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Mesoporous Silica: An Efficient Nanoreactor for Liquid−Liquid Biphase Reactions

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Periodic mesoporous silicates, which possess uniform channels with large pore size (1.5−40 nm), high surface area (up to 2000 m^2/g), and tunable structure, have attracted much attention in the past decade.[1,2] The ordered mesoporous materials have been widely explored as supports for a variety of catalysis, including acidic/basic catalysis, hydrogenation, desulfuration, oxidation, asymmetric synthesis, or enzyme catalysis.[3−8] The surface of the mesoporous silicates can be modified with different groups,[9−11] by which it can greatly adjust surface functionality and change textural properties.[5] The surface hydrophobic/hydrophilic properties of the solid catalysts have great influence on their catalytic activity. Silylated mesoporous titanosilicates which are more hydrophobic compared with the unmodified silicas can enhance the catalytic activity in olefin epoxidation.[12,13]

For a liquid−liquid biphase reaction which contains both oil and water phases, vigorous stirring, a cosolvent, or a phase transfer catalyst is required to promote the reaction, of which using a phase transfer catalyst is the most efficient method. To reuse the expensive and sometimes toxic phase transfer reagents for the consideration of economy and environment, the phase transfer catalyst tends to be immobilized onto a solid support to obtain a heterogeneous catalyst, which is more suitable for industrial fabrications. Such a concept of liquid−liquid−solid "triphase catalysis" has been well adopted in many cases.[14−16] However, usually the immobilized catalysts show relatively lower activities.

Here, we demonstrate the use of the ordered mesoporous silica (SBA-15) as a nanoreactor for liquid−liquid biphase reaction with high activity. A "triphase catalysis" reaction efficiently occurred in the absence of phase transfer reagents and cosolvents as well. It is attributed to the amphiphilic surface of the mesoporous silica which can provide a suitable accommodation for both hydrophilic and hydrophobic molecules. Using the catalyst of sodium tungstate/SBA-15, high conversions (up to 89%) are achieved with a low catalyst loading (S/C = 300) in an organic solvent-free condition for the reaction of benzylic alcohols oxidized by hydrogen

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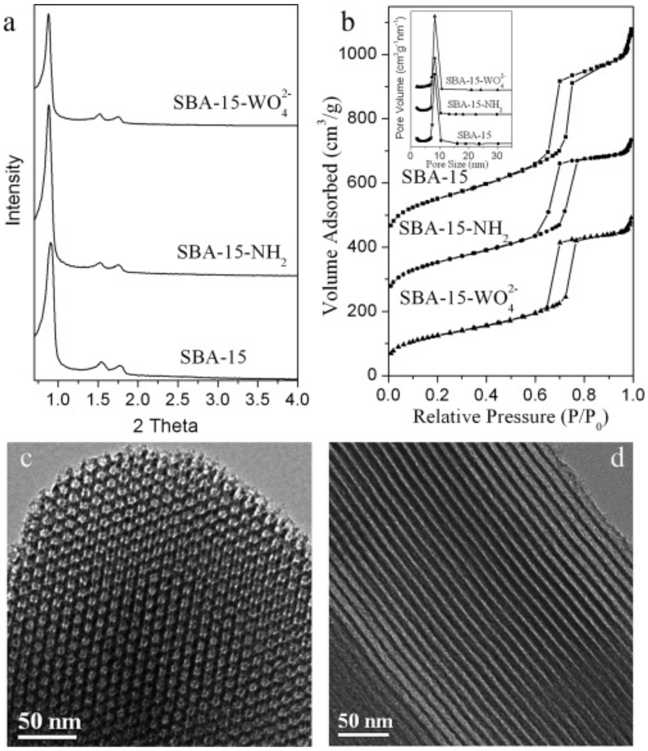

Figure 1. XRD patterns (a) and nitrogen sorption isotherms (b) and pore size distributions (inset) of SBA-15, SBA-15-NH$_2$, and SBA-15-WO$_4^{2-}$. TEM images of mesoporous silica SBA-15 along the [001] direction (c) and SBA-15-WO$_4^{2-}$ catalyst along the [110] direction (d).

peroxide, which is a typical liquid−liquid biphase reaction. Furthermore, the grafted catalysts can be recovered and reused with high conversion at least eight times.

Mesoporous silicates SBA-15 were prepared by using triblock copolymer Pluronic P123 as a structure-directing agent under acidic condition according to the previous literature.[2] The amino modified SBA-15-NH$_2$ was obtained by post-grafted method with 3-aminopropyltriethoxysilane. The grafted catalyst SBA-15-WO$_4^{2-}$ was obtained by acidification of SBA-15-NH$_2$ using trifluoromethanesulfonic acid and ion exchange by tungstate[17] (experimental details are shown in Supporting Information).

