 270-mesh (<53 μm) metal sieve.

Tetraethyl ortho-silicate (TEOS, 98%), cetyltrimethylammonium bromide (CTAB, 98%), ethanol (99.8%), aqueous ammonia solution, sodium hydroxide, sulphuric acid (H_2SO_4, 37%) and hydrochloric acid (HCl, 70%) were purchased from Sigma-Aldrich (USA).

2.2 Synthesis of mesoporous MCM-41

The synthesis of MCM-41 was modified from the previous reports (P. Kumar, Mal, Oumi, Yamana, & Sano, 2001; Meléndez-Ortiz et al., 2012; Stöber & Fink, 1968). In the first step of sample preparation, the diatomite powders were treated with sodium hydroxide in a weight ratio of 1:1.2 and transferred into a hermetically closed Teflon vessel, and heated at 150 ºC for 24 h. The supernatant had to be filtered before the further reaction. Then, the organic template (CTAB) was dissolved in a solution of aqueous ammonia and ethanol. After 15 min, the supernatant was dropwise added and the mixture was kept under the vigorous stirring for 2 h at room temperature. The pH value of solution mixture was adjusted to approximately 10-11 with sulfuric acid. In each case, the solid product was obtained was filtered and dried at room temperature. Finally, the products were heated to 550 ºC and held for 6 h. For a comparison, the sample was also synthesized from pure silica source TEOS as the same procedure. The mesoporous silica synthesized from diatomite and pure silica source TEOS were denoted as MCM-41(DM) and MCM-41(TEOS), respectively.

2.3 Characterization

All mesoporous silica samples were analyzed by several techniques as follows;

X-ray powder diffraction (XRD): Phase analysis by XRD (Bruker AXS Model D8-Discover) was carried out at room temperature using CuK_α radiation as the radiation source ($\lambda = 1.5406$ Å) at a scan speed of 0.5° min^{-1} and a step scan of 0.02°. A scan angle over the range 0.6-10° (2θ) was used to identify mesoporous material. The difference phases observed in the XRD spectra were identified with reference to standard JCPDS cards available in the system software.

X-ray Fluorescence Spectrometer (XRF): Diatomite chemical compositions were obtained by XRF method using Philips PW2400.

N_2 physisorption: Surface area and porosity were determined from nitrogen adsorption-desorption isotherms obtained (at -196 ºC) on Micromeritics Chemisorb 2750 Pulse chemisorption system instrument.

Field emission scanning electron microscopy (FESEM): The particle morphologies were observed by FESEM image using JEOL mode JSM-5410LV, at an acceleration voltage of 10 kV.

Transmission Electron Microscopy (TEM): The TEM bright field image was taken using a JEM-200CX electron microscope operated at 200kV. The sample for TEM measurements were suspended in ethanol and dropped onto holey carbon films supported on Cu grids for imaging.

3. Results and discussion

3.1 Structural properties

The hexagonal mesoporous silica is normally detected by XRD at low 2θ angles from 0.6° to 10° as shown in Fig. 1. The diffraction peaks in both the material are presented in similar patterns and exhibited one sharp peak ascribed to the peak from *h k l* reflection plane 1 0 0 plane of the highly ordered two-dimensional hexagonal structure at $2\theta = 2.40$ and $2\theta=2.28$ for MCM-41(TEOS) and MCM-41(DM), respectively(Beck et al., 1992). Decrease in peak intensities of the 1 1 0 and 2 0 0 plane were observed for both materials. These sharp signals indicated the long-range order of the uniformly hexagonal structure which is the distinctive characteristic of MCM-41 type. However, the characteristic peaks of MCM-41(TEOS) become sharper and more intense than that of MCM-41(DM), which indicates the higher degree of crystallinity.

