Synthesis and Alkylation of Phenol over Periodic Mesoporous Organosilicas Functionalized with Sulfonic Acid Group

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ABSTRACT

Sulfonic acid group have been successfully incorporated on the surface of periodic mesoporous organosilicas (PMO) by co-condensation of bis(triethoxysilyl)ethane and 3-mercaptopropyltrimethoxysilane in the presence of octadecyltrimethylammonium chloride as the structure-directing agent under basic conditions, and subsequent oxidation with hydrogen peroxide. The materials present highly ordered channel arrangements and have excellent thermal stability. The novel solid acid catalysts have been used for the alkylation of phenol with 2-propanol. The results indicate that the PMO-SO$_3$H exhibit much higher catalytic activity than ZSM-5 zeolite, and also has higher catalytic stability than MCM-41-SO$_3$H.

Keywords: Periodic mesoporous organosilica; Sulfonic acid; Functionalization; Alkylation of phenol

INTRODUCTION

Periodic mesoporous organosilicas (PMO) are hybrid organic-inorganic materials containing siloxane moieties bridged by organic group as well as ordered mesopores [1, 2]. The PMO materials have very similar structural characteristics with those of ordered mesoporous silica materials [3, 4], except of framework
structures. The presence of organic groups within the frameworks is expected to give these materials a lot of favorable properties: structural rigidity and a degree of hydrophobic character useful for applications in aqueous systems [5]. A number of studies have been performed aiming to the synthesis of the PMO materials [1, 2]. However, there are few reports on the modification and applications of PMO materials. Some studies report the synthesis of inorganic-organic hybrid mesoporous materials MCM-41 functionalized with alkylsulfonic acid [6, 7]. These mesoporous materials with high acid strength have been reported to be efficient catalysts in esterification reactions [8].

Alkylated phenols are important chemicals because they are intermediates in the agrochemical and polymer industries. They are traditionally manufactured via Friedel-Crafts alkylation promoted by strong acid catalysts such as Lewis acids (AlCl$_3$ and BF$_3$) and mineral acids (HF, H$_2$SO$_4$) [9]. The corrosive nature and potential environmental hazards as well as difficulties in recycling and disposal of the spent catalyst are drawbacks of these homogeneous catalytic systems. Therefore, heterogeneous processes using solid catalysts are highly desirable.

The aims of the present work are as follows: synthesis of hybrid solid catalyst PMO-SO$_3$H materials, structural characterization of the materials, and catalytic application of the materials for alkylation of phenol with 2-propanol.

EXPERIMENTAL

Chemicals. Bis(triethoxysilyl)ethane (BTSE), 3-mercaptopropyltrimethoxysilane (MPTMS), phenol and 2-propanol were obtained from Aldrich chemical. Octadecyltrimethylammonium chloride (ODTMA) was obtained from Kogyo, Co.. All chemicals were used as received.

Syntheses. Thiol functionalized PMO materials (PMO-SH) were synthesized using BTSE as the main framework source and MPTMS as functional group and ODTMA as the structure-directing agent. The synthesis procedure was as follows: 1.0 g of ODTMA was dissolved into 31.7 g of deionized water under stirring in a polypropylene vessel. Subsequently, 0.47 g of NaOH was added to the surfactant solution at room temperature, giving a clear solution. BTSE and MPTMS were mixed in a separate vessel for 20 min. The silica framework sources were then added to the surfactant solution, and the mixture was stirred at room temperature for 20 h. The gel compositions were (1-x) BTSE : x MPTMS : 0.57 ODTMA : 2.4 NaOH : 350 H$_2$O (x is the molar ratio of MPTMS/(MPTMS+BTSE)). Then, the gel mixtures were heated at 95 °C for 21 h. The white precipitate solids were filtered off, washed and dried at 60 °C overnight. A blank sample (Si-PMO) without thiol
functional group was synthesized under the similar conditions except that BTSE was used as the single framework source. MCM-41-SO$_3$H was prepared by post-grafting method [10].

