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## **Synthesis and characterization of analogue of mordenite and its role as a catalyst for Friedel-Crafts acylation of anisole**

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### **ABSTRACT**

*4-methoxy propiophenone used as an intermediate for the production of fine chemicals and pharmaceuticals was synthesized by Friedel-Crafts acylation of anisole with propionic anhydride using mordenite zeolite as a solid acid catalyst. Mordenite was synthesized in the laboratory by hydrothermal method, after dealumination and calcination, the sample was characterized by different techniques such as powder X-ray diffraction analysis (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS) analysis. Effect of various reaction parameters such as reaction time, molar ratio of reactants, weight of catalyst and reaction temperature were studied to optimize the reaction conditions. The optimum condition for the synthesis of 4-methoxypropiophenone was found at anisole to propionic anhydride molar ratio 8:1, using 0.5 g of the catalyst at 373K. The product was analyzed by Gas Chromatography and Gas Chromatography Mass Spectrometry analysis. The conversion of propionic anhydride to 4-methoxypropiophenone was found to be 44.7% in case of dealuminated form of HMOR zeolite and 39.4% for HMOR zeolite respectively.*

**Key words:** 4-methoxypropiophenone; Friedel-Crafts acylation; dealumination; Mordenite zeolite.

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### **INTRODUCTION**

Friedel-Crafts acetylation of aromatic compounds is one of the industrially important reactions for the production of several value-added aromatic ketones. Several solid oxide heterogeneous

catalysts such as zeolites and zeotype materials, and homogeneous catalysts have been employed for the acetylation of aromatic reactions, which are highly efficient, sustainable, recyclable, and ecofriendly [1-10]. Organic chemists make use of this reaction quite often as a convenient means to prepare aromatic ketones. These reactions are traditionally catalyzed by either Lewis acids such as  $\text{AlCl}_3$ ,  $\text{FeCl}_3$  and  $\text{BF}_3$  or Brønsted acids such as  $\text{HF}$  or  $\text{H}_3\text{PO}_4$  [11]. The use of above-mentioned liquid catalysts is undesirable from the environmental point of view as these chemicals are corrosive and generally encounter the problems of handling and transportation. Moreover, high product selectivity and reusability of the catalysts cannot be expected. Hence, there are numerous global efforts to replace these environmentally harmful chemicals with more eco-friendly and less expensive catalysts [12]. The use of solid acids such as zeolite is convenient and also effective for acid-catalyzed reactions [13]. It has the following inherent advantages over catalysis initiated by homogeneous catalysts: (a) it is non-corrosive, (b) the catalyst can be easily removed from the reaction mixture by decantation or filtration, and (c) the product selectivity can be achieved to a certain extent due to the shape-selective nature of the zeolite structure. The use of zeolites as catalysts for organic reactions began in early 1960s. Due to these properties zeolites have been found to be safe alternative for such conventional liquid acid catalysts used in synthetic organic chemistry in petroleum refining, fine chemical synthesis and pharmaceutical industries, etc. [14–16].

Mordenite is one of the high silica zeolite and has two pore channels, i.e.  $6.5 \times 7.0 \text{ \AA}$ , which is parallel to c axis are connected by tortuous pores of  $2.6 \times 5.7 \text{ \AA}$  which is parallel to b axis that form side pockets. Since the latter are too small for most molecules to enter, mordenite is generally regarded as a mono-dimensional zeolite, which is widely used in catalysis, separation and purification because of its uniform, small pore size, high internal surface area, flexible framework, and controlled chemistry. Mordenite is a zeolite with two-dimensional pores, as the structure determined by Meier in 1961 showed [17].

For industrial purposes, homogenous catalysts have shown some disadvantages, which among others are high consumption of catalyst and problems in the separation step due to similar phases of the reaction products to that of the catalyst. In addition, the use of acidic reagents in aqueous form also create environmental problems such as corrosion.

Heterogeneous catalyst has been given much attention to overcome the problems. Solid catalysts such as zeolites [18-29], phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) supported on  $\text{SiO}_2$  in the form of cerium salt [29], mesoporous molecular sieves such as MCM-41 [30] and clay such as montmorillonite [31] are among the solid acid catalysts that have been used in Friedel-Crafts acylation. Recently, solid super acid was reported to be another type of heterogeneous catalyst used in the acylation of toluene with benzoyl chloride and benzoic anhydride [32].

The electrophilic acylation of anisole (methoxybenzene) with phenyl acetate, phenyl propionic, phenylacetyl chloride, phenylpropionyl chloride [33] acetyl chloride [34] and acetic anhydride [35,36,37] have also been reported. Freese *et al.* [35] made a comparison of the activity and selectivity of zeolite H-Beta, H-Y,  $\text{NH}_4$ -Y and H-ZSM-5 catalysts in the acylation of anisole by acetic anhydride. It was observed that H-ZSM-5 showed lower activity than H-Y and H-Beta catalysts, due to smaller intersection channel in ZSM-5.

