Influence of functional silanes on hydrophobicity of MCM-41 synthesized from rice husk

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Abstract

Mesoporous molecular sieve MCM-41 was synthesized from rice husk and rice husk ash, called RH-MCM-41 and RHA-MCM-41. The sol–gel mixtures were prepared with molar composition of 1.0 SiO\textsubscript{2}: 1.1 NaOH: 0.13 CTAB: 0.12 H\textsubscript{2}O. After calcination, the polarity of MCM-41 still remained on its surface due to the existence of some silanol groups. In this study, both RH-MCM-41 and RHA-MCM-41 were silylated with two different functional silanes trimethylchlorosilane (TMCS) and phenyldimethylchlorosilane (PDMS) in order to reduce the surface polarity. The efficiency of silylation was determined based on the amount of moisture adsorbed using thermogravimetric analysis (TGA). The structure of silylating agents and silica templates were found to be important parameters affecting the hydrophobic property of the MCM-41 surface. The post-grafting silylation with aliphatic silane can decrease the surface polarity better than that with aromatic silane, probably due to less steric hindrance effect. Thus, the surface hydrophobicity of MCM-41 can be improved by the silylation of small molecular silane on RH-MCM-41.

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1. Introduction

Thailand has been the world’s largest rice exporter for many decades. The rice milling process generates abundant rice husk wastes up to 25% by the wet weight. Most of husks are commonly utilized for agricultural purposes such as animal feed and fertilizer. Additionally, it is used as an additive compound in building materials such as a component of bricks and a reinforcing material in cement. According to energy crisis, a consumption of biomass for alternative energy source has become more interesting. Rice husk can be a raw material for making fuel briquettes as well as a biomass fuel for heat and electricity generation. However, massive burning of rice husk produces some toxic gases, plenty particulate matters and ash, which has a serious impact on environment. Rice husk ash is mainly composed of silica. The extraction of silica from rice husk ash by acid treatment provides more than 95 wt% of amorphous silica. The applications of the extracted silica have been published in many papers [1–3].

Our previous study was focused on the preparation of MCM-41 synthesized from rice husk and rice husk ash. MCM-41 is a mesoporous molecular sieve in the M41S families discovered by Mobil researchers. Its molecular structure performs a uniformly and highly ordered network of silicon with hexagonal pore diameter in a range of 2–50 nm. These outstanding characteristics such as high surface area and high thermal stability results in various applications of MCM-41. For example, it can be used as a catalyst itself or being a catalyst support and as an ion exchanger [4,5]. Many authors also studied about the removal of some toxic chemicals by using a particular adsorbent such as MCM-41. However, the adsorption efficiency of some hydrophobic air pollutants on MCM-41 has been unsatisfied due to the remaining of silanols.
(Si–OH) along pore surfaces. This manner promotes a competitive adsorption of humidity and target pollutants such as adsorption BTEX in industry.

Silylation is a well-known technique for surface tailoring on several materials such as MCM-41, MCM-48, FSM-16 and silica gels [6–9]. Various functional silanes have been considered as directing agents controlling the degree of hydrophobicity on material surface. On a basis of like–dissolved–like, a silane containing resemble functional groups of a particular adsorbate is typically selected to improve an adsorption efficiency. In this study, the hydrophobic improvement of MCM-41 synthesized from rice husk and rice husk ash was carried out. The influences of molecular structures of silanes (aliphatic and aromatic silanes) and silylating condition on degree of hydrophobicity were also studied.

2. Experiment procedure

2.1. Synthesis of RH-MCM-41 and RHA-MCM-41

The synthesis methods of both RH-MCM-41 and RHA-MCM-41 were taken place at room temperature under atmospheric condition, following our earlier study [5,10]. Two different sources of silica extracted from rice husk and rice husk ash (obtained from gasification process) were mixed with hexadecyltrimethyl ammonium bromide (CTAB) with the molar composition of 1 SiO2: 1.09 NaOH: 0.13 CTAB: 120 H2O and the pH value was controlled at 10. After continuous stirring for 48h, the suspended solid was filtered and rinsed with ethanol and distilled water, then calcined at 550°C for 5h. The parent MCM-41 was synthesized from commercial silica by a method presented elsewhere [13]. The physical and chemical characteristics of synthesized samples were studied by X-ray diffraction (XRD) and Fourier transform infra red (FTIR) techniques.

