

## Functionalized mesoporous silica from rice husk for BTEX adsorption in gas phase

Thanita Areerob<sup>1,2</sup>, Siriluk chiarakorn<sup>3,\*</sup>, Nurak Grisdanurak<sup>4</sup>

<sup>1</sup>The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok, Thailand

<sup>2</sup>Center of Energy Technology and Environment, Ministry of Education, Thailand

<sup>3</sup>Division of Environmental Technology, School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi, Thailand

<sup>4</sup>Department of Chemical Engineering, Thammasat University, Thailand

### Abstract:

The BTEX, consisting of benzene, toluene, ethylbenzene, and three isomers of xylene, are volatile organic compounds (VOCs) causing the harmful effect to human health. Thus, the development of BTEX adsorbent for treatment and measurement is necessary. Two silane reagents, trimethylchlorosilane (TMCS) and *n*-propyltriethoxysilane (*n*-PTES) were used to improve the BTEX adsorption performance of RH-MCM-41. The silylated RH-MCM-41 with *n*-PTES had slightly smaller pore size and pore volume than that silylated with TMCS due to its larger molecular size and complicated structure. Additionally, it was obviously seen that small trimethylsilyl groups can easily penetrate into hexagonal pores resulting in better surface coverage. The adsorption efficiencies of BTEX on unsilylated and silylated RH-MCM-41 at various relative humidity conditions from 25 to 99% RH were measured. The BTEX adsorption efficiency increased after RH-MCM-41 was silylated with both silane reagents due to the alkylsilyl group loading. Hence, the BTEX adsorption efficiency of RH-MCM-41 could be improved by silylation. Moreover, The BTEX adsorption efficiency of RH-MCM-41 silylated by *n*-PTES was less than that silylated by TMCS. This can be explained that the complicated structure with branch and large molecular size of *n*-PTES causes less degree of silylation.

**Keywords:** mesoporous silica; silylation; rice husk; BTEX; adsorption

\*Corresponding author. Tel.: +662-470-8654 ext. 401, Fax: +662-427-9062  
E-mail: siriluk.chi@kmutt.ac.th

## 1. Introduction

Recently, MCM-41, an ordered mesoporous silica, has been introduced as an alternative adsorbent for air pollution treatment due to its high hydrothermal and chemical stability, highly homogenous hexagonal pore structure and easy to be regenerated by heating. However, it was reported that the adsorption efficiency of aromatic compounds on ordered mesoporous silica in highly humid conditions was limited, compared with dry condition (Serna-Guerrero and Sayari, 2007). The decrease of VOC adsorption capacity onto MCM-41 was found when MCM-41 was exposed to high relative humidity. Nevertheless, the mass uptake of VOCs on MCM-41 was higher than Tenax TA (a commercial adsorbent) even in low and high relative humidity (Idris et al., 2010). From this point of view, the limitation of MCM-41 adsorption performance under high humidity condition should be improved. Theoretically, the decrease of VOCs adsorption at high humidity is caused by remaining of silanol (Si-OH) on the MCM-41 surface. The elimination of hydroxyl from silanol can be achieved by silylation technique. The hydrophobic alkyl or aryl groups (R-Si) of organosilane reagents can be used to substitute the hydroxyl groups of MCM-41 (Zhao et al., 1998). In this paper, the surface of ordered mesoporous silica synthesized from rice husk (RH-MCM-41) was silylated with two different silane structures: trimethylchlorosilane (TMCS) and *n*-propyltriethoxysilane (*n*-PTES). The BTEX adsorption capacities on the modified MCM-41 under low and high RH conditions were measured in a closed static chamber.

