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Efficient solid-base catalysts for aldol reaction by optimizing the density and type of organoamine groups on nanoporous silica

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ABSTRACT

A highly efficient solid-base catalyst for aldol condensation reaction was synthesized by grafting site-isolated secondary amines onto the channel walls of mesoporous silica, MCM-41, in a polar-protic solvent. These site-isolated organoamines pair up with the neighboring residual surface silanol (weak acid) groups to form optimized acid and base groups, which cooperatively catalyze the aldol condensation reaction with high TON (turn over number) and selectivity (alcohol products over alkene products). The organoamine samples grafted in a polar-protic solvent, isopropanol, showed higher catalytic efficiency toward aldol reaction than those grafted in a non-polar solvent, toluene, because the former gave a sample with less dense loading of grafted organoamines (or more silanols present in it). To elucidate the role of surface silanols as acidic sites and their ability to activate the substrates in aldol condensation, control experiment with diethylamine as a homogeneous catalyst in the presence of MCM-41, silica microspheres, methyl-capped MCM-41 or methyl-capped catalyst was carried out. MCM-41 resulted in significant enhancement of catalytic activity compared to the corresponding reactions conducted in the absence of MCM-41, or in the presence of methyl-capped catalysts or silica spheres. By testing materials with different grafted organoamine groups as catalysts, we also found that secondary amine functionalized sample produced the best acid and base pairs and most efficient catalytic activity in aldol reaction. This was followed by primary amines, while the tertiary amine functionalized samples showed negligible catalytic property.

1. Introduction

In nature, enzymes often employ sophisticated strategies to achieve complex reactions or to drive many biological processes, the complexity and efficiency of which are often unmatched by man-made systems. The highly efficient catalytic abilities of enzymes often result from the collective efforts of several functional groups or active catalytic sites [1,2]. A recent topic of interest in synthetic methodologies to heterogeneous catalysts has been the functionalization of solid-state materials with two or more functional groups to produce efficient, cooperative catalysts [3–6] or materials capable of catalyzing multi-step, one-pot tandem [7] reactions.

Solid-base catalysts, which can be synthesized by functionalization of various solid-state materials, constitute a class of heterogeneous catalysts that are capable of catalyzing various C–C bond forming reactions such as the Henry, Knoevenagel, and aldol reactions [8,9]. These catalysts are synthesized by a variety of synthetic methods including surface functionalization of metal oxides with base catalytic groups [10], co-assembly or organosilanes [11], ammonia/amine surface reactions and surface nitridation of aluminophosphates, zeolites and mesoporous materials [12–14]. For example, by exchanging alkali metal ions of zeolites with alkaline metal ions, solid-base zeolites, whose basicity increases with decreasing charge-to-radius ratio of the alkaline metal ion, can be synthesized [15]. Similarly, by encapsulating alkali metal–oxide clusters inside zeolites, solid bases with low degree of basicity have been reported [16]. The substitution of framework oxygen atoms in metal oxide materials by NH_x groups via nitridation of amorphous silica [17–21], aluminophospates [22–26], and zeolites [27–31] with ammonia or nitrogen under high temperature also produces solid-base materials. Depending on the nitridization temperature and time, the nitrogen content as well as basicity of the resulting materials can also be tuned.

Since their discovery in 1992 [32], mesoporous silicas have been widely used as a host for catalytic moieties such as basic [33–35] and acidic [36–38] groups to form active heterogeneous nanocatalysts. Because of their ordered nanopore structures compared to amorphous silica and their large pores compared to zeolites, mesoporous silica materials are often more interesting as support materials for making heterogeneous catalysts. As in zeolites, amorphous silica and aluminophosphates, the frameworks of mesoporous materials can also undergo nitridization to form solid base,

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mesoporous aminosilica, and silicon oxynitride materials [39–44]. Another more commonly used method to produce solid base mesoporous materials has been the grafting or co-assembly of aminoorganosilanes [3–5]. This method introduces organic base catalytic groups on mesoporous silica framework at low temperature. Furthermore, it also allows the introduction of acidic groups on the same material, affording a heterogeneous catalyst containing both acidic and basic functional groups (or cooperative catalyst). For instance, Lin's group reported the synthesis of a series of bifunctional mesoporous silica nanosphere (MSN) materials containing a general acid, ureidopropyl (UDP), and a general base, 3-[2-(2-aminoethylamino)ethylamino]-propyl (AEP), and showed that the existence of the auxiliary acidic groups significantly enhanced the catalytic activity of the base-catalyzed aldol, Henry, and cyanosilylation reactions [4]. Similar enhancement effect by organic acid groups was also reported by Zeidan et al. [5b,5c], who not only found a catalytic enhancement effect by the general acid on the base-catalyzed aldol reaction, but also discovered the dependence of the catalytic performance of the catalysts on the pK_a value of the auxiliary acidic groups. They further showed that a weaker acid produces a lesser degree of neutralization and a more efficient catalyst. Although the effect of different acidic groups including weakly acidic surface silanols on the efficiency of heterogeneous base-catalyzed reactions have been reported [5,45], the effects of the type of basic sites and their relative surface density along with surface silanols on the catalytic efficiency of mesoporous silica-supported heterogeneous organocatalysts were not well investigated. Recently, our group reported the synthesis of highly efficient bifunctional catalyst for the Henry reaction by simple post-grafting of site-isolated organoamine groups in polar-protic solvents [46]. By grafting aminorganosilanes on mesoporous silica in polar-protic solvent, we produced relatively less density of surface organoamine and many residual silanol groups compared to the materials we grafted in non-polar solvents under the same condition. The primary amine and the surrounding weak acid silanol groups in the former were proved to cooperatively catalyze the Henry reaction more efficiently. However, this synthetic strategy and its applications for catalysis have not been investigated for reactions other than the Henry reaction so far.