Powder X-ray diffraction (XRD) patterns show that all the samples have highly ordered hexagonal mesostructures (Figure 1a), which remain intact during the post-grafting. Transmission electron microscopy (TEM) images (Figure 1c,d) of the mesoporous silica SBA-15 (Figure 1c) and SBA-15-WO$_4^{2-}$ (Figure 1d) also show well mesostructural regularity in large domains. In addition, the TEM image of SBA-15-WO$_4^{2-}$ shows that the tungstates are well dispersed in the pore channels. Nitrogen sorption isotherms of all the samples show representative type-IV curves, which are characteristic of mesoporous materials with uniform pore structure (Figure 1b). A decrease of the BET surface areas is observed after the post-grafted process; the BET surface areas of SBA-15, SBA-15-NH$_2$, and SBA-15-WO$_4^{2-}$ are 721, 555, and 452 m^2/g, respectively. However, the BJH pore size distributions of each sample are narrow at the mean value of 8.2 nm, suggesting an open mesopore channel (Figure 1b, inset). It also implies that the tungstates are well dispersed and accessible via the open pore channels. The UV diffuse reflection spectrum (UV-DRS) of SBA-15-WO$_4^{2-}$ shows two absorption peaks around 403 and 252 nm (Supporting Information, Figure S1), which indicates the immobilization of tungstates.

Table 1. Oxidation of Benzyl Alcohol to Benzoic Acid in Different Systems[a]

entry	system	S/C[b]	yield[c] %
1	0.022 g of $Na_2WO_4 \cdot 2H_2O$	300	5
2	0.20 g of SBA-15		<2
3	0.022 g of $Na_2WO_4 \cdot 2H_2O$ + 0.2 g of SBA-15	300	74
4	0.23 g of SBA-15-WO$_4^{2-}$	300	84

[a] For a typical reaction, the conditions are as follows: 0.02 mol of benzyl alcohol and 0.07 mol of 30 wt % H_2O_2, and the above superadditions were stirred at 90 °C for 12 h. [b] S/C is the molar ratio of benzyl alcohol to sodium tungstate. [c] Isolated yields of benzoic acid.

The oxidation of benzyl alcohol to benzoic acid by hydrogen peroxide was chosen as a probe liquid−liquid biphase reaction (Supporting Information, Scheme S1). The oxidation reactions were carried out under an organic solvent-free condition with 30 wt % H_2O_2 at 90 °C. As shown in Table 1, a low isolated yield of 5% for benzoic acid (entry 1) was obtained when sodium tungstate was used as a catalyst, probably because of the immiscibility of the oxidant and the substrate. It was also detected that mesoporous silica SBA-15 showed almost no catalytic activity (entry 2). However, when a mixture of Na_2WO_4 and SBA-15 was employed, an unexpected high yield of 74% was obtained (entry 3). It is explained that the large mesochannels of SBA-15 can accommodate Na_2WO_4 with the aid of water from aqueous H_2O_2 which promoted the oxidation reaction. Furthermore, when the grafted catalyst SBA-15-WO$_4^{2-}$ was used, a higher yield of 84% was obtained (entry 4). The yield improvement could be attributed to the rich concentration of tungstates in the mesochannels. The yield as a function of reaction time was measured, and it was found the yield achieved a plateau after 12 h (Supporting Information, Figure S2). As a result, a reaction time of 12 h was chosen for all the reactions. Further studies showed that the grafted catalyst could be recovered and reused for at least eight cycles without significant decrease of the yield (Supporting Information, Figure S3). The recovery of the catalyst could be easily realized through a filtration or centrifugation process.

Under N_2 atmosphere or airtight conditions, the benzyl alcohols can be selectively oxidized to aldehydes (Table 2, entry 2). When the molar ratio of H_2O_2/BzOH is as low as 1.2, benzaldehyde is the main product with a yield of 68% (isolated yield of 66%) and a high selectivity of 94%. In addition, SBA-15-WO$_4^{2-}$ is also an efficient catalyst for the oxidation of other benzylic alcohols and cyclohexanol (Table 2).

