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

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Periodic mesoporous organosilicas have been successfully functionalized with sulfonic acid groups. The resulting materials exhibit much higher catalytic activity than ZSM-5 zeolite and higher catalytic stability than MCM-41 functionalized with the same group.

Periodic mesoporous organosilicas (PMO) are hybrid organic-inorganic materials containing siloxane moieties bridged by organic group as well as ordered mesopores.[1–4] 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, which are useful for a lot of applications such as catalysis, separations and advanced materials design. A number of studies have been performed aiming at the synthesis of the PMO materials.[1–6] However, there have been few reports on the modification and applications of PMO materials.[7,8]

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 and mineral acids. The corrosive nature and potential environmental hazards as well as difficulties in recycling and disposal of the spent catalyst are drawbacks of theses homogeneous catalytic systems. Heterogeneous processes using solid catalysts are highly desirable. Some studies report the synthesis of mesoporous materials MCM-41 functionalized with sulfonic acid.[9,10] The mesoporous materials with high acid strength have been reported to be efficient catalysts in esterification reactions. In the present work, we have synthesized heterogenized PMO catalysts functionalized with sulfonic acid groups (PMO-SO_3H) and successfully applied the materials to the alkylation of phenol with 2-propanol.

Thiol functionalized PMO materials (PMO-SH) were synthesized using bis(triethoxysilyl)ethane (BTSE) as the main framework source and 3-mercaptopropyltrimethoxysilane (MPTMS) as functional group and octadecyltrimethylammonium chloride (ODTMA) as the structure-directing agent. In a typical batch, 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 and then added to the surfactant solution. 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_2O (x = 0–0.25). Then, the gel mixtures were heated at 95 °C for 20 h. The white precipitate solids were filtered off, washed and dried at 100 °C overnight. A PMO material without thiol group (Si-PMO) was synthesized under the similar conditions except that BTSE was used as the single framework source. The solid product was treated with a mixture ethanol and HCl under reflux condition for 12 h for removal of surfactant.[12] The resulting material was filtered, washed with ethanol and dried at 100 °C for 12 h. This washing step was repeated one more time. The PMO-SH materials were oxidized with H_2O_2 at room temperature during 24 h and subsequently acidified by H_2SO_4, and subsequently filtered, washed with doubly distilled water and dried at 100 °C for 12 h. MCM-41-SO_3H was prepared by post-grafting method,[11] in order to compare the catalytic activity. Alkylation of phenol with 2-propanol was done using a flow type reactor at 150 °C. 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.

Figure 1 shows powder X-ray diffraction (XRD) patterns for Si-PMO, PMO-SH and PMO-SO_3H, respectively. All the

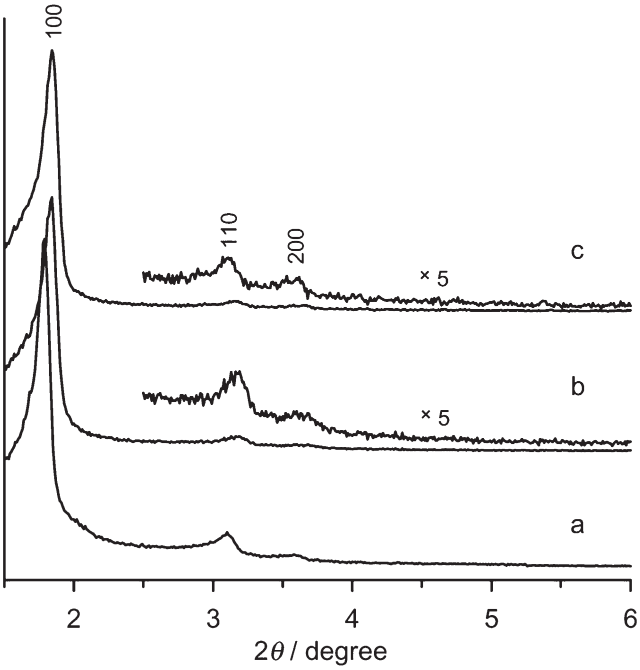

Figure 1. XRD patterns for (a) Si-PMO, (b) PMO-SH ($x = 0.1$) and (c) PMO-$SO_3$3H ($x = 0.1$).

materials give a very intense diffraction peak and two weak peaks, which are characteristic of 2-d hexagonal (*P6mm*) structure with excellent textural uniformity.[1–6] There is no significant change upon oxidation from SH group to SO_3H group. The XRD lines of PMO-SH and PMO-SO_3H materials, prepared with $x \geq 0.2$, are somewhat broad compared with those of materials with low ratios, which may be due to the screening effect between templates and framework sources by bridged organic group. A regular hexagonal arrangement in transmission electron microscopic images also reveals that all the materials have highly ordered 2-d hexagonal structures. Nitrogen adsorption-desorption isotherms for the PMO materials show Type IV with a sharp increase in the adsorption at $p/p_0 = 0.3$–0.4, which are typical of mesoporous solids.[1–6] All the samples exhibit narrow pore size distribution curves around 3 nm. BET surface areas and BJH pore diameters for the materials are listed in Table 1.

