Mesoporous Silica with Site-Isolated Amine and Phosphotungstic Acid Groups: A Solid Catalyst with Tunable Antagonistic Functions for One-Pot Tandem Reactions


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Scientists engaged in heterogeneous catalysis often cite enzymes as their model catalysts. Enzymes can efficiently catalyze multistep processes that give various types of biomolecules. Remarkably, many enzymes combine two antagonistic catalytic functions, such as acid and base functions. Attracted by this challenge, several groups synthesized homogeneous catalysts that can successfully combine chemically hostile functions. However, the difficulty lies in controlling the separation between these groups and simultaneously working at practical catalyst concentrations. In principle, both of these problems can be solved using heterogeneous catalysis. But synthesizing solid catalysts that combine hostile functions is no easy task. Not surprisingly, examples of solids with both acidic and basic functions are limited. The reported examples combine acids such as sulfonic acids, silanols, ureas, and thiols with amines. However, problems such as low catalytic activity because of weak acidity, complicated preparation, and lack of a continuous range of acidic and basic catalytic sites often significantly limit their application in organic reactions.

Here, we present a simple and straightforward route to such bifunctional solids. We combine amine base functions and heteropolyacid functions on periodic mesoporous silica, obtaining an efficient and robust bifunctional acid–base solid catalyst. This new material enables one-pot cooperative catalysis. Moreover, the synthesis permits easy tailoring of the acid/base properties by controlling the number and surface concentration of the acid and base sites, respectively.

We demonstrate the catalytic efficiency and robustness of this new system in two cascade reactions: a tandem deprotection–Henry reaction, and a tandem deprotection–aldol reaction. Excellent yields and selectivities are obtained in both cases.

Figure 1 shows the synthesis of the catalyst. We started by making a mesoporous silica support $S$ (Figure 1, top; pore diameter of 4.9 nm and surface area of 870 m$^2$ g$^{-1}$, see the Experimental Section). The base functions were then added by grafting 3-aminopropyl groups, giving the base catalyst $SB$ (Figure 1, middle). This material was then immersed in a methanolic solution of phosphotungstic acid ($H_3PW_{12}O_{40}$). The 3-aminopropyl groups immobilized the acid poly-anions, creating the acid/base catalyst $SAB$ (Figure 1, bottom). By controlling the ratio of immobilized heteropolyacids and aminopropyl tethers, we succeeded in reacting only part of the amino groups, creating bifunctional catalytic sites inside the silica mesopores.

The catalysts were characterized before and after each functionalization step. Figure 2 shows the $N_2$ adsorption isotherms of $S$ and $SAB$. Both materials are mesoporous, with average pore diameters of 4.9 and 3.4 nm, respectively. The isotherms show that grafting the base catalyst $SB$ (Figure 1, middle). This material was then immersed in a methanolic solution of phosphotungstic acid ($H_3PW_{12}O_{40}$). The 3-aminopropyl groups immobilized the acid poly-anions, creating the acid/base catalyst $SAB$ (Figure 1, bottom). By controlling the ratio of immobilized heteropolyacids and aminopropyl tethers, we succeeded in reacting only part of the amino groups, creating bifunctional catalytic sites inside the silica mesopores.

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nitrilotriacetic acid (T
\textsubscript{3}) and T
\textsubscript{2} functionalities in the 29Si CP-MAS NMR spectra (Figure 4) confirmed a strong covalent linkage between the organic groups and the silica surface (see also Figure S3 in the Supporting Information). A comparison of the W-L
\textsubscript{3} edge region in the X-ray absorption near-edge structure (XANES) spectrum of SAB with that of bulk phosphotungstic acid showed no major shifts in position and amplitude. This confirms the absence of geometrical or electronic changes in the immobilized groups (Figure 5). Moreover, 31P NMR spectroscopy also showed that the Keggin structure of the phosphotungstic acid was maintained after immobilization (singlet at −15.5 ppm, see the Supporting Information).

We then investigated the bifunctionality of catalyst SAB in the one-pot tandem conversion of dimethoxymethylbenzene (benzaldehydedimethylacetal) 1 to trans-1-nitro-2-phenylethylene 3 (Scheme 1; the functionality that catalyzes each step is shown in blue). The first step of this reaction is the acid-catalyzed deacetalization of 1 to benzaldehyde 2. In the second step, which is base-catalyzed, the benzaldehyde reacts with nitromethane, giving the nitro product 3. Table 1 shows the results. High conversions and yields were observed in the presence of the SAB catalyst (entry 1 in Table 1). When SB
Table 1: Tandem deprotection–Henry reaction.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Substrate</th>
<th>Conversion [%]</th>
<th>Yield GC/isolated [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SAB(^{[b]})</td>
<td>1</td>
<td>(\approx 98)</td>
<td>tr 97/92</td>
</tr>
<tr>
<td>2</td>
<td>SB</td>
<td>1</td>
<td>–</td>
<td>–/–</td>
</tr>
<tr>
<td>3</td>
<td>SAB(^{[c]})</td>
<td>1</td>
<td>(\approx 99)</td>
<td>95/– 5/–</td>
</tr>
<tr>
<td>4</td>
<td>SB(^{[d]})</td>
<td>2</td>
<td>&gt; 99</td>
<td>–/–</td>
</tr>
<tr>
<td>5</td>
<td>S</td>
<td>1</td>
<td>tr</td>
<td>tr</td>
</tr>
<tr>
<td>6</td>
<td>SAB(^{[e]})</td>
<td>1</td>
<td>95</td>
<td>tr 94/90</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: benzaldehyde dimethyl acetal (1 mmol), CH\(_3\)NO\(_2\) (10 mL), 50°C, 12 h. [b] Phosphotungstic acid (HPW)/amino-propyl (AP) ratio around 0.5:1 (molar). [c] HPW/AP ratio around 1:1 (molar). [d] Fourth recycle of the catalyst of entry 1. [e] For Henry reaction alone starting from entry 2. tr: trace.

