



## Effect of hydrophobic and hydrophilic properties of solid acid catalysts on the esterification of maleic anhydride with ethanol

M. Bhagiyalakshmi, S. Vishnu Priya, J. Herbert Mabel, M. Palanichamy, V. Murugesan \*

Department of Chemistry, Anna University, Chennai 600 025, India

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### ABSTRACT

Esterification of maleic anhydride with ethanol over Al-MCM-41 (Si/Al = 50, 100 and 150) and H $\beta$  zeolite was investigated in the liquid phase at 80, 100 and 120 °C. Monoesterification of maleic anhydride to monoethyl maleate (MEM) was found to be fast and independent of the presence of catalyst but subsequent esterification to diethyl maleate (DEM) was catalyst dependent. The absence of isomerisation of diethyl maleate to diethyl fumarate (DEF) over Al-MCM-41 molecular sieves is a significant advantage. Al-MCM-41 (50), Al-MCM-41 (100) and H $\beta$  are convenient replacement for hazardous sulphuric acid used in the industrial esterification of maleic anhydride with ethanol.

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### 1. Introduction

Esterification is an industrially important reaction as organic esters are important intermediates in the synthesis of fine chemicals, drugs, plasticisers, food preservatives, pharmaceuticals, cosmetics and auxiliaries [1]. These esters are produced by a batch process in industries using mineral acid catalysts such as hydrofluoric acid, sulphuric acid or Lewis acid catalysts like tin octoate [2]. Mineral acid catalysts are corrosive and need to be neutralised after the reaction for disposal. Lewis acid catalysts also require their careful removal after the reaction by adsorption on bleaching earth which also produces large amount of waste. Hence, there is a need for ecofriendly heterogeneous catalysts for esterification. Many heterogeneous catalysts viz., ion-exchange resin, H-ZSM-5, HY [3], triol-ic acid, sulphated oxides [4], hydrous zirconium oxide and supported heteropoly acids [5] were reported in the literature for esterification.

Al-MCM-41 materials with large pore diameter (20–100 Å) and scattered distribution of acid sites were proved to be an important catalyst. Esterification of acetic acid with ethanol over MCM-41 has been reported [6]. Combined alkylation and sulphonic acid functionalisation of MCM-41 type silica for esterification of glycerol with fatty acids is an interesting advancement [7]. These studies have instigated us to undertake esterification of maleic anhydride with ethanol over Al-MCM-41 molecular sieves. The ester, diethyl maleate, is used as an additive and intermediate for plastics, pig-

ments, pharmaceuticals and agriculture products. It is used as a dienophile in Diels–Alder reaction. Diethyl maleate is manufactured in industries by reacting maleic anhydride with ethanol in the presence of catalytic amount of sulphuric acid [8]. In addition, this process also yields diethyl fumarate as an additional product, thus necessitating product purification. Further, since this process is hazardous, ecofriendly solid acid catalysts could be a convenient alternative. Hence, in the present study we report the esterification of maleic anhydride with ethanol in the liquid phase over mildly acidic Al-MCM-41 molecular sieve with different Si/Al ratios. In addition the reaction was carried over H $\beta$  zeolite for comparison.

### 2. Experimental

#### 2.1. Synthesis of Al-MCM-41 and H $\beta$

The hydrothermal crystallization procedure reported by Beck et al. [9] was adopted for the preparation of Al-MCM-41 molecular sieves with Si/Al ratios of 50, 100 and 150. In a typical synthesis, 10.6 g sodium silicate nanohydrate (Merck) in demineralised water was combined with an appropriate amount of aluminum sulphate (Merck). This mixture was then acidified with 1 M H $_2$ SO $_4$  to bring down the pH to 10.5 under vigorous stirring. After 30 min stirring, an aqueous solution of cetyltrimethylammonium bromide (CTAB) (Merck) was added and the surfactant-silicate mixture was stirred for a further 30 min at room temperature. The molar gel composition of the resultant mixture was SiO $_2$ :0.2CTAB:XAl $_2$ O $_3$ :0.89H $_2$ -SO $_4$ :120H $_2$ O (X varies with Si/Al ratio). The resultant gel was autoclaved and heated at 170 °C for 12 h. The solid product

\* Corresponding author. Tel.: +91 44 22203144; fax: +91 44 22200660/22350397.  
E-mail address: [v\\_murugu@hotmail.com](mailto:v_murugu@hotmail.com) (V. Murugesan).

obtained was filtered and dried at 80 °C in air. The sample was then calcined at 550 °C for 5 h in a muffle furnace to expel the template.