In order to remove the surfactant, 1 g of solid product was treated with 150 ml of a mixture of 10:1 (wt/wt) EtOH:HCl (35 wt%) at 70 °C for 12 h [11]. The resulting material was filtered, washed and dried at 100 °C for 12 h. This washing step was repeated one more time. The PMO-SH materials were oxidized with H$_2$O$_2$ (33% w/v, solid:liquid ratio of 1:20) at room temperature during 24 h. Finally the solid products were acidified by H$_2$SO$_4$ to produce sulfonic moieties (PMO-SO$_3$H).

**Catalyst tests.** Alkylation of phenol with 2-propanol was done using a flow reactor. 0.3 g of catalyst was packed into a glass column. The column was placed inside an electrically heated oven kept at 150 °C, and a slow flow (0.6 cm$^3$h$^{-1}$, LHSV = 2 h$^{-1}$) of the reactant mixture (phenol : 2-propanol = 1 : 2) was introduced with a syringe pump. Reaction product was analyzed by M600D gas chromatograph using FID detector furnished with a 30-m HP-5 crosslinked column. The yields of products were calculated by taking in account response factor of each compound, which were determined experimentally.

**Fig. 1.** Powder X-ray diffraction patterns of as-made PMO-SH (a) $x$ = 0.1, (b) $x$ = 0.15, (c) $x$ = 0.2 and (d) $x$ = 0.25.
RESULTS AND DISCUSSION

Powder X-ray diffraction patterns were obtained for the as-made and oxidized samples (Figs. 1 and 2). All the samples showed at least one very intense low-angle Bragg peak, indicating the presence of uniformly sized pores in the materials. There are two or more weak peaks in both the oxidized samples and the as-made PMO-SH samples with low MPTMS/BTSE ratios, which are characteristic of 2-d hexagonal (P6mm) mesostructure. The diffraction patterns of the blank sample (Si-PMO) exhibit larger intensity than the functional samples, and the intensity of the d_{100} reflection decrease as the MPTMS/BTSE ratio increase. This can be related to the fact that the MPTMS precursor contains more hydrophobic groups, so that when its amount increases, the degree of cross-linking decreases. The XRD lines of PMO-SO_3H samples, prepared with more than \( x = 0.2 \), are somewhat broad compared with low ratio, which may be due to the screening effect between templates and framework sources by functional group.

Fig. 2. Powder X-ray diffraction patterns of PMO-SO_3H (a) \( x = 0 \), (b) \( x = 0.1 \), (c) \( x = 0.15 \), (d) \( x = 0.2 \) and (e) \( x = 0.25 \).
The organic components within the frameworks of the PMO materials can be identified from the FT-IR spectra. Fig. 3 shows all the PMO materials exhibit strong bands at 2920 and 2890 cm$^{-1}$, assigned to C-H stretching and deformation vibrations, 1410 and 1270 cm$^{-1}$ corresponding to C-H deformation vibrations of the framework organic group. The peaks at 780 and 690 cm$^{-1}$ assigned to Si-CH$_2$ stretching vibrations. The PMO-SH materials, obtained from higher thiol/BTSE molar ratio than 0.2, exhibit a weak peak at 2580 cm$^{-1}$, corresponding to S-H stretching vibrations. This peak is disappeared after oxidation of the -SH group to -SO$_3$H, as shown in Fig. 3.

![FT-IR spectra of PMO materials after surfactant extraction](image)

**Fig. 3.** FT-IR spectra of PMO materials after surfactant extraction: (a) Si-PMO, (b) PMO-SH ($x = 0.1$), (c) PMO-SH ($x = 0.15$), (d) PMO-SH ($x = 0.2$), (e) PMO-SH ($x = 0.25$) and (f) PMO-SO$_3$H ($x = 0.25$).

Fig. 4 shows the pore size distribution curves of Si-PMO and PMO-SH materials after surfactant extraction, obtained from the desorption branch of nitrogen sorption isotherms. All samples exhibit narrow pore size distributions around the mean pore diameters. The pore size of PMO materials, modified by -SH groups, are somewhat larger than that of Si-PMO material. The pores size gradually decreases as the amount of MPTM in the synthesis gel increases from 0.1 to 0.25. This is attribution to more MPTMS group on the pore wall surface of PMO.