2.2. Hydrophobicity improvement of RH-MCM-41 and RHA-MCM-41

The silylation method was adapted from Zhao et al. [7]. Two different functional silanes, trimethylchlorosilane (TMCS) and phenyldimethylchlorosilane (PDMCS) were used as silylating agents. Their molecular structures were shown in Fig. 1. The synthesized adsorbents were degassed at 200°C, 400 mbar for 2h, and then placed in 5 vol% of silane solutions. The silylation was taken place under a reflux condition at 30 and 80°C for 24h. After that the suspended solid was filtered, washed with toluene and acetone and dried in an oven at 105°C. To determine an improvement in surface polarity, the silylated samples were retained in a moisture saturated chamber for 48h. The degree of hydrophobicity was evaluated from weight loss of moisture using thermogravimetric analysis (TGA). The material properties after silylation such as crystallinity and surface functional groups were characterized by XRD and FTIR.

3. Results and discussion

3.1. Properties of RH-/RHA-MCM-41

Table 1 showed the amount of minerals in silica obtained by acid digestion of rice husk and rice husk ash. Silicon dioxide found in rice husk silica was more purified than that of rice husk ash, which was contaminated with some inorganic compounds during gasification process. This resulted in higher content of loss on ignition compared to rice husk silica.

The porosity properties of RH-MCM-41 and RHA-MCM-41 obtained from nitrogen adsorption isotherms were shown in Table 2. Similar to the parent, the average pore diameters of all samples were in a range of 20–30 Å, categorized in mesopore range and their surface areas calculated from the BJH model were up to 800 m² g⁻¹.

The crystallinity of the synthesized samples was determined by XRD, conducted using CuKα radiation in angular range (20) from 1° to 10° with 15 mA and 30 kV. The XRD results presented in Fig. 2 indicated that the crystalline structure of MCM-41 synthesized from both rice husk silica and rice husk ash silica were well-arranged and

![Fig. 1. Molecular structures of silylating agents (a) trimethylchlorosilane (TMCS) and (b) phenyldimethylchlorosilane (PDMCS).](image-url)
uniformly hexagonal patterns similar to that of the parent. Theoretically, the prominent characteristic of MCM-41 can be examined from an appearance of three distinctive reflections at $2\theta$ equal to 2.7°, 4.7° and 5.4° which corresponded to $hkl$ reflection planes 100, 110 and 200, respectively.

### Table 2

Porosity properties of RH-MCM-41 and RHA-MCM-41 examined by BET analysis

| Samples         | Pore diameter, BJH (Å) | Pore volume (mLg⁻¹) | $S_{BET}$ (m²g⁻¹) |
|-----------------|------------------------|---------------------|-------------------|
| Parent-MCM-41   | 22.5                   | 1.01                | 722               |
| RH-MCM-41       | 29.0                   | 0.93                | 800               |
| RHA-MCM-41      | 21.9                   | 0.87                | 730               |

Fig. 2. XRD patterns of the P-MCM-41, RH-MCM-41 and RHA-MCM-41.

Fig. 3. FTIR spectra of RH-MCM-41 and the silylated RH-MCM-41 samples.

Fig. 4. FTIR spectra of RHA-MCM-41 and the silylated RHA-MCM-41 samples.

Fig. 5. XRD patterns of RH-MCM-41 and RHA-MCM-41 before and after silylated by 5% TMCS and 5% PDMCS at 30°C.
respectively. However, it was obviously seen that the peaks of the highest intensity of RH-MCM-41 and RHA-MCM-41 were shifted to higher angle. This phenomenon is due to the presence of some impurities found in the extracted silica associated with disordered condensation of siloxane framework during crystallization.

