Design of Mesoporous Solid Acid Catalysts with Controlled Acid Strength

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Abstract: Mesoporous silica materials, SBA-15, functionalized with strong (-SO$_3$H), moderate (-PO$_3$H$_2$) and weak (-COOH) acid groups have been successfully prepared by the co-condensation or post-grafting methods. Transmission electron microscopy and powder X-ray diffraction indicate that all of the acid-functionalized SBA-15 materials possess highly ordered mesostructures. These mesoporous acid catalysts have been applied to the alkylation of phenol with tert-butanol. The acid strength as well as the reaction parameters, such as the temperature, space velocity, and molar ratio between the reactants, were found to be the main factors controlling the reactivity and selectivity of the alkylation reaction. SBA-15-SO$_3$H and SBA-15-PO$_3$H$_2$ exhibited much higher catalytic activities than SBA-15-COOH. The product selectivity of alkylation reaction strongly depends on the acid strength as well as the reaction temperature. The SBA-15-SO$_3$H revealed high selectivity for 4-tert-butylphenol and 2,4-di-tert-butyl phenol at high temperature, whereas the SBA-15-PO$_3$H$_2$ did so for 2-tert-butylphenol at moderate temperature. Ether was observed at a relatively low reaction temperature over the SBA-15-COOH catalyst.

Keywords: SBA-15, mesoporous catalyst, acid strength, alkylation, butyl phenol

Introduction

The alkylation of phenol with tert-butyl alcohol is an important process both in organic synthesis and in the chemical industry [1]. The resulting products, such as tert-butyl phenol (TBP), 2,4-di-tert-butyl phenol (2,4-DTBP), and phenyl tert-butyl ether (PTBE), are widely used as intermediates in the synthesis of pesticides, fragrances, phosphate esters, demulsifier and antioxidants. In general, Friedel-Crafts reactions are carried out in the presence of highly corrosive liquid acids, which pose loss of yield, corrosion of equipment and post-treatment pollution problems. Typically, the Friedel-Crafts alkylation is performed using various kinds of homogeneous catalysts such as Lewis acid catalysts (AlCl$_3$, FeCl$_3$, CaCl$_2$, BF$_3$) or Brönsted acid catalysts (HF, CF$_3$SO$_3$H, H$_2$SO$_4$, polyphosphoric acid) [2]. However, it is well known that the conventional Friedel-Crafts catalysts have some drawbacks, such as their corrosiveness toward the reactor system, the consumption of catalysts, the difficulty in recycling the catalysts, and the additional separation process required to avoid environmental problems. A lot of effort has been made to circumvent these problems by using heterogeneous catalysts. Cation-exchanged resins exhibit an excellent catalytic activity, but their practical application is limited by their low thermal stability [3]. Various kinds of heterogeneous catalysts, such as zeolites HY [4], H/$\beta$ [5] and clay [6], show relatively high activity for the alkylation of phenol with TBA. However, it is not easy to control the selectivity for the products, such as 4-TBP, 2-TBP,
and 2,4-DTBP, solely by adjusting the acid strength of the catalysts. Zeolite H having strong acid sites shows a relatively high selectivity for 4-TBP, whereas the other types of zeolites having medium or weak acid sites show selectivity for 2-TPB and PTBE [5]. Mesoporous silica materials, containing Fe, Zn, and Al, have also been synthesized and used as the acid catalysts for various types of alkylation reactions. However, these materials also exhibit broad ranges of acid strengths from weak to strong depending on their synthesis methods [7-11].

An alternative technique for the generation of acidity on mesoporous silica are the functionalization of the silica surfaces with various kinds of organosilane compounds [11-18], instead of the incorporation of transition metals. In the case of mesoporous catalysts containing sulfonic acid groups, the material with thiol (-SH) groups can first be obtained by grafting on the surface of mesoporous silica with 3-mercaptopropyl trimethoxysilane (MPTMS) or by the co-condensation of MPTMS and tetraethylorthosilicate (TEOS) during the synthesis. Subsequently, the oxidation of the -SH groups with H$_2$O$_2$ and the subsequent acid treatment result in the formation of active sulfonic groups on the mesoporous silica surface. Interestingly, the surface modification of mesoporous silica using organosilane compounds has opened up new possibilities of controlling not only the acid strength, but also the number of acid sites.

