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Original Research Article

H-mordenite zeolite as an efficient, rapid and recyclable catalyst for chemoselective synthesis of 1,1-diacetates under solvent-free conditions

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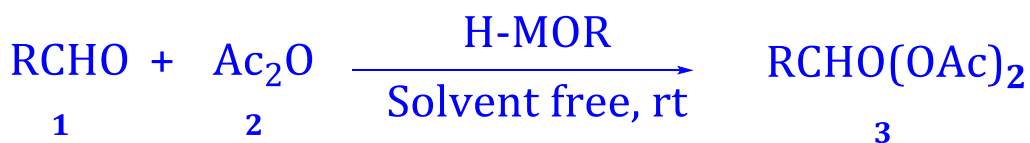
Aldehydes

Solvent-free conditions

ABSTRACT

In this investigation H-mordenite zeolite has been shown to be an efficient, rapid, green, stable, chemoselective and recyclable catalyst for the synthesis of 1,1-diacetates (acylals) of various aromatic aldehydes under solvent-free conditions at room temperature. The main advantages of this protocol include low catalyst loading, shorter reaction time, excellent yields, eco-friendly, mild-condition, easy work-up procedures and reusable catalyst. This method must be useful in future for the synthesis of similar derivatives. The synthesized zeolite was characterized by various techniques via X-ray diffraction (XRD), scanning electronic microscopy (SEM), fourier transform-infrared (FTIR spectroscopy) and brunauer–emmett–teller (BET) surface area analysis. The synthesized reaction products were characterized by FTIR and ¹H NMR technique. Further investigation of the application of H-MOR zeolite for other reactions is ongoing in our laboratory.

Graphical Abstract



R = C₆H₅, 4-ClC₆H₄, 4-BrC₆H₄, 3-NO₂C₆H₄, 4-NO₂C₆H₄, 2,4-ClC₆H₄, 4-(HO)C₆H₄

Introduction

Selective protection and deprotection of carbonyl groups plays a very excellent role in modern organic chemistry. In organic synthesis some useful available reagents are used for protection of aldehydes. 1,1-diacetate (acylals) are most useful carbonyl protecting group because of their main stability under both neutral and basic medium and under acidic conditions [1]. It is an important precursor for the synthesis of 1-acetoxydienes [2] and vinyl acetates in Diels-Alder reactions [3]. Due to their stability acylals have been used as crosslinking reagents for cellulose in cotton [4].

Various methods have been reported in the literature for the synthesis of 1, 1-diacetate from strong acids including sulfamic acids [5], sulphuric acid [6], methane sulphuric acid [7] lewis acids such as lithium bromide [8], FeCl_3 [9], PCl_3 [10], NBS [11], expensive graphite [12], zeolite HSZ-360 [13], montmorillonite clay [14], Sulphate Zirconia [15], $\text{Cu}(\text{OTf})_2$ [16], $\text{Sc}(\text{OTf})_3$ [17], and ZrCl_4 [18], P_2O_5 [19], sodium lithium perchlorate [20], zeolite Y [21], [Hmim] $[\text{H}_2\text{SO}_4]$ [22], [bmim] $[\text{BF}_4]$ [23], $\text{SO}_3\text{H-MIL-101}$ [24], aluminum chloride [25], and certain transition metal compounds and complexes [26] which are more effective for this conversion. However, above these methods have some main limitations such as formation of low yield, long reaction time, high temperature, strong acidic condition, expensive reagents, corrosive and highly toxicity.

Here we propose a simple, rapid, efficient and excellent method for the synthesis of 1,1-diacetates using H-mordenite zeolite as a heterogeneous acid catalyst. It is one of the most extensively used surface material supports for different chemical transformation in modern organic chemistry. Preparation of H-mordenite zeolite is very simple, clean, and cheap and also it can be easily removed from the reaction mixture.