Herein we report on the synthesis of highly efficient solid-base catalysts containing grafted organoamine and significant numbers of weakly acidic silanol groups for an aldol condensation reaction. The materials were synthesized by grafting a series of aminoorganosilanes in a polar-protic solvent, isopropanol. Isopropanol was chosen because the grafting of aminorganosilane in a polar-protic solvent produces less surface density and relatively greater site-isolated organoamine groups that are surrounded by many residual surface silanols or weak acid groups. We find that the surface silanol groups have significant cooperative catalytic activity with the site-isolated organoamines toward aldol condensation. Compared to the catalytic efficiency of other solid-base catalysts reported previously [3–5], in which relatively strong acidic groups were used, we find that the mildly acidic surface silanol groups provide better acidic sites to cooperatively catalyze the aldol reaction along with the amine groups possibly due to lesser degree of neutralization between the antagonistic acidic and basic groups. In order to optimize our catalytic system and to determine the best acid and base pairs for aldol reaction, different types of amines were tested and compared in our study. The results indicated that secondary amine showed the highest cooperative catalytic efficiency with silanols for aldol condensation reaction, followed by primary amine; however, tertiary amine produced negligible catalytic efficiency possibly because of its inability to form enamine intermediates. In order to prove if the enhanced catalytic activity was due to the surface silanol groups, MCM-41 and silica microspheres were used as an additive during the homogeneous catalysis of aldol reaction with diethylamine. While MCM-41 was found to significantly enhance the catalytic ability of diethylamine, no enhancement effect was observed on capping the surface silanols of MCM-41 with trimethysilyl groups although the resulting materials still had large surface area and pore size. Silica microspheres also gave no catalytic enhancement. We further synthesized and investigated mesoporous catalysts whose silanols were capped with methyl groups. These materials did also show lower catalytic efficiency. This proved that the surface silanol groups of mesoporous materials indeed enhanced the catalytic performance and proved our hypothesis to utilize weakly acidic surface silanol groups for producing the most effective solid-base catalysts for the aldol reaction.

2. Experimental

2.1. Materials and reagents

Cetyltrimethylammonium bromide (CTAB), *p*-nitrobenzaldehyde (*p*-NO_2), tetraethylorthosilicate (TEOS), 3-aminopropyltrimethoxysilane (APTS), ammonia solution (30%), and anhydrous ethanol were obtained from Sigma–Aldrich. 3-(*N*-methylaminopropyl)trimethoxysilane (MAPTS) and 3-(*N*,*N*-dimethylaminopropyl)trimethoxysilane (DMAPTS) were obtained from Gelest, Inc. Anhydrous toluene and isopropanol were purchased from Pharmco-AAEPR. Anhydrous acetone was purchased from Fischer Scientific. All reagents were used as received without any further purification.

2.2. Synthesis of mesoporous silica (MCM-41)

The synthesis of mesoporous silica, MCM-41, was performed as reported previously [32,47]. Typically, 4.0 g (1.1 mmol) cetyltrimethylammonium bromide (CTAB) was dissolved in 960 mL of Millipore water and 14 mL of 2.0 M NaOH solution. After moderately stirring the solution at 80 °C for 30 min, 22.6 mL (101.2 mmol) of tetraethoxysilane (TEOS) was added into it. The resulting solution was stirred for another 2 h at 80 °C. The hot solution was then filtered and the solid product was washed with Millipore water (4 × 80 mL), followed by ethanol (4 × 80 mL) and then dried in oven at 80 °C. This resulted in as-synthesized mesostructured MCM-41. To remove the surfactant template, 6 g of the as-synthesized MCM-41 was suspended in a mixture of 3 mL (12.1 N) hydrochloric acid and 600 mL anhydrous ethanol and stirred at 50 °C for 5 h. The resulting solution was filtered and the solid sample was washed with copious amount of Millipore water and ethanol (3 × 80 mL). The extracted mesoporous silica (MCM-41) was dried in oven at 80 °C overnight before postgrafting it with various aminoorganosilanes.

2.3. Synthesis of solid-base mesoporous catalysts by postgrafting

The postgrafting of organoamines onto mesoporous silica, MCM-41, was done by stirring 600 mg of MCM-41 in excess (4.42 mmol) aminoorganosilanes (APTS, MAPTS, or DMAPTS) in 300 mL isopropanol (or toluene) at 80 °C for 5 h. Control samples by grafting MCM-41 in excess (4.42 mmol) APTS and MAPTS in 300 mL toluene for 15 min and 30 min at 80 °C were also synthesized. The hot solution was then filtered and the solid sample was washed with dichloromethane (300 mL), followed by ethanol (600 mL) and then dried in oven at 80 °C for overnight. The resulting materials synthesized from APTS, MAPS, and DMAPS in isopropanol were designated as MCM41-API, MCM41-MAPI, and MCM41-DMAPI catalysts, respectively. While AP, MAP, and DMAP are used to denote primary, secondary, and tertiary amines, respectively (the letter "I" represents the grafting solvent, isopropanol). Similarly, samples grafted in toluene were labeled as MCM41-APT, MCM41-MAPT, and MCM41-DMAPT catalysts, respectively (the letter "T", in these cases, indicates toluene as the grafting solvent).

2.4. Synthesis of solid-base mesoporous catalysts with capped silanols

To investigate the catalytic enhancement effects of surface silanols on aldol reaction, the silanols were protected with trimethylsilyl groups by suspending 500 mg MCM-41 in a mixture of 100 mL toluene and 5 mL hexamethyldisilazane (HMDS) [48,49]. The mixture was stirred at room temperature under nitrogen atmosphere for 24 h and then filtered. The solid sample was washed by following a similar procedure mentioned above, resulting in a control sample that was designated as MCM41-CH_3. The samples were characterized by various methods (Table 1). Similarly, MCM-API-CH_3 and MCM-MAPI-CH_3 were synthesized.

2.5. Synthesis of silica microspheres

The synthesis of silica microspheres was carried out by following the Stöber method [50,51]. TEOS (5.94 g) was added to 4 mL of 12.1 N ammonia solution in 100 mL of ethanol and 3.6 g of Millipore water under stirring. The colloidal solution was then centrifuged and washed three times with 50 mL of ethanol and redispersed in 50 mL ethanol. Ten millilitre of the colloidal solution was centrifuged and washed three times with 50 mL of anhydrous acetone and then redispersed in 10 mL of anhydrous acetone. The corresponding colloidal solution was determined to have 30 mg of silica microspheres in 1 mL of solution.

2.6. Probing site-isolation of organoamine catalytic sites

The degree of site-isolation of the organoamine catalytic sites in the mesoporous materials was probed by following our recently reported procedure [52], which involved complexation of Cu^{2+} ions from dilute aqueous solution onto the organoamines and measurement of the UV–Vis absorption spectra of the resulting Cu^{2+}-amine complexes. Briefly, 20 mg of the amine-functionalized sample (MCM-API, MCM-APT, MCM-MAPI, or MCM-MAPT) was mixed with 5 mL of 2 mM aqueous Cu^{2+} solution. The sample was sonicated for 5 min and then stirred for 1 h. The solution was then filtered and the solid sample was washed with 5 mL ethanol and dried under vacuum. The reflectance UV–Vis spectrum of the solid sample was then obtained by placing the solid product between two quartz plates.

