Acid–Base Catalysis

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Multifunctional Heterogeneous Catalysts: SBA-15-Containing Primary Amines and Sulfonic Acids**

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A current area of interest in the design and synthesis of solid catalysts is the creation of materials that contain multiple types of active centers. These functionalities may be used to perform several steps in a reaction sequence or work in a cooperative manner to alter the characteristics of a single reaction, for example, rates, selectivities, and so forth. Enzymes, such as aldolases, are interesting examples of multifunctional catalysts as they are capable of conducting multistep reactions. Enzymes immobilize mutually incompat-

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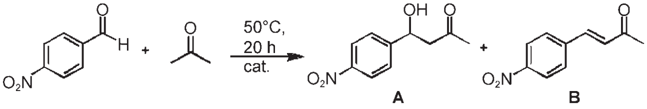
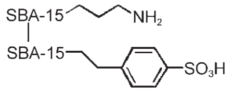
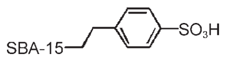
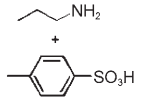
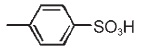
ible functional groups in a manner that maintains their independent functionality, and as such, are able to carry out multistep reaction sequences with functionalities that would not be tolerated together in solution.

Previous work on bifunctional solid-catalyst synthesis largely involved the use of metal centers with acid sites. Recently, attention has been focused on combinations of organic functional groups. Immobilized organic amines (base) have been used with supported silanols (acid)[1] to perform bifunctional catalysis, and amine functional groups have been immobilized together with thiols.[2,3] Dufaud and Davis[4] reported on the positioning of adjacent sulfonic acid functional groups, and Zeidan et al.[5] have also incorporated sulfonic acids and thiols that exhibit a cooperative effect in a condensation reaction. Also, bifunctional catalysis with different active centers on separate supports[6–9] and hydrogen-bonding ureas with amine bases[10] have been investigated. However, no reports of a material containing an organic acid and organic base that are incorporated into the same material have appeared, presumably as a result of the incompatibility of these groups. Herein, we report a solid material that contains both organic acid and base groups that together exhibit a reactivity in the aldol condensation of acetone with 4-nitrobenzaldehyde that is not achievable with these same groups in solution.

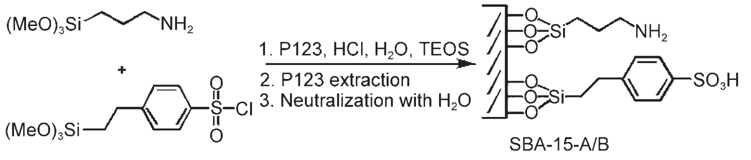
A sulfonic acid and amine were incorporated into SBA-15 (Santa Barbara Amorphous) through a "one-pot" synthesis using poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (P123), HCl, H_2O, and tetraethoxysilane (TEOS; Scheme 1) to prepare the dual-functionalized mesoporous catalyst SBA-15-A/B.

Table 1: Acid–base aldol catalysis.



Entry	Catalyst (10 mol %)	**A** [%]	**B** [%]	Conv. [%][a]
1		45	17	62
2		8	8	16
3		25	8	33
4	SBA-15-A/SBA-15-B[b]	30	14	44
5	SBA-15	0	0	0
6		0	0	0
7		3	5	8
8		3	1	4

[a] Total conversion. Yields determined through ^{1}H NMR spectroscopic analysis with THF as the internal standard. [b] 1:1 mixture of sulfonic acid functionalized SBA-15 (SBA-15-A) and amine-functionalized SBA-15 (SBA-15-B).



Scheme 1. Catalyst synthesis.

This material (as well as SBA-15 functionalized with sulfonic acid alone and propylamine alone) was analyzed by ^{13}C and ^{29}Si CP/MAS solid-state NMR spectroscopy, X-ray diffraction (XRD), N_2 adsorption, and thermogravimetric analysis (see Supporting Information).

The characterization data show that the functionalized materials have surface areas of between 600 and 800 $m^2 g^{-1}$ and pore sizes on the order of 40–60 Å, typical of SBA-15-type materials.[4,5] The ^{13}C NMR spectra indicate the presence of the intact organic functional groups, and the ^{29}Si NMR spectrum indicates the incorporation of organic functional groups.

