



Short Communication

Synthesis, characterization and catalytic application of bifunctional catalyst: Al-MCM-41-NH₂Fanpeng Shang, Heng Liu, Jianrui Sun, Bo Liu, Chunhua Wang, Jingqi Guan^{*}, Qiubin Kan^{*}

College of Chemistry, Jilin University, Changchun, 130023, PR China

ARTICLE INFO

Article history:

Received 18 October 2010

Received in revised form 6 January 2011

Accepted 7 January 2011

Available online 19 January 2011

Keywords:

Acid-base

Mesoporous materials

One-pot cascade reaction

Nitroaldol reaction

ABSTRACT

A new type of acid-base bifunctional mesoporous catalyst is prepared by the modification of Al-MCM-41 surfaces with organic amine functional groups. The ratio of acidic and basic sites on the solid surface can be adjusted by varying the amount of 3-aminopropyl-triethoxysilane (APTES) in the reaction medium (toluene). The acid-base bifunctional catalysts show high catalytic activities and selectivities in one-pot deacetalization–Knoevenagel and deacetalization–nitroaldol (Henry) reactions. The cohabiting of acidic and basic sites in the materials acting in a cooperative way to catalyze nitroaldol (Henry) reaction is also demonstrated.

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1. Introduction

Since the discovery of ordered mesoporous silicates M41S, a variety of surface-modified mesoporous materials have been extensively investigated for catalysis, drug delivery, separation and sensor design [1–4]. Recently, a number of research groups have pursued new and creative approaches towards incorporating multiple functional groups into heterogeneous catalysts, which can catalyze multistep reaction cascades in one system or work in a cooperative manner to alter the characteristics of a single reaction, for example, rates, selectivities, and so forth [5–8].

Direct co-condensation and post grafting procedures have been used for the preparation of these bifunctional materials. There are reports about the preparation of bifunctional materials through a co-condensation approach of tetraethylorthosilicate (TEOS) and organosilanes with supramolecular templates [9–13]. These antagonist functions exhibit a cooperative effect in nitroaldol condensation. However, the materials mentioned above were unable to give rise to higher activities due to mutual destruction of acids with amines in the one-pot synthetic process. As an alternative approach for the design of acid-base bifunctional catalysts, Asefa et al. synthesized bifunctionalized catalysts by simply grafting an organosilane precursor onto the MCM-41 in a polar-protic solvent. These materials contain site-isolated organoamines and neighboring residual surface silanol (weak acid) groups to cooperatively catalyze the Henry reaction and aldol condensation [14–16]. However, the utilization of those bifunctional materials is restricted by its relatively

weak acid centers. Motokura et al. have reported immobilization of organic amines as bases on inorganic solid–acid surfaces by post grafting to afford highly active acid-base bifunctional catalysts, which enabled various organic transformations including C–C coupling reactions and also performed one-pot acid-base reaction [17–20]. One drawback of these materials is the lack of uniform and controlled porosity. Therefore, these materials may be detrimental in some catalytic applications. The small pore size of the silica support also limits the scope of catalytic reactions.

Our aim in this communication is to describe a simple and effective method for the preparation of efficient acid-base bifunctional materials possessing hexagonal arrays of uniform pores, large surface area and high pore volume. Their catalytic activities for one-pot cascade reactions and nitroaldol reaction were investigated.

2. Experimental

Materials

cetyltrimethylammonium bromide (Aldrich), tetraethyl orthosilicate (TEOS) (Aldrich), 3-aminopropyl-triethoxysilane (Acros), benzaldehyde dimethylacetal (Alfa), ethyl cyanoacetate (Acros), nitromethane (A.R), benzaldehyde (A.R), benzene (A.R), AlCl₃·6H₂O (A.R) were commercially available and used as received.

2.1. Catalyst preparation

Al-MCM-41 (Si: Al = 25) was synthesized according to the method described in the literatures [21]. An ethylamine (EtNH₂) solution was added to a stirred solution containing distilled water, cetyltrimethylammonium bromide (CTAB) and AlCl₃·6H₂O. Afterwards,

^{*} Corresponding authors at: Jiefang Road 2519, Changchun, 130023, PR China. Tel./fax: +86 431 88499140.