2.7. Catalytic tests

An aldol reaction was carried out by following a procedure reported previously [4], but by using a higher substrate to catalyst ratio. To ensure that the same mole of catalyst and the same substrate to catalyst (S/N) ratio were used in each of our reactions and to make comparison of catalytic efficiency of the samples easier, we used mesoporous catalysts containing the same number of catalytic groups (2.5 μmol organoamines) in the case of samples grafted in isopropanol (Table 2). The corresponding mass of catalyst was calculated based on the wt.% N obtained from the elemental analysis data, which was found to be 25, 17, and 19 mg for MCM41-API, MCM41-MAPI, and MCM41-DMAPI, respectively (Table 2). In a typical reaction, the calculated mass of catalyst was added to a solution containing 152 mg (1 mmol) of *p*-nitrobenzaldehyde in 10 mL of acetone, which is to serve both as a substrate and solvent. The reaction mixture was stirred at 50 °C under nitrogen. Aliquots of ~0.05 mL reaction mixture were taken out with a syringe at different time intervals and analyzed by ^1H NMR as reported previously [4]. For catalysts grafted in toluene, the same procedure was employed, except 25 mg of sample was used in each case since the 2.5 μmol organoamine corresponds to a rather low mass of catalyst in these samples. The 25 mg of catalyst corresponded to 64 and 58 μmol of organoamine for MCM41-APT and MCM-41-MAPT, respectively. The comparisons of catalytic efficiencies in this case were done based on catalytic turn-over-numbers (TONs).

2.8. Enhancement effect tests and control experiments

In order to prove the enhancement effect by surface silanol groups on the aldol reaction, MCM-41, MCM41-CH_3, or silica microspheres were added to a homogeneous catalytic system containing diethylamine as a catalyst. Briefly, the homogeneous catalyst, diethylamine (0.2 mmol), was added to a solution of 152 mg *p*-nitrobenzaldehyde (1 mmol) in 10 mL of acetone, followed by 25 mg of MCM-41, (MCM41-CH_3, or silica microspheres). The reaction mixture was stirred at 50 °C under nitrogen atmosphere and analyzed at different time intervals as mentioned above.

In other control experiments the surface silanol groups of MCM-API and MCM-MAPI were capped with trimethysilyl groups, or samples MCM-API-CH_3 and MCM-MAPI-CH_3, respectively were used as catalysts and their catalytic properties were then tested by following the same procedure as the one conducted for MCM-API and MCM-MAPI (see Section 2.7 for details).

2.9. Instrumentation

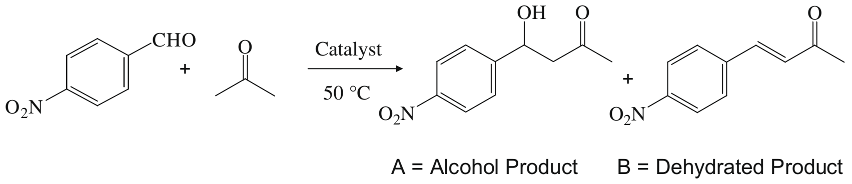
The TEM (transmission electron microscopy) images were taken by using an FEI Tecnai G-20 TEM/STEM microscope working at an accelerating voltage of 120 KeV. The XRD (powder X-ray diffraction) patterns were obtained by using a Scintag powder diffractometer. The BET gas adsorption–desorption measurements were carried out on Micromeritics Tristar 3000 volumetric adsorption analyzer after degassing the samples at 160 °C for 12 h. The solid-state ^{13}C (75.5 MHz) and ^{29}Si (59.6 MHz) NMR spectra were acquired on a Bruker AVANCE 300 NMR spectrometer. For ^{13}C CP-MAS NMR experiments, 7.0 kHz spin rate, 5 s recycle delay, 1 ms

Table 1
Wt.% N content and structural information of the mesoporous catalysts.

Catalyst	Wt.% C	Wt.% N	Number of N (nm^2)	BET surface area (m^2/g)	BJH pore diameter[a] (Å)	Pore volume[a] (cm^3/g)
MCM-41	0	0	0	1069	30.2	1.04
MCM41-API	9.15	1.44	0.72	849	27.8	0.75
MCM41-MAPI	11.35	2.16	1.06	873	27.1	0.63
MCM41-DMAPI	12.4	1.87	0.91	886	26.4	0.62
MCM41-APT	10.37	3.7	1.79	899	27.1	0.57
MCM41-MAPT	12.31	3.43	1.70	875	27	0.53
MCM41-CH_3	10	0	0	973	27.2	0.66

[a] The BJH pore diameter and the pore volume were calculated from the desorption branch of the isotherm.

Table 2
Catalytic reaction and results of the aldol condensation reaction catalyzed by acid–base mesoporous catalysts.



Acid–base mesoporous catalyst[a]	mg (μmol) of catalyst used	S/N[b]	% Yield in 6 h[c]	% Yield in 20 h	TON at 6 h[c]	TON at 20 h	*A*/*B*
MCM-41[d]	25 (0)	0	0	NA[e]	0	NA[e]	NA[e]
MCM41-API	25 (25)	40/1	43.8	94.6	17.5	38.0	9.0/1
MCM41-MAPI	17 (25)	40/1	97.0	NA[e]	38.8	NA[e]	9.0/1
MCM41-DMAPI	19 (25)	40/1	0	5.1	0	1.9	
MCM41-APT	25 (64)	15.6/1	15.1	NA[e]	2.35	NA[e]	9.2/1
MCM41-MAPT	25 (58)	17.1/1	95.6	NA[e]	16.4	NA[e]	10.5/1
MCM41-MAPT-15 min Grafting[f]	18 (25)	40/1	93.2	NA[e]	34.0	NA[e]	9.4/1

[a] The grafting of the samples was performed by stirring the organosilanes in isopropanol or toluene for 5 h unless mentioned otherwise.

[b] The S/N (substrate to amine) ratio was calculated based on the elemental analysis and the quantity of catalysts used, the quantity of catalysts grafted in isopropanol was chosen to make S/N content as 40/1, while the mass of other catalysts was chosen to be constant (25 mg).