The immobilized catalysts were tested for activity in the aldol condensation of 4-nitrobenzaldehyde with acetone to give the resulting aldol addition and dehydration products. SBA-15-A/B was used as a catalyst for this reaction (Table 1, entry 1), and in all experiments the total amount of amine and/or sulfonic acid functional groups was kept constant at 0.05 mmol. Significant production of both products occurred and gave a total conversion of 62 %. Use of SBA-15 functionalized only with a sulfonic acid or amine functionality gave significantly lower levels of conversion (Table 1, entries 2 and 3). A physical mixture of acid-functionalized SBA-15 and amine-functionalized SBA-15 showed an intermediate level of conversion that was significantly lower than the dual-functionalized acid/base catalyst (Table 1, entry 4). The support alone caused no conversion (Table 1, entry 5). Interestingly, the homogeneous analogues of the sulfonic acid and amine showed no conversion of the starting materials into either product, as these functionalities apparently neutralize each other and salt out of the reaction mixture (Table 1, entry 6). Also, the individual acid and base homogeneous analogues gave rise to very low conversions (Table 1, entries 7 and 8), much less than the acid/base bifunctional catalyst. The observed cooperative effect indicates some level of acid/base pairing in this material. With the two functional groups being dispersed randomly in the synthesis, it was expected that there would be acid sites neighboring acid sites, base sites neighboring base sites, and some acid sites in proximity to base sites. If the catalytic activity is due to single acid or base sites, or neighboring acid/acid or base/base sites, the level of conversion in entries 2 and 3 (Table 1) would be the maximum achievable. The enhancement of reactivity beyond those cases is likely due to interactions between neighboring acid and base sites (see Supporting Information for the mechanism).

It is expected that the acid and base groups in SBA-15-A/B would be in equilibrium between the free acid and base and the ion pair that results from neutralization, and that the solvent would have a dramatic effect on this equilibrium, that is, protic solvents would confer different properties to aprotic solvents as a result of differing abilities to stabilize the neutralized ion pair. The equilibrium would lie towards the ion pair in polar, protic solvents, as proton exchange would be rapid and the protic solvent would stabilize the ion pair the most. Nonpolar, aprotic solvents would cause slower exchange of the protons and would stabilize an ion pair much less than a protic solvent, thus forcing the equilibrium in favor of the free acid and base. To investigate these possibilities, reactions were carried out in a variety of cosolvents to examine the effect of solvent polarity on conversion. The conversion into both products is nearly 30% in polar, protic solvents, such as water and methanol (Table 2, entries 1 and 2). The conversion more than doubles to about 70% upon moving to polar, aprotic solvents, such as diethyl ether and chloroform (Table 2, entries 3 and 4). Nonpolar, aprotic solvents, such as hexane and benzene (Table 2, entries 5 and 6), give further improvements in conversion, which approach 90% in the case of hexanes (Table 2, entry 5). Thus, there is a clear effect on conversion that is related to solvent polarity, thereby suggesting that the nature of the solvent does affect the equilibrium of proton exchange and hence the effective concentration of free acid and base.

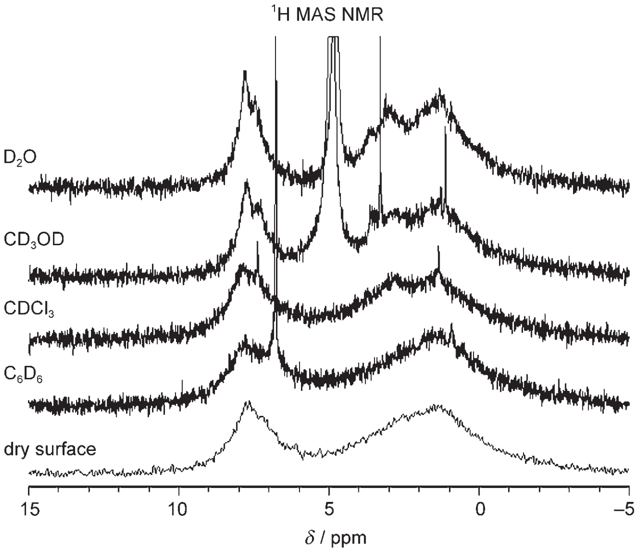
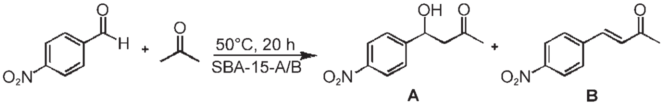


Figure 1. Solvent effect on the line shape of ^{1}H MAS NMR spectra. Sharp lines are due to incomplete deuteration of the solvents.

Table 2: Solvent effect on the catalysis.



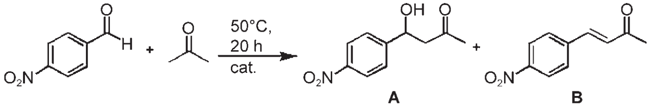
Entry	Cosolvent (1:1)[a]	**A** [%]	**B** [%]	Conv. [%][b]
1	H_2O	27	7	34
2	MeOH	14	9	23
3	Et_2O	52	13	65
4	$CHCl_3$	60	9	69
5	hexane	75	13	88
6	benzene	62	12	74

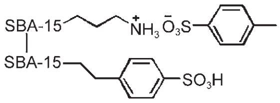
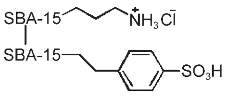
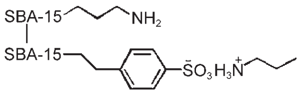
[a] 50:50 mixture of acetone/cosolvent. [b] Total conversion. Yields determined through ^{1}H NMR spectroscopic analysis with THF as the internal standard.

