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LETTER

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Rational Catalyst Design: A Multifunctional Mesoporous Silica Catalyst for Shifting the Reaction Equilibrium by Removal of Byproduct

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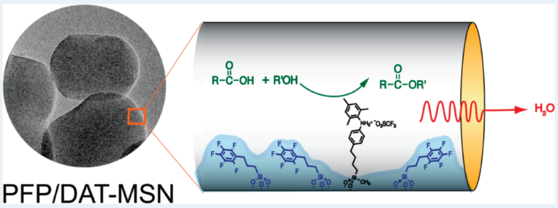
Supporting Information

ABSTRACT: Bifunctional mesoporous silica nanoparticle (MSN) catalysts for esterification reaction, containing a Brønsted acid site of diarylammonium triflate (DAT) and a pentafluorophenyl propyl (PFP) group, were synthesized and thoroughly characterized. Their high reactivity is attributed to the formation of a surface-bound hydrophobic layer of PFP molecules, which facilitates the extrusion of one of the reaction products (water) from the mesopores by suppressing water adsorption onto the surface, thereby shifting the reaction equilibrium to completion.



KEYWORDS: heterogeneous catalysis, rational catalyst design, mesoporous materials, fluorinated surface, esterification, solid-state NMR

Recent advancements in designing mesoporous silica nanoparticle (MSN) materials with surface-anchored functional groups have shown promising potential for applications in heterogeneous catalysis.[1−6] Not only can such catalysts be easily separated from the products and recycled, but their large surface area (>700 m^2/g), tunable pore diameter (2−10 nm) and well-ordered pore structure allow for precise regulation of mass-transport properties that are crucial for many chemical transformations. Several classes of single-site catalytic systems have been developed using the MSN materials as supports, including organometallic catalysts,[5,7−9] acid catalysts,[4,10,11] base catalysts,[12] and immobilized enzymatic catalysts.[13] In addition, by introducing multiple functional groups onto the three-dimensional (3D) controlled mesoporous surface our group,[14,15] as well as others,[3,16−19] have demonstrated that the selectivity and reactivity of MSN-supported catalysts can be effectively enhanced.

In our recent report,[20] we detailed the conformations of 3-(pentafluorophenyl)propyl (PFP) groups covalently anchored to the "dry" MSN support (i.e., in the absence of any solvent molecules inside the pores). We demonstrated that the silica-bound PFP groups exist in two different conformations: (1) the molecules located in the proper vicinity of accessible siloxane groups assume the prone orientation with the aromatic rings centered near the siloxane oxygens, and (2) the remaining PFP functionalities are oriented roughly upright with respect to the silica surface and are more mobile. Both structures were determined by a number of two-dimensional (2D) solid-state NMR experiments and further substantiated by theoretical calculations.[20] In particular, the fingerprints of both conformations were obtained in terms of ^{19}F chemical shifts.

We have since discovered that the conformations of PFP groups change when the pores are filled with solvents. For example, in the presence of heptane, only the resonances representing molecules in prone positions can be detected (Figure 1). Second, it has been demonstrated by others, both experimentally and theoretically, that fluorine bound to aromatic carbon is a poor hydrogen-bond acceptor, and thus poorly interacts with water.[21,22]

These findings inspired us to design a new perfluorinated MSN catalyst for the esterification reaction, containing a Brønsted acidic diarylammonium triflate (DAT) group serving as a catalyst[11,23−26] and PFP as a secondary functionality (Scheme 1). Rather than controlling the diffusional penetration of the reactants to the catalytic sites inside the mesopores,[14] we incorporated the PFP groups to suppress the interactions between the reaction byproduct (water) and the silica surface. The benefits of using other secondary functional groups to increase the hydrophobicity of mesoporous catalysts have been already reported for several reactions involving dehydration.[27−29] Here, we demonstrate that the PFP functionality significantly enhances the catalytic activity in the esterification reaction, and performs better in this capacity than the commonly used trimethylsilyl group (TMS). Furthermore, we compare the catalytic performance of this bifunctional MSN-system with commercially available heterogeneous acid catalysts, such as Amberlyst-15 and Nafion NR-50, in the esterification of carboxylic acids with benzyl alcohol under our reaction conditions.