[c] Reaction was run twice for each catalyst with little variation in percentage yield and TON (mole of starting materials converted into products per mole of amines), and the results shown here are the averages of two runs.

[d] Parent material before grafting.

[e] NA = Not available.

[f] The grafting of this sample was performed for 15 min, which has produced similar density of grafted organoamine groups as sample MCM41-MAPI. The mmol of catalytic sites for these samples was calculated from TGA traces and not from elemental analysis.

contact time, $\pi/2$ pulse width of 5.6 μs, and 600 scans using TPPM ^1H decoupling were employed. For the ^{29}Si CP-MAS NMR experiments, 7.0 kHz spin rate, 10 s recycle delay, 10 ms contact time, $\pi/2$ pulse width of 5.6 μs, and 600 scans by using TPPM ^1H decoupling were employed. The solution ^1H NMR was measured by using a Bruker DPX-300 NMR spectrometer. The elemental analysis was performed at Quantitative Technologies, Inc.

3. Results

3.1. Synthesis and characterization of mesoporous base catalysts for aldol condensation reaction

We employed a synthetic strategy to produce efficient solid-base catalysts containing site-isolated organoamine groups along with many residual silanols for aldol condensation reaction. Mesoporous silica, MCM-41, was grafted with organosilanes containing primary, secondary, or tertiary amine in isopropanol producing MCM41-API, MCM-41-MAPI, and MCM41-DMAPI catalysts, respectively. Similarly, MCM-41 was grafted with organosilanes containing primary, secondary, or tertiary amines in toluene producing MCM41-APT, MCM41-MAPT, and MCM41-DMAPT catalysts, respectively. The samples grafted with aminoorganosilanes in isopropanol are expected to have relatively more site-isolated amine catalytic groups while samples grafted in toluene are anticipated to have more aggregated organoamine groups [46]. Control samples were also synthesized by grafting the surface silanols of MCM-41, MCM-API, and MCM-MAPI with methyl groups, which produced MCM41-CH_3, MCM-API-CH_3, and MCM-MAPI-CH_3, respectively (see Section 2 for details).

All the mesoporous materials and catalysts were characterized by XRD, TEM, elemental analysis, solid-state ^{13}C and ^{29}Si NMR spectroscopies, and nitrogen gas adsorption. The low angle XRD patterns (Fig. 1a) showed three well-defined peaks with 2θ values that can be indexed as (1 0 0), (1 1 0), and (2 0 0) Bragg reflections, which are typical of the *P6mm* honeycomb structure of mesoporous materials [48]. These peaks remained observable after functionalization of the mesoporous silica with organoamines, indicating the stability of the mesostructure during the chemical modification process. The TEM images of the mesoporous materials or catalysts before and after the chemical modification also showed well-ordered mesoporous structures. The low and high magnification TEM images of MCM-41 are shown in Fig. 1b and c, respectively, while a high magnification TEM image of a representative organoamine functionalized sample, MCM41-API, is shown in Fig. 1d. Mesoporous particles with spherical morphology are clearly observed under low magnification while their well-ordered mesoporous structures are seen under high magnification. Similar images were also obtained for the remaining materials that were modified with secondary and tertiary amine groups (not shown).

The results from elemental analysis (Table 1) showed that after aminoorganosilane grafting, the materials showed a significant increase in the wt.% of N and C indicating the functionalization of mesoporous silica material with the organoamines. Samples grafted with aminorganosilanes in toluene had much higher wt.% N (e.g., 3.7 wt.% for MCM41-APT) than the corresponding samples grafted in isopropanol (e.g., 1.44 wt.% for MCM41-API). This result is consistent with the data reported previously [46,52]. The functionalization of the materials with the organoamine groups was further confirmed by ^{13}C CP-MAS NMR and ^{29}Si CP-MAS NMR spectroscopies (Supplementary Fig. 1S). The ^{13}C CP-MAS NMR spectra showed typical chemical shifts that can be assigned to the carbon atoms of the different organoamine groups containing primary, secondary, and tertiary amines (see Supplementary Fig. S1). The assignment of the peaks was similar to that reported previously in Ref. [48]. The ^{29}Si CP-MAS NMR spectra showed T peaks centered at around -50 ppm, which correspond to silicon atoms that are attached to the organoamine groups. Furthermore, additional peaks were also observed between -80 and -115 ppm on the ^{29}Si CP-MAS NMR spectra, which correspond to silicon atoms of the parent MCM-41 framework ($SiO_x(OH)_{4-x}$).

The surface areas and pore diameters of the materials were characterized by nitrogen gas adsorption. The samples were degassed at 160 °C for 12 h before the measurement. The nitrogen

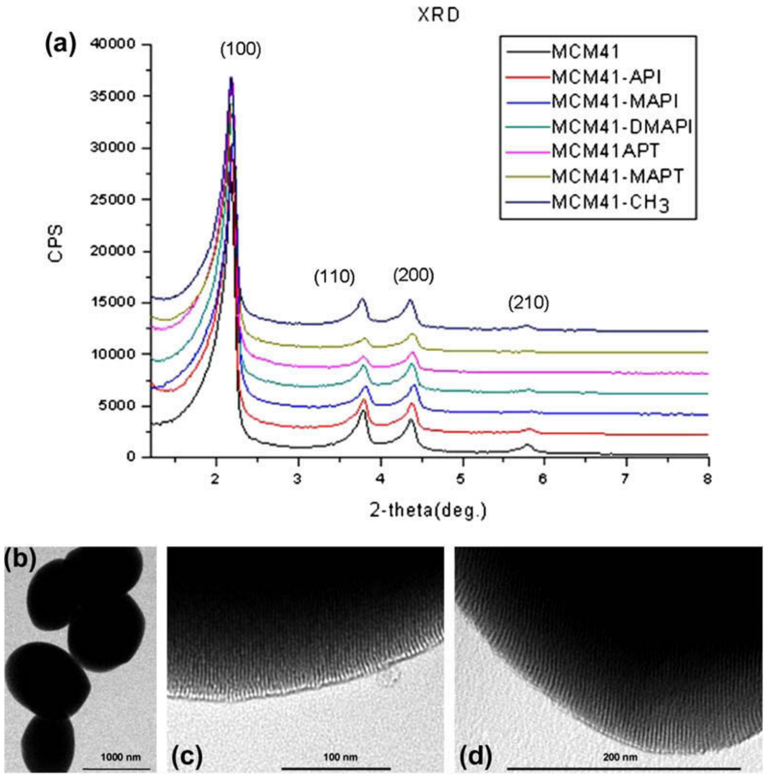


Fig. 1. (a) Powder X-ray diffraction (XRD) spectra of MCM-41 and different organoamine-functionalized catalysts (the XRD patterns were vertically spaced for clarity). (b and c) Low and high magnification TEM images of MCM-41. (d) High magnification TEM image of MCM41-API.