3.2. Properties of the silylated samples

3.2.1. Functional group determination
The chemical changes in functional groups after silylation were detected by FTIR technique. As shown in Figs. 3 and 4, the reduction of peak intensity appeared at 3436 and 963 cm$^{-1}$ which were assigned to symmetric stretching vibration of Si–OH groups. All silylated samples also exhibited the presence of methyl groups at 2964 and 845 cm$^{-1}$, attributed to symmetrical C–H stretching vibration. For the samples modified by PDMCS, small transmittance peak belonging to phenyl groups was found at 1430 cm$^{-1}$. In comparison between two templates, FTIR spectra suggested a better surface silylation degree for RH-MCM-41 than that for RHA-MCM-41. However, there was not any significant change for all samples silylated at different temperatures.

3.2.2. Crystallinity characteristics
The structural properties of the MCM-41 samples before and after silylation were characterized by XRD measurements. The crystallinity patterns of all silylated MCM-41 presented in Fig. 5 were not different from that of the unsilylated one even being modified at 30 and 80°C. Three main reflections of silicon dioxide crystals were found at 2.7, 4.7 and 5.4°; however, the main reflection peak (100) of the silylated samples shifted to lower degree. It can be explained that the partial removal of Si–OH groups during silylation produced more siloxane bonds that brought about better structural forming.

3.2.3. SEM micrographs
Fig. 6. presented the SEM micrographs of RH-MCM-41 and the silylated RH-MCM-41. The agglomerated particles of RH-MCM-41 exhibited uniform distribution with the estimated particle size of approximately 0.3–0.5 μm. Silylation increased this particle size to 0.5–0.7 μm. This indicated that the outer surface of RH-MCM-41 was covered by multiple layers of silylating agents, usually found as the characteristics of the post silylation technique [11]. Many authors have suggested that the in situ grafting silylation results in more uniformly silylated surface compared to the post-silylation. However, the existence of silane molecules assembled inside the grafted MCM-41 affects the crystal orientation and also decreases the specific surface area [12,13].

3.2.4. Thermogravimetric analysis
Thermogravimetric weight loss curve of the RH-MCM-41 and the silylated RH-MCM-41 after the experiment of the water adsorption were shown in Fig. 7. It can be seen that the unsilylated MCM-41 gave a major weight loss during 50–100°C due to an evaporation of water adsorbed. As presented in Table 3, the amount of moisture adsorbed dramatically decreased after the surface silylation. This

![SEM micrographs](image)

Fig. 6. SEM micrographs of (a) RH-MCM-41, (b) silylated RH-MCM-41 by 5% TMCS at 30°C and (c) silylated RH-MCM-41 by 5% PDMCS at 30°C.
result confirmed the appreciable surface coverage of silanes on material surfaces. The degree of hydrophobicity achieved by TMCS was increased up to 83% on RH-MCM-41, much more than that on RHA-MCM-41. Nevertheless, it was observed that the silane coverage of TMCS on RH-MCM-41 (19.3 \mu mol m^{-2}) was lower than that on TMCS-RHA-MCM-41 (32.7 \mu mol m^{-2}). This is resulted from the presence of some impurities such as potassium and calcium oxides (as shown in Table 1) which were not able to remove from rice husk ash. These metal oxides could adsorb moisture and change to hydroxide forms which then react with the silane molecules during the post silylation. When the silylated RHA-MCM-41 was exposed to moisture, the Si–O bonding with metal oxides could be hydrolyzed and returned to hydroxide forms. Consequently, silylation of RHA-MCM-41 with small silane molecule like TMCS, exhibited high silane coverage but low degree of hydrophobicity. The different functional silanes were proved to be an effect on the surface polarity. The silicon surface modified by aliphatic silane (trimethyl coverage) can reduce the possibility of water adsorption more than that modified by aliphatic silane (phenyl coverage). In case of the silylation by TMCS, its small molecular size can be distributed thoroughly on material surfaces. While, the large size of the PDMCS molecules could produce sterric hindrance effect that retards the reaction of silanes.

4. Conclusion

In this study, by using different silanes and silica templates to modify surface of MCM-41, it was found that both structure of silylating agents and type of silica templates strongly influence the degree of hydrophobicity. The post-grafting silylation with aliphatic silane (TMCS) can reduce the surface polarity better than that with aromatic silane (PDMCS) which was possibly caused by
less steric hindrance. The enhancement of surface hydrophobicity was obtained from the silylation with a small molecular silane on RH-MCM-41.

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