



# Synthesis and characterization of BEA-SO<sub>3</sub>H as an efficient and chemoselective acid catalyst

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## ARTICLE INFO

### Article history:

Received 6 March 2010

Received in revised form 29 October 2010

Accepted 14 November 2010

Available online 21 November 2010

### Keywords:

Beta zeolite

Chlorosulphonic acid

Aldehyde protection

Deprotection

1,1-Diacetates

## ABSTRACT

BEA zeolite was synthesized under hydrothermal condition and modified with various amounts of chlorosulphonic acid. It was characterized by XRD, XRF, FT-IR, BET, thermogravimetric analysis and SEM techniques. Catalytic activity of BEA-SO<sub>3</sub>H was tested for the synthesis of 1,1-diacetates from a variety of aromatic and aliphatic aldehydes including those carrying electron donating or withdrawing substituents by acetic anhydride. At optimized conditions, The BEA-SO<sub>3</sub>H (28 wt.%) catalyst showed good yield at very short time for the synthesis and deprotection of 1,1-diacetates. Furthermore, BEA-SO<sub>3</sub>H was found to be recyclable for the protection of aldehydes with acetic anhydride under solvent-free and room temperature conditions. This method is a green approach for the protection of aldehydes in the presence of ketones.

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## 1. Introduction

The protection of carbonyl groups plays an important role in organic synthesis as well as in the chemistry of drug design [1].

Acylal formation is one of the most widely used processes for protection of carbonyl compounds. Due to the remarkable stability of 1,1-diacetates (acylals) toward a variety of reaction conditions, such as aqueous acids, neutral and basic media [2], synthesis of them is one of the methods of choice to protect a carbonyl compound in multi-step organic synthesis. Despite that numerous electrophilic catalysts were shown to be effective in forming 1,1-diacetates by the reaction of aldehydes or ketones with acetic anhydride, new reports are still being published, disclosing the use of new reagents. Strong protic acids, such as sulphuric acid [3,4], phosphoric acid and methane sulphonic acid [5], NH<sub>2</sub>SO<sub>3</sub>H [6], and Lewis acids, such as Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O [7], ZrCl<sub>4</sub> [8], FeCl<sub>3</sub> [9], anhydrous FeSO<sub>4</sub> [10], Bi(OTf)<sub>3</sub> [11], PCl<sub>3</sub> [12], and LiBr [13] have been employed for the synthesis of 1,1-diacetates. Furthermore, there are several inorganic heterogeneous catalysts, such as SiO<sub>2</sub> [14], zeolite [15], montmorillonite [16], amberlyst [17], AlPW<sub>12</sub>O<sub>40</sub> [18] and H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>·24H<sub>2</sub>O [19] for this purpose. However, many of

these methods have drawbacks, such as harsh acidic conditions, long reaction times, need for expensive catalyst, stoichiometric or excess amounts of reagents.

Many heterogeneous catalysts are less active than the homogeneous catalysts because the reaction rates are limited by the transport of the reactant to the active sites on the particle surfaces. The utility of heterogeneous catalysts can be improved by using high surface area materials since the transport of the reactants to the active site on particle surface can be enhanced by this method. Among mesoporous silica zeolites, beta zeolite is one of the most important high silica zeolites which have special catalytic properties because of its interconnected large pore network and strong acidity [20–23]. There has been a great deal of investigations on its synthesis and application [24–28].

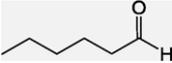
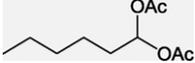
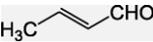
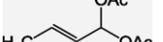
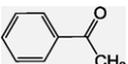
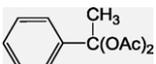
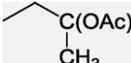
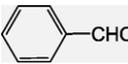
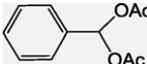
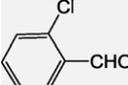
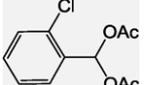
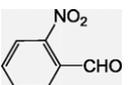
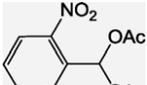
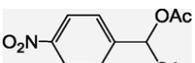
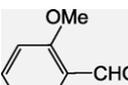
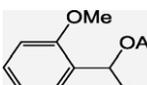
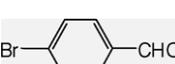
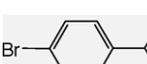
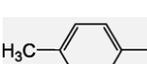
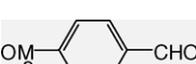
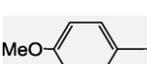
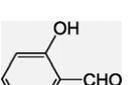
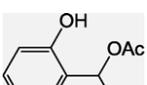
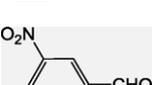
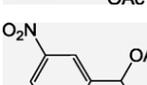
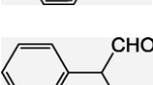
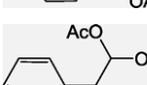
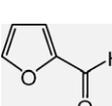
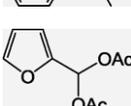
In most cases, the incorporation of SO<sub>3</sub>H species into the mesoporous silica and other inorganic materials is performed with the organosilica or bridged organosilanes precursors. They have extensively improved the hydrophobicity of mesoporous silica material [29–53]. However, the organosilica and bridged organosilane precursors either involve complicated synthesis and purification method or are very expensive. Therefore, preparation of acidic catalyst without using organosilica and bridged organosilane precursors is highly desirable.

In this work, BEA zeolite was synthesized under hydrothermal condition and modified with various amounts of chlorosulphonic acid. Then the influence of the catalytic activity and the acidity of the surface anchored sulphonic acid groups on the synthesis and deprotection of acylals is considered.