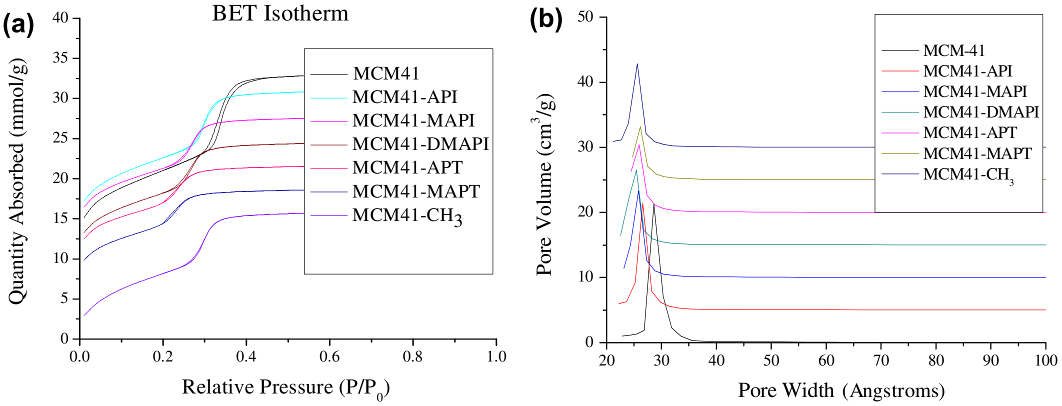


Fig. 2. (a) BET gas adsorption isotherms and (b) BJH pore-size distributions MCM-41 and different organoamine-functionalized catalysts and control samples. The pore size distributions were obtained from the desorption branch of the isotherms. All the graphs were vertically spaced on the *y*-axis by six data points in (a) and by five data points in (b) for clarity.

gas adsorption and desorption measurements resulted in type IV isotherm for all the catalysts, indicating further that all the samples have mesoporous structures (Fig. 2 and Table 1). While all the materials showed high surface areas (Table 1), upon modification by the organoamine groups, the surface area, pore width, and pore volume decreased compared to the unmodified MCM-41. The surface area of all the organoamine functionalized samples (Table 1, entry 2 through entry 6) fell in the range between 850 and 900 m^2/g, with only marginal differences in the values. Although the choice of solvents isopropoanol and toluene was made to produce different loading and surface density of organoamines on the mesoporous materials [46,52], no significant difference in surface area between the samples grafted in isopropanol and toluene was observed (see Table 1). However, the pore size and pore volume decreased more significantly in samples grafted in toluene compared to the corresponding samples grafted in isopropanol.

The relative degree of site-isolation of the primary and secondary organoamine groups was probed by using the copper-complexation method as we have reported recently [52]. Representative reflectance UV–Vis spectra of solid mesoporous samples, after being treated with dilute aqueous Cu^{2+} solution, are shown in Supplementary Fig. 2S. Sample MCM41-MAPI, which was grafted in isopropanol for 5 h, showed a red-shifted absorption maximum at 717 nm, which indicated the presence of CuO_5N_1 structure and relatively less densely populated or more site-isolated organoamine groups in it. However, the corresponding sample grafted in toluene for 5 h, MCM41-MAPT, showed a blue-shifted absorption maximum at 676 nm, which indicated the presence of CuO_4N_2

structure and more densely populated (or more aggregated) organoamine groups in it (Fig. S2). On the other hand, the control samples synthesized by grafting 3-(*N*-methylaminopropyl)trimethoxysilane (MAPTS) in toluene for relatively short periods of times of 15 and 30 min showed similar low density of grafted organoamine groups as the corresponding sample grafted in isopropanol for 5 h as observed on thermogravimetric analysis (see Fig. S3). These samples further exhibited red-shifted absorption maxima at ~700 upon complexation with Cu^{2+} ions (Fig. S4). This indicates that samples grafted in toluene for shorter periods of time can indeed produce less densely populated, more spatially distributed amine groups and CuO_5N_1 structures as much as the samples grafted in isopropanol (Fig. S4). While we have used this copper-complexation method successfully to monitor the degree of site-isolation of primary amine groups in mesoporous materials previously [55], our experiment here further proved of the method's versatility in probing the degree of site-isolation of secondary organoamine groups for the first time.

3.2. Catalysis tests

The catalytic activity of all the amine-functionalized materials and control samples were then investigated in aldol reaction. We describe catalysis results for all the samples containing primary, secondary, and tertiary amine groups. But, in order to simplify our arguments, we will discuss in more detail the samples containing primary and secondary amines (and their corresponding control samples), which we have found to be the most efficient catalysts for aldol reaction. Since we also have found that the samples containing tertiary amines were found to be very inefficient in the aldol reaction, the results for these materials are only briefly discussed. From Table 2 and Fig. 3, we observe that the catalysts that were grafted with primary amines in isopropanol and toluene (MCM41-API and MCM41-APT, respectively) showed different catalytic performances. Sample MCM41-API exhibited a more efficient catalytic activity than MCM41-APT (Table 2 and Table 1S). For example, sample MCM41-API gave a total conversion of 43.8% and a TON value of 17.5 in 6 h while the corresponding sample MCM41-APT afforded a total conversion of 15.1% and a TON value of 2.4 in 6 h. It is also worth noting that the catalytic efficiency obtained for MCM41-API in aldol reaction, i.e. a total conversion of 94.6% and a TON value of 38 in 24 h, is much higher than those recently reported for acid–base bifunctional catalysts by Zeidan et al. [5b,5c] as well as by Huh et al. [4] (see Supplementary Table 1S).