Methoxy propiophenones are found to have wide applications in the area of fine chemical synthesis. 4-Methoxypropiophenone is an intermediate for the production of anethole, which is widely used in preparation of perfumes and flavors. It is also used for the synthesis of secoverine, a spasmolytic agent with specific antimuscarinic properties [38]. The current study deals with the acylation of anisole using propionic anhydride over mordenite zeolite crystals under atmospheric pressure. The reaction parameters such as, reaction time, reaction temperature, anisole : propionic anhydride molar ratio and catalyst quantity were optimized.

## EXPERIMENTAL SECTION

### 2.1. Chemicals

Sodium Silicate (Aldrich), Aluminium Nitrate, Sodium Hydroxide (Aldrich), Ammonium Nitrate (Merck), Anisole and Propionic Anhydride were commercial samples from Merck .

### 2.2. Synthesis of the catalyst (Mordenite)

The composition of the gel was  $6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:30\text{SiO}_2:780\text{H}_2\text{O}$ . Aluminium Nitrate as the aluminum source was mixed with an aqueous solution of NaOH. Then sodium silicate was added to the mixture and the mixture was homogenized by stirring. Finally, the gel was transferred to a Teflon-lined autoclave and crystallization was carried out at 453 K under autogenous pressure without agitation for 24 h. The product was recovered by filtration, washed thoroughly with deionized water and dried at 393 K overnight, then calcined in air at 823 K for 2 h. The mordenite was then ion-exchanged three times with 1 M  $\text{NH}_4\text{NO}_3$ . Mordenite with Si/Al ratio of 15 was hydrothermally synthesized according to Ref. [39].

### 2.2. Catalyst characterization

The catalysts were characterized by XRD, SEM, FTIR and EDS analysis. The elements present in the zeolite were determined by energy dispersive X-ray (EDS) analysis using JEOL 5400 scanning microscope equipped with the microprobe analyzer LINK ISIS (Oxford Instrument). Powder X-ray diffraction pattern for all the materials were recorded at room temperature on PW 1710 diffractometer. Samples were scanned using  $\text{Cu-K}\alpha$  radiation of wavelength 1.54056 Å and the diffractograms were recorded in the range  $2\theta = 0^\circ - 65^\circ$  at the scanning speed of 1 step / second. Powder diffraction pattern data is most commonly used as a “fingerprint” in the identification of a material. If possible, the diffraction experiment should be adopted to optimize that feature which provides the desired information. The morphology and crystal size of the synthesized material was examined by SEM. Samples were analyzed by using JSM-5600 microscope and the images obtained shows the morphology of these materials. FT-IR spectroscopy was performed on SHIMADZU FT-IR spectrometer. The sample were prepared with KBr and pressed into wafer/pellet. Spectra were collected in the mid-IR range of 400 to  $4000\text{ cm}^{-1}$  with a resolution of  $1\text{ cm}^{-1}$ .

### 2.3. Catalytic activity studies

The liquid phase acylation of anisole was carried out in a 100 ml round bottom flask fitted with water cooled condenser in the temperature range 333 K to 393 K under atmospheric pressure. The temperature was maintained by using an oil bath connected to thermostat. Both the reactants anisole and propionic anhydride were taken directly into the RB flask along with the catalyst. The reaction mixture was continuously stirred during the reaction using a magnetic stirrer and

then the clear solution of the reaction mixture was withdrawn periodically and was analyzed by Gas Chromatograph (Varian vista 6000) fitted with a (AT-WAX column diameter 0.25mm, thickness 0.2mm and length 30m) FID detector and qualitatively by GC-MS (Shimadzu QP - 2000).

The conversion was expressed by the percentage of propionic anhydride (PA) converted into the acylated product. Experiment was designed by varying amount of catalyst, molar ratio of the reactants, reaction temperature and reaction period to obtain optimum reaction condition.

$$\% \text{ Conversion of PA} = \{(\text{PA in feed} - \text{PA in product}) / \text{PA in feed}\} \times 100$$

## RESULTS AND DISCUSSION

### 3.1. Characterization

#### 3.1.1. XRD

Powder X-ray diffraction pattern of synthesized materials was recorded at room temperature on PW 1710 diffractometer. Samples were scanned using Cu-K $\alpha$  radiation of wavelength 1.54056 Å and the diffractograms were recorded in the range  $2\theta = 0^\circ - 65^\circ$  at the scanning speed of 1 step / second.

The XRD pattern of Mordenite zeolite samples (sodium form and hydrogen form) are shown in Fig. 1. The peaks are characteristic of MOR zeolite which was compared to the diffraction pattern of MOR zeolite.