E-mail addresses: guanjq@jlu.edu.cn (J. Guan), qkan@mail.jlu.edu.cn (Q. Kan).

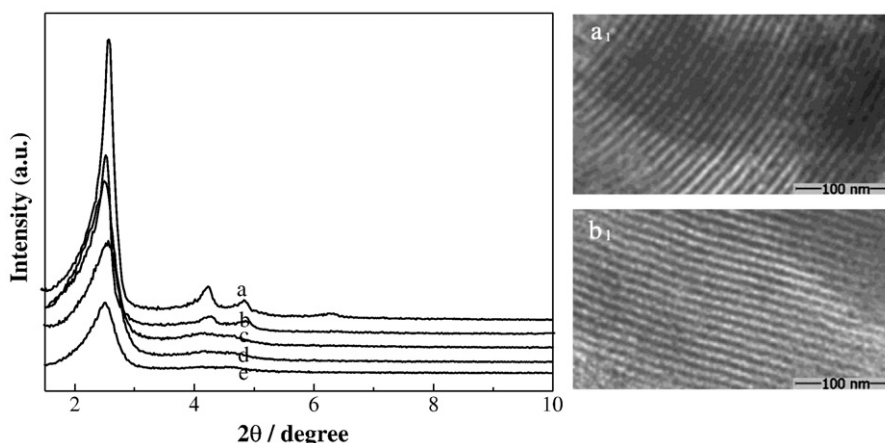


Fig. 1. XRD patterns of the Al-MCM-41 (a), Al-MCM-41-NH₂-1% (b), Al-MCM-41-NH₂-3% (c), Al-MCM-41-NH₂-5% (d), Al-MCM-41-NH₂-10% (e) and TEM images of (a₁) Al-MCM-41-NH₂-3%, (b₁) Al-MCM-41-NH₂-5%.

tetraethylammonium orthosilicate (TEOS) was added dropwise, leading to a composition of 1.0 SiO₂:0.04 Al₂O₃:0.14 CTAB:2.4 EtNH₂:100 H₂O. The reaction mixture was further stirred for 4 h at room temperature before being heated at 110 °C for one day. The solution was filtered and the precipitate was washed with distilled water. After being dried at ambient temperature, the product was heated in air at 550 °C for 7 h, with a heating rate of 1 °C min⁻¹ from room temperature to 550 °C. Pure MCM-41 was prepared by the same procedure without addition of AlCl₃·6H₂O. Then, 2 g dehydrated Al-MCM-41 or MCM-41 was stirred vigorously in 80 ml dry toluene containing different amount of 3-aminopropyl-triethoxysilane (N/Si = 1, 3, 5, 10 mol%). This solution was heated to 383 K under nitrogen for 10 h. The powder was collected by filtration, washed with 2-propanol and dried at 373 K, resulting in silica material Al-MCM-41-NH₂-x or MCM-41-NH₂-x, where x (x = 1, 3, 5, 10%) is the theoretical proportion of the amino-organoalkoxysilane in the Si source.

2.2. Catalytic experiments

2.2.1. One-pot deacetalization–Knoevenagel reaction

This one-pot reaction was performed according to our previous work [13]. Toluene was used as a solvent in this study instead of benzene, which is less toxic.

2.2.2. One-pot deacetalization–Henry reaction

Into a reaction vessel were placed the catalyst (0.05 g), benzaldehyde dimethylacetal (1.0 mmol) and nitromethane (5 ml). The resulting

mixture was vigorously stirred at 90 °C under nitrogen. The products were analyzed with a BEIFEN-3420A gas chromatograph (GC) equipped with an OV-101 capillary column and FID detector.

2.2.3. Nitroaldol reaction

The catalyst was added (0.05 g) into a Pyrex glass reactor, then nitromethane (5 ml) and benzaldehyde (0.1 ml, 1 mmol) were added. The resulting mixture was vigorously stirred at 70 °C under nitrogen. After 2 h, the catalyst was separated by filtration, and the filtrate was analyzed quantitatively by GC-FID.