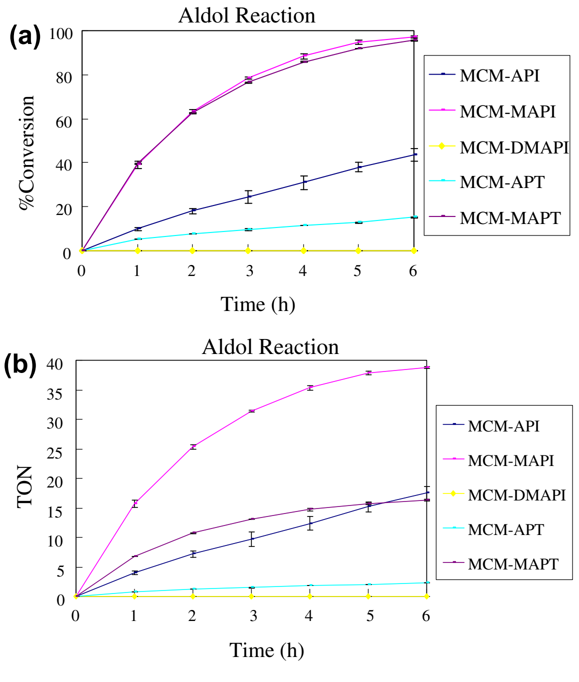


Fig. 3. Time-dependent study of the catalytic performance of the mesoporous catalysts in an aldol reaction. (a) Percentage conversion and (b) TON (moles of starting materials converted to products per mole of amines).

It is also worth noting that our amine functionalized materials gave much more selective alcohol product than the dehydrated, olefin product compared to those reported by Davis group [5b,5c]. The aldol reaction can produce significant amount of dehydrated, olefin products along with an alcohol product in aldol reaction, with ratios of dehydrated olefin : alcohol products as high as 49%:42% and 45%:17% [5b,5c]. The olefin product from aldol reaction is most likely resulted from dehydration of the alchol product. So, it also appears that some of the olefin products we observed are also products of dehdydration of the alcohol product under the reaction conditions we used, although produced less so than the ones observed in Refs. [5b,5c]. This further makes our materials not only efficient catalysts for aldol reaction but also more suitable, selective catalysts for producing a higher relative ratio of alcohol/olefin. This may be due to the fact that our reaction goes to almost completion within 6 h and the tendency of the alcohol products to undergo dehydration over this relatively shorter time period is less than it would be over 24 h, which is a reaction time employed in Zeidan et al. [5b,5c].

After demonstrating the highly effective catalysis in aldol reaction by the primary amine functionalized material, we tested the two other samples containing secondary and tertiary amines. *N*-Methylaminopropyl (MAP) and *N*,*N*-dimethylaminopropyl (DMAP)-functionalized catalysts were synthesized in isopropanol and toluene and their catalytic properties were compared with the corresponding samples containing primary amine groups (Fig. 3). Interestingly, the secondary amine grafted samples, MCM41-MAPI and MCM41-MAPT, showed more efficient catalytic activity than the corresponding primary amine grafted samples, MCM41-API and MCM41-APT. On the other hand, both MCM41-DMAPI and MCM41-DMAPT exhibited negligible catalytic activity (Fig. 3). Interestingly, samples grafted in toluene for shorter times gave similar wt.% organoamine groups as the corresponding sample grafted in isopropanol for 5 h. However, the former still showed weaker catalytic efficiency than the latter (Table 2 and Fig. S5). For instance, the sample grafted with APTS in toluene for 15 min, which has similar number of amine (or silanol groups) as sample MCM41-API, showed significantly lower catalytic efficiency than the latter (Table 2 and Fig. S5).

One can speculate that the higher catalytic activity of MCM41-API and MCM41-MAPI compared to that of MCM41-APT and MCM41-MAPT, respectively, might be due to the fact that the densely populated organoamine groups grafted in the latter reduce the surface area and pore size of the material, which subsequently may result in lower catalytic efficiency [53,54]. However, nitrogen adsorption–desorption experiment on samples grafted in isopropanol versus toluene did not show significant differences in surface areas, pore size, and pore volume between the two samples, despite the samples had significant differences in organoamine loading (Table 1). Although the latter difference is expected to cause some differences in catalytic efficiency, it alone could not explain the significant difference in catalytic efficiency between the two samples, especially after normalizing the catalytic efficiency per unit surface area [55]. In other words, there must be reasons such as possible cooperative catalytic activity [3–5,46,52,55] that may have resulted in the higher catalytic performance in aldol reaction by the samples grafted in isopropanol compared to those grafted in toluene. We recently reported that the primary amine functionalized samples that were synthesized by grafting in isopropanol for

6 h were proved to have enhanced catalytic performance in the Henry reaction than the corresponding samples grafted in toluene for the same period of time because of the improved cooperative effect between the site-isolated amine groups and many residual silanols in the former [56]. Based on this previous report for primary amine functionalized samples for the Henry reaction, we have hypothesized that the samples grafted with the different amines in isopropanol for 5 h here also should have many surface residual silanol groups surrounding amine groups and produce cooperative catalytic activity in the aldol reaction compared to the corresponding samples grafted in toluene for 5 h. Similarly, the samples grafted in toluene for shorter times of 15 and 30 min may have similarly higher numbers of ungrafted silanol groups, which result in higher catalytic efficiency. This hypothesis is reasonable considering the fact that surface silanol groups are weak acids, and base-catalyzed aldol reactions are activated by acidic groups [3–5]. Furthermore, mesoporous silica (MCM-41) has been shown to produce enhanced catalytic effect on base-catalyzed aldol reaction in homogeneous catalysis [45].

In order to prove the enhancement effect of silanols in aldol reaction by the samples grafted in isopropanol for 5 h and samples grafted in toluene for 15 and 30 min, we did several control experiments. We first performed an experiment similar to the one done by Kubota et al. [45] by adding MCM-41 in the reaction mixture. We also did reactions by using samples MCM41-CH_3, MCM-API-CH_3, and MCM-MAPI-CH_3 whose silanols were functionalized with trimethylsilyl groups but have large surface area and pore diameter as their corresponding unfunctionalized samples (see Section 2 for details). When MCM-41 was added to the reaction mixture in which diethylamine was used as a homogeneous catalyst, the catalytic ability was significantly improved. However, when the surface silanol groups were capped with trimethylsilyl groups (MCM41-CH_3), no enhanced catalytic effect was observed (Table 3). Furthermore, the catalytic activity of the amine-functionalized catalysts decreased after functionalization of their silanols with methyl groups (Fig. 4). For instance, upon grafting the silanol groups of MCM-API (or upon using MCM-API-CH_3), the catalytic efficiency decreased significantly (Fig. 4), confirming the role of surface silanol groups as a general acid. Although not significant, similar decrease in catalytic efficiency was also observed for sample MCM-MAPI-CH_3 compared to its unfunctionalized counterpart, MCM-API (Fig. 4b). Interestingly the sample grafted with APTS for 15 min, which gave similar density of organoamine (or silanol groups) as sample MCM-API (MAPTS-grafted sample in isopropanol for 5 h), showed significantly lower catalytic efficiency than sample MCM-API (Table 2 and Fig. S5). However, the former showed higher catalytic efficiency than the corresponding sample grafted in toluene for 5 h.