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**Table 1**  
BEA-SO<sub>3</sub>H (28%) catalyzed protection of aldehydes under solvent-free condition.<sup>a</sup>

Entry	Aldehyde	Molar ratio (aldehyde:acetic anhydride)	Protection		
			Product	Time (min)	Yield (%) <sup>b</sup>
1		1:1		1	90
2		1:1		1	90
3		1:1		30	0
4		1:1		30	0
5		1:1		1	96
6		1:1		1	90
7		.1:15		3	95
8		.1:15		4	95
9		1:1		2	98
10		.1:15		2	90
11		1:1		1	90
12		1:1		2	80
13		1:1		20	10
14		.1:15		4	85
15		.1:15		30	0
16		1:1		1	90

<sup>a</sup> Reaction conditions: acetic anhydride (2 mmol), catalyst (0.015 g), benzaldehyde (2 mmol), solvent-free, and room temperature.

<sup>b</sup> Isolated yield.

## 2. Experimental

### 2.1. Instruments and characterization

The catalyst was characterized by X-ray diffraction (Bruker D8ADVANCE, Cu K $\alpha$  radiation), X-ray fluorescence (XRF) (Bruker D8ADVANCE), FT-IR spectroscopy (Nicolet 400D in KBr matrix in the range of 4000–400 cm<sup>-1</sup>), BET specific surface areas and BJH pore size distribution (Series BEL SORP 18, at 77 K), thermal analyzer TGA (Setaram Labsys TG (STA); in a temperature range of 30–700 °C and heating rate of 10 °C/min in N<sub>2</sub> atmosphere) and SEM (Philips, XL30, SE detector).

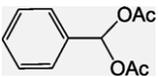
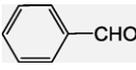
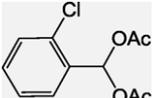
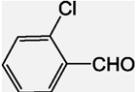
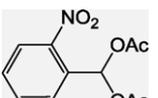
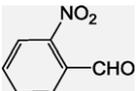
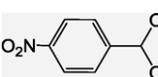
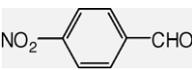
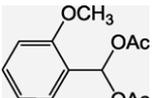
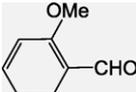
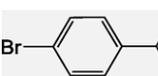
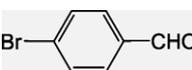
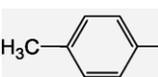
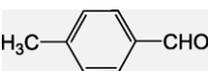
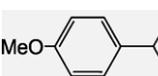
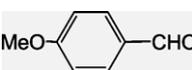
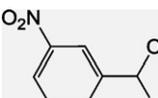
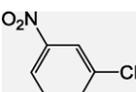
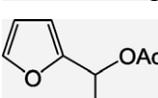
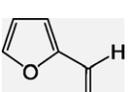
The products were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra (Bruker DRX-500 Avance spectrometer at 500.13 and 125.47 MHz, respectively), GC (Agilent 6820 equipped with a FID detector) and GC-MS (Agilent 6890). Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. All the products are known compounds; they were characterized by IR, <sup>1</sup>H NMR

and <sup>13</sup>C NMR. All melting points compared satisfactorily with those reported in the literature.

### 2.2. Catalyst preparation

Beta zeolite seeds (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 50) were synthesized according to a previously published method [54]. 0.189 g of aluminum hydroxide (54% Al<sub>2</sub>O<sub>3</sub>, 46 wt.% H<sub>2</sub>O) was added to tetraethylammonium hydroxide (TEAOH, 20%, aqueous solution) at room temperature and the mixture was stirred for 15 min. Then, fume silica (6 g, 99.8%) was added drop-wise to the solution under stirring at room temperature. After the mixture was homogenized, the temperature was ramped to 75 °C and maintained at this temperature for 1 h. The homogenous final gel was transferred into a Teflon-lined stainless autoclave and placed at 140 °C for 12 days. Finally, the solution was filtered and washed with deionized water and then dried at 100 °C overnight. Template removal was performed by calcination in air at 550 °C for 6 h.

**Table 2**  
Deprotection of 1,1-diacetates over BEA-SO<sub>3</sub>H (28 wt.%) in ethanol.

Entry	Substrate	Deprotection		
		Product	(min) Time	Yield (%) <sup>a</sup>
1			40	85
2			45	80
3			30	100
4			30	100
5			60	80
6			30	80
7			60	90
8			60	90
9			30	100
10			25	80
11			5	100

<sup>a</sup> Isolated yield.

**Table 3**  
The experimental results in synthesis of beta zeolite.

Product	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	(TEA) <sub>2</sub> O/SiO <sub>2</sub>	H <sub>2</sub> O/SiO <sub>2</sub>	Temperature (°C)	Time (day)	XRD crystallinity (%) <sup>b</sup>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>
Zeolite beta (BEA)	50	0.15	7	140	12	100	34.2

<sup>a</sup> Used in the synthesis procedure.

<sup>b</sup> Reference zeolite crystallinity is calculated from the intensity of the most intense (3 0 2) reflection peak appearing at 22.4°.

<sup>c</sup> Estimated by XRF.

To synthesize BEA-SO<sub>3</sub>H (28 wt.%), 0.50 g of zeolite beta (BEA) was added to a round-bottomed flask, then 0.192 g (1.65 mmol) of chlorosulphonic acid was added dropwise during 30 min under nitrogen atmosphere. The reaction mixture was stirred with a magnetic stirrer. After all chlorosulphonic acid was added, the reaction mixture was stirred for another 30 min under nitrogen atmosphere. Then the solution was filtered and washed with water (2 × 10 mL) to remove the unreacted chlorosulphonic acid. Finally, the white solid powder of BEA-SO<sub>3</sub>H (28 wt.%) was obtained. The composition of the catalyst samples was obtained using XRF analysis. BEA-SO<sub>3</sub>H (15 wt.%) and BEA-SO<sub>3</sub>H (34 wt.%) were synthesized similar to this procedure with various amounts of chlorosulphonic acid.

