

# Acid–base cooperativity of heterogeneous catalyst containing acidic framework and sterically hindered base for aldol condensation

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## Abstract

A bifunctional heterogeneous catalyst containing two mutually incompatible acidic and basic sites, which exhibits cooperative catalytic behavior in the aldol condensation of acetone and various aldehydes, was synthesized by postgrafting of 1,5,7-triazabicyclo[4.4.0] dec-5-ene (TBD, a sterically hindered organic base) onto Al-MCM-41 molecular sieve.

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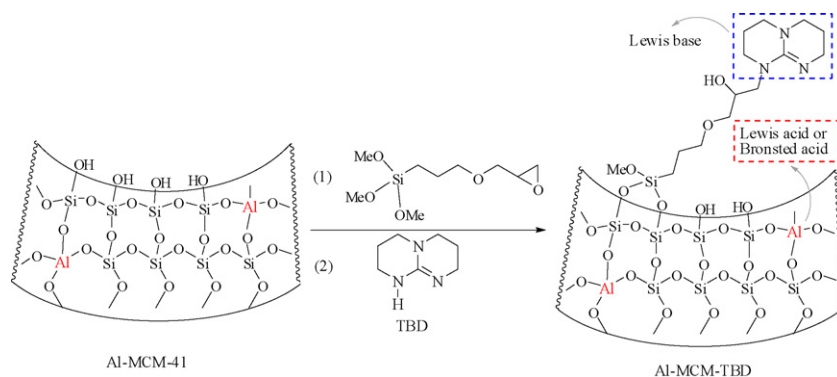
**Keywords:** Bifunctional catalyst; Acid–base cooperative catalysis; Mesoporous material; Aldol reaction

Many enzymatic and antibody catalytic processes concern acid–base cooperativity, in which two mutually antagonistic molecular groups, one acidic and one basic, coexist peacefully due to the stable microenvironment with certain steric hindrance. By mimicking these extraordinary systems found in nature, the design and synthesis of solid catalysts with multiple types of active centers have received much attention in recent years [1–6]. Immobilized organic amines as basic sites have been used with supported silanols or simultaneously immobilized thiols as acidic sites to perform bifunctional catalysis in the Henry and Michael reactions [7–9]. Recently, Davis group reported on mesoporous materials functionalized with incompatible acid and base groups that showed reactivity not achievable by these organic groups in solution for an aldol condensation reaction [10]. Notably, both antagonistic organic groups located at nanometric scale were highly accessible and can cohabit independently without mutual destruction [11].

Herein, we report the synthesis of bifunctional mesoporous catalysts containing an acidic site in the framework and a basic site on the porous surface by postgrafting of 1,5,7-triazabicyclo[4.4.0] dec-5-ene (TBD, a sterically hindered organic base with a comparable strength to KOH) onto Al-MCM-41 molecular sieve (Scheme 1). Al-MCM-41 usually has relatively weaker Brønsted acid sites and stronger Lewis acid sites [12–15]. There are two possible routes to form Lewis acid sites: one is formed by tetrahedrally coordinated framework aluminum atoms [12,13]; the other is formed by extra-framework aluminum atoms [14,15]. Because of the space hindrance between the acidic sites in the framework and the immobilized TBD base sites, they can cohabit independently without mutual destruction. Therefore, a cooperative catalysis originated from the acidic and basic sites of the bifunctional heterogeneous catalyst was expected to be confirmed in the aldol reaction of acetone and various aldehydes.

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Scheme 1.

The synthesis of bifunctional mesoporous catalyst (designated as Al-MCM-TBD), containing an acidic site in the framework and a basic site on the porous surface, was achieved by the reaction of the N–H group of TBD with oxirane groups bound onto Al-MCM-41 molecular sieve. For a comparison purpose, TBD being bound siliceous MCM-41 without acidic site in the framework (designated as MCM-TBD), no or low sterically hindered imidazole bound Al-MCM-41 (designated as Al-MCM-Im) as well as siliceous MCM-41 molecular sieves (designated as MCM-Im) were also synthesized.

