Malaysian Journal of Microscopy Vol.8 (2012) pg. 22-27

EFFECT OF POLYETHYLENIMINE LOADING ON THE PHYSICOCHEMICAL PROPERTIES OF AMINE–FUNCTIONALIZED Si–MCM–41

S. Ahmed[1], A. Ramli[2*], and S. Yusup[1]

[1]Department of Chemical Engineering, University Teknologi PETRONAS (UTP), Bandar Seri Iskandar, 31750, Tronoh, Perak, MALAYSIA.
[2]Department of Fundamental and Applied Sciences, University Teknologi PETRONAS (UTP), Bandar Seri Iskandar, 31750, Tronoh, Perak, MALAYSIA.

Si – MCM-41 with highly ordered uniform mesopores was synthesized hydrothermally at 100 °C. The calcined Si-MCM-41 was then functionalized with 10-50% (w/w) polyethylenimine (PEI) via impregnation method. The physicochemical properties of these samples were characterized using FTIR, TGA, FESEM, TEM and CHNS analysis. Results show that the Si-MCM-41 was successfully functionalized with PEI. FTIR analysis shows that all the characteristic peaks of Si-MCM-41 i.e. 794, 1080 & 1240 cm^{-1} are still present in PEI-functionalized Si-MCM-41, which means that the mesoporous frame work is preserved. TGA analysis shows that the PEI-functionalized Si-MCM-41 is thermally stable up to 200-250 °C. FESEM images show that as the PEI weight percent increases to 50wt%, the PEI-functionalized Si-MCM-41 became agglomerated, which indicates that the PEI is distributed into the pores and on the external surface of the Si-MCM-41. TEM results also show that the hexagonal pore structure remains intact and the pores are filled with PEI. CHNS analysis confirms the presence of nitrogen in the PEI-functionalized Si-MCM-41.

Keywords: Si – MCM - 41, Mesopores, Functionalization, Polyethylenimine, Impregnation method

INTRODUCTION

In 1992, a new family of Mesoporous Molecular Sieves named as M41S, was discovered by scientists of Mobil Research and Development Corporation. Numerous members of this family have been synthesized, exhibited different morphologies and a periodic pore system. MCM-41, a member of this family possessed a hexagonal arrangement of uniform mesopore channels and controllable pore size in the range of 15 Å to above 100 Å. The pore dimensions can be tailored by using through the choice of surfactant, auxiliary organic chemicals and reaction conditions.

A liquid crystal templating (LCT) mechanism was proposed for the formation of mesoporous material, in which liquid crystal structures serve as organic templates and inorganic material (silicate) form inorganic walls between the ordered surfactant micelles [1, 2]. J. S. Beck *et al.* described the role of surfactant in the formation of mesoporous molecular sieves. The surfactant act as a structure directing agent for formation of mesoporous molecular sieve framework [3]. In the absence of the surfactant the product is completely amorphous, when the surfactant is added the rate of silicate polymerization increases by a factor of more than 2000 [4]. C-F Cheng *et al.* optimized the parameters for the synthesis of mesoporous molecular sieve (Si-MCM-41). The properties of the product depend on the source and concentration of reactants, the gel aging time, the temperature and the duration of the synthesis [5]. Pore size of mesoporous molecular sieve MCM-41 can be controlled by using surfactant with different tail lengths [6], organic auxiliary chemicals *i.e.* methyl-substituted benzene, Isopropyl-substituted benzene, alkane during hydrothermal process [7, 8] or by controlling the reaction conditions [9].

MCM – 41 possesses numerous special features *i.e.* variable pore size, high surface area < 700 m^2/g, pore volume 0.7 – 1.2 cm^3/g, high thermal and hydrothermal stability, uniform pore size and shape over micrometer length scales, [1,4]. Due to these prominent features, this material is potentially useful for number of applications like adsorption, catalysis [1], separation of proteins, selection of large molecules from effluents, processing of tar sand, high distillates of crude oils to valuable low boiling products [5].