Zeolite  $\beta$  was obtained from SUD Chemie India Ltd. and converted to  $\text{NH}_4^+$  form by ion-exchange with 0.5 M ammonium chloride solution. One gram of the catalyst was mixed with 20 ml of the exchange solution in a round-bottom flask fitted with a reflux condenser. The solution was stirred magnetically for 3 h; then the content of the flask was cooled and filtered. The residue was dried at 100 °C for 6 h in an air oven and then calcined at 550 °C for 6 h. The procedure was repeated thrice. After calcination, the ammonium chloride-exchanged zeolite gave the protonic form of H $\beta$  zeolite. This H $\beta$  was used for the esterification reaction in order to compare its catalytic activity with that of mesoporous Al-MCM-41 molecular sieves.

## 2.2. Characterization

The XRD powder diffraction patterns of calcined mesoporous Al-MCM-41 (Si/Al = 50, 100 and 150) molecular sieves were recorded on a Siemens D5005 Stereoscan diffractometer using nickel-filtered  $\text{CuK}\alpha$  radiation and a liquid nitrogen cooled germanium solid-state detector. The diffractograms were recorded in the  $2\theta$  range from 5 to 60° in steps of 0.02° with a count time of 15 s at each point for H $\beta$  zeolite, and in the  $2\theta$  range 0–10° for Al-MCM-41 molecular sieves. Surface area, pore volume and pore size distribution were measured by nitrogen adsorption at 77 K with an ASAP 2010 porosimeter from Micromeritics Corporation (Norcross, GA). The samples were degassed at 623 K under a pressure of  $10^{-5}$  mbar overnight prior to adsorption experiments. The mesopore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.5, assuming that all the mesopores were filled with condensed nitrogen in the normal liquid state. Pore size distribution was estimated using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP 2010 built-in software from Micromeritics). Mid-IR spectra of mesoporous Al-MCM-41 molecular sieves were recorded on a FT-IR spectrometer (Nicolet Avatar 360) using KBr pellet technique. About 10 mg of the sample was ground with 200 mg of spectral grade KBr to form a pellet under hydraulic press. The pellet was used to record the IR spectrum in the range 4000–400  $\text{cm}^{-1}$ .

The acidity of catalysts was determined by *in situ* DRIFT pyridine adsorption–desorption technique. The *in situ* DRIFT spectra of samples were recorded on a FT-IR spectrometer (Nicolet Avatar 360) equipped with a high temperature vacuum chamber. Approximately 30 mg of the sample was taken in the sample holder and dehydrated at 400 °C for 6 h under vacuum ( $10^{-5}$  mbar). The sample was then cooled to room temperature and the spectrum was recorded. Then pyridine was adsorbed at room temperature. The physically adsorbed pyridine was removed by heating the sample at 150 °C under vacuum ( $10^{-5}$  mbar) for 30 min. The sample was then cooled to room temperature and the spectrum was recorded in the range 1700–1400  $\text{cm}^{-1}$  (pyridine adsorption region). The acidity was calculated using extinction coefficients of the bands of Brønsted and Lewis acid sites adsorbed pyridine.

## 2.3. Esterification procedure

Esterification of maleic anhydride with ethanol was carried out in the liquid phase. Maleic anhydride (1 mol), ethanol (3 mol) and catalyst (0.1 g) were taken in a 25 ml round-bottom flask fitted with a reflux condenser. The flask with its content was heated at a constant temperature in an oil bath and stirred simultaneously magnetically. In order to monitor the progress of the reaction, aliquots of the hot mixture were withdrawn at regular intervals (3, 6 and 9 h), centrifuged and analyzed in a gas chromatograph (Hewlett-Packard 5890A) equipped with a SE-30 column and an FID

detector. Nitrogen was used as the carrier gas at a flow rate of 20  $\text{ml min}^{-1}$ . After completion of each reaction, the catalyst was regenerated by activation at 500 °C in air and reused again.

