Mesoporous Materials

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Efficient Bifunctional Nanocatalysts by Simple Postgrafting of Spatially Isolated Catalytic Groups on Mesoporous Materials**

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Multistep and efficient synergistic catalytic processes to various types of biomolecules by biological catalysts (enzymes) are very common in living organisms.[1] Many notable examples of such enzymatic and antibody catalytic processes involve acid–base cooperative or efficient bifunctional catalysts.[2] By mimicking these extraordinary systems found in nature, some conventional homogeneous bifunctional acid–base catalysts have been synthesized.[3] However, the efficiency and selectivity of these catalysts, which often depend on the relative separation between the acid and base catalytic sites, are often poor because the materials lack a continuous range of acidic and basic catalytic sites.[4] Hence, a considerable amount of effort has recently been directed towards the synthesis of heterogeneous solid-state, acid–base catalysts that have well-controlled, high concentrations of acidic and basic catalytic sites.[5]

A family of mesoporous materials, which were first reported in 1992, have been widely and effectively used as hosts for a variety of catalytically active functional groups, including acidic and basic sites, to produce efficient heterogeneous catalysts.[6] By postgrafting of the residual surface silanol groups of the mesoporous materials with organosilanes, high-surface-area and tunable nanopores have been synthesized that contain solid acid and solid base catalytic sites for reactions such as the Knoevenagel condensation, catalytic oxidations, and Michael addition.[7] However, almost all postgrafting syntheses of catalysts reported to date are typically carried out by stirring mesoporous materials with an excess amount of organosilanes in nonpolar solvents such as toluene at reflux (112 °C).[8]

Postgrafting of organosilanes onto mesoporous materials in toluene at reflux indeed allows an effective inclusion of densely populated or high concentrations of covalently bound organic functional groups, including organoamines. However, this synthetic approach also has drawbacks as it grafts most of the surface silanol groups of the materials. The latter groups, which can act as weak acids, generally increase the efficiency of a number of organoamine-catalyzed reactions such as the Henry reaction and nitroaldol condensations.[9] Furthermore, the presence of densely populated organic groups reduces the surface areas and pore volumes of the materials. Therefore, densely populated organoamine catalysts synthesized in toluene are typically accompanied by loss of catalytic efficiency. For instance, metallocene catalytic groups immobilized on densely populated postgrafted organoamines synthesized in toluene show lower catalytic efficiency for polymerization reactions than corresponding samples containing sparsely populated metallocene groups.[10] However, the synthesis of the latter materials involves a lengthy multistep procedure that consists of the preparation of bulky imine-containing organosilanes and postgrafting the groups in toluene to form densely populated imine-functionalized mesoporous materials. Upon subsequent hydrolysis of the bulky imine groups, spatially spaced organoamines and silanol groups are formed.

Recently, Katz and co-workers described the synthesis of organoamine-functionalized silica gel catalysts that contain silanol groups.[11] These bifunctional catalysts showed increased efficiency and selectivity for the Michael and Henry reactions compared to the corresponding materials without silanols. However, the surface area of silica gel is low, the number of the bifunctional groups in the material is limited, and the distribution of the two groups is difficult to control. Davis and co-workers have also reported the synthesis of sulfonic acid and organoamine bifunctionalized catalysts for aldol reactions by self-assembly.[12] However, these materials have a low number of randomly distributed acid and base groups.

