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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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.[1] Remarkably, many enzymes combine two antagonistic catalytic functions, such as acid and base functions.[2] Attracted by this challenge, several groups synthesized homogeneous catalysts that can successfully combine chemically hostile functions.[3] 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.[4] 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, 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-aminomethylpropyl 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-aminomethylpropyl 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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nitrogen than $S$, because a fraction of the pores is already occupied by the aminopropyl and phosphotungstic groups. However, the pores are still wide enough to allow easy diffusion of reactant and product molecules. The structure retention after immobilization was also confirmed by X-ray diffraction (see the Supporting Information).

$^{13}$C cross-polarization (CP) magic angle spinning (MAS) NMR spectra showed peaks at 11, 22, and 43 ppm (Figure 3). These peaks are typical for the SiCH$_2$CH$_2$CH$_2$NH$_2$ chain, indicating the successful grafting of the aminopropyl groups on $S$.

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>98</td>
<td>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[d]</td>
<td>1</td>
<td>99</td>
<td>5/-</td>
</tr>
<tr>
<td>4</td>
<td>SB[b]</td>
<td>2</td>
<td>99</td>
<td>99/91</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[d]</td>
<td>1</td>
<td>95</td>
<td>94/90</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: benzaldehyde dimethyl acetal (1 mmol), CH₃NO₂ (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.

Table 2: Tandem deprotection–aldol 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>&gt; 98</td>
<td>99/91</td>
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<tr>
<td>2</td>
<td>SB</td>
<td>1</td>
<td>–</td>
<td>–/–</td>
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<tr>
<td>3</td>
<td>SAB[d]</td>
<td>1</td>
<td>99</td>
<td>5/-</td>
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<tr>
<td>4</td>
<td>SB[b]</td>
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<td>99/92</td>
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<tr>
<td>5</td>
<td>S</td>
<td>1</td>
<td>tr</td>
<td>tr</td>
</tr>
<tr>
<td>6</td>
<td>SAB[d]</td>
<td>1</td>
<td>95</td>
<td>95/91</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: benzaldehyde dimethyl acetal (1 mmol), CH₂(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.[9] 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 stored in a methanolic solution of required amounts of phosphotungstic acid in dry toluene for 24 h to obtain aminopropyl-grafted mesoporous silica. [6] The signal at 85% H₃PO₄.

The spectra were referenced with respect to 85% H₃PO₄. The spectral referencing is with respect to neat, external tetramethylsilane. 31P NMR spectra were obtained with a Varian VNMRS 150 MHz spectrometer operating at 161.88 mHz.

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**Keywords:** heterogeneous catalysis - mesoporous materials - NMR spectroscopy