#### 3.1.2. FTIR analysis

FT-IR spectroscopy was performed on SHIMADZU FT-IR spectrometer. The samples were prepared with KBr and pressed into wafer/pellet. Spectra were collected in the mid-IR range of 400 to 4000  $\text{cm}^{-1}$  with a resolution of 1  $\text{cm}^{-1}$ .

Fig.2 shows the peaks between 700-850  $\text{cm}^{-1}$  and 1000-1150  $\text{cm}^{-1}$  are assigned to symmetric and antisymmetric T-O-T stretching vibration, broad band in the region of 3410  $\text{cm}^{-1}$  due to asymmetric stretching of OH group and the bands at 1621 and 1386  $\text{cm}^{-1}$  due to bending vibration of (H-OH) and -(O-H-O)- band respectively.

#### 3.1.3. EDS analysis

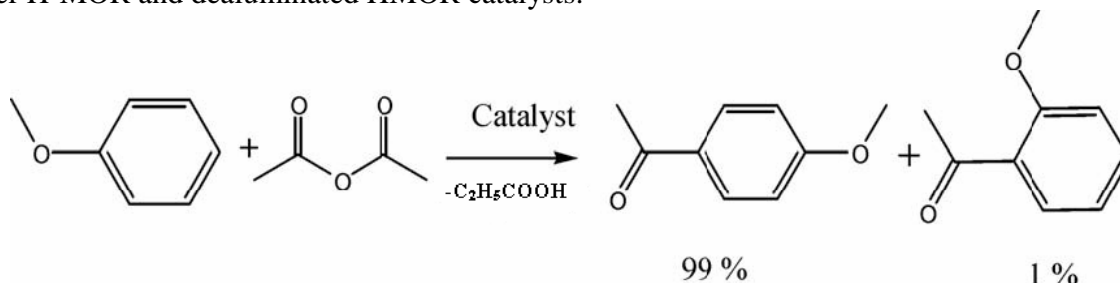
The EDS spectra of the samples are presented in Fig.3 & 4, were measured on a JEOL 5400 scanning microscope equipped with the microprobe analyzer LINK ISIS (Oxford Instrument) for the analysis of the element. EDS analysis showed the presence of Si, Al and Na in the synthesized material.

#### 3.1.4. SEM analysis

For SEM analysis samples were analyzed by using JSM-5600 microscope, Fig.5 represents the SEM micrograph of the synthesized material. The particle size of the synthesized material was found to be 20 micrometer.

### 3.2. Catalytic activity

The catalytic activity of the calcined mordenite was examined in the Friedel-Crafts acylation of anisole with propionic anhydride. The GC and GC-MS analysis showed the presence of only four components, i.e., anisole, propionic anhydride, 4-methoxypropioophenone and propionic acid over H-MOR and dealuminated HMOR catalysts.



#### 3.2.1. Effect of reaction time

Reaction was carried out at different reaction (refluxing) times. The reaction time was varied from 0.6 to 12 hrs. The conversion increased rapidly in the beginning and gradually leveled off after 4 hrs (Fig. 7). For further study the reaction time was fixed as 4 hrs.

#### 3.2.2. Effect of molar ratio of the reactants

The effect of anisole to propionic anhydride molar ratio was studied at 2:1,4:1,6:1,8:1 and 10:1 by keeping the total volume constant (Fig. 8). The conversion of propionic anhydride was found to increase with increase in concentration of anisole up to eight and thereafter remained almost constant. The increasing conversion of propionic anhydride is attributed to easy desorption of propionic acid and 4-methoxypropiophenone formed through the zeolite pores by the excess anisole as anisole is a self-solvent [40]. Further increase in molar ratio has no appreciable effect in propionic anhydride conversion. Therefore, all reactions were studied by using anisole: propionic anhydride molar ratio of 8:1.