Herein, we report the synthesis of bifunctional mesoporous catalysts that contain spatially distributed organoamine and silanol groups and which are the most efficient catalysts, to the best of our knowledge, to be reported for the Henry reaction. The catalysts were prepared by carrying out either a simple, one-step postgrafting of an excess amount of aminoorganosilanes under reflux onto mesoporous silica in a polar solvent, ethanol, at lower temperature (78 °C) or by postgrafting a smaller amount of aminoorganosilanes in toluene during a shorter reaction time at 78 °C (see the Supporting Information for details of the latter approach). The advantages of the spatially distributed organoamines and silanols for catalysis was demonstrated for 3-aminopropyl-functionalized mesoporous materials, the use of which resulted in a fourfold increase in catalytic efficiency or turnover (TON) number for the Henry reaction compared to similar materials prepared in toluene at reflux as most commonly done previously.[8] These materials afforded a 99.4% yield for the

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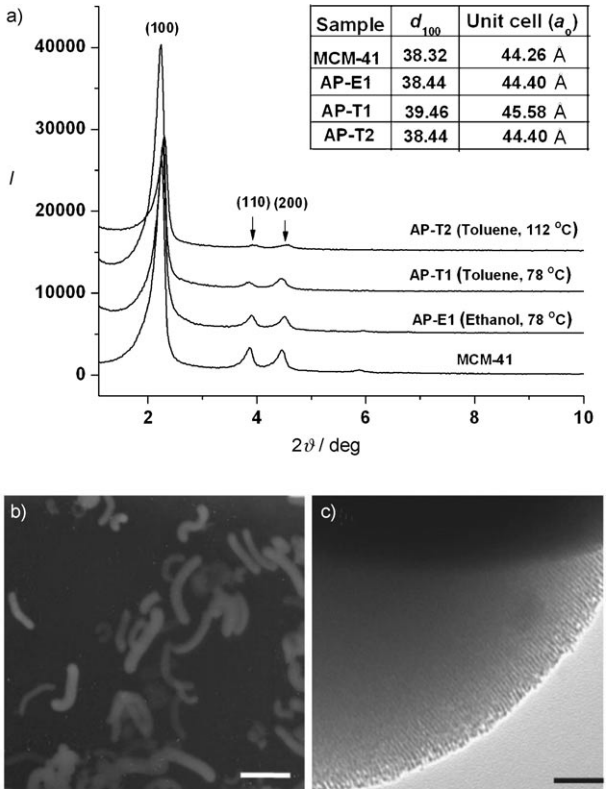
Henry reaction within 15 min, the highest catalytic efficiency of any mesoporous catalyst reported for the Henry reaction.

The synthesis of the bifunctional, spatially isolated organoamine and silanol groups was obtained by stirring an excess amount of 3-aminopropytrimethoxysilane with MCM-41 in ethanol at 78 °C to produce AP-E1. To obtain control samples, an excess amount of the same organosilane was postgrafted onto MCM-41 in toluene at 78 °C (AP-T1) and at reflux at 112 °C (AP-T2). These materials, both before and after postgrafting, were characterized by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM; Figure 1). The XRD patterns of all the samples



Sample	d_{100}	Unit cell (a_o)
MCM-41	38.32	44.26 Å
AP-E1	38.44	44.40 Å
AP-T1	39.46	45.58 Å
AP-T2	38.44	44.40 Å

Figure 1. a) Powder XRD patterns of MCM-41 and corresponding organoamine-functionalized samples prepared by grafting 3-aminopropytrimethoxysilane on MCM-41 in ethanol at reflux or 78 °C (AP-E1), in toluene at 78 °C (AP-T1), and in toluene at reflux (112 °C; AP-T2). Inset shows d_{100} and unit cell (a_o) values of the samples ($a_o = 2d_{100}/3^{1/2}$ Å) for 2D hexagonally ordered materials). b,c) TEM images of AP-E1. Scale bars: 2 μm (b) and 200 nm (c).

showed a sharp peak corresponding to the (100) peak as well as at least two more Bragg reflections corresponding to the (110) and (200) peaks and indicate that the materials have highly hexagonally ordered mesostructures, which remain intact during postgrafting (Figure 1a). The peaks were indexed to give unit cell sizes of approximately 4.4–4.5 nm, which barely changed during postgrafting. The slight decrease in XRD intensity of the postgrafted sample AP-T2 relative to AP-E1 and AP-T1 may be caused by the decrease in electron contrast between the channel pores and the walls of the mesoporous material, which can be caused by the presence of more organoamine groups in the former than the latter and/or by a slight loss of structural order in the latter as a result of the higher temperature for postgrafting. The TEM images of the samples before and after postgrafting also showed well-ordered mesoporous structures (Figure 1b,c). N_2 gas adsorption measurements of all the materials showed type IV isotherms, which are characteristic of mesoporous materials (see the Supporting Information). Furthermore, their BET surface areas range between 1030–60 $m^2 g^{-1}$ depending on grafting density while their BJH pore size distributions are monodisperse.