3. Results and discussion

3.1. Characterization of the silica structures

The XRD patterns of the synthesized samples are shown in Fig. 1. The XRD results are consistent with the literature results [13], indicating that the target OMS phase is obtained. The peak intensity of the samples weakens as the organic loading increases, indicating the formation of less ordered mesostructure. The mesostructure ordering and symmetry inferred from the XRD patterns can also be confirmed by the TEM images (Fig. 1). The hexagonally arranged pore arrays of the samples can be clearly seen. N₂ adsorption–desorption isotherms and pore size distributions of Al-MCM-41, Al-MCM-41-NH₂-3% and Al-MCM-41-NH₂-5% are shown in Fig. 2. It shows that all samples display a type IV isotherm with H1 hysteresis and a sharp increase in volume adsorbed at P/P₀ = 0.2–0.4, characteristic of highly

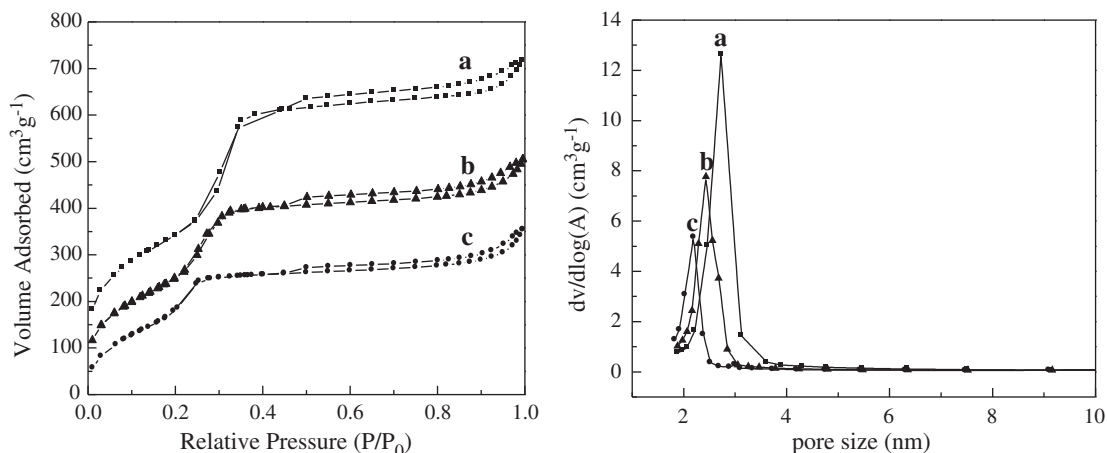


Fig. 2. N₂ adsorption–desorption isotherms and pore size distribution profiles of samples: (a) Al-MCM-41, (b) Al-MCM-41-NH₂-3% and (c) Al-MCM-41-NH₂-5%.