In this study, we have designed mesoporous solid acid catalysts with different acid strengths, and investigated the effects of the acid strength on their reactivity and selectivity in the Friedel-Crafts alkylation reaction. The surface modified SBA-15 catalysts with -SO$_3$H and -COOH groups were synthesized using the co-condensation method. The acid functionalized SBA-15 catalyst with -PO$_3$H$_2$ group was prepared using the surface grafting of H$_3$PO$_4$. These heterogeneous catalysts prepared by surface modification were used to demonstrate the feasibility of phenol alkylation with TBA. The acid strength of the catalysts as well as the reaction parameters, such as the reaction temperature, space velocity and molar ratio of TBA to phenol, were observed to be the important reaction parameters affecting the conversion and selectivity of the tert-butylation reaction.

**Experimental**

**Preparation of Functionalized SBA-15**

Pluronic triblock copolymer P123 (Aldrich, $M_w = 5800$, $EO_mPO_nEO_m$) was used as a structure-directing agent. Tetraethylorthosilicate (TEOS, Aldrich), (3-mercaptopropyl) trimethoxysilane (MPTMS, Aldrich), and 4-(triethoxysilyl)butyronitrile (TESBN, Aldrich) were the main framework sources and organic modifiers.

Phenol and TBA was obtained from Samchun Chemical and Shinyo Pure Chemical, respectively. All chemicals were used as received.

The SBA-15 materials modified with -SH (SBA-15-SH) and -CN (SBA-15-CN) groups were obtained by the co-condensation of TEOS and MPTMS or TESBN in the presence of P123 under acidic conditions. The typical synthesis procedure was as follows: 4.0 g of P123 and 25 g of HCl (35 wt%) were added to 98 g of deionized water in a polypropylene vessel under stirring conditions at room temperature for 2 h to give a clear solution. 7.7 g of TEOS was added and the resulting mixture was stirred for 1 h at room temperature. Subsequently, 0.81 g of MPTMS (or 0.95 g of TESBN) was added. The mixture was aged at 40 °C for 20 hrs under vigorous magnetic stirring. The gel compositions were 1 P123: 54 TEOS: 6 MPTMS (or TESBN): 340 HCl : 9500 H$_2$O. Then, the gel was heated in an oven at 100 °C for 24 h. The white precipitate was filtered off, washed with deionized water and dried in a vacuum oven at 60 °C overnight. A pure silica sample (Si-SBA-15) was also synthesized under the same conditions except that only TEOS was used as the framework source. In order to remove the template, 1 g of solid was treated with 150 mL of a mixture of 10:1(wt/wt) EtOH:HCl (35 wt%) at 70 °C for 12 h. Then the material was filtered, washed with EtOH and dried in a vacuum oven at 60 °C for 12 h. This washing step was repeated twice more in order to remove the template completely.

The SBA-15-SH and SBA-15-CN were oxidized with H$_2$O$_2$ (33 % wt/v, solid:liquid ratio of 1:20) at room temperature for 24 h. Finally, the solid products were acidified by H$_2$SO$_4$ to produce the SBA-15 materials modified with sulfuric acid (SBA-15-SO$_3$H) and that with acetic acid (SBA-15-COOH). The SBA-15 material modified with phosphoric acid (SBA-15-PO$_3$H$_2$) was prepared by the post-grafting method. 1 g of the washed Si-SBA-15 was impregnated with 0.17 g of H$_3$PO$_4$ (85%) using a rotary evaporator. Subsequently, the resulting material was dried in a vacuum oven at 60 °C for 12 h, and finally calcined at 500 °C for 4 h under static air conditions.