## 2. Material and methods

### 2.1 Synthesis and modification of mesoporous silica molecular sieves

The extracted silica from rice husk by hydrochloric acid (HCl) was used to prepare sodium silicate solution (Grisdanurak et al., 2003). The rice husk silica was dissolved with sodium hydroxide and mixed with cetyltrimethylammonium bromide solution (CTAB) ((C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>3</sub>)Br, Fluka) as a

template. The mixture of sodium silicate and CTAB was with molar ratio of 1 SiO<sub>2</sub>: 1.09 NaOH: 0.13 CTAB: 120 H<sub>2</sub>O. After stirring for 30 min, the clear solution was adjusted the pH to 10, then the mixture was continuously stirred for 48 h at room temperature. The filtered solid was calcined at 550°C for 5 h. Then, RH-MCM-41 were fabricated via silylation technique followed the procedure described in Chiarakorn et al., (2007). The analytical grade of silane reagents were used such as trimethylchlorosilane (TMCS 95%, Fluka) and n-propyltriethoxysilane (n-PTES 98%, Fluka). The RH-MCM-41 was functionalized by placing into 100 mL of 5% v/v of silane reagent in toluene and constantly stirred at room temperature for 24 h in the closed system container. The functionalized RH-MCM-41 were washed with toluene and acetone, then heated in a drying oven at 100°C.

## 2.2 Characterization

Then, the crystallinity of RH-MCM-41 samples were characterized by a powder small-angle X-ray diffraction (XRD) (D8 Advance with Eulerian Cradle; Bruker) in range of 1° to 8°. Porosity properties of mesoporous silica samples were determined by N<sub>2</sub> adsorption/desorption via BEL model (BELSORP-miniII, Osaka, BEL Japan Inc.). Fourier transformed infrared (FTIR) spectra were used to analyze the organosilane functional groups on RH-MCM-41 with Spectrum one, Perkin Elmer, GX. The surface grafting ( $\Gamma$ ) and the surface density ( $\alpha$ ) were calculated from percentage of carbon content using ultimate analysis (Liu et al., 2004).

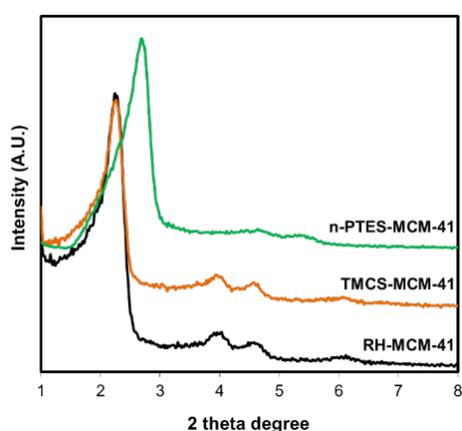
## 2.3 BTEX adsorption at various relative humidity

BTEX adsorption efficiency of functionalized RH-MCM-41 was determined in a batch adsorption system. The 10 mg of degassed adsorbents at 200°C for 2 h were placed into the bottom of chamber with a capacity of 16 L and then BTEX concentration of 1000 ppm was injected to the closed container. The humidity in the chamber was controlled at 25, 70 and 99%. After the equilibrium adsorption, BTEX were desorbed from the functionalized adsorbents thermal desorption unit (TDU, UNITY 2<sup>TM</sup> thermal desorber, Marks) and analysed by GC-FID.

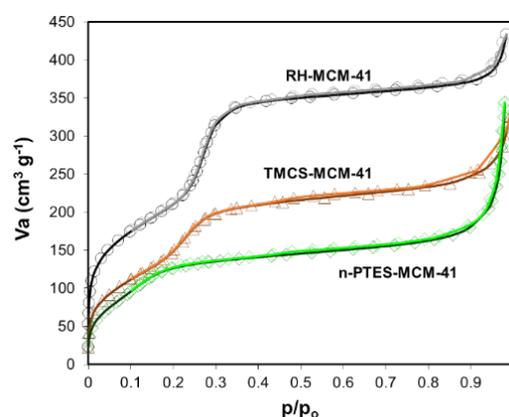
## 3. Results and discussion

### 3.1 Crystallinity and porosity

The XRD patterns of RH-MCM-41 and RH-MCM-41 silylated with TMCS and n-PTES were displayed in Fig. 1. Although, the XRD diffractograms of all samples exhibited three reflection peaks that represent the characteristic of RH-MCM-41, the main peak positions of n-PTES samples shifted to higher contact angle and the intensity of their reflection peaks were decreased. These effects are related with the decrease of hexagonal pore due to the surface coverage of n-propyltriethoxysilyl