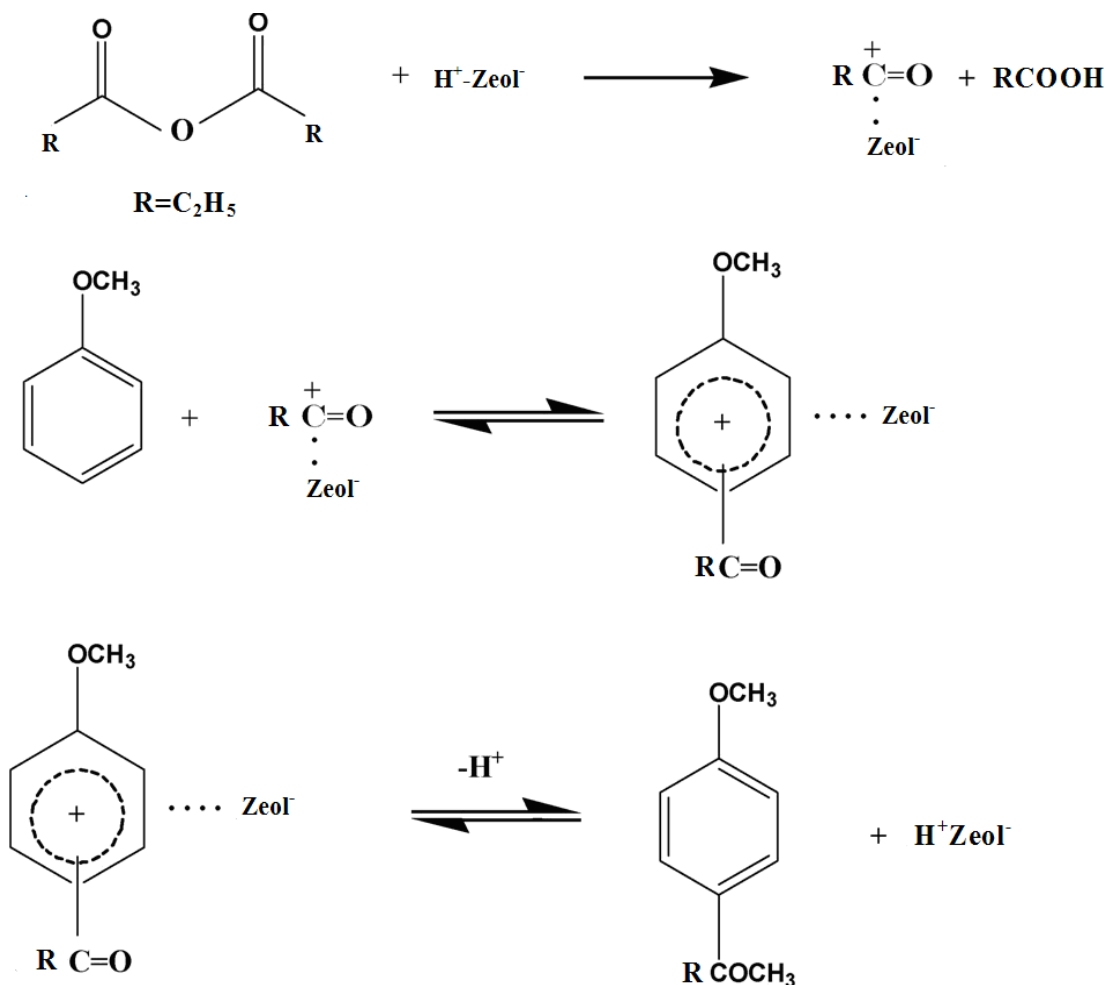
#### 3.2.3. Effect of amount of catalyst

The effect of catalyst quantity was studied over a range of 0.1– 1.5 g for acylation of anisole at 373K (Fig. 9). The conversion of propionic anhydride was found to increase with increase in catalyst amount, which is due to the proportional increase in the number of active sites and then increase becomes less significant beyond 0.5 g. This indicates that beyond 0.5 g, the additional active sites do not increase the adsorption of reactants at a given concentration.

#### 3.2.4. Effect of reaction temperature

The effect of reaction temperature on the conversion of propionic anhydride was studied over a range of 333–393 K (Fig. 10). The conversion was found to increase significantly with increase in temperature till 373 K and thereafter a slight decrease was observed. The slight decrease in conversion at high temperature is probably due to the inhibiting effect of 4-methoxypropiophenone, which can be strongly adsorbed on the catalyst at higher conversion. A decrease in conversion at high temperature was also observed for the acylation of toluene with acetic anhydride due to the strong adsorption of methylacetophenones [41]. For this study the reaction temperature was fixed as 373K.

**4. p-methoxypropiophenone-** MOR zeolite (0.5 g) was added to a mixture of anisole and propionic anhydride, and the mixture was heated at 100°C for 4 h. The zeolite was filtered off, washed with diethyl ether (5x20 ml) and evaporated. The residue was distilled under reduced pressure to give colourless crystals (m.p. 27–29°C (28°C.;  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 1681 (C=O);  $\delta_{\text{H}}$  (3H, t, *J* 7, CH<sub>3</sub>CH<sub>2</sub>CO), 2.93 (2H, q, *J* 7, COCH<sub>2</sub>), 3.84 (3H, s, OCH<sub>3</sub>), 6.92 (2H, d, *J* 9, 3-H and 5-H), 7.95 (2H, d, *J* 9, 2-H and 6-H),  $\delta_{\text{d}}$  8.4 (CH<sub>3</sub>CH<sub>2</sub>), 31.4 (CH<sub>2</sub>), 55.4 (OCH<sub>3</sub>), 113.7 (C-3 and C-5), 130.1 (C-1), 130.2 (C-2 and C-6), 163.3 (C-4), 199.5 (C=O); *m/z* (EI) 164 (M<sup>+</sup>, 14%), 135 (100), 107 (15), 92 (24), 77 (35), 64 (11).