**Catalyst Characterization and Reaction Studies**

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku ATX-G diffractometer operated at 3 kW using Cu Kα radiation at room temperature. For the transmission electron microscopic (TEM) observation, the sample was mixed with epoxy resin, and the mixture was cut via microtoming process. The TEM images were collected using a JEOL JEM-2100F operated at 300 kV. In-situ elemental analysis was done using energy dispersive X-ray spectroscopy (EDX) in conjunction with the TEM instrument. The N$_2$ adsorption-
Table 1. Physical Properties of Functionalized SBA-15 catalysts

<table>
<thead>
<tr>
<th>Materials</th>
<th>Lattice parameter (a) (nm)</th>
<th>Surface area (b) (m²/g)</th>
<th>Pore volume (c) (cm³/g)</th>
<th>Pore size (d) (nm)</th>
<th>Wall thickness (e) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-SO₃H</td>
<td>11.7</td>
<td>801</td>
<td>0.93</td>
<td>5.9</td>
<td>5.8</td>
</tr>
<tr>
<td>SBA-15-PO₃H₂</td>
<td>11.6</td>
<td>757</td>
<td>0.99</td>
<td>6.4</td>
<td>5.2</td>
</tr>
<tr>
<td>SBA-15-COOH</td>
<td>11.1</td>
<td>781</td>
<td>0.86</td>
<td>5.2</td>
<td>5.9</td>
</tr>
</tbody>
</table>

¹Lattice parameters calculated from XRD data using the equation \(a_0 = d_{100} \times (2/\sqrt{3})\).
²Surface areas obtained by the BET method.
³Total pore volumes estimated from the \(N₂\) sorption isotherms at \(p/p₀ = 0.99\).
⁴Mesopore diameters obtained from the \(N₂\) adsorption branches using the BJH method.
⁵The wall thickness was calculated from the lattice parameter and pore size.

Figure 1. XRD patterns of (a) Si-SBA-15, (b) SBA-15-SH, (c) SAB-15-CN, (d) SBA-15-PO₃H₂, (e) SBA-15-SO₃H, and (f) SBA-15-COOH.

Figure 1. XRD patterns of (a) Si-SBA-15, (b) SBA-15-SH, (c) SAB-15-CN, (d) SBA-15-PO₃H₂, (e) SBA-15-SO₃H, and (f) SBA-15-COOH.

desorption isotherms were obtained on a Quantachrome Autosorb-1 instrument at liquid \(N₂\) temperature. All of the samples were evacuated at 100 °C for 24 h prior to the measurement. The FT-IR data were collected using a Thermo Nicolet Nexus 670.

The alkylation of phenol with TBA over the functionalized SBA-15 catalysts was carried out at atmospheric pressure using a fixed-bed down flow vertical reactor (catalyst weight = 0.1 g). The reactor was placed inside an electrically heated furnace. The reactant mixture of phenol and TBA was injected by a calibrated syringe pump with a weight hourly space velocity (WHSV) of the reactant of \(1 \sim 5 \text{ h}^{-1}\). In order to measure the effect of reaction conditions, the reactions were operated in the temperature range of \(90 \sim 150 \text{ °C}\) with the molar ratio of phenol to TBA (P/B) in the range of \(0.5 \sim 4\). The reaction temperature was measured using a K-type thermocouple attached to the catalyst bed. The products were collected every 30 min for analysis over a period of 5 h. The products were analyzed by gas chromatography (Younglin 600D) using a flame ionization detector furnished with a 30 m HP-5 capillary column. The alkylation of phenol with TBA produced 4 types of products: 2-TBP, 4-TBP, 2,4-DTBP, and PTBE. The yield of each product was calculated taking into account its response factor. The reactants, products and their synthetic mixtures were used to calibrate the chromatograms and to deduce the quantitative information.

Results and Discussion

Figures 1(a) ~ (c) show the XRD patterns of Si-SBA-15 and functionalized SBA-15 (SBA-15-SH and SBA-CN), which exhibit well resolved peaks corresponding to the 100, 110, and 200 planes of the 2-D hexagonal mesostructures. The XRD patterns indicate that the 2-D hexagonal structures of SBA-15-SH and SBA-15-CN are maintained in spite of the co-condensation of organosilane with TEOS for the functionalization of SBA-15. The prepared SBA-15-SH and SBA-15-CN samples were treated with \(H₂O₂\) and then washed with \(H₂SO₄\) for the oxidation of the -SH and -CN groups to -SO₃H and -COOH groups, respectively. As shown in Figures 1(e) and (f), there is no significant change in the XRD patterns after these treatments. Compared with the pure silica SBA-15, the functionalized SBA-15 materials showed a slight decrease in the XRD peak intensity. The synthesis procedure used to prepare the functionalized SBA-15 is very similar to that of Si-SBA-15, except for the co-addition of organosilanes with TEOS. It is well known that the addition of organosilanes disturbs the formation and self-assembly of the SBA-15 mesostructure, because the organosilane has both organic and inorganic moieties even after hydrolysis [12,13].

