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Research Note

The effect of acid–base pairing on catalysis: An efficient acid–base functionalized catalyst for aldol condensation

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Abstract

Acid–base bifunctionalized heterogeneous catalysts may be capable of exhibiting reactivity not achievable with homogeneous catalysts. We investigated the effect of pK_a of the acid component of mesoporous solids containing acid–base bifunctionality on their catalytic ability toward aldol condensation between 4-nitrobenzaldehyde and acetone. We found that higher levels of aldol product conversion were obtained when weaker acid components (phosphoric, carboxylic vs sulfonic) were used, an indication of the importance of the equilibrium between free acid and free base and the resulting neutralized ion pair in the catalytic capability of acid–base functionalized materials. A catalyst containing primary amine groups in combination with carboxylic acid groups (with similar chemical functionalities to proline) was found to be a superior catalyst in this aldol reaction with a number of different electrophilic components.

Keywords: Acid–base; Heterogeneous; Aldol reaction; Mesoporous materials; Bifunctional catalyst

1. Introduction

The design of multifunctional materials capable of carrying out heterogeneous catalysis though the incorporation of organic functional groups capable of cooperative catalysis has been of growing utility. Numerous individual functional groups have been incorporated into solids and have been shown to have unique properties alone or in combination with other functional groups [1–9]. Recently our group reported on mesoporous materials functionalized with incompatible acid and base groups that showed reactivity not achievable by the organic group combination in solution for an aldol condensation reaction [10]. The equilibrium between acids and bases when immobilized together is not well defined but likely is very important in understanding the catalysis properties of such materials. In the present study, we investigated the effect of the equilibrium between acid and base groups by varying the pK_a of the acid group.

Interest in materials bearing sulfonic acids and amine groups has been growing recently, due to these materials' inherent acid and basic properties. Corriu et al. reported a material bearing sulfonic acid and amines isolated from one another [11], whereas our group previously reported on the reactivity of immobilized acid/base pairs wherein the sulfonic acid and amines are incorporated together to create a material with accessible sulfonic acid and amine sites exhibiting cooperative catalytic behavior [10]. The nature of the equilibrium between the acid and base groups in this material could be very important to the tuning and understanding of its catalytic behavior; as reported previously, a dramatic solvent effect was observed for this system. In this particular reaction, acetone (the only component bearing an acidic alpha-proton) is deprotonated to generate a nucleophilic enolate (possibly assisted through imine formation), which then attacks the electron-deficient aldehyde to generate the aldol product. The proposed mechanism for acid/base cooperative catalysis (Fig. 1) demonstrates the potential importance of acid/base interactions. Presumably, the regeneration of the active catalytic species relies on the rate of proton exchange between the acid and base groups, which would be facilitated by surface silanols and water when immobilized on mesoporous supports.