### 2.3. General procedure for the synthesis of 1,1-diacetate

In the typical experiment, 2 mmol of acetic anhydride was added to the mixture of catalyst (0.03 g, BEA-SO<sub>3</sub>H (28 wt.%) and benzaldehyde (2 mmol) in a round-bottomed flask. The reaction mixture was stirred with a magnetic stirrer at solvent-free and room temperature conditions. Course of the reaction was monitored by TLC and GC. At the end of the reaction, the catalyst was separated by filtration and washed with ethyl acetate (2 × 10 mL). The solvent was evaporated under reduced pressure to give the corresponding pure 1,1-diacetate (acylal). The yield of 1,1-diacetates with various aldehydes was tested at the optimized condition over BEA-SO<sub>3</sub>H (28 wt.%) and the results are given in Table 1.

### 2.4. General procedure for deprotection of 1,1-diacetate

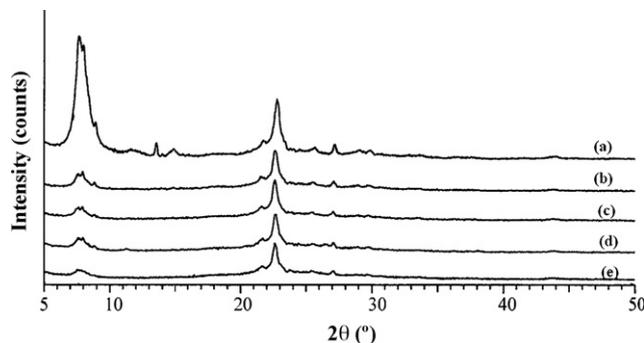
A mixture of 1-phenylmethanediacetate (1 mmol) and BEA-SO<sub>3</sub>H (28%) (0.02 g) in ethanol (96%, 5 mL) was stirred vigorously for specified time at 50 °C (Table 2). After completion of the reaction, as indicated by TLC, the catalyst was filtered and washed with Et<sub>2</sub>O (2 × 10 mL). The solvent was evaporated under reduced pressure. The resultant product was passed through short column of silica gel (n-hexane–ethylacetate, 9:1) to afford pure aldehyde. The yield of aldehydes with various 1,1-diacetates was tested at the optimized condition over BEA-SO<sub>3</sub>H (28%) and the results are given in Table 2.

## 3. Results and discussion

### 3.1. Characterization of the catalyst

The synthesis experimental results are summarized in Table 3. In the reaction, the maintained time of the alumino silicate solution into the Teflon-lined stainless autoclave has a great influence on the size of the product. By increasing maintained time, the size of the zeolite beta crystals increased.

XRD powder patterns of the calcinated samples of zeolite beta with different amount of loaded chlorosulphonic acid (a–e) are presented in Fig. 1. Fig. 1a exhibited the typical pattern of highly crystalline zeolite beta with broad and sharp reflections [55] and no other phase impurities were observed. Relative crystallinity is calculated from the intensity of the most intense (3 0 2) reflection peak appearing at 22.4° of highly crystalline zeolite beta (Table 1). The XRD analysis of the BEA-SO<sub>3</sub>H zeolites (Fig. 1) shows that by loading the zeolite with ClSO<sub>3</sub>H and during the calcination processes,



**Fig. 1.** XRD powder patterns of the calcinated samples of zeolite beta catalysts containing different amounts of loaded chlorosulphonic acid: (a) 0%, (b) 15%, (c) 28%, (d) 34%, and (e) 56%.

its crystallinity is lost to some extent, possibly by dealumination of the zeolite. It can be seen that SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio is about 34 wt.% for synthesized beta zeolite (Table 3). After loading ClSO<sub>3</sub>H on the beta zeolite (BEA-SO<sub>3</sub>H (28 wt.%)), the amount of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is about 37.5 wt.% (Table 4). These results show some dealumination of the zeolite after loading ClSO<sub>3</sub>H. However, the crystallinity of the BEA zeolite with 34% loaded acid still remained (Fig. 1d).

In addition, the X-ray fluorescence (XRF) results also show the elemental composition of catalyst before and after washing the catalyst with water (BEA-SO<sub>3</sub>H (28 wt.%)). It can be seen that the proportion of SO<sub>3</sub> in the catalyst was 22 wt.%, which was close to 28% ClSO<sub>3</sub>H of the value set in the catalyst design (Table 4). From these data we can conclude that SO<sub>3</sub>H was grafted on the surface of the catalyst by covalent bond. However, the amount of SO<sub>3</sub> on the surface of the catalyst did not change after washing the catalyst with water. In addition, the proportion of SO<sub>3</sub> in the catalyst was estimated after the first and third cycles of the reaction (Table 4). It can be seen that the amount of SO<sub>3</sub> was constant. So it can be concluded that there were no leaching of SO<sub>3</sub> in the solution after the third cycle of the reaction.