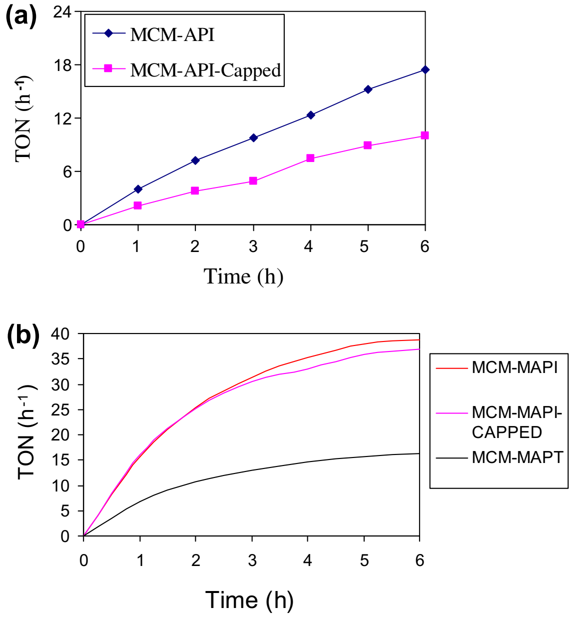
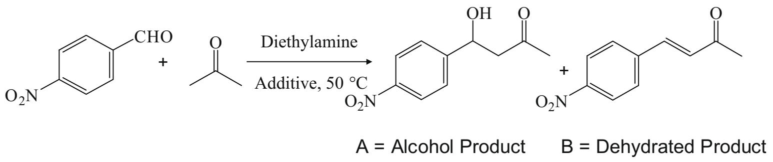


Fig. 4. Time-dependent study of the catalytic performance of the mesoporous catalysts in an aldol reaction before and after capping with silanol groups of the catalysts: Samples with (a) primary amine and (b) secondary amine groups.

From the results shown in Table 2, Table 1S, Figs. 3 and 4, and Fig. S5, three trends in catalytic activity can be drawn, i.e. (1) the catalytic efficiency of catalysts grafted in isopropanol > corresponding catalysts grafted in toluene; (2) the catalytic efficiency of catalysts grafted with secondary amine > primary amine > tertiary amine; and (3) the catalytic activity was significantly reduced after capping the silanols with methyl groups in the case of primary amine containing sample and in a moderate degree in the case of the sample containing secondary amine groups (Fig. 4). The lower degree of catalytic activity by the sample containing tertiary amine groups was consistent with what was reported previously [45], suggesting that the enamine formation may be the key intermediate in the catalysis by our materials as well and that the tertiary amines have difficulty in forming enamine intermediates.

Based upon all the discussion above, a mechanistic explanation for the difference in catalytic performance between the catalysts grafted in isopropanol and those grafted in toluene is proposed in Fig. 5, where MCM41-MAPI and MCM41-MAPT were used as examples. Samples grafted in isopropanol, which have relatively more site-isolated organoamines that are surrounded by many sil-

Table 3
Catalytic activity of diethylamine with and without additives.



Additive used	No additive	MCM-41	MCM41-CH_3	Silica microspheres
Percentage yield at 1 h[a]	NA[b]	9.6	NA[b]	NA[b]
% Yield at 6 h[a]	10.5	36	9.9	8.7

[a] % Yield is the sum of *A* and *B*.

[b] NA = Not available since the product peaks were so small in the NMR spectra that it could not be integrated to get reliable data. All reactions were run twice and the obtained data were similar.

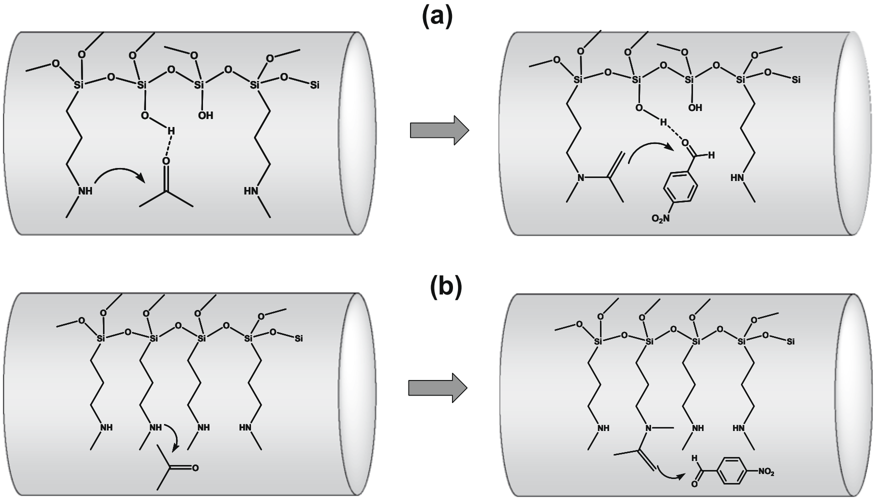


Fig. 5. Mechanistic-based explanation for the difference in catalytic efficiency between MCM41-MAPI (a) and MCM41-MAPT (b).

anol groups [46], not only activate the acetone molecules to form enamines but also help the aldehyde to be more susceptible for nucleophilic addition [51]. This combined effect produces more efficient catalysis. Since the samples grafted in toluene produce more aggregated organoamines [46,55] and have only few surface silanol groups surrounding the amines, this cooperative catalytic activity by the surface silanols to activate both acetone and benzaldehyde in the aldol reaction is reduced significantly (Figs. 4 and 5).