Experimental

Materials and methods

^1H NMR spectra were obtained on JNM-ESC 400 MHz spectrophotometer with CDCl_3 as solvent using tetramethylsilane (TMS) as an internal standard; the chemical shift values are in δ . From powder X-ray diffraction (XRD) studies, the catalyst was analyzed by using Shimadzu XRD 6000 model equipment. The operational detailed technique was set as follows: Copper $\text{K}\alpha$ radiation at 40 kV/30 mA, with a goniometer speed of $2^\circ/\text{min}$ and a step of 0.02° in the 2θ range scanning from 10° to 70° for H-MOR Zeolite. SEM images H-MOR zeolite were obtained by using SEM instrument. SEM image of this material was taken at 10,000 x magnifications to show their surface morphology and to obtain the clearest view of crystals. For FT-IR analysis, H-MOR zeolite and reaction products were subjected to physical treatment in accordance with the KBr method, which contains 0.007 g of

the sample and 0.1 g KBr were mixed and grinding and pressing the solid mixture to 5 tons for 30 s to form a pellet that allows the passage of light. The H-MOR zeolite was performed using an infrared spectrophotometer Shimadzu FT-IR in the wavelength ranging from 500 to 4000 cm^{-1} and the reaction products was also performed using an infrared spectrophotometer Shimadzu FT-IR in the wavelength ranging from 500 to 3500 cm^{-1} . BET surface area measurement was performed on ASAP 2020 by N_2 adsorption at liquid nitrogen temperature using multipoint N_2 BET method.

Preparation of Modernite Zeolite

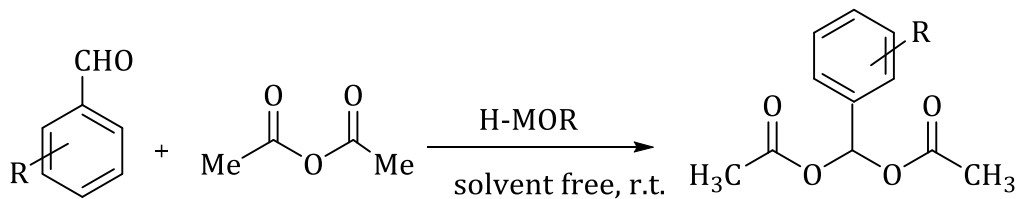
19 g of sodium hydroxide was dissolved in 40 mL distilled water and the mixture was stirred until dissolved. After then 14.3 g sodium aluminate was to it. The mixture was continuously stirred until dissolved 654 mL of distilled water was added to this solution and then 98.2 g of silica powder was added to it. The mixture was stirred for 30 minutes to form a thick gel like solution. The thick gel was kept in a PTFE- lined stainless steel Autoclave and heated in an oven at 180 $^{\circ}\text{C}$ for 40 h. After synthesis, the product was filtered, washed with distilled water and dried in an oven at 105 $^{\circ}\text{C}$ for 24 h.

Conversion of modernite zeolite into H-form

Na-form of mordenite zeolite was converted into H-form by the following procedure: 9.0 g of mordenite zeolite, 7.23 g of NH_4Cl and 13.80 mL of distilled water were mixed with 0.01 mol/L hydrochloric acid (HCl) solution so as to maintain the pH = 4 of the solution. The mixture was stirred at 60 $^{\circ}\text{C}$ for 6 h. After that the required material was filtered and washed 2-3 times with distilled water. After filtration and washing with distilled water, chlorides were removed then NH_4 -zeolite was placed in an oven at 60 $^{\circ}\text{C}$ for 24 h. Finally the ammonium form of mordenite zeolite was converted into the H-form by calcination over 60 min at 500 $^{\circ}\text{C}$.