The infrared spectra of the BEA zeolite and the samples with various amounts of ClSO<sub>3</sub>H supported on BEA zeolite are presented in Fig. 2. In the sample BEA zeolite the broad peaks in the range of 3200–3600 cm<sup>-1</sup> may be attributed to the hydroxyl stretching of hydrogen bonded internal silanol groups and O–H stretching of water, while the peak at 1620–1640 cm<sup>-1</sup> corresponds to bending mode of O–H of water. Besides those, the peaks around 800

**Table 4**  
Summary of composition of BEA-SO<sub>3</sub>H (28 wt.%) determined by XRF.

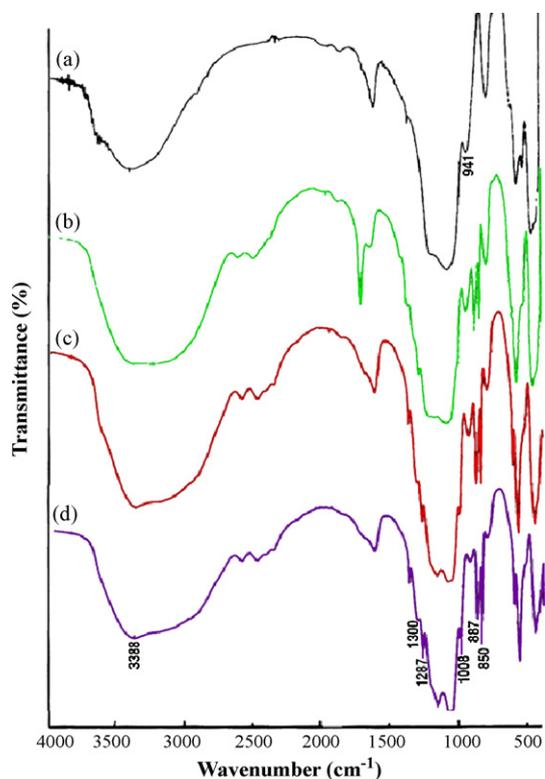
Catalyst	Composition of catalyst by XRF (wt.%)		
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>
BEA-SO <sub>3</sub> H (28 wt.%) <sup>a</sup>	74.11	1.91	22.52
BEA-SO <sub>3</sub> H (28 wt.%) <sup>b</sup>	76.32	2.03	21.87
BEA-SO <sub>3</sub> H (28 wt.%) <sup>c</sup>	76.23	2.03	21.79
BEA-SO <sub>3</sub> H (28 wt.%) <sup>d</sup>	76.19	2.03	21.68

<sup>a</sup> Before washing with water.

<sup>b</sup> After washing with water.

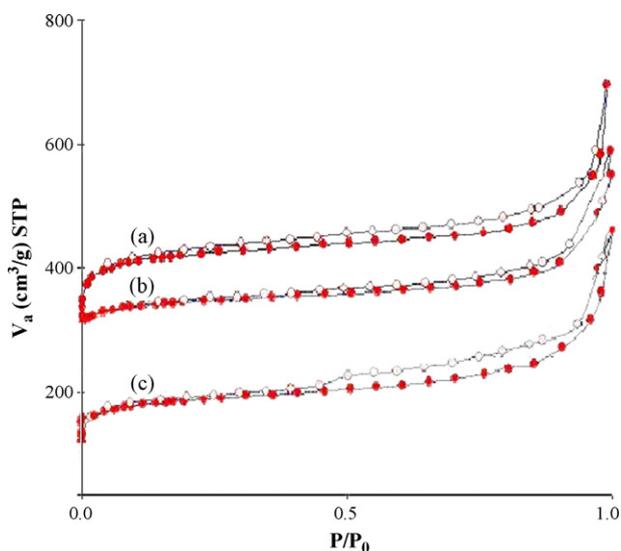
<sup>c</sup> After first cycle of the reaction.

<sup>d</sup> After third cycle of the reaction.



**Fig. 2.** FT-IR spectra of the calcinated samples of zeolite beta catalysts containing different amounts of loaded chlorosulphonic acid: (a) 0%, (b) 15%, (c) 28%, and (d) 34%.

and  $1090\text{ cm}^{-1}$  are attributed to the symmetric and asymmetric stretching vibrations of the Si–O–Si groups, respectively [56]. The band at  $470\text{ cm}^{-1}$  is assigned to the bending vibrations of Si–O–Si or Al–O–Si groups. The high crystallinity of zeolite samples can be ascertained from their framework IR spectra, which show in the  $500\text{--}650\text{ cm}^{-1}$  region the features characteristic of zeolite beta [55]. In the samples with various amounts of  $\text{ClSO}_3\text{H}$  loaded on BEA zeolite, some additional peaks; the asymmetric and symmetric stretching of S=O bond at  $1229\text{--}1290$  and  $1177\text{ cm}^{-1}$ , respectively, confirm the presence of  $\text{SO}_3\text{H}$  in BEA- $\text{SO}_3\text{H}$  [57,58]. The other peaks



**Fig. 3.** Nitrogen adsorption-desorption analysis of beta zeolite with various amounts of loaded chlorosulphonic acid: (a) 15%, (b) 28%, and (c) 34%.

in the range of  $750\text{--}1000\text{ cm}^{-1}$  may be attributed to the S–O bond. It should be mentioned that with increasing amount of  $\text{ClSO}_3\text{H}$  loaded on the BEA zeolite, the intensity of the peaks related to S=O and S–O increases.

The  $\text{N}_2$  adsorption-desorption isotherm of beta zeolite with various amounts of loaded chlorosulphonic acid is summarized in Fig. 3. The pore volume data of all these materials are summarized in Table 5. It is known that calcined BEA zeolite has a large pore volume ( $0.271\text{ cm}^3/\text{g}$ ), indicative of its potential application as a host in materials. After being modified with  $\text{ClSO}_3\text{H}$  it exhibits a lower pore volume in comparison with that of pure BEA zeolite, which might be due to the presence of  $\text{SO}_3\text{H}$  groups on the pore surface. The pore volume decreased with increasing amount of loaded chlorosulphonic acid. This means that the chlorosulphonic acid is grafted onto the pore wall surface of beta zeolite materials (Table 5).