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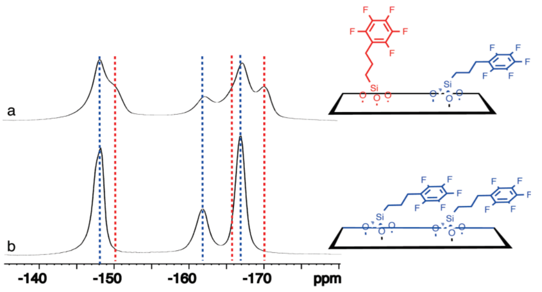
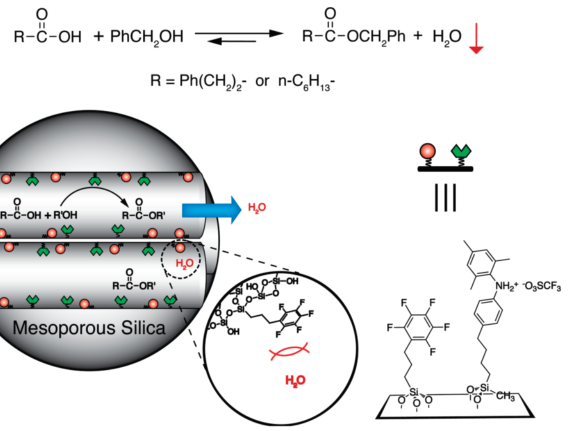
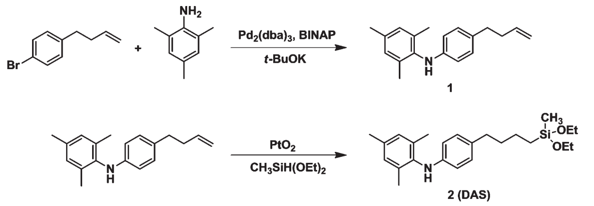


Figure 1. ^{19}F solid-state MAS NMR spectra of PFP groups on MSN support measured in dried condition (a) and with the mesopores filled with heptane (b). Blue and red lines indicate resonances representing fluorines in "prone" and "upright" PFP functionalities, which are depicted on the right side of the figure. In the presence of solvent, all molecules remain close to the silica surface.

Scheme 1. Schematic Representation of a Bifunctional PFP/DAT-MSN



Scheme 2. Synthesis of Diarylamine-Functionalized Methyldiethoxo-Silane (DAS)



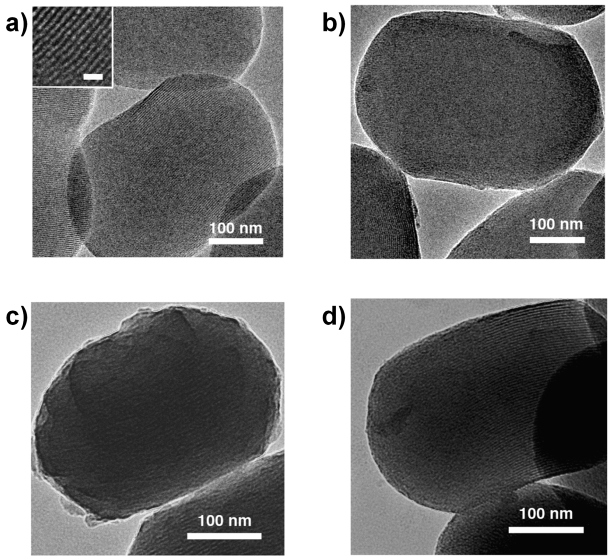


Figure 2. TEM images of Cat A (a), Cat B (b), Cat C (c), and Cat D (d). Scale bars are 100 nm. The inset in (a) represents parallel mesoporous channels of Cat A. Scale bar = 10 nm.