General procedure for the synthesis of 1, 1-diacetates

With a mixture of 4-Chloro benzaldehyde (1 mmol), acetic anhydride (1 mmol) and catalyst H-MOR zeolite (0.05 g) was added at room temperature under solvent free condition. The mixture was magnetically stirred for certain specific time. Upon completion (monitored by TLC), dichloro methane was added to remove the catalyst by simple filtration (Scheme 1). After removal of the solvent, the product was further recrystallized with suitable solvent such as (ether or chloroform). The product structure was confirmed by ^1H NMR, FTIR and compared with samples already obtained by reported methods.



R = C₆H₅, 4-ClC₆H₄, 4-BrC₆H₄, 3-NO₂C₆H₄,
4-NO₂C₆H₄, 2,4-ClC₆H₄, 4-OHCH₄

Scheme 1.

Selected spectral data of the products

Synthesis of 1,1-diacetoxy-1-(4-chlorophenyl) (Entry 2)

IR (KBr) (ν_{max} / cm⁻¹): 763, 1061, 1092, 1318, 1683, 1733, 1933, 2561, 2852, and 3094 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 1.87 (s, 6H, 2Ac), 7.52 (d, 2H, Ar-H), 7.89 (d, 2H, Ar-H).

Synthesis of 1,1-diacetoxy-1-(3-nitrophenyl) (Entry 4)

IR (KBr) (ν_{max} / cm⁻¹): 688, 812, 1087, 1350, 1533, 1700, 1717, 1985, 2133, 2435, and 2550 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 7.73-7.77 (t, 1H), 8.20-8.22 (d, 1H), 8.43-8.46 (m, Ar-H), 8.66-8.77 (t, 1H), 10.0 (s, 1H).

Synthesis of 1,1-diacetoxy-1-(2,3-dichlorophenyl) (Entry 6)

IR (KBr) (ν_{max} / cm⁻¹): 574, 823, 1199, 1287, 1374, 1683, 1790, 1976, 2332, 2576, and 2755 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 2.26 (s, 6H, 2Ac), 7.58 (d, 2H, Ar-H), 7.79-7.84 (t, 1H), 10.24 (s, 1H, CH).

Synthesis of 1,1-diacetoxy-1-(4-hydroxyphenyl) (Entry 7)

IR (KBr) (ν_{max} / cm⁻¹): 604, 832, 1219, 1457, 1669, 1906, 2074, 2881, and 3212 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 2.24 (s, 6H, 2Ac), 6.58-6.60 (t, 1H), 7.37-7.39 (t, 1H), 9.71 (s, 1H, CH).

Results and discussion

X-ray diffraction analysis of H-MOR zeolite is shown in Figure 1. It shows that H-MOR zeolite is highly crystalline in nature without any amorphous phase. From X-ray diffraction analysis the sharp peak 2θ value is obtained at 28.14 which are clearly observed.

The scanning morphology of H-MOR zeolite is shown in Figure 2. From SEM image of H-MOR zeolite it is clearly observed that the particles appear to have irregular shape with highly excellent crystal edges .

The FT-IR analysis of H-MOR zeolite is shown in Figure 3. It shows that peaks between 700-830 cm^{-1} and 1000-1120 cm^{-1} are assigned to symmetric and asymmetric T-O-T stretching vibrations, broad band in the region of 3460 cm^{-1} due to asymmetric stretching of OH group and the bands at 1600 and 1350 cm^{-1} due to bending vibration of (H-OH) and(O-H-O) band respectively.

Adsorption-desorption of nitrogen gave an isotherm plot type 4V/A of (Brunauer Emmett and Teller theory). Pore volume, pore size and surface area of H-MOR zeolite are shown in Table 1.