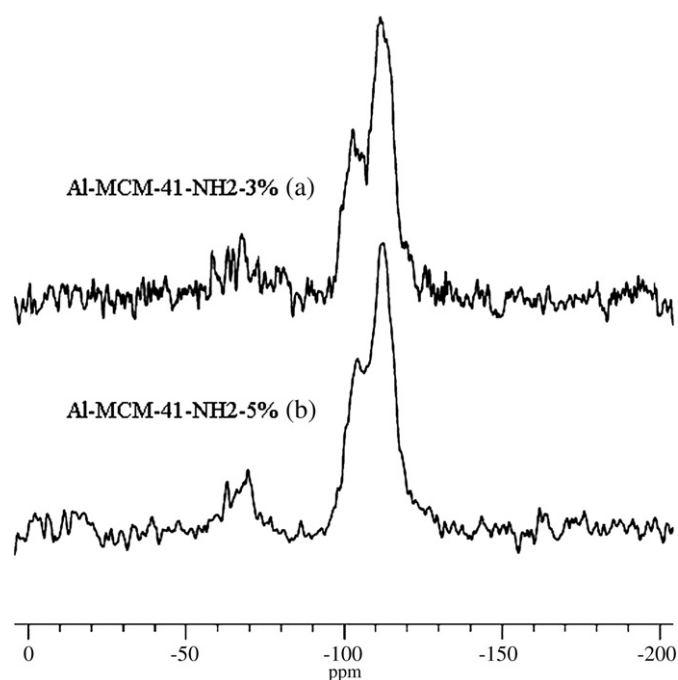


Fig. 3. ^{29}Si MAS NMR spectra of Al-MCM-41-NH₂-3% (a), and Al-MCM-41-NH₂-5% (b).

ordered mesoporous materials [22]. In addition, as shown in Table 1, with the introduction of organic functional groups, the BET specific surface area, pore size and pore volume gradually decreases. The results imply that organic moieties are successfully incorporated by grafting in toluene.

3.2. Confirmation of the base and acid sites

Solid-state ^{29}Si MAS NMR spectra of samples in Fig. 3 show two distinct peaks at about -100 ppm due to Q^3 ($\text{Si}(\text{OSi})_3\text{OH}$) and -110 ppm due to Q^4 ($\text{Si}(\text{OSi})_4$) silicon sites. In addition to these peaks, samples display a resonance peak at -65 ppm, assigned to T^3 ($\text{RSi}(\text{OSi})_3$). This peak is due to the Si atoms in the organosilane APTES. It is also seen that sample Al-MCM-41-NH₂-5% possesses a higher intensity of T sites than sample Al-MCM-41-NH₂-3%, demonstrating a higher content of amine groups in the former than that in the latter [23]. Quantification of amine loading in some materials was performed using elemental analysis (CHN). The results indicate that Al-MCM-41, Al-MCM-41-3% and Al-MCM-41-5% contains 0, 0.43 and 0.62 mmol/g of NH₂, respectively (Table 1).

Pyridine is employed as a test molecule to confirm the acidic sites on the selected samples [24,25]. IR spectra of pyridine adsorption on Al-MCM-41, Al-MCM-41-NH₂-3% and Al-MCM-41-NH₂-10% at 373 K were shown in Fig. 4. The peaks associated with pyridine coordinated to Lewis acid sites (~ 1455 , 1623 and 1490 cm^{-1}) and to Brønsted acid sites (~ 1546 , 1639 and 1490 cm^{-1}) can be clearly seen in Al-MCM-41 and Al-MCM-41-NH₂-3%, indicating that aluminium incorporation in the framework of MCM-41 generates both Brønsted and Lewis sites. However, for Al-MCM-41-NH₂-10%, the peaks associated with acid sites intensively weaken or even disappear implying that the acid sites

Table 1
The structure parameters and elemental analysis results of samples.

Samples	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore vol. ($\text{cm}^3 \text{g}^{-1}$)	Pore size ^a (nm)	N content ^b (mmol/g)
Al-MCM-41	1250	1.23	2.91	0
Al-MCM-41-NH ₂ -3%	934	0.88	2.70	0.43
Al-MCM-41-NH ₂ -5%	746	0.61	2.45	0.62

^a Calculated by using the BJH model on the adsorption branch of the isotherms.

^b Based on the N elemental analyses.

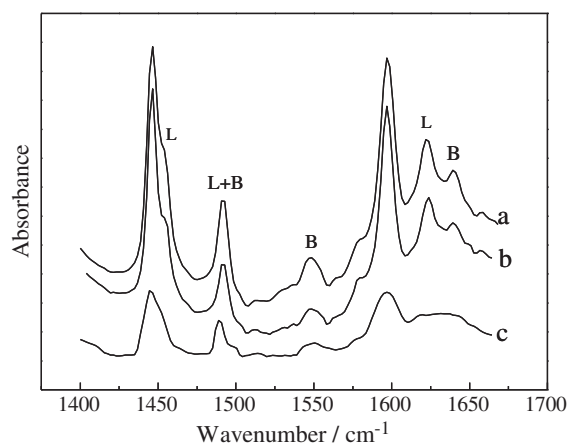


Fig. 4. IR spectra of pyridine adsorption on Al-MCM-41 (a), Al-MCM-41-NH₂-3% (b) and Al-MCM-41-NH₂-10% (c) at 373 K.

are lacking in this sample. Therefore, it is supposed that appropriate amount of amine (basic sites) could friendly coexist with the acid on the surface of the solid without destroying the original acid. However, densely populated amines will destroy the acid sites because of the neutralization.