**Proposed mechanism for the acylation reaction of anisole by propionic anhydride**

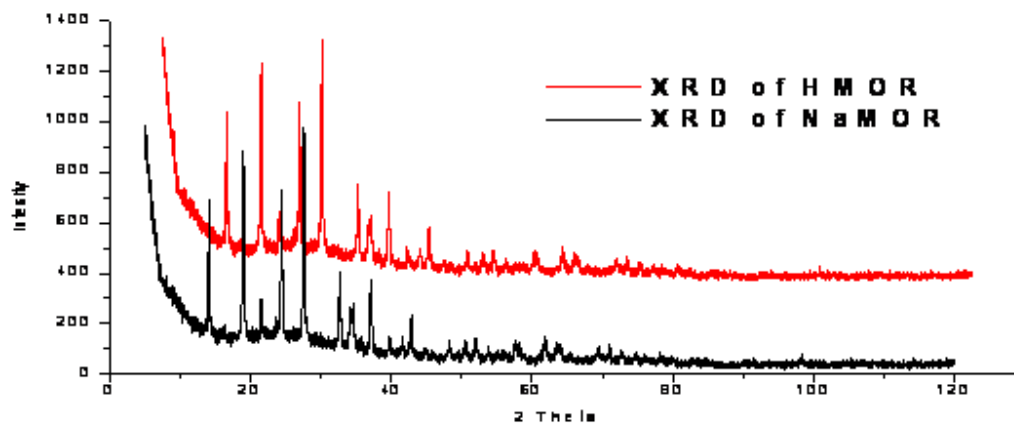


Fig.1 XRD of Mordenite zeolite

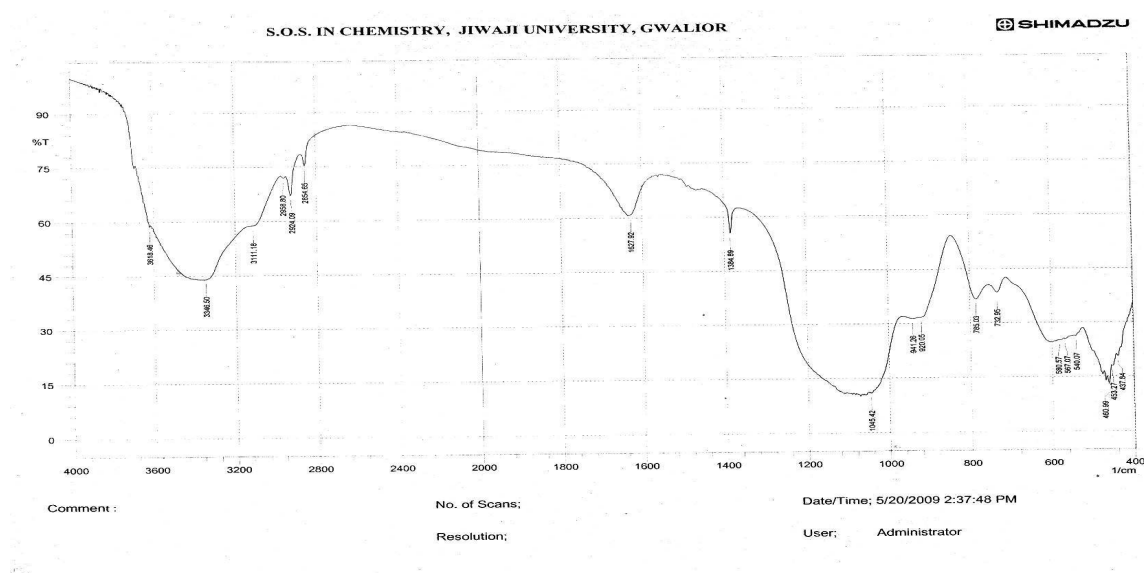


Fig.2 FTIR spectra of of Mordenite zeolite



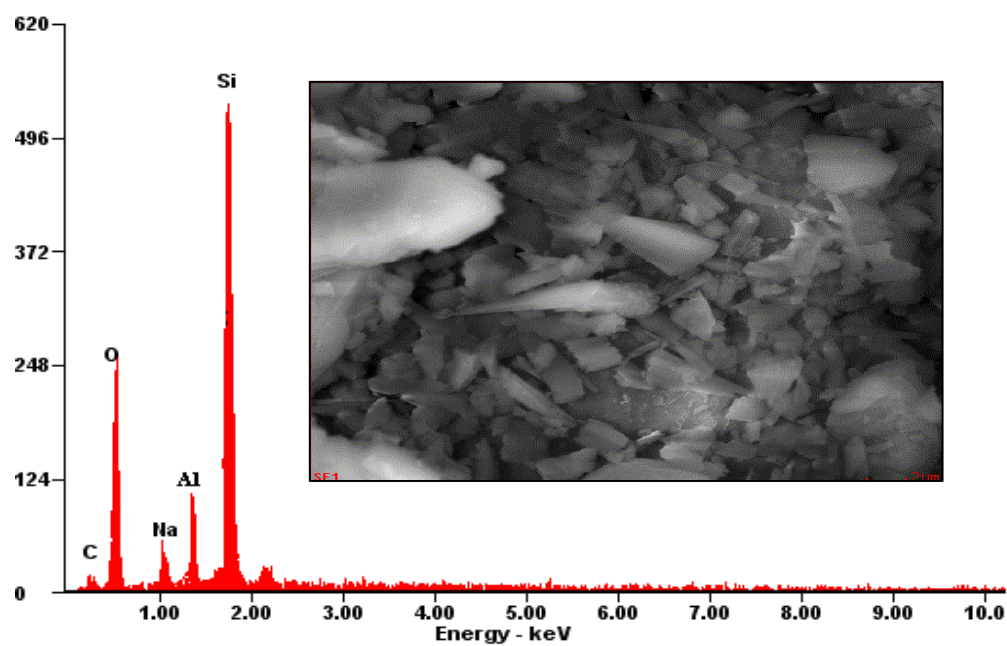


Fig.3 EDS spectra of H-Mordenite zeolite (before dealumination)