Figure 1. X-ray diffraction pattern of H-MOR Zeolite

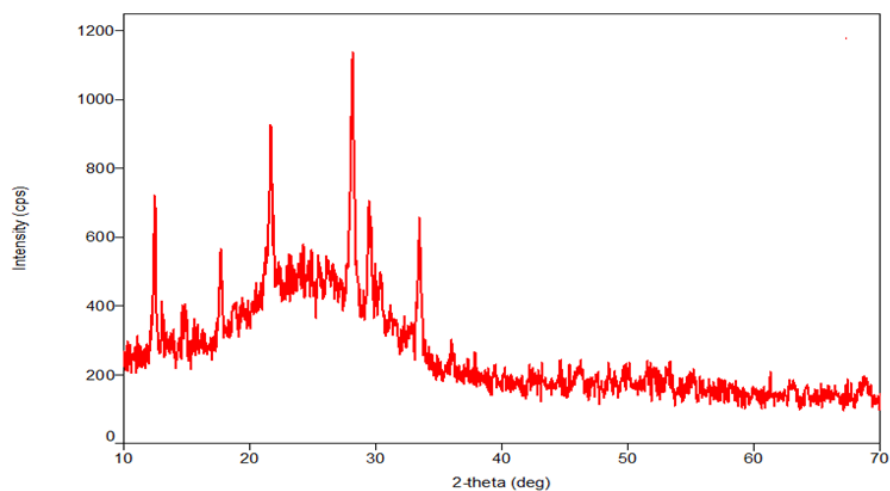
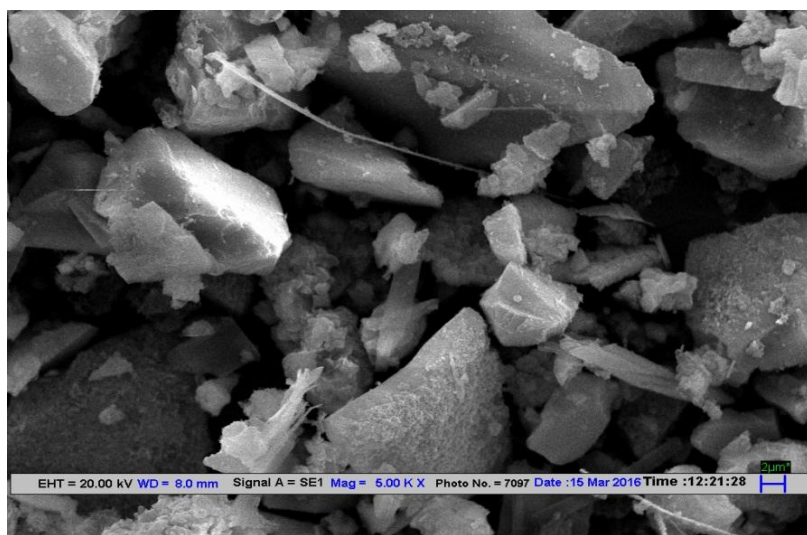