The thermogravimetric traces (Figure 2) indicated a weight loss below 100 °C in all the samples which corresponded to the loss of physisorbed water. However, the

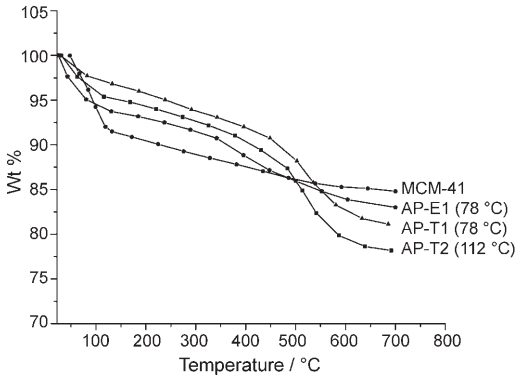
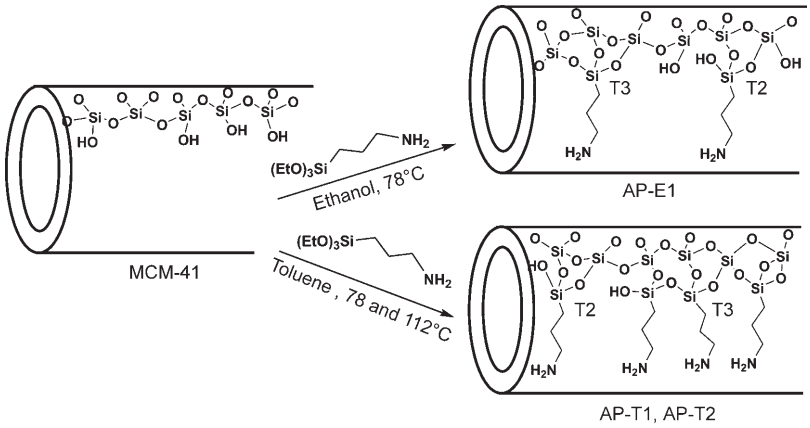


Figure 2. Thermogravimetric traces of MCM-41, AP-E1, AP-T1, and AP-T2.

weight loss of the samples between 100 and 600 °C, which corresponds to the loss of organoamine groups and some condensed water, showed an interesting trend. The AP-E1 sample showed the lowest weight loss (10.7%) followed by AP-T1 (14.8%) and then AP-T2 (16.8%). These differences in weight loss are more significant if we consider that the removal of silanol groups from the materials during postgrafting is greatest for AP-T2 and therefore results in the lowest weight loss from TGA traces as a result of condensation of water. These results were further corroborated by solid-state NMR spectroscopy (see the Supporting Information). ^{29}Si MAS NMR qualitatively and quantitatively confirmed the presence of the highest density of organoamine groups in AP-T2 (4.3 mmol g^{-1}), followed by AP-T1 (4.1 mmol g^{-1}), and then AP-E1 (1.3 mmol g^{-1}). Similarly, the ^{13}C CP-MAS NMR spectra showed peaks corresponding to aminopropyl groups at $\delta = 43.1$, 24.7, and 8.4 ppm after postgrafting. The intensities of these peaks were highest for AP-T2, then AP-T1, and AP-E1, consistent with the TGA and ^{29}Si MAS NMR spectroscopy results. Both the TGA and solid-state NMR spectroscopy results confirmed that AP-E1 has a smaller number of organoamine groups and more silanol groups, and the organoamines are likely to be spatially distributed relative to AP-T1 and AP-T2, which have densely populated organoamine groups and fewer silanol groups (Scheme 1).[9,10]



Scheme 1. Reaction scheme for postgrafting aminopropyl groups in ethanol at 78 °C (AP-E1) and in toluene at 78 °C (AP-T1) and at reflux at 112 °C (AP-T2).