Solid-state CP/MAS NMR spectroscopic analysis was used to probe the local motion of the bifunctional catalyst. SBA-15-A/B was fully deuterated and then slurried in different deuterated solvents to study the changes in motion of the functional groups in these different environments (Figure 1). The resolution of the ^{1}H NMR resonances in D_2O and CD_3OD (from non-exchanging protons in the organic functional groups) sharpened, thus indicating a more mobile structure. However, the resonances broadened in the nonpolar solvents CD_3Cl and C_6D_6, thus suggesting more restricted motion of the two groups as the acid and base functional groups associate to avoid unfavorable interactions with nonpolar solvents. The trend is in full agreement with the catalysis data as reactions in nonpolar solvents cause the polar acid and base groups to associate to a greater extent, thus allowing for an increased cooperative effect. The groups are more mobile in polar solvents as they favorably interact with the solvent and are less likely to interact with one another for cooperative catalysis to occur. Taken together, the catalytic and NMR spectroscopic data suggest that the catalytic behavior of SBA-15-A/B is clearly dictated by multiple factors, two of which seem to be the state of the equilibrium between the acid and base and the ion pair and the interactions between the two functional groups as caused by polar/nonpolar interactions with the solvent.

To probe the bifunctionality of the catalyst, SBA-15-A/B was treated with acid to neutralize the amine functional groups, thus leaving only the sulfonic acid sites. SBA-15-A/B was washed with 1M HCl or aqueous *para*-toluenesulfonic acid (*p*-TSA; Table 3, entries 1 and 2, respectively), and it is clear that the material behaves as the immobilized sulfonic acid alone (Table 1, entry 2). Likewise, SBA-15-A/B was treated with propylamine (Table 3, entry 3) and the resulting material, in which the sulfonic acid sites are neutralized, behaved the same as the amine-functionalized catalyst (Table 1, entry 3). These results illustrate the bifunctionality of SBA-15-A/B and the coexistent acidity and basicity. These experiments highlight the interesting properties achievable by immobilization of multiple functional group types. The amine and sulfonic acid salt out in solution and give rise to no conversion (Table 1, entry 6), and when the heterogeneous catalyst SBA-15-A/B is treated with homogeneous acids or bases the opposing functional group salts out and the respective behavior is lost. On the other hand, the two opposing functional groups do not lose catalytic activity when the amine and sulfonic acid are immobilized on SBA-15-A/B

Table 3: Catalyst quenching experiments.



Entry	Catalyst	**A** [%]	**B** [%]	Conv. [%][a]
1		7	7	14
2		8	7	15
3		31	7	38

[a] Total conversion. Yields determined by ^{1}H NMR spectroscopic analysis with THF as the internal standard.

but rather function in a cooperative manner to give the most active catalyst used in this study.

In summary, a new approach to carrying out heterogeneous catalysis with functional groups that are incompatible and incapable of catalyzing reactions in solution has been reported. By immobilizing functional groups that can not coexist in solution as active catalytic sites, it has been demonstrated that reactivity can be restored and a cooperative, catalytic effect is observed between the functional groups. Advanced solid-state NMR experiments are in progress to study the proton motion and spacing of functional groups in these materials, and further catalytic applications are being investigated.

Experimental Section

"One-pot" synthesis of catalyst: HCl (120.0 mL, 240.0 mmol, 2.0 M) and H_2O (6.0 mL, 333.0 mmol) were added to triblock copolymer P123 (4.0 g, 0.688 mmol, $M_n = 5800$) and stirred at 40 °C until the P123 was fully dissolved. TEOS (8.2 mL, 37.8 mmol) was then added, and the reaction mixture was allowed to stir at 40 °C for 45 min. Then 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (0.65 g) in dichloromethane (1.0 mmol, 50/50 (w/w)) was added followed by 3-aminopropyltrimethoxysilane (0.19 mL, 1.0 mmol). The reaction mixture was then stirred at 40 °C for 20 h, and then left at 100 °C for 24 h. The resulting solid was filtered and rinsed with excess H_2O (4 × 500 mL) until the slurry reached a neutral pH value. The solid was then allowed to dry overnight on a filter. The dried solid was then extracted with EtOH (400 mL per gram) by refluxing in EtOH for 24 h to remove the P123. The solid was filtered and rinsed repeatedly with EtOH (4 × 500 mL), washed with copious amounts of water until neutral, and dried overnight to obtain a dry white solid. The solid was then further dried at 80 °C under vacuum for 24 h.

Catalytic experiments (using the following general procedure for the aldol condensation):[10] Catalyst was added (0.05 mmol total amines and/or sulfonic acids) to a solution of 4-nitrobenzaldehyde (76 mg, 0.5 mmol) in acetone (10 mL), and the reaction flask was then sealed under Ar and heated at 50 °C for 20 h. Acetone was then removed in vacuo, and the product was analyzed by ^{1}H NMR spectroscopy in $CDCl_3$ with THF as an internal standard. In the case of the cosolvent studies, 10 mL of a 50:50 mixture of acetone and cosolvent was used.

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