Typical SEM images are displayed in Fig. 4. No amorphous and impurity phase existed in the all samples. The pure silica BEA zeolite showed truncated square bipyramidal morphology and the crystal size was  $200\text{ nm}$  (Fig. 4a). The decrease in crystals size and bipyramidal morphology was observed when the amount of loaded acid in the sample was increased. However, the crystal size and morphology of the BEA zeolite with 34% loaded acid still remained.

TG/DTA measurement of the samples showed three weight loss intervals mainly at  $160\text{--}190^\circ\text{C}$ ,  $200\text{--}300^\circ\text{C}$  and  $800\text{--}820^\circ\text{C}$  (Fig. 5). The first step at  $160\text{--}190^\circ\text{C}$  is in a good agreement with the weight loss of chlorosulphonic acid, which is on the external or nearby surface of beta zeolite. The peak is observed at  $200\text{--}300^\circ\text{C}$  due to the weight loss of  $\text{SO}_2$  and  $\text{Cl}_2$  molecules on the silica surface [59]. These observations can be seen in the DSC curve of beta zeolites with various amounts of loaded chlorosulphonic acid (Fig. 6). DSC isotherms of BEA- $\text{SO}_3\text{H}$  catalysts show two endothermic processes due to the decomposition of  $\text{ClSO}_3\text{H}$ . The other weight loss intervals correspond to the concurrent decomposition of beta zeolite structure by increasing temperatures. To prove this speculation, XRD data of the catalyst post-TGA were used. As we can see from Fig. 7, the XRD pattern of the catalyst was completely changed because of the decomposition of beta zeolite structure by increasing temperature. The XRD pattern displays the characteristic spectral profile of an amorphous aluminosilicate, with an amorphous halo present in the  $2\theta = 23$ . This typical halo results from the dispersion of the angles and bond distances between the basic structural units (silicates and aluminates), which destroys the structure periodicity and produces a non-crystalline material.

### 3.2. Catalytic activity for synthesis and deprotection of 1,1-diacetate (acylal)

A wide variety of aromatic and aliphatic aldehydes (Table 1) underwent smooth reaction to give the corresponding acylals in good yield. As shown in Table 1, the results reveal that the BEA- $\text{SO}_3\text{H}$  catalysis generally results in good yields with aromatic aldehydes including those carrying electron donating or withdrawing substituents even when moderately hindered aldehydes were used, with the advantages of mild reaction conditions. The tolerance of various functional groups under the present reaction

**Table 5**

The BET results of beta zeolite (BEA) and BEA- $\text{SO}_3\text{H}$  synthesized with different amounts of chlorosulphonic acid.

Sample	$V_p$ ( $\text{cm}^3\text{ g}^{-1}$ )
BEA	0.271
BEA- $\text{SO}_3\text{H}$ (15%)	0.115
BEA- $\text{SO}_3\text{H}$ (28%)	0.104
BEA- $\text{SO}_3\text{H}$ (34%)	0.069