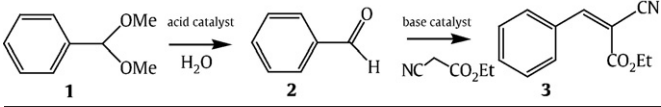
NH₃-TPD measurement was employed to estimate of the number and strength of acidic sites. The NH₃-TPD profile of Al-MCM-41 (not shown here) shows only one peak at 190 – 200 °C, which may be corresponding to the desorption of NH₃ from the weak acid sites of the materials. The lack of strong acid on Al-MCM-41 may be due to the amorphous nature of the pore wall of the mesoporous materials. The number of acidic sites in Al-MCM-41 is 0.60 mmol/g, which is similar to the results materials reported [26].

3.3. Catalytic properties

The acid-basic properties of the bifunctionalized catalysts were first evaluated in two tandem reactions: the catalytic conversion of benzaldehyde dimethyl acetal (**1**) into benzylidene ethyl cyanoacetate (**3**) and (2-nitrovinyl) benzene (**4**), as shown in Table 2 and Table 3. These reaction sequences involve two separate steps: an acid-catalyzed deprotection to give the intermediate benzaldehyde (**2**) and the subsequent base-catalyzed Knoevenagel reaction or nitroaldol (Henry) reaction to yield benzylidene ethyl cyanoacetate or 2-nitrovinyl benzene. Deacetalization is used to recover protected aldehydes in organic chemistry.

One-pot synthesis of benzylidene ethyl cyanoacetate (**3**) from benzaldehyde dimethylacetal (**1**) was demonstrated over various catalysts (Table 2). From the table, benzaldehyde is the main product (entry 1) over Al-MCM-41 and only a negligible formation ($<1\%$) of **3** was formed over MCM-41-NH₂-3% (entry 2). Thus the monofunctionalized catalyst on its own cannot perform the one-pot cascade reaction. Addition of equivalent amounts of structurally similar free acid (*p*-toluenesulfonic acid) or base (tert-butylamine) to bifunctionalized catalysts cannot catalyze the tandem reaction sufficiently, as these homogeneous species diffuse into the pore channels and then destroy the catalytic sites by formation of ion pairs (entry 7 and entry 8). Al-MCM-41-NH₂-1% gave almost 100% conversion of benzaldehyde dimethylacetal within 40 minutes, but the yield to the final product **3** (42.8%) is low, indicating the lack of base sites on this catalyst (entry 3). Remarkably, Al-MCM-41-NH₂-3% showed the highest activity in tandem deacetalization–Knoevenagel condensation. It gave almost 100% conversion of benzaldehyde dimethylacetal and afforded **3** in yield of 97.3% (entry 4). The conversion of benzaldehyde dimethylacetal decreased with raising concentration of organosilanes in the catalysts (entries 5 and 6). The probability of neutralization from acid and base

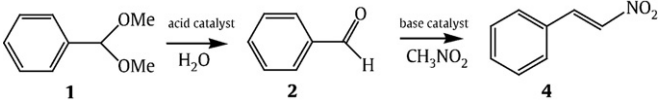
Table 2
One-pot deacetalization–Knoevenagel reaction over different catalysts.