We first synthesized a diarylamine-functionalized alkoxysilane (DAS), *N*-(4-(4-(diethoxymethylsilyl)butyl)phenyl)-2,4,6-trimethyl-aniline, as a precursor for the synthesis of the aforementioned bifunctional MSN materials as shown in Scheme 2. The 4-(4-bromophenyl)-1-butene was coupled with 2,4,6-trimethylaniline through a palladium-mediated amination to yield a diarylamine **1**, followed by a hydrosilylation reaction with methyldiethoxysilane to synthesize the desired DAS compound **2**. Two bifunctional MSN catalysts were prepared by introducing DAS and PFP-trimethoxysilane in molar ratios 1:1 (sample A) and 1:4 (sample B), to a NaOH-catalyzed, cetyltrimethylammonium bromide (CTAB)-templated co-condensation reaction of tetraethoxysilane, as detailed in the Supporting Information.[30] Additionally, two monofunctional MSN catalysts with only the DAS (sample C) and the PFP (sample D) group were synthesized via the same method. After the removal of CTAB, these MSN samples were treated with triflic acid to yield the corresponding catalysts, labeled Cat A, Cat B, Cat C, and Cat D, respectively.[30] The physisorbed triflic acid on the surface was removed under vacuum, as indicated by the thermogravimetric analysis (TGA).[30] The transmission electron microscopy (TEM) images showed that all silica particles exhibited an elliptical shape with the aspect ratio of 1.5−2.0 and average length of 350−400 nm, as shown in Figure 2. The mesoporous channels were arranged in a 2D hexagonal array, as observed by TEM and powder X-ray diffraction (XRD).[30] These studies indicated that the porous structure of these MSN materials remained intact after treatment with triflic acid. The N_2 sorption analysis of the samples showed a type IV isotherm, which is characteristic of a cylindrical mesoporous structure. The measured Brunauer−Emmett−Teller (BET) surface areas of Cat A, B, C, and D were 792, 861, 874, and 837 m^2/g, respectively. The average pore size calculated using the Barrett−Joyner−Halenda (BJH) method is 2.6 ± 0.2 nm for all materials.

The total concentration of covalently bound surface organic functionalities was evaluated by solid-state ^{29}Si NMR, based on the relative intensities of resonances representing Q^n, T^n, and D^n sites, as detailed in the Supporting Information[30] and summarized in Table 1. In addition, the concentrations of DAT groups were quantified using ^{1}H MAS NMR spectra, in which the resonances representing aromatic protons were clearly resolved.[30] The ^{13}C CPMAS NMR spectra were measured to confirm the covalent immobilization of all functional groups and the integrity of their chemical structures.[30]

To examine the effect of PFP groups on the catalytic performance of DAT, catalysts A−D were tested in the esterification reactions of 3-phenylpropionic acid or heptanoic acid with benzyl alcohol in heptane. As illustrated in Figure 3, the bifunctional PFP/DAT MSNs (Cat A and Cat B) exhibit the best

Table 1. Loading and Relative Ratio of Organic Functional Groups in the MSN Catalysts Based on Quantitative Solid-State ^{29}Si MAS NMR

sample	PFP (mmol/g)[a]	DAT (mmol/g)[a]	PFP:DAT ratio
Cat A	0.70 (35%)[b]	0.12	6:1
Cat B	0.76 (35%)[b]	0.05	15:1
Cat C	0	0.15	NA
Cat D	0.62 (30%)[b]	0	NA

[a] The loading in mmol/g was measured with an error of ±8% for PFP and ±15% for DAT. [b] The surface coverage of PFP was calculated assuming that the inner pore surface area in MSNs constitutes 90% of the total surface, and the footprint area of the PFP compound is ~0.6 nm^2. The DAT groups were not included.

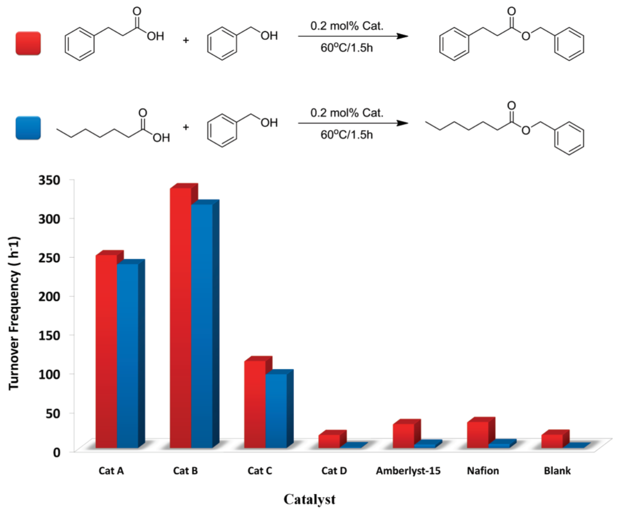


Figure 3. Esterification reactions of 3-phenylpropionic acid (red) and heptanoic acid (blue) with benzyl alcohol catalyzed by various heterogeneous acid catalysts.

reactivity among all catalysts. The turnover frequency (TOF, measured after 1.5 h of reaction time) of Cat B is higher than that of Cat A, which may be attributed to the higher relative concentration of PFP. The TOF of Cat C is considerably lower than those of Cat A and Cat B, which shows that the DAT groups alone are less efficient in both esterifications. Cat D exhibits negligible activity, that is, the PFP groups do not catalyze these reactions.