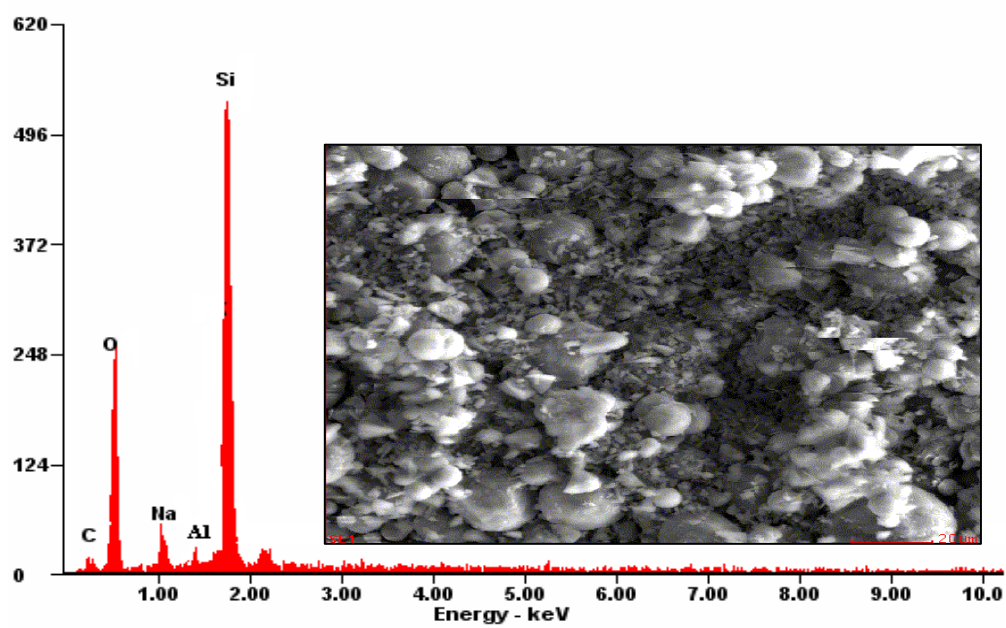
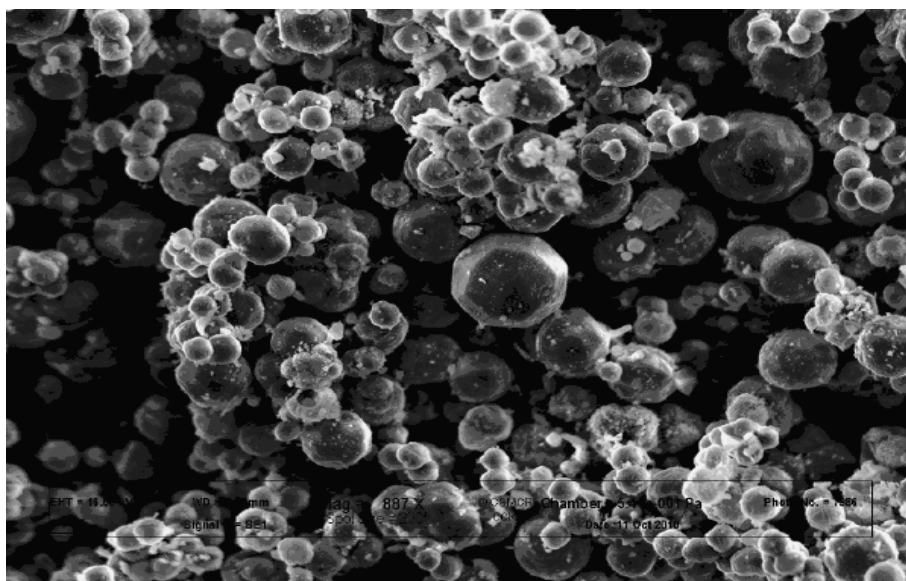