In order to investigate in the degree of ordering, the unit cell parameter (a_0) of hexagonal structure was calculated according to the formula $a_0 = 2d_{100} / \sqrt{3}$, where d_{100} is the inter-planar spacing as a function of Miller indices 1 0 0 plane. The a_0 values can be calculated using XRD data of the profiles shown in Fig. 1 and summarized in Table 1. A slight decrease the d (1 0 0)-spacing and the unit cell parameter (a_0) of MCM-41(DM) were observed as compared to MCM-41(TEOS). This can be partly attributed to the lower degree of polymerization of silicate species under strong alkaline conditions.

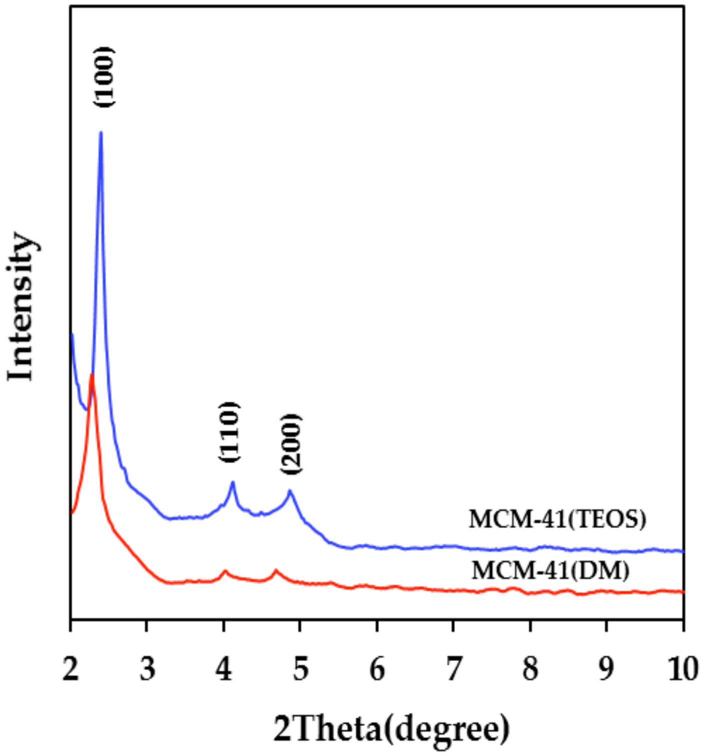


Figure 1**:** XRD patterns of MCM-41(TEOS) and MCM-41(DM) materials

Table 1. The unit cell parameter (a_0) of MCM-41(TEOS) and MCM-41(DM) materials

Sample designation	$d_{1\,0\,0}$ (nm)[a]	Unit cell parameter a_0 (nm)[b]
MCM-41(TEOS)	3.68	4.25
MCM-41(DM)	3.87	4.47

[a] The observed length of 1 0 0 plane to another as obtained from XRD data.

[b] Unit cell parameter calculated as $a_0 = 2d_{100} / \sqrt{3}$.

3.2 Textural properties

The porosity structures were investigated by using the nitrogen sorption isotherms as given in Fig. 2. Data of their specific surface area, pore volume, pore diameter and wall thickness are summarized in Table 2. It can be observed from Fig. 2 that, the isotherms of both materials exhibit the typical isotherm type IV with the hysteresis loops of type H1, which are the characteristic feature of the ordered mesoporous materials with uniform cylindrical pores open at both ends, defined by IUPAC(Kruk & Jaroniec, 2001). Moreover, the steep curve and hysteresis loop take place in the range of relative pressure of $0.3 < P/P_0 < 0.5$ which is typical for the filling of mesoporous systems(Wang, Guo, Wang, Liu, & Wang, 2010) The inflection point of MCM-41(DM) slightly shifted toward a higher relative pressure (p/p0), which indicated the broadening of the pores to larger pores sizes compared to MCM-41(TEOS). This observation was corresponding with the XRD results.

The BET surface area of MCM-41(DM) was lower approximately by 26.72 % when compared to MCM-41(TEOS). This result may be associated with the reactivity of the chosen silica source, which pure silica sources produce the higher specific surface area.