Entry	Catalyst	Conv. of 1 (%)	Yield of 2 (%)	Yield of 3 (%)
1	Al-MCM-41	~100	97.3	2.7
2	MCM-41-NH ₂ -3%	Trace	Trace	Trace
3	Al-MCM-41-NH ₂ -1%	~100	63.2	36.8
4	Al-MCM-41-NH ₂ -3%	~100	3.7	96.3
5	Al-MCM-41-NH ₂ -5%	83.7	3.2	80.5
6	Al-MCM-41-NH ₂ -10%	10.5	2.2	8.3
7	Al-MCM-41-NH ₂ -3% + tert-butylamine	Trace	Trace	Trace
8	Al-MCM-41-NH ₂ -3% + p-toluenesulfonic acid	60.2	57.4	2.6

Reaction conditions: **1** (4 mmol), **2** (4 mmol), catalyst (0.2 g), toluene (12 ml), 40 min, 80 °C.

Table 3
One-pot deacetalization–Henry reaction over different catalysts.



Entry	Catalyst	Reaction time (h)	Conv. of 1 (%)	Yield of 2 (%)	Yield of 4 (%)
1	Al-MCM-41	1	~100	97.6	2.4
2	MCM-41-NH ₂ -3%	1	Trace	Trace	Trace
3	Al-MCM-41-NH ₂ -1%	1	~100	69.1	30.9
4	Al-MCM-41-NH ₂ -3%	1	~100	11.9	89.1
5	Al-MCM-41-NH ₂ -5% (1st)	1	~100	1.2	98.8
6	Al-MCM-41-NH ₂ -5% (2nd)	1	97	1.7	95.3
7	Al-MCM-41-NH ₂ -5% (3rd)	1	95	1.5	93.5
8	Al-MCM-41-NH ₂ -10%	1	11.7	2.6	9.1
9	MSN-NH ₂ -SO ₃ H [11]	5	55	17.6	37.4
10	PMO-SO ₃ H-NH ₂ [12]	20	100	2.5	97.5
11	SO ₃ H-M-NH ₂ -0.15[13]	5	~100	14.8	85.2

Reaction conditions: **1** (1 mmol), nitromethane (5 ml), catalyst (0.05 g), 90 °C, 1 h.

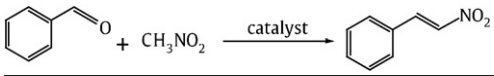
sites increases with the increasing NH₂ loading, leading to the lower catalytic activities. These results illustrate the coexistence of acidic and basic sites for this one-pot reaction on Al-MCM-41-NH₂-3%. Furthermore, the one-pot reaction system did not need the addition of water probably because the successive aldol reaction produced water to efficiently accelerate the deprotection of **1**.

Deacetalization-nitroaldol (Henry) reaction was employed to evaluate the acid-base bifunctional catalyst MSN-NH₂-SO₃H by Thiel et al. [11], the catalyst afforded **4** in yield of 37.4% after 5 hours. Recently, they reported a synthetic procedure to generate a successful cohabitation of two antagonistic functional groups in a periodic mesoporous organosilica [12], which afforded **4** in yield of 97.5% after 20 h. We reported a method to synthesize MCM-41 that contains organic amines and organic acids through protection of amino group [13] and afforded **4** in yield of 85.2% after 5 hours. Data for deacetalization–Henry reaction over Al-MCM-41-NH₂ catalysts are collected in Table 3. Amazingly, under the same reaction condition, Al-MCM-41-NH₂-5% with appropriate acidic and basic sites afforded **4** in yield of 98.8% after 1 hour (entry 5), which is the best result reported up to now. It is proven that Al-MCM-41-NH₂-5% exhibits excellent acid-basic properties. However, catalytic activities decreased with raising NH₂ loading (entry 8). To determine whether leaching and/or deactivation of the catalysts occur, Al-MCM-41-NH₂-5% was reused three times in this reaction. The catalyst was recovered by filtering, washing with ethanol, and dried at 100 °C for 2 h, and then reused without any activation. As shown in Table 3, only a slight deactivation occurred for the material after used three times (entries 5, 6, and 7). The

decrease in conversion is probably due to the incomplete removal of adsorbed species from the active sites by ethanol.