We believe that the activation effect to the carbonyl carbons via the single hydrogen bonding would be significant enough to explain the observed difference in catalytic efficiency (or catalytic promotional effect of silanols) between the sample grafted in isopropanol (or that containing more silanols) versus the one grafted in toluene (or that containing less silanols). This hydrogen bonding makes that carbon more electrophilic or more susceptible to nucleophilic attack [3c] and more so in samples containing more density of silanols than in those samples containing fewer silanols. Furthermore, as shown in Fig. 5, the activation occurs to both reactants (*p*-nitrobenzaldehyde and acetone) making the activation or promotional effect by silanols to be even more significant.

4. Discussion

Recently, extensive efforts toward the synthesis of heterogeneous catalysts containing multiple functional groups that are capable of cooperatively catalyzing various chemical processes have continued [3–5,46,52,55]. Enhancement of catalytic activity by acidic groups in base-catalyzed reactions has been reported [3–5,46,55,56]. For example, Zeidan et al. [5b,5c] recently reported enhanced base catalysis in an aldol condensation by placing organic acid and organic base groups on the same solid support. They further found that the efficiency of the catalysts was dependent on the pK_a value of the acid. A weaker organic acid group provides a better acid and base pair to catalyze the reaction owing to lowered degree of neutralization between the acidic and basic groups [5b,5c]. However, during the synthesis of these catalysts, the acidic and basic groups are not protected from each other [3–5]; therefore, neutralization cannot be completely avoided. In another work, attempts were made to isolate the acidic and basic groups by administering them separately in the pores and within the frameworks of the mesoporous materials [56]. This, however, produces greater distance between the acid and base groups, making them not capable of exercising effective cooperative activity. In either of the above two cases, one could expect low catalytic efficiency. Our group recently developed a new method to achieve more site-isolated organoamine basic groups and many residual silanol weak acid groups in the pores of mesoporous materials by using polar-protic solvents such as isopropanol [46,55]. The advantage of this approach has been the weakly acidic silanol groups, which are barely capable of "killing" the site-isolated organoamine basic groups, leaving both acidic and basic sites intact in close proximity within the material. We have probed the degree of site-isolation of the organoamine catalytic groups colorimetrically and demonstrated an enhanced catalytic activity of the material for the Henry reaction [46,55].

Here we employed a similar strategy to achieve site-isolated basic groups along with many residual silanols for aldol condensation reaction. Furthermore, by a systematic change of the basic sites, the most optimum and efficient site-isolated catalyst for the reaction was determined. While grafting different aminoorganosilanes in isopropanol was proved to result in site-isolated organoamine and many weakly acidic silanol catalytic groups, samples grafted in toluene produced more aggregated organoamine groups and fewer silanols. The samples grafted with primary and secondary amines showed significant catalytic activity in aldol condensation reaction, with the one with secondary amine being the most efficient. The latter observation is interesting compared to our previous study for the Henry reaction where the sample with primary amine was obtained to be the most effective cooperative catalyst [57]. The sample grafted with tertiary amines showed negligible catalytic ability whether it has site-isolated organoamine groups or not. Control samples synthesized by grafting the surface silanols of MCM-41, MCM41-API, and MCM41-MAPI with methyl groups exhibited less catalytic activity, proving the importance of the silanol groups (Fig. 4).

Generally, the samples that were synthesized in isopropanol simply contained the surface silanol groups in large numbers around site-isolated organoamines, enabling a cooperative catalytic activity in aldol reaction to take place efficiently. The uniqueness in our materials is the presence of many residual surface silanol groups, which are weakly acidic, around the site-isolated organoamine groups. There are several advantages of using surface silanol groups to produce acid–base bifunctional catalysts over the different organic acid groups that were employed previously [3–5]: (1) weak acidity results in less degree of neutralization with the amine groups, giving higher catalytic activity; (2) weak acids favor less dehydration of the alcohol product (A) into dehydrated product (B) during the aldol reaction, giving higher selectivity toward

A as shown in Table 2 and Supplementary Table 1S, which is a product often preferred in industry; and (3) silanol groups make it unnecessary to introduce an additional auxiliary acidic group as done in Refs. [3–5]. Having the surface silanol groups not only produces more effective acidic sites for the aldol reaction but also makes the synthesis less costly and safer.

The aldol reaction that we chose to test the catalytic performance here has not only allowed us to investigate cooperative catalytic properties of our catalysts further but also is one of the most important C–C bond-forming reactions in organic synthesis. Thus, the systematic investigation of cooperative solid catalysts containing acidic and basic groups for aldol reaction provided us with valuable insight about cooperative catalysis and may facilitate the development of efficient heterogeneous catalysts mimicking biocatalysts [1,2,52] for other reactions. Furthermore, the investigation of the properties of the catalysts in aldol reaction allowed us to demonstrate the versatility of amine-functionalized mesoporous materials that are synthesized by solvent-assisted grafting [46,52,55] to beyond the Henry reaction.

5. Conclusion

A highly efficient solid-base catalyst for the aldol condensation reaction was synthesized by placing site-isolated organoamine groups along with many residual silanols on mesoporous materials. The synthesis was carried out by grafting aminoroganosilanes in a polar-protic solvent. The mesoporous catalysts were characterized by various methods. The surface silanol groups, which were proved to be more in samples grafted in isopropanol compared to the corresponding samples grafted in a non-polar solvent, toluene, were found to be responsible for the enhanced catalytic activity in aldol reaction. Control experiments were carried out to investigate the importance of silanol groups for the cooperative catalytic activity in base-catalyzed aldol reaction. By systematically investigating a series of organoamines including primary, secondary, and tertiary amines, the most optimum basic catalyst for the reaction was determined to be the one with a secondary amine group that was grafted in isopropanol (MCM41-MAPI). This observation is interesting compared to our previous study for the Henry reaction where the sample with primary amine was obtained to be the most effective cooperative catalyst [57]. Upon comparison of the catalysis on the basis of catalytic yield and turn-over-number, sample MCM41-MAPI showed the highest acid–base cooperative catalytic activity and efficiency for aldol reaction, even when compared to other materials reported previously. A mechanism was proposed revealing the cooperative catalytic activity between the site-isolated organoamine groups and residual silanols, where the surface silanol groups not only participate in the formation of enamine intermediate but also facilitate the nucleophilic addition. This new solid-base catalyst, which contained many residual surface silanols, has enhanced cooperative catalytic activity and selectivity while its synthesis involves no need of additional secondary organic acid group and proceeds through a less costly procedure.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2009.04.018.

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