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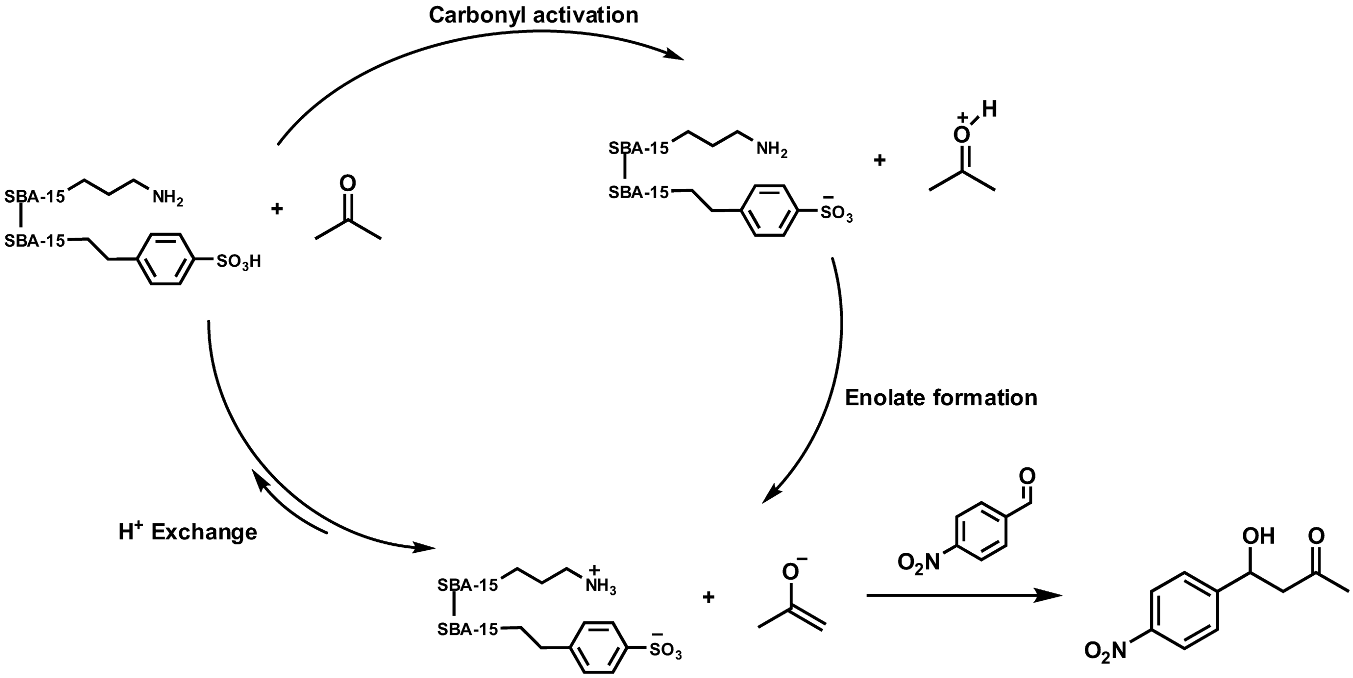


Fig. 1. Proposed catalytic cycle.

In the case of sulfonic acids and amines, the equilibrium would be expected to lie heavily in favor of the inactive, neutralized ion pair, with only small amounts of the nonneutralized acid/base species containing free sulfonic acids and amines. Sulfonic acids, being strong acids, should protonate the primary amine, readily causing the equilibrium to lie heavily in the direction of the neutralized ion pair.

2. Experimental

2.1. "One-pot" catalyst synthesis

Siloxane starting materials were purchased from Gelest. Triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) P123 (4.0 g, 0.688 mmol, Mn 5800) was weighed into a Teflon bottle. Then 2.0 M HCl (120.0 mL, 240.0 mmol) and H_2O (6.0 mL, 333.0 mmol) were added and stirred at 40 °C until the P123 was fully dissolved. TEOS (8.2 mL, 37.8 mmol) was then added to the reaction, and the mixture was stirred at 40 °C for another 45 min prehydrolysis time. Then 2-(4-chlorosulfonylphenyl)-ethyltrimethoxysilane (0.65 g, 50/50 w/w solution in dichloromethane, 1.0 mmol) was added, to allow for hydrolysis of the sulfonyl chloride, followed by 3-aminopropyltrimethoxysilane (0.19 mL, 1.0 mmol). The respective acid component was substituted for the sulfonyl chloride for different acid functionalizations. This mixture was stirred at 40 °C for 20 h, then aged at 100 °C for 24 h. The mixture was then cooled to room temperature, and the resulting solid was filtered and rinsed repeatedly with excess H_2O (4 × 500 mL), then allowed to dry overnight on an aspirating filter. The dried solid was then extracted with EtOH (400 mL per g) by refluxing in EtOH for 24 h to remove P123. The solid was again filtered and rinsed repeatedly with EtOH (4 × 500 mL), then dried overnight on the aspirator to obtain a dry white solid, which was further dried at 80 °C under vacuum for 24 h.