The thermal stabilities of the as-made Si-PMO and PMO-SH materials were analyzed by the thermogravimetric analysis (TGA) under nitrogen atmosphere. Fig. 5 shows the derivative TGA curves for the materials. As shown in Fig. 5, a weight
loss below 120 °C is appeared, which is attributable to the loss of small amounts of residual water adsorbed to the materials. This is followed by a weight loss from 120 to 250 °C due to surfactant decomposition. A weight loss from 350 °C is attributed to the decomposition of the -SH group from the surface of PMO. This weight loss cannot be observed from Si-PMO sample. An additional weight loss above 500 °C is attributed to the decomposition of organic moiety within the frameworks.

The degrees of incorporation of –SO$_3$H groups are shown in Table 1. The percent incorporations are almost 100 %, till $x = 0.15$, which means that all organosilane species can be incorporated and functionalized within mesopores. However, the –SH incorporation degree decrease as the ratio of MPTMS/BTSE increase above 0.2, as shown in Table 1.

Fig. 6 shows the catalytic activity of the materials for the alkylation of phenol with 2-propanol. The reaction results indicate that the mesoporous materials functionalized with sulfonic acid group (PMO-SO$_3$H and MCM-41-SO$_3$H) have much higher activities than ZSM-5 zeolite catalyst. This may be attributed to large pore size of the mesoporous materials compared with that of ZSM-5, from a diffusional point of view. Fig. 6 indicates that the catalytic activities of PMO-SO$_3$H
(x = 0.25) and MCM-41-SO$_3$H (x = 0.25) are almost same at the beginning of the reaction. However, the activity of MCM-41-SO$_3$H decreases rapidly above 10 h, whereas PMO-SO$_3$H exhibits similar activity. This may be because the PMO materials contain organic group (-CH$_2$CH$_2$-) within the frameworks, so that the materials have excellent hydrothermal stability than MCM-41.

Fig. 5. Derivative TGA curves: (a) Si-PMO, (b) PMO-SH (x = 0.1), (c) PMO-SH (x = 0.15), (e) PMO-SH (x = 0.2) and (f) PMO-SH (x = 0.25).

Table 1.
Incorporation degrees of -SO$_3$H groups

<table>
<thead>
<tr>
<th>Sample</th>
<th>Incorporation (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMO-SO$_3$H (0.1)</td>
<td>100</td>
</tr>
<tr>
<td>PMO-SO$_3$H (0.15)</td>
<td>98.8</td>
</tr>
<tr>
<td>PMO-SO$_3$H (0.2)</td>
<td>80.9</td>
</tr>
<tr>
<td>PMO-SO$_3$H (0.25)</td>
<td>73.8</td>
</tr>
</tbody>
</table>

$^a$Obtained by comparison between the calculated and the titrated –SO$_3$H groups.
The frameworks of the mesoporous materials can be attacked by water, which produced during the reaction as a byproduct. The hydrothermal stabilities of PMO-SO$_3$H have been characterized by the XRD patterns of the sample after the reaction. The results indicate that the structures of the PMO-SO$_3$H materials are not changed, whereas the framework of MCM-41-SO$_3$H material is destroyed after the reaction.

**CONCLUSION**

The PMO-SH materials have been synthesized by the co-condensation of BTSE and MPTMS under basic conditions. The amount of MPTMS in the initial synthetic mixture has been varied and its effect on the structural and chemical properties of these materials has been characterized. Successful removal of the surfactant templates has been accomplished by extracting with acidified ethanol. X-ray diffraction patterns indicate that the materials have hexagonally packed arrays of mesopores. No significant changes in the XRD after oxidation step to produce the PMO-SO$_3$H materials. TGA data show that the -SO$_3$H group is stable up to 300 °C and the ethane group within the framework of PMO materials are thermally stable at 500 °C. The results of alkylation of phenol with 2-propanol show that PMO-SO$_3$H and has higher activity than ZSM-5, and higher hydrothermal stability than MCM-41-SO$_3$H.
REFERENCES