Figure 2. SEM image of H-MOR Zeolite



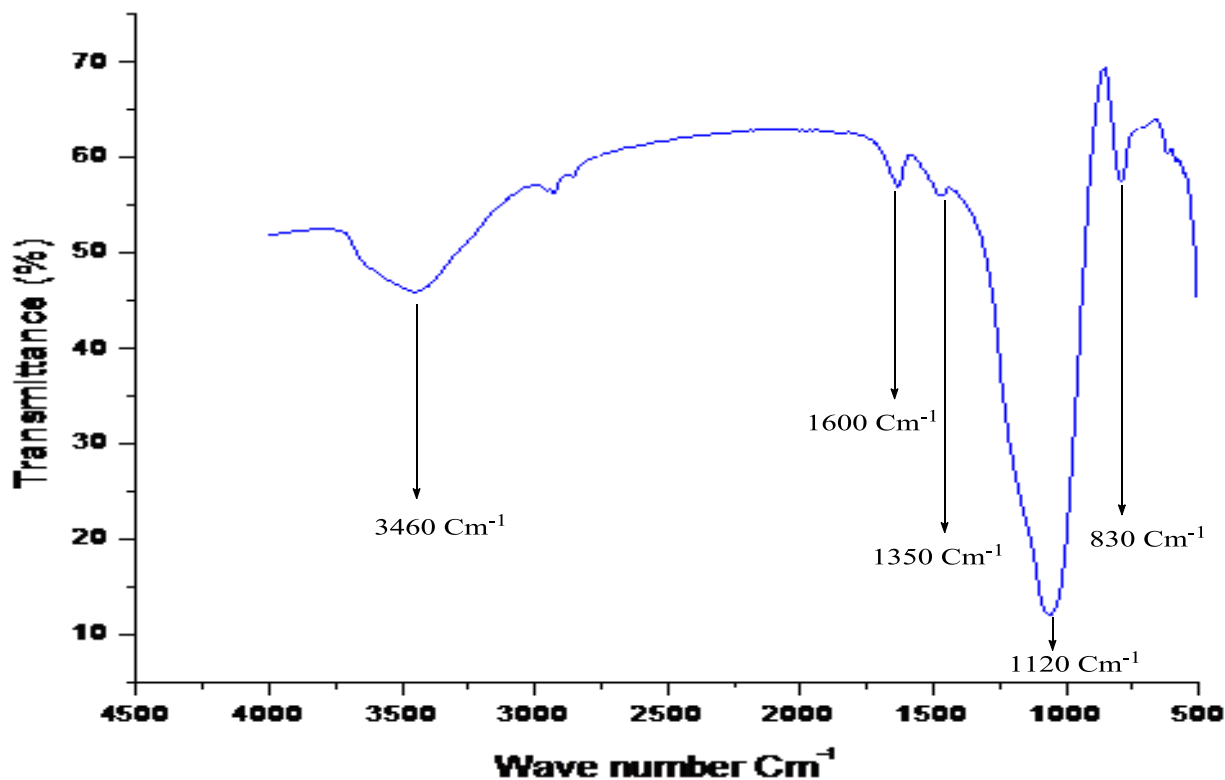


Figure 3. FT-IR Spectrum of H-MOR zeolite

Table1. H-MOR zeolite surface features

BET analysis for H-MOR zeolite	
Pore volume	0.206754 cm ³ /g
Pore size	72.470 m ² /g
Surface area	60.4114 m ² /g

We have developed an efficient, rapid, and an excellent method for synthesis of 1,1-diacetates under solvent-free condition at room temperature in the presence of catalyst H-MOR zeolite. So the model reaction was carried out between 4-chlorobenzaldehyde and acetic anhydride (as shown in Scheme 1). The model reaction was carried out in various solvents such as EtOH, CH₂Cl₂, CHCl₃ and also solvent free condition at room temperature in presence of catalyst H-MOR zeolite. The results are shown in Table 2. As it is shown in Table 2, the reaction yield under solvent free condition was the highest and the reaction time was the shortest. Aprotic solvents such as CH₂Cl₂ and CHCl₃ gives the desired product in low yield and longer reaction time (Table 2, entry 3-4). In protic solvents such as ethanol and water (Table 2, entry 1-2), this reaction proceeds longer reaction time and very

low yield which may occur due to instability of acetic anhydride and corresponding product in protic solvents. The next study carried out the catalytic amount of the model reaction on the activity of the catalyst H-MOR zeolite was observed under solvent free condition at room temperature. The results are shown in Table 3.

Table 2. Solvent effect for synthesis of 1,1 diacetates^a

Entry	Solvent	Time	Yield (%) ^b
1	EtOH	45 min	35
2	H ₂ O	55 min	20
3	CH ₂ Cl ₂	18 min	80
4	CHCl ₃	18 min	76
5	Solvent free	5 min	97