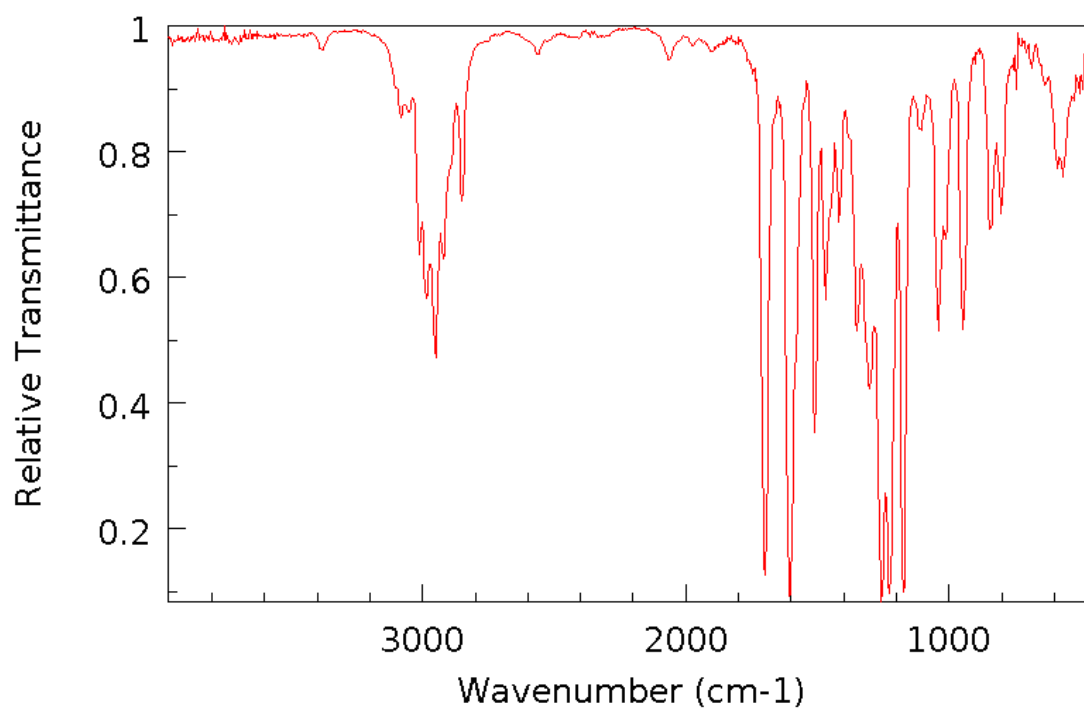
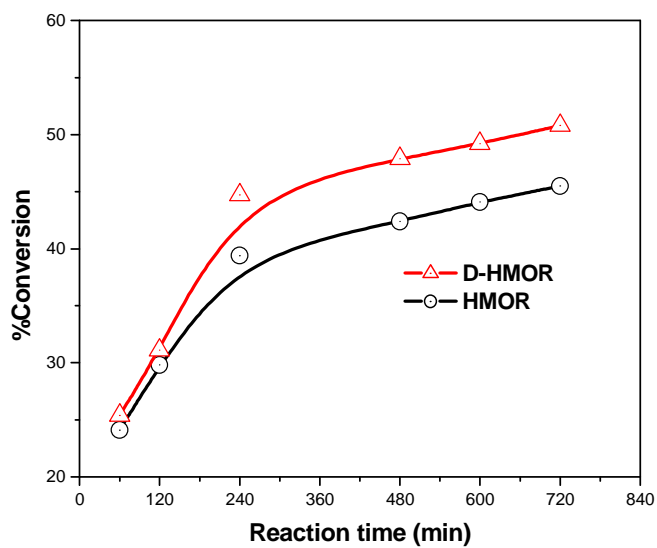