MCM – 41 can be used as a good adsorbent for CO_2 removal due to its high surface, large pore size and large pore volumes. CO_2 is one of the main green house gases and responsible for environmental change that is known as global warming. Fossil fuel is the main source of energy in this present time and in future. Combustion of fossil fuels like gasoline, coal *etc.*, and burning of biomass are the main

**Corresponding author: Tel: +605-3687639; Fax: +605-3655905*
E-mail address: anita_ramli@petronas.com.my (Anita Ramli)

sources of CO_2 emission. The emission control of CO_2 is the most challenging issue for scientists. Efforts to reduce the emission of CO_2 are of prime importance to make this globe clean and secure. Adsorption is the most favorable method that could be appropriate for separating CO_2 from gas mixtures. Because of low energy requirement, cost advantage, and ease of applicability over a relatively wide range of temperatures and pressures, adsorption separation attracts much interest [10].

For the practical use of adsorption method, the first and most important issue is to develop a suitable adsorbent, with high CO_2 selectivity and high adsorption capacity, which can also be operated relatively at higher temperatures. For this purpose, an adsorbent is needed with high surface area, large pore size and large pore volume that can adsorb large amount of CO_2. These features are present in mesoporous molecular sieve MCM-41. Pure MCM-41 showed low adsorption of CO_2 even at high pressure [11]. This may be due to the weak interaction between Si-MCM-41 and CO_2. For high adsorption uptake, high selectivity and use at high temperature, MCM-41 can be functionalized with different kinds of amines due to large pores and silanol groups. Literature showed that Amine functionalized MCM-41 showed high adsorption and selectivity for CO_2.

Herein, laboratory synthesized Si-MCM-41 has been functionalized with different weight percent of polyethylenimine (PEI) *i.e.*, 10, 20, 30, 40 and 50 wt%, in order to study the effect of polyethylenimine loading on the physicochemical properties of amine-functionalized Si-MCM-41.

MATERIALS AND METHODS

Materials

Mesoporous Molecular Sieve (MCM – 41) was synthesized hydrothermally at 100 °C for 8-days duration in our laboratory, Polyethylenimine (PEI, M_w 2000, Sigma Aldrich) was used as an amine source impregnated on MCM-41, Methanol (Sigma Aldrich; purity >= 99.8%) was used as a solvent for impregnation method.

Synthesis of PEI – functionalized MCM – 41

For the synthesized of PEI functionalized MCM–41 by impregnation method [12], the required amount of PEI was dissolved in 10 g of methanol under stirring for about 15 min, after that 2 g of calcined MCM-41 was dispersed into the solution. The resultant slurry was vigorously stirred for about 30 min, and then dried at 70 °C for 16 h under 700 mmHg vacuum. The as-prepared adsorbent was denoted as X-PEI-MCM-41, where X represents the loading of PEI as weight percentage in the sample.

Characterization.

Fourier Transformed Infra – Red Spectroscopy (FTIR)

Fourier transformed infrared (FTIR) spectra of all amine-functionalized samples were recorded at room temperature on a SHIMADZU 8400S spectrometer. The samples were ground using an agate mortar and pestle until it had approximately the same consistency as the KBr powder. KBr powder was added, mixed thoroughly, and then pressed at 9000 tons. The FTIR spectra were obtained over the range of 400-4000 cm^{-1} in transmittance mode.

Thermogravimetric Analysis (TGA)

Thermal stability and decomposition studies of all PEI impregnated samples were carried out in nitrogen atmosphere by using Thermogravimetric Analyzer TG/DTA EXSTAR 6300, SII (Japan). Samples were heated from room temperature to 1000 °C with heating rate of 10 °C/min in atmosphere of nitrogen (100 ml/min).

Field Emission Scanning Electron Microscopy (FESEM)

Surface morphology of calcined MCM-41 and polyethylenimene modified MCM-41 samples were determind by Field Emission Scanning Electron Microscopy (FESEM). FESEM images were recorded on a ZEISS 55 Supra VPFESEM microscope operated at 10.00 kV and at 30,000 magnification.

Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) micrographs of the polyethylenimine modified MCM–41 samples were obtained using a Zeiss Libra 200FE transmission electron microscope with an acceleration voltage 200 kV. In the typical sample preparation, ground samples were dispersed in a little quantity of isopropanol and sonicated for 1 h to settle down the heavy particles at bottom and thin particles remain suspended in the solution. The samples were deposited on grid 300 mesh by dipping the grid in the solution, air dried at ambient temperature and then were loaded into the microscope chamber for analysis.

CHN Analysis

The percentage of C, H and N present in polyethylenimine modified MCM-41 were obtained by using CHNS analyzer LECO CHNS-932 USA with sulfamethazine as a standard.

RESULTS AND DISCUSSIONS

FTIR spectra of synthesized calcined MCM–41 sample and all polyethylenimine modified MCM-41 samples with weight percent of 10, 20, 30, 40 and 50 were obtained in the range of 4000–400 cm^{-1} in transmittance mode and are shown in Fig. 1. Fig. 1 depicts spectrum of pure calcined MCM-41 and the spectra of all PEI functionalized MCM-41 samples. Synthesized calcined MCM-41 showed a broad peak at around ~3450 cm^{-1} (in the region of 3100–3700 cm^{-1}) is corresponding to –OH stretching vibration of surface silanol groups (Si–OH) and water molecules adsorbed while a peak at around ~1635cm^{-1} represents bending vibration of the adsorbed water molecules (H–O–H). The band at around 1080 cm^{-1} with a shoulder at ~1240 cm^{-1} and a band at 794 cm^{-1} are characteristic of asymmetric and symmetric stretching vibration of Si–O in Si–O–Si. The band at around ~964 cm^{-1} is corresponding to stretching vibration of $Si–O^-$ (Si–OH) present on the surface of the mesoporous material which is the characteristic of mesoporous molecular sieve MCM-41 [13-17].

After modifications with polyethylenimine, noticeable changes were observed in the FTIR spectra of PEI modified MCM-41 as compared to the spectrum of MCM-41. When the mesoporous molecular sieve MCM-41 was modified with Polyethylenimine (PEI), FTIR spectra showed changes as follows; the intensity of the peaks at ~3450 cm^{-1}, ~1635 cm^{-1} and 964 cm^{-1} due to –OH stretching or bending vibration is quite reduced due to attachment of amine groups in the channels and on surface. The intensity of these peaks gradually reduced as the weight percent of PEI increased. It was suggested that there is a chemical interaction between the silanol groups on the surface of the MCM-41 and the amine groups in PEI, which may form $Si\text{-}O^-N^+H_3R$ or $Si\text{-}O^-N^+H_2R$. Such chemical interaction functioning as an anchor to the PEI molecules on the surface of MCM-41 and keeps PEI in the pore channels, resulting in an increase of the thermal stability of the sorbent and decrease the fluidity of PEI on the surface [18]. These sites act as active sites for CO_2 capture.

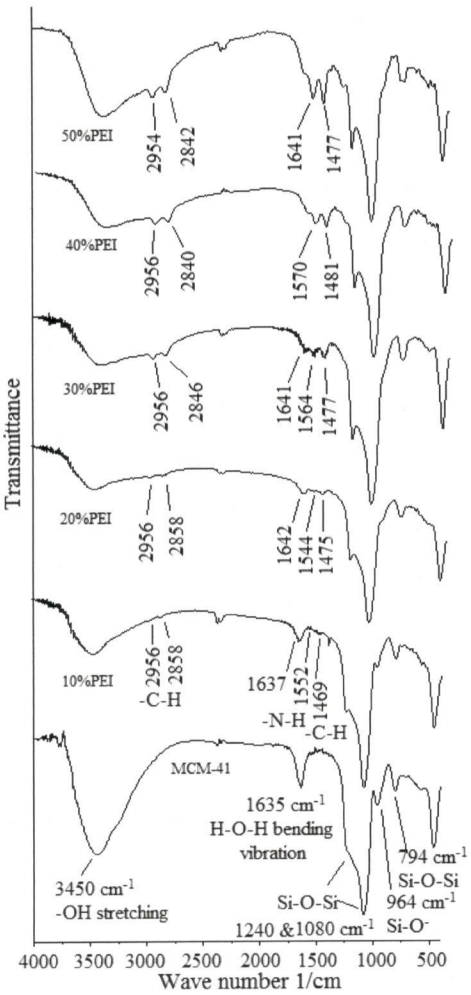

Fig. 1. FTIR spectra of calcined MCM-41and 10, 20, 30, 40 and 50 wt% polyethylenimine impregnated MCM-41