In contrast to the co-condensation of organosilane, the surface functionalization of phosphoric acid moiety is
Figure 2. Transmission electron microscopy image and in-situ elemental analysis of SBA-15-SO$_3$H: (a) TEM image of SBA-15-SO$_3$H, (b) STEM image of SBA-15-SO$_3$H, an elemental analysis by EDS was performed and is indicated by the straight line in this image, (c) distribution of S and Si elements detected by EDS at the corresponding region indicated in the image.

Figure 3. FT-IR spectra of functionalized SBA-15: (a) SBA-15-SO$_3$H, (b) SBA-15-PO$_3$H$_2$, (c) SBA-15-COOH.

done by the impregnation of H$_3$PO$_4$ on the Si-SBA-15, based on the method reported by Kawi and coworkers [17]. They reported that the -PO$_3$H$_2$ or -PO$_2$H groups were formed on the surface of mesoporous silica through the interaction of the P-OH bonds of H$_3$PO$_4$ and the surface silanols of mesoporous silica. When the MCM-41 was functionalized with phosphoric acid, the structural integrity of the materials decreased as the amount of grafted acid increased. The structure of MCM-41 collapsed when an excess amount of acid (Si/P < 25) was used for the grafting process. In the present work, SBA-15 was functionalized with phosphoric acid instead of MCM-41. As shown in the XRD patterns of Figure 1(d), the uniformly-arranged hexagonal mesoporous framework is still well maintained even after the excess loading of phosphoric acid (Si/P ∼ 10) onto the surface of SBA-15. The high stability of SBA-15 for the grafting of phosphoric acid is mainly attributed to the thicker walls of SBA-15 compared with those of MCM-41. As shown in Table 1, the pore wall thickness of SBA-15 determined by XRD and N$_2$ sorption was about 5 nm, which is much higher than the value of approximately 1 nm for MCM-41 reported elsewhere [19]. It was also confirmed by the N$_2$ sorption experiments that all of the functionalized SBA-15 catalysts had high surface areas (∼ 800 m$^2$/g), large pore volumes (∼ 0.9 cm$^3$/g), and mesopores (5 ∼ 6 nm), as summarized in Table 1.

As shown in the TEM image in Figure 2(a), the SBA-15-SO$_3$H showed the same well-resolved pore structure as that of SBA-15 even after the modification of surface with -SO$_3$H. Also, the local distribution of sulfur on the functionalized SBA-15-SO$_3$H particles was monitored by in-situ EDX in conjunction with the TEM (Figures 2(b) and (c)). The sulfur was evenly distributed throughout the particles, which means that the organosilanes are grafted uniformly over the whole SBA-15 particles during the co-condensation. Figure 3 shows the FT-IR spectra of functionalized SBA-15 catalysts. The SBA-15-COOH and SBA-15-SO$_3$H catalysts exhibit the bands centered at 2928 and 2854 cm$^{-1}$, corresponding to C-H stretching [20], which are likely originated from the organic moieties of silane compounds (MPTMS and TESBN). These IR data also indicate the existence of organic functional groups within the material in agreement with the EDX results in Figure 2. On the other hand, no C-H stretching band from organic moieties was observed for SBA-15-PO$_3$H$_2$ because the surface of SBA-15 was functionalized directly with phosphoric group (-PO$_3$H$_2$) by treating it with H$_3$PO$_4$ without any organic coupling agent. From the results of XRD, TEM, N$_2$ sorption, and FT-IR, it could be concluded that the surface of the 2-D hexagonally structured SBA-15 could be functionalized successfully with -COOH, -SO$_3$H, and -PO$_3$H$_2$ groups by direct functionalization or co-condensation combined functionalization.