The XRD patterns of all the samples showed two or three peaks that are assigned to the (1 0 0), (1 1 0), and (2 0 0) reflections of hexagonally ordered MCM-type structures, indicating that the support material remains intact during postgrafting (see Supporting Information Fig. S1). Measurement of the N<sub>2</sub>-adsorption isotherm demonstrated that the anchoring of TBD unit results in an average pore size from 3.45 nm decreasing to 2.38 nm, pore volume from 0.93 mL to 0.47 mL, and BET surface area from 1073 m<sup>2</sup> to 796 m<sup>2</sup>. The chemical immobilization of TBD was also confirmed by solid-state NMR spectroscopy. Fig. 1a shows the <sup>29</sup>Si MAS NMR spectra of various samples. There are three peaks at –110, –101 and –92 ppm which can be assigned to Q<sup>4</sup> (Si(OSi)<sub>4</sub>), Q<sup>3</sup> (Si(OSi)<sub>3</sub>(OH)) and Q<sup>2</sup> (Si(OSi)<sub>2</sub>(OH)<sub>2</sub>) species, respectively [14,16]. Moreover, some new broader signals appear at –60 to –70 ppm, which are ascribed to T<sup>n</sup> sites (RSi(OSi)<sub>n</sub>(OMe)<sub>3–n</sub>) [17–19]. These results indicate the organic functional groups have been incorporated on the surface of mesoporous host. Several peaks in the <sup>13</sup>C CP/MAS NMR spectrum of Al-MCM-TBD can be assigned to the anchored TBD and linking space groups (Fig. 1b). This suggests the presence of the intact TBD groups.

The immobilized catalysts were tested for activity in the aldol reaction of acetone with various aldehydes to afford the resulting addition and dehydration products (Table 1). In sharp contrast to that of the systems containing protic acid, the selectivity of β-hydroxycarbonyl compound was more than 99% in the resulting condensation products [10]. With Al-MCM-TBD as catalyst for the reaction of acetone and 4-nitrobenzaldehyde, a conversion of 77.2% was obtained at 50 °C for 20 h, while use of MCM-TBD without acidic sites in the framework gave significantly lower conversion at the same conditions (Entries 2 and 3). It is worth noting that a very low conversion of only 2.5% was observed in the system of Al-MCM-41 as catalyst (Entry 1). These results demonstrate that the enhanced activity is due to a cooperative catalysis between the acidic sites in the framework and the immobilized TBD basic sites of Al-

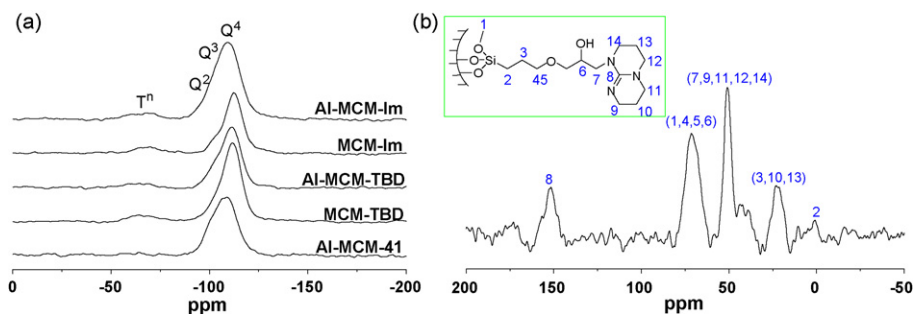
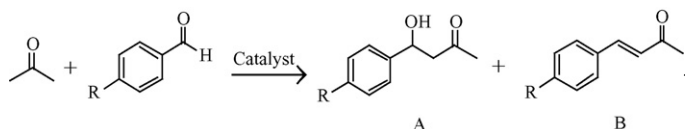
Fig. 1. (a) <sup>29</sup>Si MAS NMR spectra of various samples and (b) <sup>13</sup>C CP/MAS NMR spectrum of Al-MCM-TBD.

Table 1

Aldol reaction of acetone with various aldehydes catalyzed by various heterogeneous catalysts.<sup>a</sup>

| Entry | R               | Catalyst                   | Time (h) | A conv. (%) <sup>b</sup> | B conv. (%) <sup>b</sup> |
|-------|-----------------|----------------------------|----------|--------------------------|--------------------------|
| 1     | NO <sub>2</sub> | Al-MCM-41                  | 20       | 2.5                      | 0                        |
| 2     | NO <sub>2</sub> | MCM-TBD                    | 20       | 40.6                     | 0.1                      |
| 3     | NO <sub>2</sub> | Al-MCM-TBD                 | 20       | 76.6                     | 0.6                      |
| 4     | NO <sub>2</sub> | MCM-Im                     | 60       | 42.2                     | 0.1                      |
| 5     | NO <sub>2</sub> | Al-MCM-Im                  | 60       | 1.9                      | 0                        |
| 6     | NO <sub>2</sub> | Al-MCM-TBD/ <i>N</i> -MeIm | 20       | 60.7                     | 0.5                      |
| 7     | CN              | Al-MCM-TBD                 | 20       | 53.9                     | 0.1                      |
| 8     | CN              | MCM-TBD                    | 20       | 42.3                     | 0                        |
| 9     | CF <sub>3</sub> | Al-MCM-TBD                 | 20       | 20.7                     | 0.7                      |
| 10    | CF <sub>3</sub> | MCM-TBD                    | 20       | 7.7                      | 0.6                      |
| 11    | F               | Al-MCM-TBD                 | 60       | 53.4                     | 0.3                      |
| 12    | F               | MCM-TBD                    | 60       | 18.6                     | 0.1                      |