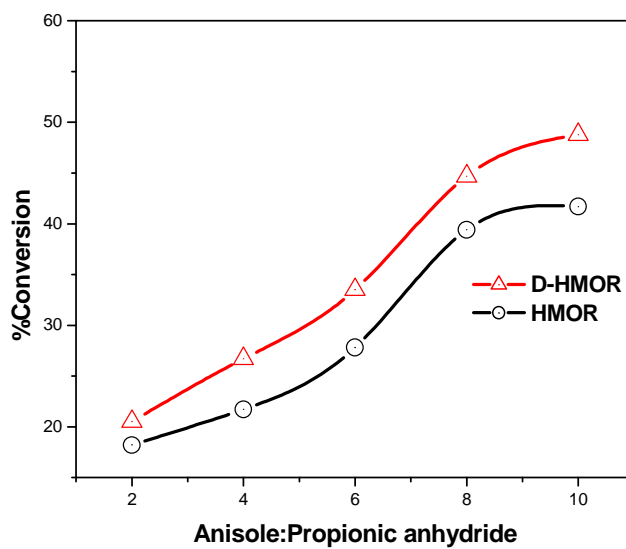
Fig.4 EDS spectra of H-Mordenite zeolite (after dealumination)



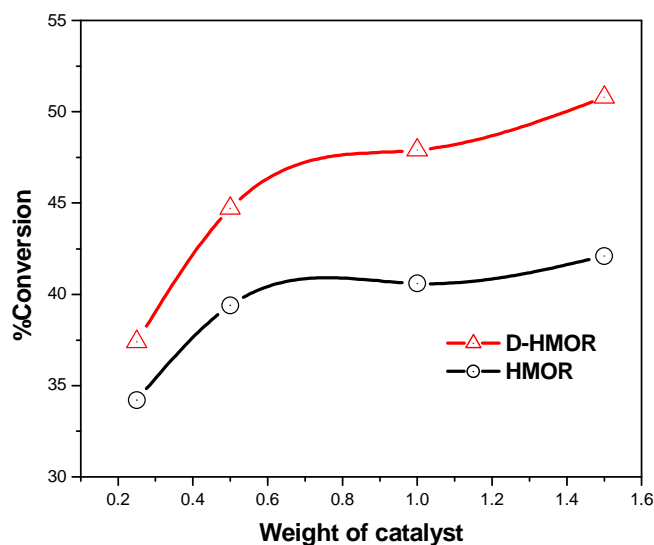
**Fig.5** SEM image of H-Mordenite zeolite**Fig.6** FTIR spectra of p-methoxypropiphenone



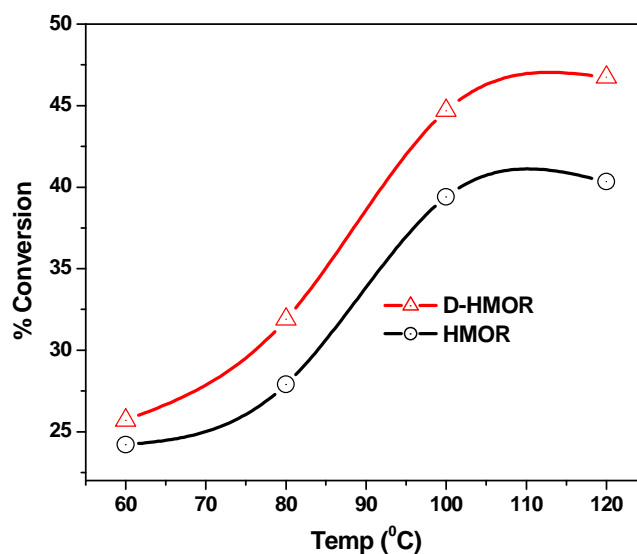
**Fig.7** Effect of reaction time on conversion of propionic anhydride



**Fig.8** Effect of molar ratio of reactants on conversion of propionic anhydride



**Fig.9** Effect of catalyst loading on conversion of propionic anhydride



**Fig.10** Effect of temperature on conversion of propionic anhydride

## CONCLUSION

The present work deals with the synthesis of mordenite zeolite, its dealumination and use as a solid acid catalyst for acylation of anisole by propionic anhydride. The reaction parameters such as reaction time, temperature, anisole: propionic anhydride molar ratio and catalyst quantity were optimized. It was observed that after dealumination the pore size of zeolite becomes larger and facilitate the reactant to get entered into it and promoted the conversion of propionic anhydride to 4-methoxypropiofenone, but there was no significant effect of dealumination on acylation

was observed. Under the optimum reaction conditions (373K, anisole: propionic anhydride mole ratio of 8:1, and reaction time for 4 hrs) conversion of propionic anhydride to 4-methoxypropiophenone was found 44.7% and 39.4% in case of dealuminated form of HMOR zeolite and HMOR zeolite respectively.

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