Phenol alkylation with TBA was carried out for the three types of acid-functionalized SBA-15 materials under the following conditions and the results are summarized in Figure 4. The reactant molar ratio between phenol and TBA was 2:1 and the space velocity (WHSV) was 1 h$^{-1}$. The reaction was carried out at one of two different temperatures depending on the activity of catalysts, 120 °C for SBA-15-SO$_3$H and SBA-15-PO$_3$H$_2$ having relatively high activity and 150 °C for SBA-15-COOH having low activity. Among the three types of catalysts, SBA-15-SO$_3$H having the highest acidity showed the highest phenol conversion at 120 °C, whereas SBA-15-COOH having the lowest acidity showed the lowest conversion even at high reaction temperature of 150 °C. This means that the activity of phenol alkylation
Figure 4. Product distribution and conversion of phenol for the alkylation with *tert*-butyl alcohol using the SBA-15-COOH, SBA-15-PO$_3$H$_2$ and SBA-15-SO$_3$H catalysts. The reaction temperatures for SBA-15-PO$_3$H$_2$ and SBA-15-SO$_3$H were 120 °C and that for SBA-15-COOH was 150 °C. The phenol/TBA molar ratio was 2.0 and WHSV was 1 h$^{-1}$.

Figure 5. Effect of reaction temperatures on the product distribution and conversion for phenol alkylation with TBA using (a) SBA-15-PO$_3$H$_2$ and (b) SBA-15-SO$_3$H. The phenol/TBA molar ratio was 2.0 and the WHSV was 1 h$^{-1}$.

is closely related to the acid strength. A different trend was observed for the selectivity. Depending on the acid strength, three different main products, viz. PTBE, 2-TBP and 4-TBP, were obtained. In the case of PTBE, the highest selectivity was obtained over SBA-15-COOH having the lowest acid strength. This means that the weak acid sites are more helpful for the formation of the ether product. These results are similar to the previously reported ones in the weak acid or base catalysts lead to the formation of ether product [8,20]. On the other hand, a higher acid strength is required to obtain alkylated products such as 2-TBP and 4-TBP. 2-TBP was mainly obtained over SBA-15-PO$_3$H$_2$ having moderate acid strength, whereas 4-TBP was obtained over SBA-15-SO$_3$H having the highest acid strength [5].

The dependence of the activity and selectivity on the reaction temperature was monitored in the alkylation of phenol with TBA over the SBA-15-SO$_3$H and SBA-15-PO$_3$H$_2$ catalysts, respectively. SBA-15-COOH was excluded from this test due to its low phenol conversion. The other reaction conditions were as follows; WHSV $= 1$ h$^{-1}$ and phenol:TBA $= 2:1$ (mol). Figure 5 shows that the phenol conversion of the two catalysts increased as the reaction temperature increased, and reached a maximum at around 130 °C under the present reaction conditions. The effect of the reaction temperature on the product selectivity strongly depends on the acid strength of catalysts, as shown in Figure 5. In the case of SBA-15-PO$_3$H$_2$, 2-TBP and PTBE were obtained preferentially at a low reaction temperature of 90 °C while the 4-TBP was obtained without PTBE at a high reaction temperature of 150 °C (Figure 5(a)). The other interesting findings were that the selectivity of PTBE decreased more rapidly than that of 2-TBP as the temperature increased and 4-TBP was formed preferentially above 130 °C. From these results, it was speculated that 2-TBP is formed preferentially through the interaction of TPA with the ortho-positioned carbon relative to the hydroxyl (-OH) of phenol at low temperature. At high reaction temperature, the increase of 4-TBP selectivity probably occurred because the reaction temperature is high enough to activate the para-position for the alkylation, or because the 2-TBP, which is first formed, is transformed into the para-positioned 4-TBP through an isomerization reaction. In contrast to SBA-15-PO$_3$H$_2$ with moderate acidity, a considerable amount of 4-TBP together with 2-TBP were obtained at an even lower temperature of 90 °C over SBA-15-SO$_3$H having strong acidity. As the reaction temperature increased, the doubly alkylated 2,4-DTBP began to be formed, while the 4-TBP selectivity reached a maximum and a monotonous decrease of the 2-TBP selectivity was observed. The selectivity of 2,4-DTBP reached 15% at 150 °C. Based on the results of Figures 4 and 5, it can be suggested that the desired product could be obtained selectively by controlling the acid strength of the catalyst and the reaction temperature. That is, a low temperature and weak acid catalyst
Figure 6. Effect of reactant molar ratios (phenol : TBA) on phenol alkylation with TBA over SBA-15-PO$_2$H$_2$. The reaction temperature was 120 °C and the WHSV was 1 h$^{-1}$.