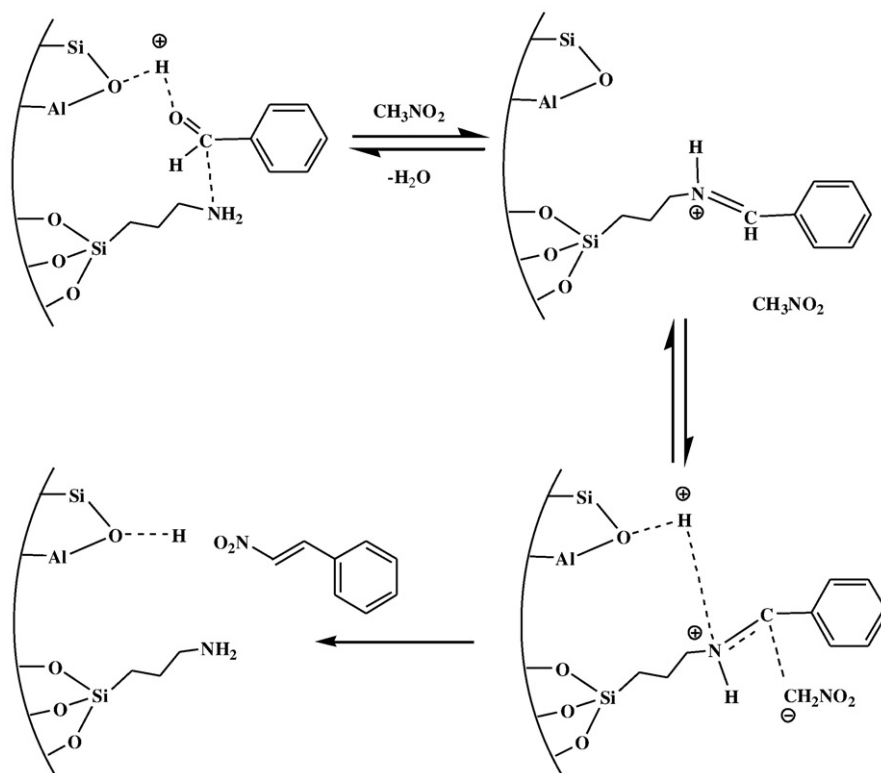
Acid and base work in a cooperative manner to catalyze nitroaldol reaction is also investigated and the results were collected in Table 4. Al-MCM-41-NH₂-5% exhibits a much better catalytic activity than the single acid or base functional MCM-41 indicating that acid-base cooperation effect should be involved in the catalytic reaction. A cooperative acid-base mechanism for the imine intermediate pathway of Henry reaction is proposed in Scheme 1. (1) The aldehyde gets activated by the surface acidic sites which allow the immobilized -NH₂ groups to attack the carbonyl group of the aldehyde. (2) Water is released in the formation of imine intermediate. (3) The nitromethane reacts with the intermediate. (4) The (2-nitrovinyl) benzene is formed and the amine is regenerated. The mechanism is reasonable

Table 4
Nitroaldol reaction over different catalysts.



Entry	Catalyst	Yield (%)
1	Al-MCM-41	<1
2	MCM-41-NH ₂ -5%	55.1
3	Al-MCM-41-NH ₂ -5%	99.2

Reaction conditions: benzaldehyde (1 mmol), nitromethane (5 ml), catalyst (0.05 g), 70 °C, 2 h.



Scheme 1. Proposed cooperative mechanism for the Henry reaction.

because both the imine formation step and the attack of the nucleophile on the imine are known to be acid catalyzed.

4. Conclusions

A type of an efficient acid-base bifunctional catalyst possessing hexagonal arrays of uniform pores, large special surface area and high pore volume was synthesized by simply grafting 3-aminopropyltriethoxysilane (APTES) onto the Al-MCM-41 surfaces. The materials were used as catalysts in one-pot cascade reactions and the acid-base reaction sequences were successfully promoted. An acid-base cooperative manner to catalyze Henry reaction was also found. We expect that this bifunctional material also can serve as an efficient heterogeneous catalyst for many other one-pot incompatible systems and catalytic nucleophilic reactions.

Acknowledgments

The authors greatly appreciate the support of the National Natural Science Foundation of China (20673046) and Jilin province (20090591).

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