**Fig. 1** XRD diffractograms of RH-MCM-41 before and after silylation with TMCS and n-PTES.



**Fig. 2** N<sub>2</sub> adsorption-desorption isotherms of before and after silylation with TMCS and n-PTES.

after silylation. This causes an increase of wall thickness and decrease of pore size and surface area. The N<sub>2</sub> adsorption-desorption isotherms of all samples gave typical type-IV isotherms according to the IUPAC classifications that was the peculiarity of mesoporous material with a steep curve in a range of p/p<sub>0</sub> 0.1 - 0.3 and no hysteresis was observed (Fig. 2). This characteristic is a unique property of the ordered mesoporous material with the uniform size of pores. Table 1 listed the porosity properties of the samples. It is found that all silylated RH-MCM-41 samples had the significant decreasing of surface area, pore sizes and pore volumes. However, n-PTES had much lower surface area than that silylated with TMCS. This might be the steric hindrance effect of n-PTES (Impens et al., 1999 and Yoshitake et al., 2002).

**Table 1** Loading of the alkylsilyl groups and surface density of loaded functional groups of the unsilylated and silylated RH-MCM-41

Sample	$\Gamma$ (mmol/g SiO <sub>2</sub> )	$\alpha$ (groups nm <sup>-2</sup> )	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{\text{total}}$ (cm <sup>3</sup> g <sup>-1</sup> )	$D_{p, \text{Naono}}$ (Å)	$W$ (Å)
RH-MCM-41	-	-	797.85	0.57	29.21	16.3
TMCS-MCM-41	1.34	1.02	632.10	0.48	28.49	16.6
n-PTES-MCM-41	0.55	0.42	438.50	0.53	27.88	9.6

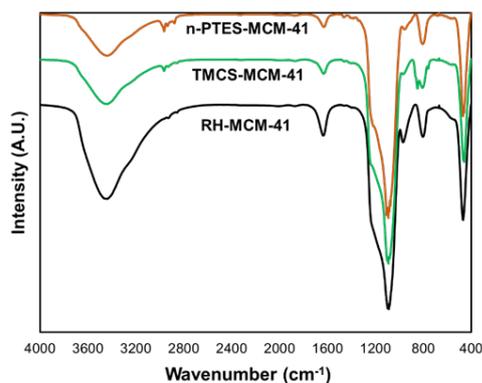
\*The mean pore diameter corresponding to the maximum peak value in the pore size distribution curve by Naono's calculation method.

$S_{\text{BET}}$ : BET surface area;  $V_{\text{total}}$ : total pore volume;  $D_p$ : pore diameter;  $d_{100}$ : d-spacing of 100 (Bragg's law,  $2d_{100}\sin\theta = n\lambda$ )

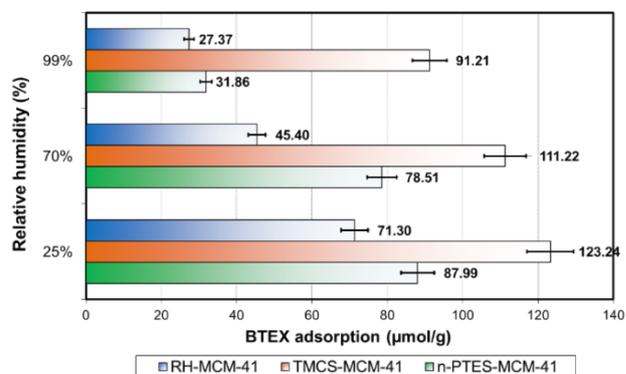
$a_0$ : unit-cell parameter ( $a_0 = 2d_{100}/\sqrt{3}$ );  $W$ : wall thickness ( $W = a_0 - D_p$ )