Scheme 1. One-pot tandem conversion of benzaldehydedimethacetal 1 to trans-1-nitro-2-phenylethylene 3. The acid sites of SAB catalyze the deacetalization first and the base sites then catalyze the Henry condensation.

Scheme 2. Tandem deacetalization–aldol reaction of dimethoxymethylbenzene 1 through 2 to benzylidine malononitrile 4.

Table 2: Tandem deprotection–aldol reaction.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entry</th>
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<th>Substrate</th>
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<td>SB</td>
<td>1</td>
<td>–</td>
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<tr>
<td>3</td>
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<td>(\approx 99)</td>
<td>95/– 5/–</td>
</tr>
<tr>
<td>4</td>
<td>SB(^{[d]})</td>
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<td>&gt; 99</td>
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</tr>
<tr>
<td>5</td>
<td>S</td>
<td>1</td>
<td>tr</td>
<td>tr</td>
</tr>
<tr>
<td>6</td>
<td>SAB(^{[e]})</td>
<td>1</td>
<td>95</td>
<td>tr 95/95</td>
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[a] Reaction conditions: benzaldehyde dimethyl acetal (1 mmol), CH\(_2\)(CN)\(_2\) (10 mL), 50°C, 12 h. [b] HPW/AP ratio around 0.5:1 (molar). [c] HPW/AP ratio around 1:1 (molar). [d] Fourth recycle of the catalyst in entry 1. [e] For the aldol reaction alone starting from 2. tr: trace.
base tandem conversions in a single pot. We can prepare this catalyst as well as tune it easily. The catalyst can be made predominantly basic, or predominantly acidic, or equally acidic and basic by changing the ratio of polyacid and amine groups. Similar types of catalysts can be synthesized using other heteropolyacids, which further widens the scope of these materials.

**Experimental Section**

Catalyst synthesis: Mesoporous silica SBA-15 (S) was synthesized by route using block copolymer templates following a literature report. Pluronic P123 (average molecular weight of 5800, EO20PO70EO20, BASF; 4.0 g) was dissolved in a solution of distilled water and 2 M HCl (125 and 25 g, respectively) and stirred at 25 °C. After stirring for 3 h, tetraethyl orthosilicate (TEOS, Aldrich; 8.6 g) was added slowly under stirring. The solution was vigorously stirred at 40°C for 24 h. The mixture was aged at 80°C for 48 h. The resulting white solid was filtered off, washed, and air-dried at room temperature for 24 h. The sample was calcined in air at 550°C for 5 h.

SBA-15 was heated at reflux with 3-aminopropyltriethoxysilane in dry toluene for 24 h to obtain aminopropyl-grafted mesoporous silica (SB). The amount of grafted amino groups were determined by elemental analysis.

Immobilization of heteropolyacids: SB was stirred with a methanolic solution of required amounts of phosphotungstic acid (Aldrich) based on grafted amino groups for 12 h. The solid was then filtered off, washed, and air-dried at room temperature for 24 h. Elemental analysis.

The spectra were referenced with respect to 85% H3PO4. A major signal at 13.7 ppm, which may be due to distortion of the HPW cubic structure because of the functionalization. However, this is only a negligible fraction of the immobilized HPW.

X-ray absorption spectra around the W-L 3 edge were recorded at 161.88 mHz instrument operating at 100.56 mHz spectrometer operating at 15406 mHz/C138. N2 adsorption–desorption isotherms were measured at 77 K on a micromeritics ASAP-2000 after evacuation C for 24 h. N2 adsorption–desorption isotherms were taken periodically and analyzed by gas chromatography (GC, Perkin–Elmer Clarus 500) using a 50 m BPS capillary column and an free induction decay (FID) detector. After the completion of the reaction, the catalyst was separated by filtration. The filtrates was analyzed by GC and the products were confirmed by GC-MS and 1H NMR spectroscopy. The recovered catalyst was washed with nitromethane and acetone, and was then reused for the above one-pot reaction. Deacetalization–aldol reaction of benzaldehyde dimethylacetal and malononitrile was also conducted in a similar way. Ethyl acetate hydrolysis was carried out in a round bottom flask, fitted with a condenser and a magnetic stirrer. A dilute aqueous solution of ethyl acetate (10 wt%) was stirred with catalyst powder (2 wt%) at 343 K and the catalytic activity was measured by GC.

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