<sup>a</sup> Reaction conditions: catalyst (0.05 mmol based on the immobilized organic base) and aldehyde (0.5 mmol) in acetone (10 mL) were stirred at 50 °C under a nitrogen atmosphere.

<sup>b</sup> Based on HPLC analysis.

MCM-TBD. Interestingly, MCM-Im material, in which imidazole was anchored onto siliceous MCM-41 molecular sieves, also showed certain activity for the aldol reaction, but nearly complete loss in activity was observed in the system of Al-MCM-Im as catalyst (Entries 4 and 5). When Al-MCM-TBD was treated with *N*-methylimidazole (*N*-MeIm, a non-sterically hindered organic base), an obvious decrease in activity was observed (Entry 6). We can reasonable assume that interactions between the acidic sites in the framework and the anchored imidazole groups with non-steric hindrance cause mutual destruction. The result also suggests the steric hindrance of TBD group maintains the coexistence of the acidic sites in the framework and the immobilized TBD basic sites of Al-MCM-TBD, while the addition of *N*-MeIm resulted in neutralization with some acidic sites in the framework of Al-MCM-TBD. Moreover, the similar cooperative catalysis was observed in the aldol condensation of acetone with other aldehydes with the use of Al-MCM-TBD bifunctional catalyst (Entries 7–12). Of importance, the Al-MCM-TBD bifunctional catalyst is easily recovered by simple filtration, and was subjected to utilization for 8 times without obvious loss in activity (see Supporting Information Fig. S2).

In conclusion, we have prepared a bifunctional mesoporous material containing an acidic site in the framework and a basic site originated from postgrafting of a sterically hindered organic base TBD on the porous surface. Because of the space hindrance of the immobilized TBD, the mutually incompatible acidic and basic site can cohabit independently without mutual destruction, and shows an acid–base cooperativity in catalyzing the aldol condensation of acetone and various aldehydes to selectively give β-hydroxycarbonyl compounds.

## 1. Experimental

Siliceous MCM-41 and Al-MCM-41 (Si/Al = 10/1) molecular sieve were synthesized according to the previously described methods with hexadecyltrimethylammonium bromide as the template [20,21]. The activated MCM-41 or Al-MCM-41 (2.00 g) at 160 °C under vacuum was allowed to react with 3.47 g (14.72 mmol) of trimethoxysilylpropoxymethyloxirane in 20 mL dried toluene under reflux for 24 h. The resulting product was filtered and washed with toluene and ethanol, respectively. The mixture of glycidylated MCM-41 suspended in 20 mL dried toluene and 1.00 g (7.25 mmol) of TBD was stirred for 10 h at 80 °C under a nitrogen atmosphere [22,23]. Residual TBD was removed by Soxhlet extraction with a mixture of methylene chloride and methanol (vol/vol, 1/1) for 72 h. Finally, the resulting solid was further dried under vacuum for 6 h. TBD modified MCM-41 and Al-MCM-41 were designated as MCM-TBD and Al-MCM-TBD, respectively.

MCM-Im or Al-MCM-Im was synthesized as the similar procedure for TBD immobilization.

*N*-methylimidazole (*N*-MeIm) treated Al-MCM-TBD sample was prepared and designated as Al-MCM-TBD/*N*-MeIm. Al-MCM-41 (0.5 g) was treated with 140 mg (1.6 mmol) of *N*-MeIm in 10 mL toluene at room temperature for 5 h. Residual *N*-MeIm was removed by Soxhlet extraction with a mixture of methylene chloride and methanol (vol/vol, 1/1) for 24 h. Finally, the resulting solid was further dried under vacuum for 6 h.

The content of the immobilized organic bases in molecular sieves was calculated from their nitrogen content determined by element analysis. These materials, both before and after postgrafting, were characterized by powder X-ray diffraction (XRD), NMR spectroscopy and adsorption and desorption isotherms of N<sub>2</sub>.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ccl.2009.04.011](https://doi.org/10.1016/j.ccl.2009.04.011).

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