Nevertheless, the pore diameter of both materials were rather close to each other and ranging between 2 – 10 nm. The wall thickness was calculated by the different between the unit cell parameter (a_0) and the pore diameter (D_p) as given in Table 2. It is obvious that the wall thickness of both materials were in the range of 1.91–2.24 nm, which is typical of traditional mesoporous MCM-41 materials.

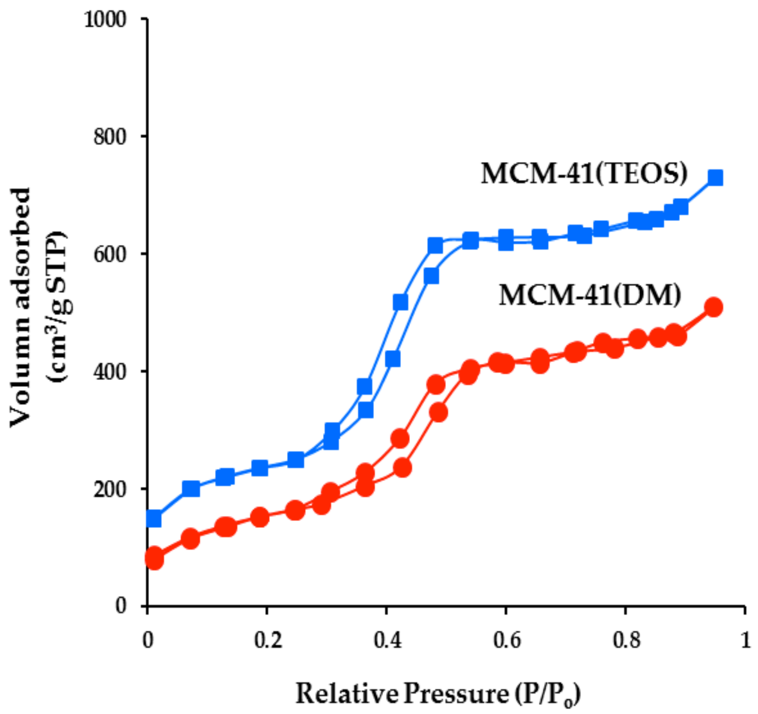


Figure 2: Nitrogen adsorption and desorption isotherms at 77 K on MCM-41(TEOS) and MCM-41(DM) materials. STP: standard temperature and pressure.

Table 2. Textural properties of MCM-41(TEOS) and MCM-41(DM) materials.

Sample designation	S_{BET} $(m^2g^{-1})^a$	V $(cm^3g^{-1})^b$	D_p $(nm)^c$	W_t $(nm)^d$
MCM-41(TEOS)	1077.00	0.94	3.3	1.61
MCM-41(DM)	789.24	0.58	2.3	2.17

[a] BET specific surface area

[b] V is the total pore volume were obtained by the BJH adsorption curves.

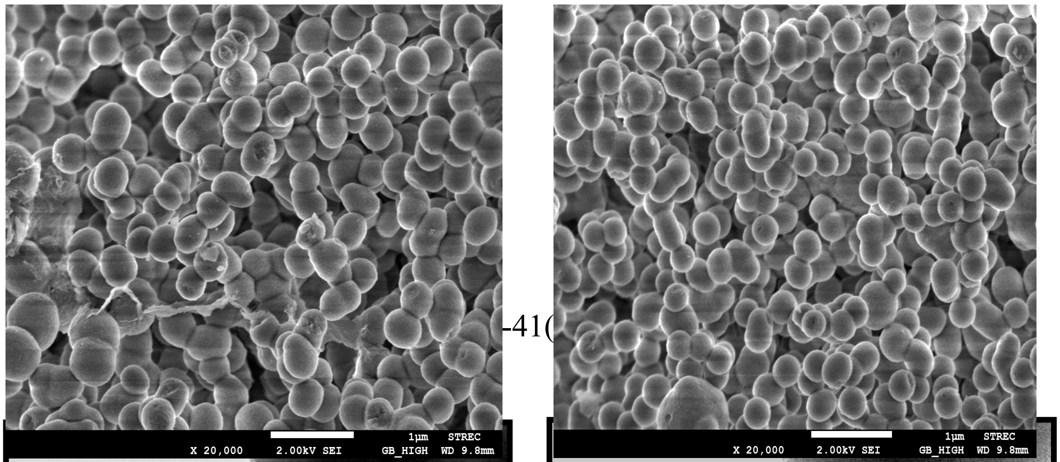
[c] D_p is the average pore diameter calculated using BJH method.