To demonstrate the usefulness of our bifunctional materials with spatially isolated organoamine and silanol groups, we performed the Henry reaction using the materials as catalysts (Figure 3). Many organoamine-functionalized mesoporous

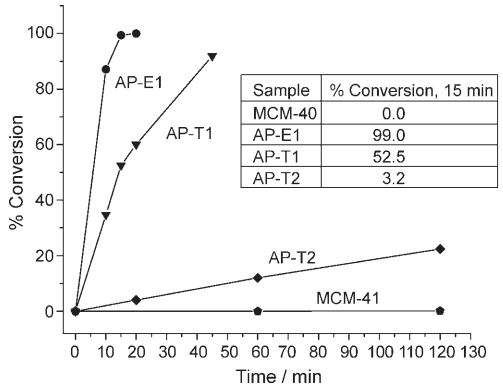
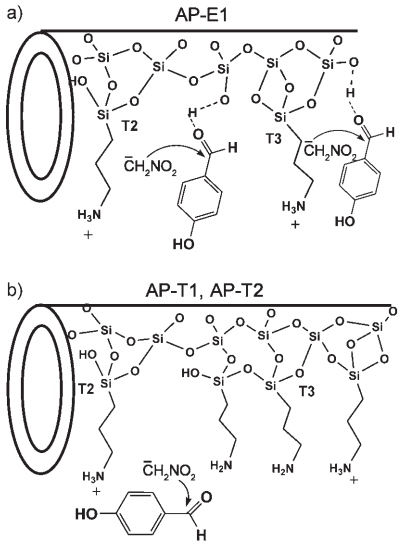


Figure 3. Percentage conversion of reactant versus time of the Henry reaction between *p*-hydroxybenzaldehyde and nitromethane at 90 °C to form nitrostyrene as catalyzed by AP-E1, AP-T1, and AP-T2.

materials synthesized under reflux in toluene are reported to catalyze the Henry reaction.[2,9,14] The highest yield (96 %) and TON values reported so far with such samples were obtained with 50 mg catalyst and 2.5 mmol reactant with 1 h reaction time[9] (see Table S2 in the Supporting Information).

Interestingly, the Henry reaction with sample AP-E1 gave a yield of 99.4 % in around 15 min, while the same amounts of AP-T1 and AP-T2 afforded yields of 52.4 and 8.4 %, respectively, in 15 min (Figure 3). This result reveals at least a twofold increase in yield and a fourfold increase in turnover number for AP-E1 relative to AP-T1 and AP-T2, and it is the highest efficiency compared to any mesoporous catalyst previously reported for the Henry reaction (see the Supporting Information). These results are more significant given the fact that AP-E1 has fewer organoamine groups per unit mass than both AP-T1 and AP-T2 and also as mesostructures in all the samples remained intact as shown by XRD and TEM. The enhanced catalytic efficiency of AP-E1 compared to AP-T1 and AP-T2 may, therefore, be a result of two reasons: 1) The higher number of silanol groups in AP-E1 can activate the carbonyl group of benzaldehyde to undergo the nitroaldol reaction more efficiently as shown in Scheme 2 and as reported by Katz and coworkers.[11] 2) The higher surface area of AP-E1 owing to its lower density of grafted organoamines relative to AP-T1 and AP-T2 may also have contributed to the differences in catalytic efficiency. Further experiments may, however, be required to determine the possible contribution of each.