To compare the effect of PFP with other commonly used hydrophobic groups, the surface of Cat C was further passivated with a TMS group to make the TMS/DAT MSN material.[30] The esterification reaction yield of methyl 3-phenylpropionate catalyzed by TMS/DAT MSN (57%, corresponding to TOF = 190 h^{-1}) was slightly higher than that of Cat C, but proved to be lower than observed in Cat A and Cat B. We also note that the reaction of 3-phenylpropionic acid and benzyl alcohol catalyzed by homogeneous triflic acid under the same conditions only gave 18.3% of yield (TOF = 61.3 h^{-1}). Given the low reactivity and high acidity (pK_a = −14) of triflic acid, this result indicates that the acid strength of the catalyst is not the only factor affecting the equilibrium of this reaction.[31]

The enhancement of catalytic properties observed in bifunctional catalysts Cat A and Cat B is attributed to the aforementioned formation of a surface-bound layer of PFP molecules, whose prone orientation in the presence of heptane prevents direct interaction between water and the surface silanol groups. It appears that in spite of the incomplete PFP coverage (see Table 1), the catalyst surface became sufficiently hydrophobic to effectively reduce the concentration of water inside the mesopores and thereby drive the chemical equilibrium toward the completion of the esterification reaction. Indeed, following the reaction the amount of water byproduct observed on the walls of reaction tubes containing Cat A and Cat B was much higher than for Cat C and TMS/DAT MSN. Cat D did not produce any water because of its negligible activity.

The bifunctional PFP/DAT MSNs and DAT-MSN proved to be recyclable at least five times with identical yields,[30] indicating that the reactivity difference between bi- and monofunctional catalysts is not because of the decomposition of DAT groups. We also note that the pK_a values of all relevant chemical species in our catalytic system do not favor the proton transfer from these groups.[32] Finally, all studied DAT-MSNs showed higher reactivity than the commercial polymeric solid acid catalysts Amberlyst-15 and Nafion NR-50 under the examined reaction conditions. It is noted, however, that Amberlyst-15 and Nafion NR-50 use a different functionality (sulfonic acid), for which the conditions used in our tests were not optimized. Although these resin-based catalysts bear high density of acid sites,[33] they often require the use of swelling solvents to enhance the accessibility of reactants to these sites.[34]

In conclusion, we have reported on a bifunctional MSN catalytic system with a superior reactivity in the equilibrium reaction, whose improved yield is the result of a nanoenvironment designed to efficiently remove the byproduct (water) through incorporation of the secondary functional group. This study integrated a novel synthetic approach with state-of-the-art characterization and theory,[20] which served as predictive tools in the design of an efficient new catalyst for the esterification reaction. We expect that similar principles can be used in designing new heterogeneous acid catalysts for other important reactions involving dehydration.

■ EXPERIMENTAL SECTION

Catalytic Esterification Reactions. The reactions were carried out using equal amount of catalytic sites in a capped tubular reactor. For example, the reaction mixture consisting of heptanoic acid (49.8 mg, 0.383 mmol), benzyl alcohol (41.4 mg, 0.383 mmol), and catalysts (0.2 mol %) in 1 mL of heptane was heated at 60 °C for 1.5 h. The catalysts were isolated by centrifuge and washed with 10 mL of heptane. Diphenyl ether (ca. 100 mg) was added into the combined heptane solution as an internal standard. The reaction conversion and product yield were determined by gas chromatography using a HP-5 column. The oven temperature was initially set at 40 °C for 4 min, then increased to 250 °C with a ramp rate of 10 °C/min, and kept at 250 °C for 5 min. The peaks corresponding to all reagents and products were separated, and their integrated intensities were calibrated using an internal standard. For the recyclability test, the reaction mixture of 3-phenylpropanoic acid (57.5 mg, 0.383 mmol), benzyl alcohol (41.4 mg, 0.383 mmol), and 0.4 mol % of Cat B in 1 mL of heptane was stirred at 70 °C for 2.5 h. The filtered catalyst was dried under vacuum for 24 h and recharged with the same amount of starting material for each run.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and characterization data of materials. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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