[d] Pore wall thickness, $W_t = a_0 - D_p$.

3.3 Particle morphology

SEM images of MCM-41(TEOS) and MCM-41(DM) materials are shown in Fig. 3. The morphologies of both materials are spherical shape. It can be observed that, The MCM-41(TEOS) particles can be clearly seen as spherical particles with uniform size distribution whereas the MCM-41(DM) particles are almost spherical with a slightly rough surface and partially non-uniform size distribution. TEM study was performed to further determine pore geometry structure. As shown in Fig. 4, both of materials possessed ordered hexagonal pore systems (honeycomb porous structure). These observations were in agreement with the results of XRD patterns and corresponding with that other reported MCM-41 materials (Beck et al., 1992; D. Kumar, Schumacher, Hohenesche, Gru, & Unger, 2001; Matsumoto, Chen, Tsutsumi, Gru, & Unger, 1999).

Eventually, all of these result suggest that the successful formation of mesoporous silica MCM-41 materials with two-dimensional hexagonal pore structure using sodium silicate derived from natural diatomite. Thus, natural diatomite was proved to be an alternative of a cheap silica source for the production of mesoporous silica MCM-41 materials.



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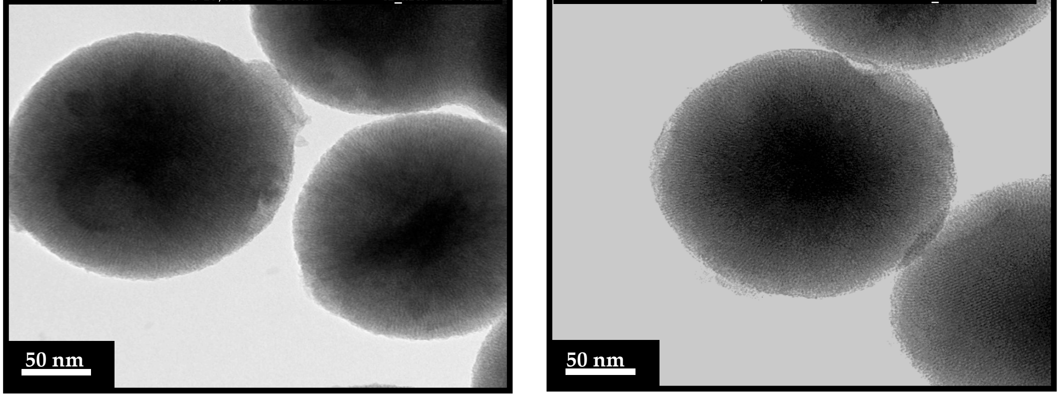

Figure 4: TEM images of MCM-41(TEOS) and MCM-41(DM) materials

4. Conclusion

In this study, well-ordered mesoporous MCM-41 materials has been successfully synthesized by condensation-polymerization with diatomite as a silica source. The morphological features of the mesoporous silica produced from diatomite was in good agreement with that derived from using pure commercial silica source. The XRD result indicated that the long-range order structure and the regular mesoporous hexagonal structure of typical MCM-41 was achieved. The specific surface area was slightly lower when compared to the former materials. The morphology of particles have shown spherical shape with fused particle were partly formed. This method can reduce the cost of preparation and also expand the commercial utilization of diatomite. Therefore, the diatomite has the potential to be used as an alternative and cheap source of silica in the production of mesoporous silica MCM-41 materials.

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