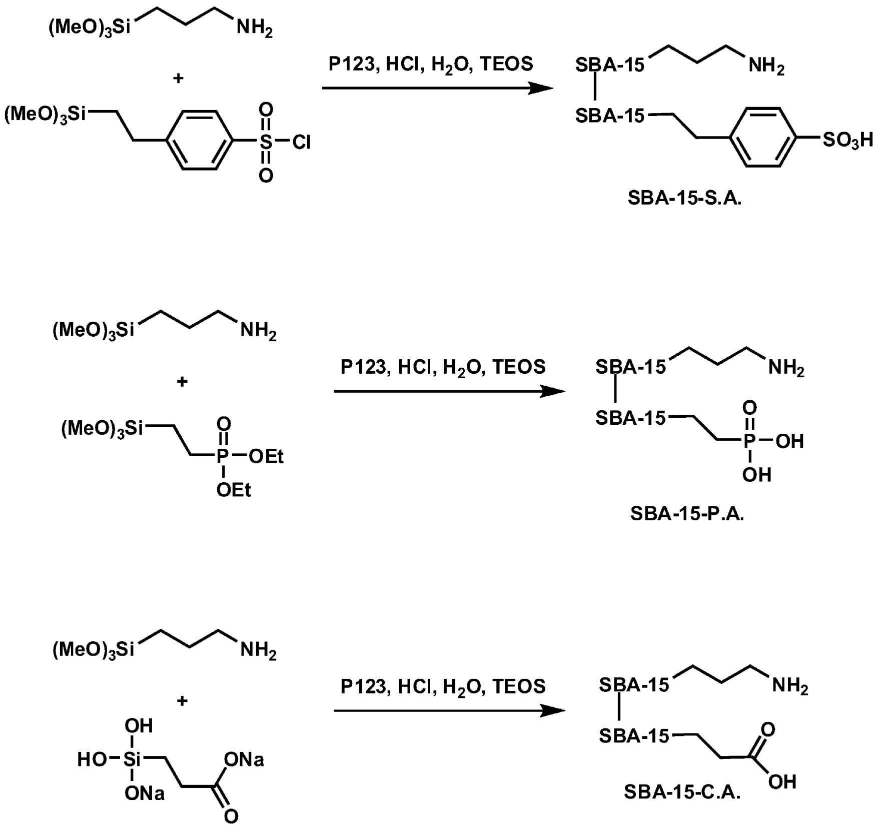
Solids were characterized by solid-state NMR on a Bruker 200-MHz NMR using CP/MAS with spinning at 4 kHz. TGA analysis was carried out on the dry solids on a Netzsch STA 449C with a heating rate of 10 °C/min. N_2 adsorption was carried out after drying the catalysts at 90 °C for 24 h on a Micromeritics 2010 instrument. The organic loading per functional group was 0.55 mmol/g for SBA-15-S.A., 0.57 mmol/g for SBA-15-P.A., and 0.62 mmol/g for SBA-15-C.A. Characterization data for SBA-15-S.A. was reported previously [1].

2.2. Catalytic experiments

The following general procedure was used for the aldol condensation. First, 4-nitrobenzaldehyde (76 mg, 0.5 mmol) was dissolved in acetone (10 mL), and the respective catalyst was added (0.05 mmol total amines and/or acids). The reaction was then sealed under Ar and heated at 50 °C for 20 h. The reaction was then filtered to remove the solid catalysts, and washed with acetone and then chloroform (3 × 10 mL each). The filtrate was concentrated in vacuo, and the resulting product was analyzed by ^1H NMR in $CDCl_3$ with THF as an internal standard. The aldol addition product was quantified on the basis of the triplet occurring at 5.3 ppm, and the aldol dehydration product was clearly distinguished by the olefin doublet at 6.9 ppm in comparison with the internal standard.

3. Results and discussion

When examining this equilibrium, we reasoned that a careful choice of acids to pair with the amino group could allow



Scheme 1. Catalyst syntheses.

for a change in the equilibrium toward an increased number of free acid/base sites and potentially lead to higher catalytic activity if less strong acids with a higher $\mathrm{p}K_\mathrm{a}$ were chosen. The $\mathrm{p}K_\mathrm{a}$ of sulfonic acids is approximately -2; weaker phosphoric acids have a $\mathrm{p}K_\mathrm{a}$ near 3, and even weaker carboxylic acids have a $\mathrm{p}K_\mathrm{a}$ around 5. These three acids of varying strengths were incorporated into SBA-15 though a one-pot synthesis procedure under acidic conditions with P123 as a structure-directing agent (Scheme 1).