Similar studies of materials postgrafted with organodiamine groups using ethanol and toluene also revealed an increased efficiency for samples synthesized in ethanol relative to



Scheme 2. Reaction mechanism to explain the enhanced efficiency of AP-E1 (a) in the Henry reaction relative to AP-T1 and AP-T2 (b). The presence of a significant number of spatially isolated silanol groups in AP-E1 leads to activation of the carbonyl group of benzaldehyde for nucleophilic attack.[11]

corresponding samples synthesized and grafted in toluene. Postgrafting the remaining silanol groups of the ethanol product (or AP-E1) with more organic groups using toluene resulted in a significant reduction in catalytic efficiency, further confirming the importance of spatially isolated organoamine and silanol groups for increased efficiency. Detailed synthesis of these materials and their catalytic properties will be reported elsewhere. We hypothesize that postgrafting spatially distributed organoamines in ethanol occurs because of the competition for the aminoorganosilane by ethanol (a polar protic solvent, dielectric constant = 24 D) and the hydrophilic surface silanol groups. Because of the absence of hydrogen bonding between the organoamines and toluene (a nonpolar solvent, dielectric constant = 2.4 D), the aminoorganosilanes aggregate and preferentially interact with the surface silanol groups. Aggregation of aminoorga-

nosilanes in toluene has been previously proposed to cause grafting of very densely populated organic groups.[10b] However, by lowering the concentration of aminorganoosilane and shortening the reaction times, we have also synthesized similar site-isolated samples that display efficient catalytic properties in toluene at lower temperature (Supporting Information).

In conclusion, we have described the synthesis of the most efficient mesoporous catalysts reported to date for the Henry reaction by postgrafting spatially distributed organoamine groups on mesoporous silica. This was achieved by reacting excess amounts of aminoorganosilanes in ethanol or by postgrafting smaller amounts of aminoorganosilanes in toluene for a short reaction time. Despite the lower number of catalytic sites, the resulting materials with increased cooperative properties and higher surface areas revealed the most enhanced catalytic properties. This procedure should allow the synthesis of various bifunctional catalysts for a number of other reactions in which cooperative effects by two functional groups and higher surface areas are required. We have confirmed that such one-pot synthetic methods allow the preparation of spatially isolated bifunctional catalysts, which until now were only attainable through lengthy and costly multistep methods.[10] In contrast, this approach is very simple, involving one step, and versatile compared to all previously reported procedures.

Experimental Section

Postgrafting of spatially isolated organoamines onto mesoporous silica, MCM-41: MCM-41 was synthesized as reported previously (see the Supporting Information).[13] The sample of MCM-41 was kept in an oven at 80 °C to remove physisorbed water prior to postgrafting. For AP-E1, MCM-41 (500 mg) was stirred with excess 3-aminopropyltrimethoxysilane (APTMS; 0.66 g, 3.68 mmol) under reflux in ethanol (250 mL) at around 78 °C for 6 h. The solution was filtered, and the precipitate was washed with dichloromethane (200 mL) and ethanol (500 mL) and then dried in air. Two other samples were prepared in toluene, one of which was prepared by stirring MCM-41 (500 mg) with APTMS (0.82 g, 3.68 mmol) in toluene (250 mL) at 78 °C (AP-T1), and the other was prepared similarly but under reflux at about 112 °C (AP-T2). These samples were washed and dried as above, and the resulting mesoporous samples were characterized instrumentally (see the Supporting Information for details).

Henry (nitroaldol) reaction: The Henry reaction was performed as reported before.[9,14] Typically, the aminofunctionalized mesoporous sample (20 mg) was added to a mixture of *p*-hydroxybenzaldehyde (122 mg, 1 mmol) and nitromethane (10 mL). The reaction mixture was stirred at 90 °C under nitrogen, and aliquots of the mixture were removed with a filter syringe and characterized by solution ^{1}H NMR spectroscopy and GC-MS over the course of the reactions. The percentage yields and conversions were determined from ^{1}H NMR spectra measured in deuterated acetone.

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