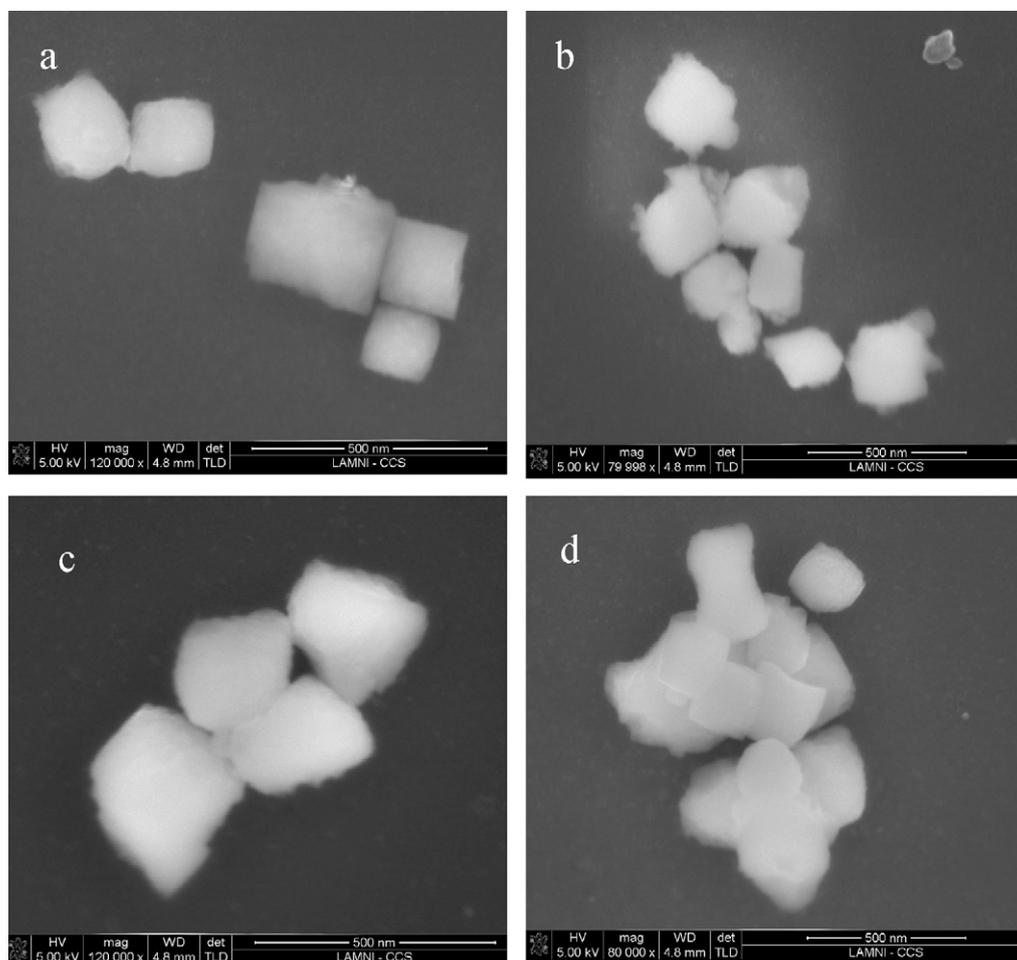


Fig. 4. SEM images of the calcinated samples of beta zeolite catalysts containing different amounts of loaded chlorosulphonic acid: (a) 0%, (b) 15%, (c) 28%, and (d) 34%.

conditions is worthy of mention, where the acid sensitive or oxidizable groups such as methoxy, nitro, chloro, and double bonds do survive under such condition. Aldehydes with withdrawing substituents gave high although unmaximized yields, for example it is worth that *o*-nitrobenzaldehyde and *m*-nitrobenzaldehyde acetalised produced good yields (entries 7 and 14, 95% and 85%). Moreover, it should be noted that aliphatic aldehydes afforded the corresponding acylals within a short reaction time and good yield (entries 1 and 2). Compounds such as acetophenone (entry 3) and

2-butanone (entry 4) were not converted into the corresponding 1,1-diacetates at optimum conditions even for 30 min. Furthermore, the results reveal that BEA-SO<sub>3</sub>H shows good activity for the deprotection of 1,1-diacetates (Table 2).

### 3.2.1. Effect of the amount of loaded chlorosulphonic acid

In order to investigate the effect of the amount of loaded acid, the activities of catalysts including various amounts of loaded chlorosulphonic acid on zeolite beta for synthesis of 1,1-diacetate (acylal) were compared. The results are listed in Table 6. The variation in

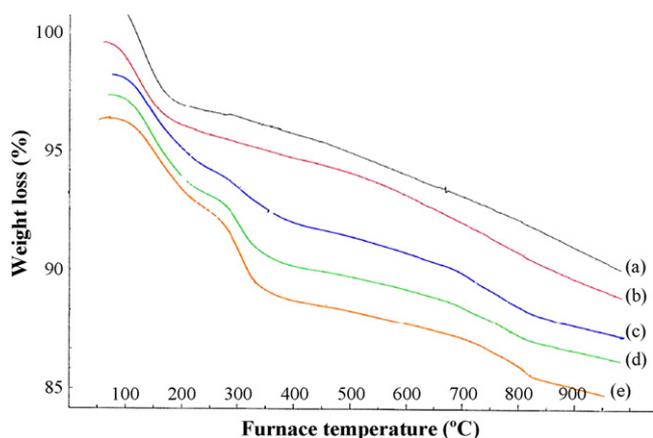


Fig. 5. Thermogravimetric analysis (TG) of beta zeolite catalysts containing different amounts of loaded chlorosulphonic acid: (a) 0%, (b) 15%, (c) 28%, and (d) 34%.

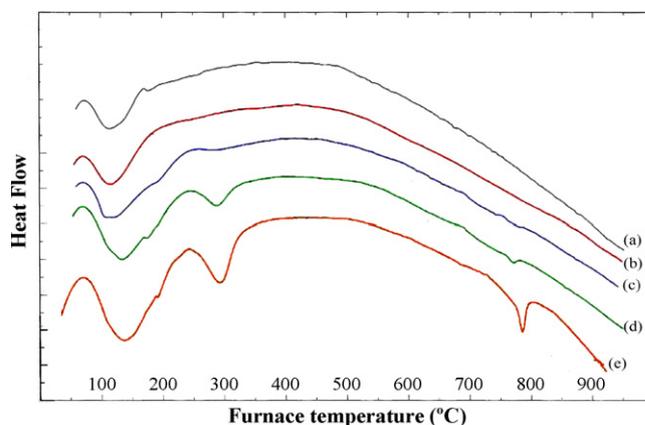


Fig. 6. DSC curves of beta zeolite catalysts containing different amounts of loaded chlorosulphonic acid: (a) 0%, (b) 15%, (c) 28%, and (d) 34%.

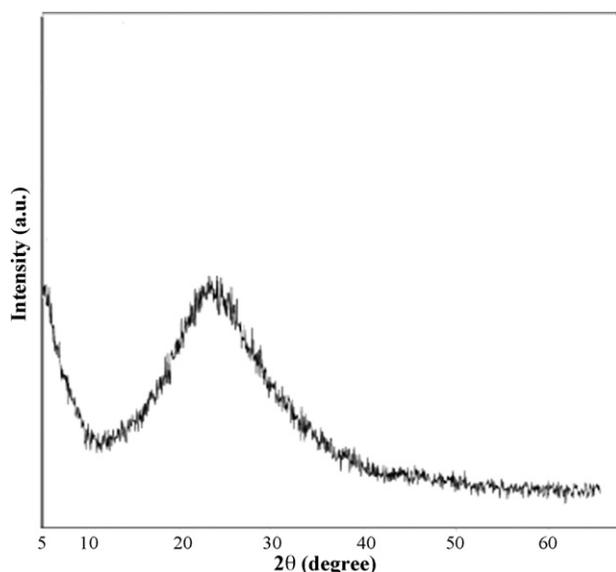


Fig. 7. XRD powder pattern of BEA-SO<sub>3</sub>H (28 wt.%) catalyst post-TGA.