Table 1. Physical properties for PMO-SO_3H materials

x	S_{BET} /m^2/g	D_p /nm[a]	Calculated acid capacity/mmol/g	Observed acid capacity/mmol/g[b]
0.00	1050	2.8	—	—
0.10	1043	3.0	0.57	0.57
0.15	1116	2.9	0.85	0.84
0.20	873	2.8	1.15	0.93

[a]Pore diameters obtained by BJH method. [b]Obtained by titration with 0.01 M NaOH (aq) after dispersion of materials in 0.1 M NaCl solution.

FT-IR spectra show all the PMO materials have 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 PMO-SH materials exhibit a weak peak at 2580 cm^{-1}, corresponding to S–H stretching vibrations. This peak is disappeared after oxidation of the PMO-SH materials, which means that SH groups are changed to SO_3H groups. The thermal stabilities of the PMO materials were analyzed by the thermogravimetric analysis (TGA) under nitrogen atmosphere. TGA curves show a weight loss below 120 °C, 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 moeity from the surface of PMO. This weight loss is not observed from Si-PMO sample. An additional weight loss above 500 °C is attributed to the decomposition of organic moiety within the frameworks. The acid capacities of the PMO-SO_3H materials are shown in Table 1. The observed acid capacities are very close to the calculated ones, till $x = 0.15$. The results mean that all MPTMS can be successfully incorporated and functionalized within mesopores. However, the observed acid capacity is lower than the calculated one above $x = 0.2$.

Figure 2 shows the catalytic activity of the solid acid catalysts for the alkylation of phenol with 2-propanol. The reaction results indicate that the mesoporous materials functionalized with sulfonic acid group (both PMO-SO_3H and MCM-41-SO_3H) 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. The catalytic activities of PMO-SO_3H and MCM-41-SO_3H are almost the same at the beginning of the reaction, as shown in Figure 2. However, the activity of MCM-41-SO_3H gradually decreases over 10 h, whereas PMO-SO_3H exhibits similar activity. This may be due to the loss of sulfonic acid groups of the MCM-41-SO_3H. The frameworks of the mesoporous materials can be attacked and disintegrated by water, which produced during the reaction as a by-product. The XRD patterns indicate that the structures of the PMO-SO_3H materials are not changed during the reaction, whereas the structure of MCM-41-SO_3H material is destroyed after the reaction. The acid capacity of MCM-41-SO_3H also becomes about half of the initial amount after reaction, which may give the decrease in catalytic activity. The bridged organic moieties within the framework of PMO materials result in excellent catalytic as well as hydrothermal stability, compared with those of MCM-41 material.

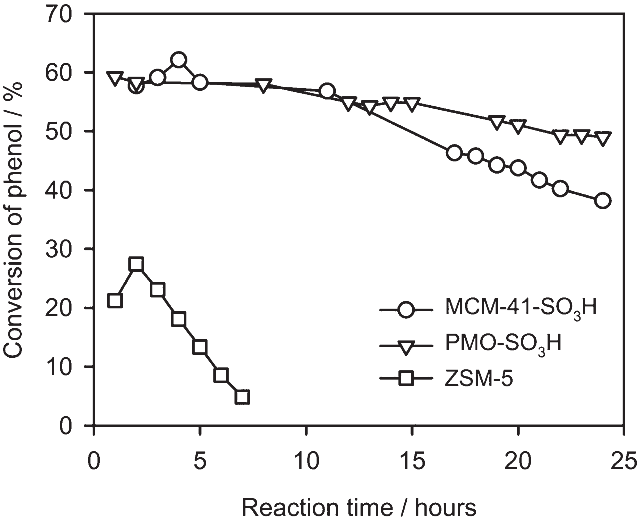

Figure 2. Alkylation of phenol with 2-propanol over ZSM-5 (Si/Al = 30), MCM-41-SO_3H ($x = 0.1$) and PMO-SO_3H ($x = 0.1$). 0.3 g of catalyst was packed into a flow reactor, which was placed inside an electrically heated oven kept at 150 °C. A slow flow (0.6 cm^3 h^{-1}, LHSV = 2 h^{-1}) of the reactant mixture (phenol:2-propanol = 1:2) was introduced using a syringe pump.

In conclusion, the highly ordered PMO-SO_3H materials have been synthesized by co-condensation of BTSE and MPTMS and subsequent oxidation. The resulting PMO materials exhibit excellent catalytic activity as well as catalytic stability.

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