### 3.2 Surface modification of RH-MCM-41 and grafting efficiency

In FTIR spectra of unsilylated and silylated samples (Fig. 3), all the spectra showed a broad band due to the hydroxyl group (-OH) stretching vibration at region 3446 cm<sup>-1</sup> and a peak at 963 cm<sup>-1</sup> which belongs to the stretching vibration of terminal or geminal silanol groups (Si-OH). The FTIR spectra of the silylated samples show the specifically asymmetric bending and stretching C-H at 2960 and 1442 cm<sup>-1</sup> corresponding to the methyl group (-CH<sub>3</sub>) formed during the silylation process. However, the amount of silane loading on RH-MCM-41 was difficult to be observed from the FTIR results. The loading of the alkylsilyl groups ( $\Gamma$ ) and surface density ( $\alpha$ ) were examined by elemental analysis as presented in Table 1. Among all silylated samples, the RH-MCM-41 silylated with TMCS had the highest silylating degree and surface density.



**Fig. 3** FTIR spectrum of RH-MCM-41 before and after silylation with TMCS and n-PTES.



**Fig. 4** BTEX adsorption on unsilylated and silylated RH-MCM-41 at 25%, 70%, and 99% relative humidity.

### 3.3 BTEX adsorption

The amounts of BTEX adsorption on unsilylated and silylated RH-MCM-41 at various relative humidity conditions from 25 to 99% RH were presented in Fig. 4. The BTEX adsorption efficiency increases after RH-MCM-41 were silylated with TMCS and n-PTES even high humidity. This is a result of the alkylsilyl moieties (R-Si) that attached on RH-MCM-41. The BTEX adsorption efficiency of RH-MCM-41 silylated with TMCS was more than that of RH-MCM-41 silylated with n-PTES because TMCS has smaller molecular structure than n-PTES, which can easily reacted with silanol groups.

### 4. Conclusion

The gaseous BTEX adsorption capacity of RH-MCM-41 at high humidity was significantly improved after silylation with two different functional groups of silane reagents, TMCS and n-PTES. Silane functional group plays an important role in the BTEX adsorbability of RH-MCM-41. Small silane, like TMCS, is a suitable reagent for increasing BTEX adsorption capacity of RH-MCM-41 via silylation.

### 5. Acknowledgement

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### 6. References

- Chiarakorn, S. Areerob, T. and Grisdanurak, N. Influence of functional silanes on hydrophobicity of MCM-41 synthesized from rice husk. *Science and Technology of Advanced Materials* 8: 110–115.
- Grisdanurak, N., Chiarakorn, S. and Wittayakun, J. 2003. Utilization of mesoporous molecular sieve synthesized from natural source rice husk silica to chlorinated volatile organic compounds (CVOCS) adsorption. *Korean Journal of Chemical Engineering* 20: 950-955.
- Idris, S. A., Robertson, C., Morris, M. A. and Gibson, L. T. 2010. A comparative study of selected sorbents for sampling of aromatic VOCs from indoor air. *Analytical Methods* 2(11): 1803-1809.
- Impens, N.R.E.N. van der Voort, P. and Vansant, E.F. 1999. Silylation of micro-, meso- and non-porous oxides: a review. *Microporous and Mesoporous Materials* 28: 217-232.
- Liu, Y.H. Lin, H.P. and Mou, C.Y. 2004. Direct method for surface silyl functionalization of mesoporous silica. *Langmuir* 20(8): 3231-3239.
- Serna-Guerrero, R. and Sayari, A. 2007. Applications of Pore-expanded MCM-41 Silica: 7. Adsorption of Volatile Organic Compounds. *Environmental Science & Technology* 41: 4761-4766.
- Yoshitake, H. Yokoi, T. and Tatsumi, T., 2002. Adsorption of Chromate and Arsenate by Amino-Functionalized MCM-41 and SBA-1. *Chemistry of Materials* 14(11): 4603-4610.
- Zhao, X. S. and Lu, G.Q. 1998a. Modification of MCM-41 by Surface Silylation with Trimethylchlorosilane and Adsorption Study. *Journal of Physical Chemistry B* 102: 1556-1561.