Table 6

Effect of amount of loaded chlorosulphonic acid on synthesis of 1,1-diacetate.<sup>a</sup>

Catalyst	Yield of acylal (%) <sup>b</sup>	Time (min)
BEA	15	30
BEA-SO <sub>3</sub> H (15%)	50	1
BEA-SO <sub>3</sub> H (28%)	96	1
BEA-SO <sub>3</sub> H (34%)	70	1

<sup>a</sup> Reaction conditions: acetic anhydride (2 mmol), catalyst (0.015 g), benzaldehyde (2 mmol), solvent-free, and room temperature.

<sup>b</sup> Isolated yield.

loaded chlorosulphonic acid (15–34 wt.% acid) has different effects on the yield of the product. In the presence of the optimized catalyst (BEA-SO<sub>3</sub>H (28 wt.%)), over 95% yield is observed. In order to investigate effect of the support (BEA-SO<sub>3</sub>H) for synthesis of 1,1-diacetate, we used ClSO<sub>3</sub>H (with the same ratio of the optimized catalyst) without any support as catalyst by keeping other parameters constant. After 40 min, about 46% yield was observed. Therefore, BEA zeolite as a support is very useful for the synthesis of 1,1-diacetate.

### 3.2.2. Effect of solvent

For optimization of the reaction conditions, we have tried the conversion of benzaldehyde (2 mmol) to the corresponding acylal with acetic anhydride (2 mmol) in the presence of various solvents and also under solvent-free conditions at room temperature. In comparison with conventional methods, the yield of the product under solvent-free conditions is higher and reaction time is less (Table 7). Therefore, we have employed the solvent-free conditions for the conversion of various aldehydes to the corresponding acylals (Table 1).

Table 7

Effect of solvent on synthesis of 1,1-diacetate.<sup>a</sup>

Solvent	Time (min)	Yield of acylal (%) <sup>b</sup>
Ethylacetate	4	50
Acetonitrile	3	70
Dichloromethane	3	80
n-Hexane	3	70
Solvent-free	1	96

<sup>a</sup> Reaction conditions: acetic anhydride (2 mmol), catalyst (0.015 g), benzaldehyde (2 mmol), and room temperature.

<sup>b</sup> Isolated yield.

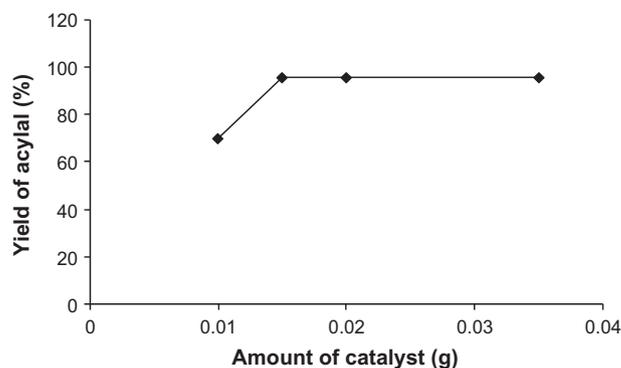


Fig. 8. Effect of catalyst amount. Reaction conditions: acetic anhydride (2 mmol), benzaldehyde (2 mmol), catalyst (BEA-SO<sub>3</sub>H (28%)) solvent-free, room temperature, 1 min.

Table 8

Recyclability of the catalyst for synthesis of 1,1-diacetate.<sup>a</sup>

Cycle	Yield of acylal (%) <sup>b</sup>	Time (min)
1	96	1
2	96	1
3	94	1
4	93	1

<sup>a</sup> Reaction conditions: acetic anhydride (2 mmol), catalyst (0.015 g), benzaldehyde (2 mmol), solvent-free, and room temperature.

<sup>b</sup> Isolated yield.

### 3.2.3. Effect of catalyst amount

Fig. 8 displays the effect of the amount of BEA-SO<sub>3</sub>H (28 wt.%) on the yield of 1,1-diacetate (acylal). It can be seen that the yield of acylal increased from 70% to 96% when the amount of BEA-SO<sub>3</sub>H (28 wt.%) increased from 0.01 g to 0.015 g. With excess amount of catalyst, the yield obviously increased, because of the availability of more acid sites. With further increase in catalyst amount, the percentage of yield remains constant. 0.015 g catalyst is selected for further experimental studies due to its optimum performance.

### 3.3. Reusability study

Reusability of the catalyst is tested by carrying out repeated runs of the reaction on the same batch of the catalyst. After each cycle the catalyst was filtered off, washed with ethyl acetate and dried at 120 °C and then reused for successive cycles. It is evident that the catalyst worked well up to the third cycle. The results are summarized in Table 8.

XRD powder pattern of the reused catalyst (after third cycle of the reaction) is presented in Fig. 9. These data showed that the

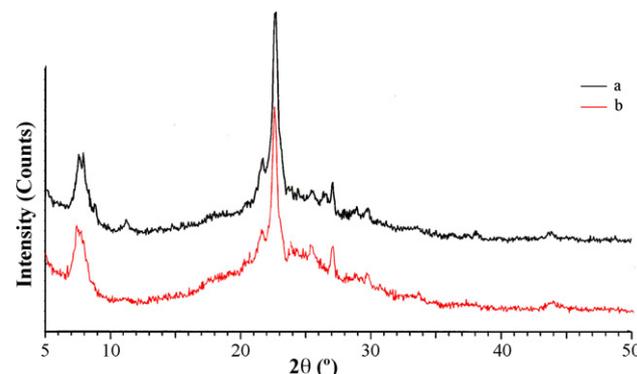
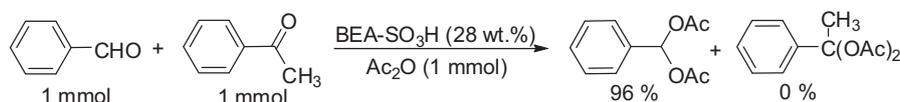


Fig. 9. XRD powder pattern of (a) fresh BEA-SO<sub>3</sub>H (28 wt.%) catalyst and (b) BEA-SO<sub>3</sub>H (28 wt.%) catalyst after the third cycle of the reaction.