A peak at around ~1470 cm^{-1} attributed to C-H scissoring vibration and a peak at around ~1550 cm^{-1} assigned to N-H bending [19], increased as the weight percent of PEI is increased. The appearance of the peaks at around ~2850 cm^{-1} and ~2950 cm^{-1} assigned to C–H stretching vibration associated with amine groups increased gradually as the weight percent of PEI increased.

The thermochemical and physical properties of polyethlylenimine impregnated MCM-41 were determined by TGA. TGA profiles of Mesoporous

molecular seive MCM-41 impregnated with different amount of PEI i.e 10, 20, 30, 40 and 50wt%, are shown in Fig. 2. Literature [20] showed that pure PEI began to decompose above 150 °C and a sharp weight loss appeared at 205 °C. When the temperature was increased above 225 °C, the rate of weight loss decreased, indicating that a different decomposition process took place. At 600 °C, the PEI was completely decomposed and removed as volatiles. When the PEI was impregnated on MCM-41, it showed different behaviour.

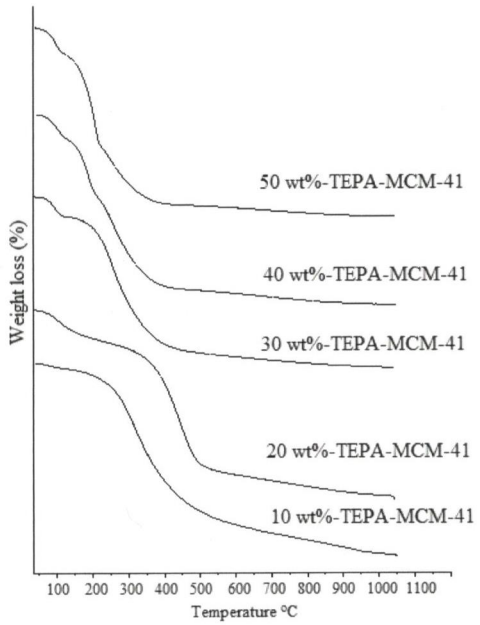

Fig. 2. TGA profiles of polyethylenimine (PEI) impregnated MCM-41 with 10, 20, 30, 40 and 50 wt%.

TGA profiles of all PEI impregnated MCM-41 samples were observed in the temperature range of 30 °C to 1000 °C. TGA profiles of PEI impregnated MCM-41 samples showed different behaviour as compared to pure PEI, all profiles can be divided into three stages, (i) weight loss from 30 °C to 150 °C due to moisture present in the sample or removal of physically adsorbed water, (ii) a sharp weight loss appeared at ~250 °C to 500 °C due decomposition of PEI, (iii) after 500 °C the rate of weight loss decreases, as the pure PEI decompose completely at 600 °C and removed as volatile [20].

From this analysis it was found that pure PEI almost decompose in the temperature of 200 to 225 °C and completely at 600 °C. But when the PEI was impregnated with MCM-41, its thermal stablity increases in the range of 250 to 500 °C and PEI completely decompose at 1000 °C, thus thermal stablity increases due to the attachment with support MCM-41. This behaviour of increase in thermal stablity of PEI is suggested due to chemical interaction with silica surface. PEI-MCM-41 showed a sharp weight loss at around ~ 250 °C due to the decomposition of amines attached to the pore walls [21].

Surface morphology of synthesized calcined mesoporous molecular sieve MCM-41 and polyethylenimine modified MCM-41was determined by Field Emission Scanning Electron Microscopy (FESEM). FESEM micrographs of all samples are shown in Fig. 3. FESEM micrographs showed that the synthesized calcined MCM-41 composed of spherical with irregular shaped particles and agglomerates with variable size.