Our results reveal that the oxidation that occurred in the mesochannels is quite similar to that reported by Noyori and co-workers[18,19] in which quaternary ammonium hydrogen sulfate was used as a phase transfer agent. In our case, the loading of catalysts (S/C = 300) is much lower than that of

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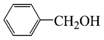
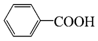
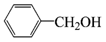
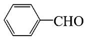
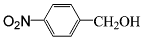
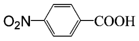
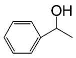
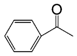
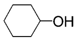
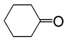
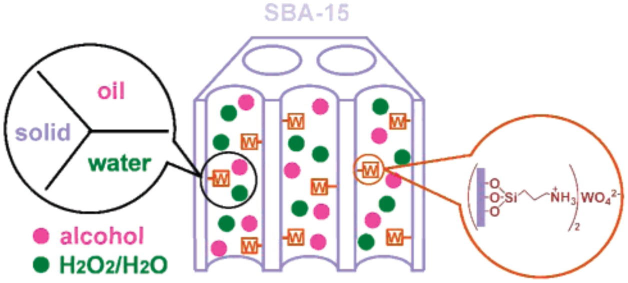
Table 2. Oxidation of Alcohols Using SBA-15-WO_4^{2-} as a Catalyst[a]

Entry	Substrate	Product	H_2O_2/ alcohol	Yield%	Selectivity %
1			3.5	84	94
2			1.2	68[b]	94
3			3.5	89	96
4			3.5	87	> 99
5			2.5	55	91

[a] Reaction conditions: S/C = 300, stirring at 90 °C for 12 h. The yields of the acid products (entries 1, 2) were calculated from those of the isolated products, while those of the other entries were calculated from GC analysis. [b] The reaction occurred in an airtight bottle.

Scheme 1. Reaction of Alcohol Oxidation Using SBA-15-WO_4^{2-} as a Catalyst under a Triphase Condition



the phase transfer catalyst (S/C = 50) used for primary alcohols, implying that the mesochannels as a nanoreactor can enrich the substrate and make the oxidation be more efficient.

It has been known that the approachability of the two liquid phases to the solid catalyst is a key factor for a triphase reaction. It is necessary with the aid of a cosolvent or a phase transfer agent. In our case, the reaction occurs in the channels of mesoporous silica where the tungstates are immobilized (Scheme 1). The mesochannels are amphiphilic as a result of the abundant hydrophilic Si−OH groups and hydrophobic Si−O−Si groups on the surface.[20] They can accommodate both hydrophobic alcohol substrate and hydrophilic oxidant H_2O_2. Therefore, a high yield reaction may occur.

To confirm the influence of the hydrophobic/hydrophilic properties, SBA-15 was modified with hydrophobic organic groups by methyltriethoxysilane (MTES). After modification, a remarkable decrease of the yield was observed (Supporting Information, Table S2, entry 6), implying that the hydrophobic environment is disadvantageous for the oxidation. It is speculated that the oxidation greatly depends on the interaction ability of alcohols with both hydrophilic H_2O_2 oxidant and silica mesochannels. The more hydrophobic the mesochannel surface is, the lower the yield is. Simultaneously, the hydrophobic mesochannels may also influence the diffusion of the reactants and products, thus resulting in lower isolated yield.

Mesoporous silicates with different pore size and surface area were used as supports for the oxidation reaction (Supporting Information, Table S1). With the increase of the pore size and surface area, the yield tends to increase a little. When MCM-41 with small pore size (2.4 nm) was used as the support, a relatively low yield (71%) was obtained (entry 1). It may arise from the difficulty for both the substrates and the products to enter and escape from the mesochannels. When the pore size is large enough (>6.8 nm) for the interphase mobility of the substrates and products, a small decrease of the yield is observed, which may be due to the drop of the surface area (entries 3−5). Similar phenomena have been observed for the photooxidation of olefins using Pt-loaded SBA-15.[21]

In summary, we demonstrate a "triphasic catalysis" reaction occurred in the channels of mesoporous silica without any phase transfer reagent and organic cosolvent. The amphiphilic mesochannels of SBA-15 can provide a suitable accommodation for both hydrophilic hydrogen peroxide and hydrophobic benzylic alcohols, which acts as not only a support for tungstate catalyst but also a "solid phase-transfer reagent". High conversion is obtained with a low catalyst loading for the oxidation of benzylic alcohols with hydrogen peroxide, which can be attributed to the enrichment effect of the mesochannels. It is a green and economical process for the oxidation industry. Furthermore, it is also expected that mesoporous silica materials may have potential applications in other liquid−liquid biphase reactions by controlling the hydrophobic/hydrophilic properties of the mesochannels.

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Supporting Information Available: Experiment details, scheme of the reactions, UV-DRS of SBA-15-WO_4^{2-}, kinetics study, catalyst reuse, FTIR spectra of modified SBA-15, and reaction results with different mesoporous silica supports (PDF). This material is available free for charge via the Internet at http://pubs.acs.org.

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