**Scheme 1.** Chemoselectivity of the catalyst (BEA-SO<sub>3</sub>H (28%)).

crystallinity of the catalyst did not change after the third cycle of the reaction. In addition, the XRF results also show the elemental composition of the catalyst after the first and third cycle of the reaction (Table 4). However, the amount of SO<sub>3</sub> on the surface of the catalyst was not changed after the reaction. Also, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the catalyst did not change after the reaction and we can conclude that the catalyst is stable in these conditions.

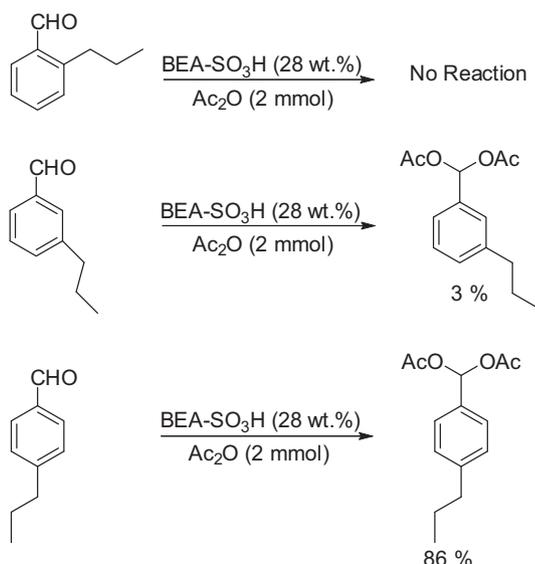
### 3.4. Chemoselectivity and shape-selectivity of the catalyst

In order to examine the chemoselectivity of the present method, equimolar mixtures of ketone (acetophenone) and aldehyde (benzaldehyde) were allowed to react with acetic anhydride in the presence of BEA-SO<sub>3</sub>H (28 wt.%) as a catalyst. As shown in Scheme 1, the catalyst was able to discriminate between ketone and aldehyde and showed a high chemoselectivity. Therefore, the present procedure is a selective preparation of the 1,1-diacetates from aldehydes in the presence of ketones.

In order to examine the shape-selectivity of the catalyst, 2-propylbenzaldehyde, 3-propylbenzaldehyde and 4-propylbenzaldehyde were allowed to react with acetic anhydride in the presence of the BEA-SO<sub>3</sub>H (28 wt.%) as a catalyst. As shown in Scheme 2, the catalyst was able to discriminate between the aldehydes with different steric effects. As we can see from Scheme 2, 1,1-diacetate was produced only from 4-propylbenzaldehyde. From these data we can conclude that the reaction just occurs in the micropores of the catalyst and it does not occur on the outer surface of the catalyst or in the solution with leached SO<sub>3</sub>H species.

### 3.5. Comparison with other catalysts in synthesis of acylal

A comparison of the catalytic activity values of various catalysts for the synthesis of acylals is given in Table 9. As can be seen, the BEA-SO<sub>3</sub>H (28%) catalyst shows good yield for the protection of 4-



**Scheme 2.** Shape-selectivity of the catalyst (BEA-SO<sub>3</sub>H (28%)).

**Table 9**

Comparison of the efficiency of BEA-SO<sub>3</sub>H with other catalysts in the protection of 4-nitrobenzaldehyde using acetic anhydride as acylation reagent.

Catalyst	Molar ratio (aldehyde:acetic anhydride)	Temperature	Time	Yield (%)	Reference
NBS	1	Room temperature	8 h	98	[60]
InCl <sub>3</sub>	2	Room temperature	4 h	88	[61]
LiBF <sub>4</sub>	2	60 °C	23 h	90	[62]
ZrCl <sub>4</sub>	3	Room temperature	30 min	92	[8]
LiOTf	8–5	Room temperature	15 h	94	[63]
Cu(OTf) <sub>2</sub>	3	Room temperature	4 h	94	[64]
Sc(OTf) <sub>2</sub>	1.5	Room temperature	10 min	99	[65]
Y zeolite	3	70 °C	7 h	93	[66]
Beta zeolite	1	60 °C	1.5 h	93	[67]
HZSM-5 (15) <sup>a</sup>	3	Room temperature	4 h	24	[68]
BEA-SO <sub>3</sub> H (28 wt.%)	1	Room temperature	4 min	95	This work

<sup>a</sup> Si/Al molar ratio.

nitrobenzaldehyde using acetic anhydride as an acylating reagent at very short time.

## 4. Conclusion

In conclusion, herein we report a mild and efficient catalyst for the preparation of 1,1-diacetates from aldehydes in the presence of acetic anhydride under solvent-free conditions at room temperature. This method is selective for the preparation of 1,1-diacetates from aldehydes in the presence of ketones. 1,1-Diacetates can be conveniently deprotected by using BEA-SO<sub>3</sub>H in methanol. Good yields were obtained within short reaction times; reusability of the catalyst, non-toxic nature and mild conditions are some of the notable features of this protocol.

## Acknowledgement

The support from Islamic Azad University, Shahreza Branch (IAUSH) Research Council and Center of Excellence in Chemistry is gratefully acknowledged.

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