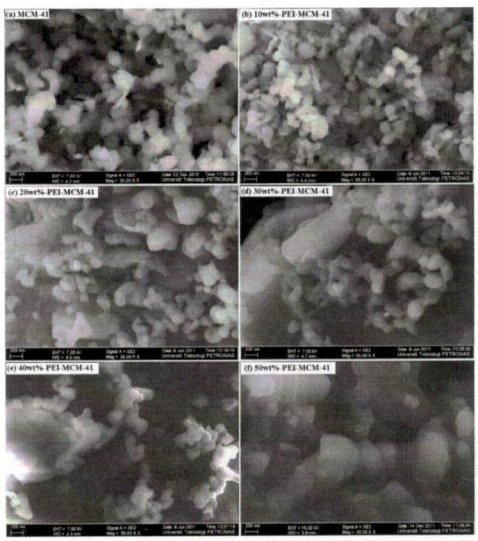

Fig. 3. FESEM images of (a) pure calcined MCM-41, (b) 10wt%, (c) 20wt%, (d) 30wt%, (e) 40wt% and (f) 50wt% polyethylenimine impregnated MCM-41.

Due to impregnation of MCM-41 with PEI, PEI starts to disperse into the pores of MCM-41. As the weight percent of PEI increases, pores become filled with PEI and then attached with the surface. As the weight percent of PEI increases, the mesoporous material become agglomerated. This shows that when

the pores were filled with PEI, then PEI attach with surface of the mesoporous material. Due to attachment of PEI on the surface, the particles become associated with each other and bcome agglomerates.

HRTEM images of pure calcined MCM-41, and PEI impregnated MCM-41 with weight percent of 10, 20, 30, 40 and 50 wt% are shown in Fig. 4. TEM image of pure calcined MCM-41showed uniform pores of hexagonal shape. After impregnation with PEI, TEM images showed uniform pores in all samples are clearly noticeable. There was not found any damage in the pore arrangement after modification with polyethylenimine (PEI).

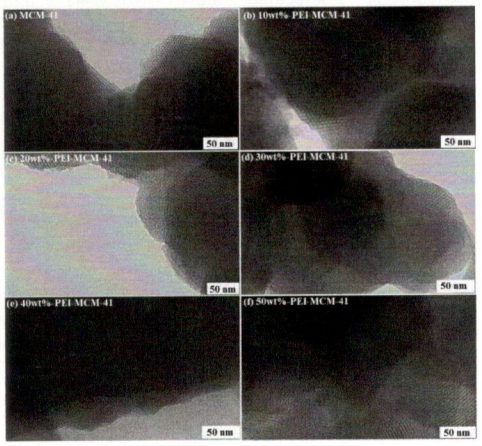

Fig. 4. HRTEM images of (a) Pure calcined MCM-41, (b) 10wt%, (c) 20wt%, (d) 30wt%, (e) 40wt% and (f) 50wt% PEI modified MCM-41

Table 1. CHN elemental analysis of PEI modified MCM-41

compounds	C wt%	H wt%	N wt%
10%PEI-MCM-41	4.93	4.18	3.00
20%PEI-MCM-41	10.04	3.87	5.70
30%PEI-MCM-41	15.24	4.25	8.60
40%PEI-MCM-41	21.12	5.78	11.63
50%PEI-MCM-41	24.53	6.08	13.53

Elemental analysis of the percentage of C, H and N present in the PEI modified MCM-41 is shown in table 1. The elemental analysis showed that MCM-41 successfully functionalized with polyethylenimine. As the weight percent of polyethylenimine increased, the percentage of C, H and N increased.