^a The reaction was carried out with 1 mmol Ac₂O at room temperature

^b Isolated yield

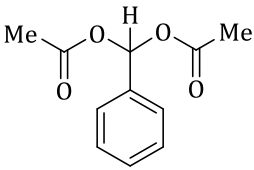
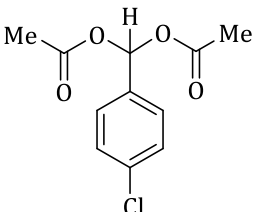
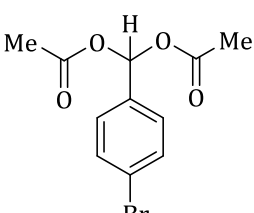
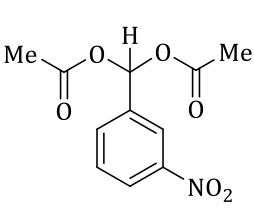
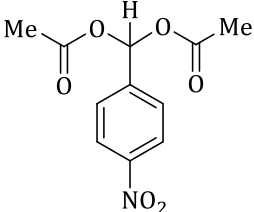
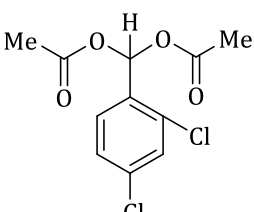
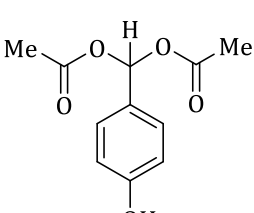
As it is shown in Table 3, it was shown that best result was found with (0.05 g or 5 mol %) of the catalyst. Further increase the amount of catalyst in the above mentioned did not have any change in the reaction product. The reason is that the additional acid sites cause no effect because the reactants may reduce sufficient sites to bind with.

To study the scope of the reaction we utilized various derivatives of aromatic aldehydes to evaluate this procedure. The reaction time and % yield are shown in Table 4. The result shows that the substitution group of aromatic aldehyde, whether they were electron-donating or electron-withdrawing groups, provides less effect on the reaction. The reaction could be carried out at room temperature smoothly with much less reaction time than that of the literature methods.

Table 3. Effect of amount of catalyst for the synthesis of 1,1 diacetates

Enter	Catalyst (g)	Solvent	Time(min)	Temperature (°C)	Yield (%)
1	0.01	Solvent free	15	R.T	57
2	0.02	Solvent free	12	R.T	64
3	0.03	Solvent free	10	R.T	78
4	0.04	Solvent free	8	R.T	89
5	0.05	Solvent free	5	R.T	97
6	0.06	Solvent free	5	R.T	97

Table 4. Synthesis of 1, 1-diacetates catalyzed by H-MOR zeolite

Entry	Product	Time (min)	Yield (%)	m.p./°C (found)
1		8	95	43-45
2		5	97	53-56
3		7	94	89-90
4		6	96	62-63
5		6	95	123
6		6	94	99-100
7		8	93	120-123

The next study carried out reusability of H-MOR zeolite for the synthesis of 1,1-diacetates. After each run, the catalyst was recovered, washed with solvents viz chloroform and ethyl acetate, dried in an oven at 100 °C for 2 h before to use and tested for its activity in the consecutive runs with no fresh catalyst added. The catalyst was tested for four runs as shown in Table 5. The small reduction in the catalytic activity is because mainly due to the loss of the catalyst structure during recovery process.

Table 5. Reusability of H-MOR zeolite for synthesis of 1,1 diacetates

Entry	Yield (%)
1 st run	97
2 nd run	94
3 rd run	91
4 th run	89

Conclusion

In conclusion, we developed a rapid, reliable, excellent and environmentally benign method for the synthesis of 1,1-diacetate from acetic anhydride and various aromatic aldehydes under solvent-free condition at room temperature in presence of H-MOR zeolite as a heterogeneous acid catalyst. After completion of the reaction, the catalyst was separated by simple filtration and washed with suitable solvents via chloroform and ethyl acetate and recycled 2-4 times without loss of any catalytic activity. The main advantages of this method are short reaction time, high excellent yield, no solvent and low catalyst loading. Further investigation on the application of H-MOR zeolite for other reactions is ongoing in our laboratory.

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