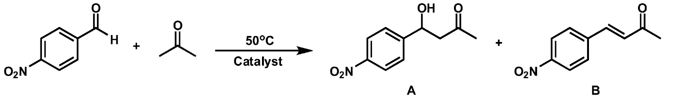
These different acid-functionalized materials were used in the aldol condensation between acetone and 4-nitrobenzaldehyde. The catalysis data are given in Table 1. The hypothesized trend in catalytic behavior is clearly realized and illustrated by these results in that the conversion increases significantly with decreasing acid strength. The combination of sulfonic acid with amines (entry 1, Table 1) gives rise to 62% conversion of aldol product, illustrating cooperative catalysis between these groups. When using a slightly weaker acid in the phosphoric acid/amine catalyst (entry 2, Table 1) a significant improvement in conversion (to 78%) is observed. When using an even weaker acid, the carboxylic acid/amine material (entry 3, Table 1), further enhancement is observed, and the reaction is nearly quantitative. Entries 4–7 serve as control experiments to illustrate the catalytic ability of these functional groups when used independently and to exemplify the type of improvements than can be achieved by immobilizing different functional groups that have the ability to behave in a cooperative manner.

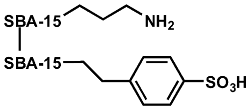
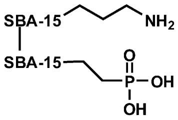
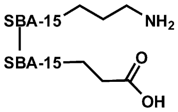
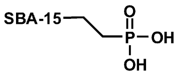
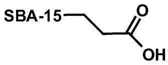
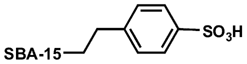
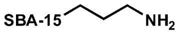
The data from kinetic experiments run on the carboxylic acid catalyst (entry 3) show that the conversion is linear with time and gives a constant selectivity throughout the course of the reaction (see Supplementary material).

To examine the effect of the electron density of the aldehyde partner on conversion, we chose a variety of aldehyde partners for the aldol condensation and used SBA-15-C.A. as the catalyst. Entries 1–4 in Table 2 illustrate the importance of an electron-withdrawing group at the para position for this reaction. The conversion varies with the electron-donating ability of the para substituent. When a chloro group is at position 4 (entry 1), poor conversion to the aldol product is observed. However, when switching to a fluoro-, nitro-, and trifluoromethyl (entries 2–4) groups, conversion improves significantly, according to these groups' electron-withdrawing capability ($Cl < F < NO_2 < CF_3$). When these electron-withdrawing groups are moved to the *ortho* position, where they may be able to impart a steric blockage of the aldehyde position, conversions decrease significantly, but in this case they seem to track with the steric bulk of the substituent rather than the electron-withdrawing nature (i.e., $F > NO_2 > CF_3$).

In conclusion, we have prepared a catalytic material capable of providing excellent conversion toward the aldol reaction that is rationalized by the proper pairing of weaker acid groups with amine groups. Mesoporous materials functionalized with carboxylic acids and amines (similar to proline) provide a very efficient catalyst capable of near-quantitative conversion in the aldol condensation. This particular pair of functional groups

Table 1
Catalysis data



Entry	Catalyst (10 mol%)	% A	% B	Total conversion
1		45	17	62
2		62	16	78
3		75	24	99
4		0	0	0
5		0	0	0
6		8	8	16
7		25	8	33

indicates, through the effects on conversion, that the equilibrium lies more in favor of the nonneutralized material than in the case of stronger acids paired with amines and gives rise to dramatically enhanced reactivity. The detailed mechanism and characterization of the neutralization equilibrium are under investigation using NMR techniques and will be reported in due course.

Acknowledgments

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Supplementary material

The online version of this article contains additional supplementary material: kinetic analysis data, solid-state NMR data, TGA data, XRD data.

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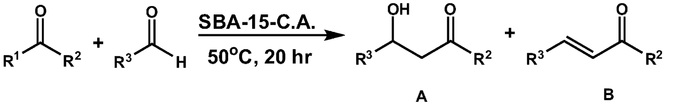
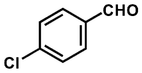
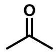
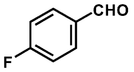
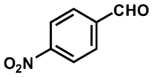
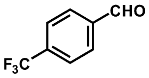
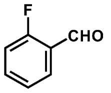
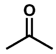
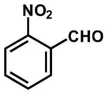
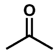
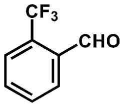
Table 2
Substrate scope



Entry	Ketone	Aldehyde	Alcohol product (% A)	Olefin product (% B)	Total conversion (%)
1			12	12	24
2			49	42	91
3			75	24	99
4			66	33	99
5			40	20	60
6			32	14	46
7			26	8	34

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