CONCLUSION

Laboratory synthesized highly ordered Si MCM-41 with uniform hexagonal pore structures was functionalized with polyethylenimine (PEI) via impregnation method. Si-MCM-41 was functionalized with different weight percent of PEI *i.e.*, 10-50% (w/w). The effect of PEI loading on the physicochemical properties of Si-MCM-41 was studied thoroughly. All the characterization results showed that Si-MCM-41 successfully functionalized with PEI. FTIR analysis showed that all the characteristic peaks of Si-MCM-41were present after functionalization, this showed that framework of mesoporous material remain preserved. Due to the functionalization with PEI new peaks appeared in the spectra of samples due to presence of C, H and N. PEI-functionalized MCM-41 showed that thermal stablity of the material at around 250 ^{0}C analysed by TGA. FESEM results showed that as the weight percent of PEI increased in the samples, it dispersed in the pores and then on the surface resulting particles becomes agglomerated. HRTEM showed the uniform hexagonal pore arrangement of Si-MCM-41 after functionalization remain undamaged. The elemental analysis of all samples confirmed the presence of C, H and N, this showed the successful functionalization of Si-MCM-41 with PEI.

ACKNOWLEDGEMENT

The authors are grateful for financial support provided by University Technology PETRONAS (UTP) Malaysia for this research.

REFERENCES

[1] Beck, J. S., Vartuli, J. S., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Schmitt, K. D., Chu, C. T-W., Olson D. H., Sheppard, E. W., McCullen, S. B., Higgins, J. B., Schlenker J. L. (1992). *J. Am. Chem. Soc.* 114, 10834-10843

[2] Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C., Beck, J. S. (1992). *Nature.* 359, 710-712

[3] Beck, J. S., Vartuli, J. S., Kennedy, G. J., Kresge, C. T., Roth, W. J., Schramm, S. E. (1994). *Chem. Mater.* 6, 1816-1821

[4] Cheng, C-F, Luan, Z., Klinowski, J. (1995). *Langmuir.* 11, 2815-2819

[5] Cheng, C-F., Park D. H., Klinowski, J. (1997). *J. Chem. Soc., Faraday Trans.* 93 (1), 193-197

[6] Jana, S. K., Atsushi. M., Namba, S. (2004). *Catalysis Surveys from Asia.* 8 (1), 1-13

[7] Jana, S. K., Nishida, R., Shindo, K., Kugita, T., Namba, S. (2004). *Microporous and Mesoporous Materials.* 68, 133-142

[8] Namba, S., Mochizuki, A. (1998). *Res. Chem. Intermed.* 24 (5), 561-570

[9] Corma, A., Kan, Q., Navarro, M. T., Perez-Pariente, J., Rey, F. (1997). *Chem. Mater.* 9, 2123-2126

[10] Xu, X., Song, C., Miller, B. G., Scaroni, A. W. (2005). *Fuel Processing Technology.* 86, 1457-1472

[11] Belmabkhout, Y., Serna-Guerrero, R., Sayari, A. (2009). *Chemical Engineering Science.* 64, 3721 – 3728.

[12] Xu, X., Song, C., Andresen, J. M., Miller, B. G., Scaroni, A. W. (2002). *Energy &Fuels.* 16, 1463-1469

[13] Jiang, T., Lu, L., Yang. X., Zhao, Q., Tao, T., Yin, H., Chen, K. (2008). *J Porous Mater.* 15, 67-73

[14] Liu, L., Zhang, G. Y., Dong, J. X. (2004) *Chinese Chemical Letters*, 15 (6), 737-740

[15] Grisdanurak, N., Chiarakorn, S., Wittayakun, J. (2003). *Korean J. Chem. Eng.* 20 (5), 950-955

[16] Romero, A. A., Alba, M. D., Zhou, W., Klinowski, J. (1997). *J. Phys. Chem. B.* 101, 5294-5300

[17] Jiang, T., Shen, W., Tang, Y., Zhao, Q., Li, M., Yin, H. (2008). *Applied Surface Science.* 254, 4797-4802

[18] Ma, X., Wang, X., Song, C. (2009). *J. Am. Chem. Soc.* 131, 5777-5783

[19] Bhagiyalakshmi, M., Yun, L. J., R. Anuradha, R., Jang, H. T. (2010*). Journal of Hazardous Materials.* 175, 928-938

[20] Xu, X., Song, C., J. M. Andresen, J. M., Miller, B. G., Scaroni, A. W. (2003) *Microporous and Mesoporous Materials.* 62, 29-45

[21] Parida, K. M., Rath, D. (2009). *Joural of Molecular Catalysis A: Chemical.* 310, 93-100