Figure 7. Catalytic stabilities for the phenol alkylation depending on the reaction time. The phenol/TBA ratio, reaction temperature and the WHSV were 2.0, 150 °C and 1 h$^{-1}$, respectively.

(SBA-15-COOH) are required for the formation of ether product (PTBE), a moderate acid catalyst (SBA-15-PO$_2$H$_2$) and medium temperature (110 ∼ 130 °C) for the formation of 2-TBP, and a strong acid catalyst and high temperature for the formation of 4-TBP as well as 2,4-DTBP.

Figure 6 shows the effect of reactant molar ratio (Phenol:TBA) on the phenol alkylation with TBA over SBA-15-PO$_2$H$_2$ at 120 °C with a space velocity (WHSV) of 1 h$^{-1}$. At a low TBA molar ratio (phenol : TBA = 4 : 1), the phenol conversion was around 10 %. That is, the phenol conversion was limited by the concentration of TBA. As the fraction of TBA in the reactants increased, the phenol conversion, as well as the selectivity of 2,4-DTBP, increased. As shown in Figure 6, the phenol conversion reaches 75 % at the higher TBA molar ratio (Phenol:TBA = 1:2), because the TBA is no longer a limiting factor for the alkylation. Similar results were reported elsewhere [8,21,22] where such an increase of the reactivity might be attributed not only to the excess amount of TBA, but also to the competition between the polar TBA and non-polar phenol at the adsorption and active sites of the catalyst. The results indicate that the reactant molar ratio is also one of the important factors controlling the activity and selectivity in the phenol alkylation with TBA, together with the reaction temperature and acid strength.

In order to evaluate the stability of the catalysts, the reaction was carried at a higher reaction temperature (150 °C) for more than 16 h, and then the used catalysts were characterized by XRD. This long-run test results for the three types of acid functionalized SBA-15 catalysts are presented in Figure 7. At the beginning of the reaction, somewhat low phenol conversions were obtained over the whole catalysts and it took a certain time to reach a steady state conversion. All of the catalysts revealed maximum conversion within 5 h and then maintained a steady state conversion up to 10 h. When the reactions proceeded further, the conversion decreased slowly although not to a great extent. This may be due to the formation of coke on the acid sites of the catalysts. Figure 8 shows the XRD patterns of the functionalized SBA-15 catalysts before and after the alkylation reaction for 16 h. All of the catalysts showed XRD patterns of mesoporous structures even after their lengthy exposure under...
the reaction conditions. From this result, it could be concluded that the functionalized SBA-15 catalysts have sufficiently high thermal stability to be applied in the alkylation of phenol with TBA.

**Conclusion**

Acid-functionalized SBA-15 catalysts with different acid strengths were synthesized by the co-condensation of an acid moiety or surface-grafting. It was confirmed by XRD, \( \text{N}_2 \) adsorption, TEM, and FT-IR that all of the acid-functionalized SBA-15 catalysts maintained their 2-D hexagonal structure even after the alkylation reaction. Through the alkylation of phenol with TBA over the acid-functionalized SBA-15 catalysts, it was found that the activity and selectivity depended strongly on the acid strength of the catalysts. The phenol conversion was in the order of SBA-15-SO\(_3\)H > SBA-15-PO\(_3\)H\(_2\) > SBA-15-COOH. In the analysis of the product selectivity, certain products could be obtained preferentially by controlling the acid strength of the catalyst and the reaction temperature, viz. the ether product at a lower reaction temperature over SBA-15-COOH having weak acid sites, 2-TBP at a moderate temperature over SBA-15-PO\(_3\)H\(_2\) having medium acid strength, and 2,4-DTBP at relatively high temperature over SBA-15-PO\(_3\)H\(_2\) having strong acid strength. The selectivity was also sensitively influenced by the molar ratio of reactants, viz. 2,4-DTBP was obtained selectively at a low phenol to TBA molar ratio and 2-TBP at a high molar ratio of reactants.

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