## 3. Results and discussion

### 3.1. Physico-chemical characterisation

The XRD powder diffraction patterns of as-synthesized and calcined Al-MCM-41 (Si/Al = 50, 100 and 150) are shown in Fig. 1A and B. The XRD patterns are similar to those already reported in the literature [11,12]. The XRD patterns of calcined Al-MCM-41 (Si/Al = 50, 100 and 150) materials exhibit an intense signal at about 1.8° due to [100] plane and weak broad signals between 2.5° and 4.5° ( $2\theta$ ) due to [110], [200] and [210] planes. These peaks confirm the hexagonal mesophase of the material. Their  $d_{100}$  spacings calculated as per the literature procedure [12] are 37.43, 39.86 and 47.90 Å while the lattice parameters ( $a_0$ ) are 43.29, 45.89 and 55.29 Å for Al-MCM-41 of Si/Al = 50, 100 and 150, respectively. These XRD patterns coincide with a data already reported in the literature for mesoporous aluminosilicate molecular sieves [13,14]. The calcined materials possess well-defined pore structure due to condensation of defective Si–OH groups. The X-ray

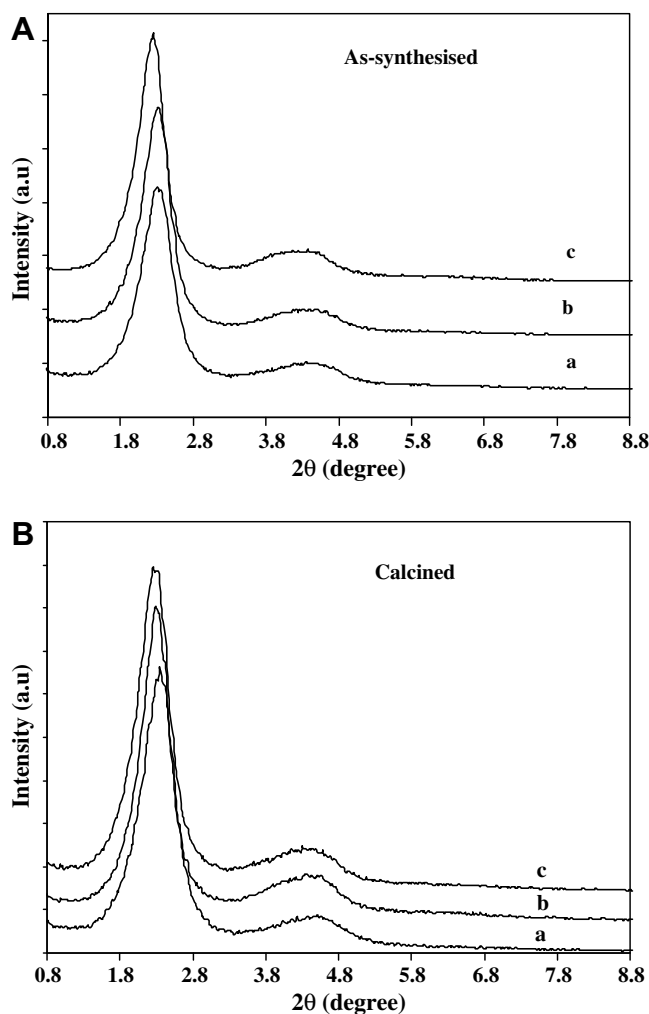


Fig. 1. XRD patterns of (A) as-synthesized Al-MCM-41 (a) AlMCM-41 (50), (b) Al-MCM-41 (100) and (c) Al-MCM-41 (150) and (B) calcined Al-MCM-41 (a) Al-MCM-41 (50), (b) Al-MCM-41 (100) and (c) Al-MCM-41 (150).

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