



## Short Communication

## Esterification of levulinic acid to ethyl levulinate over bimodal micro–mesoporous H/BEA zeolite derivatives



C.R. Patil, P.S. Niphadkar, V.V. Bokade, P.N. Joshi\*

Catalysis &amp; Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008, India

## ARTICLE INFO

## Article history:

Received 5 June 2013

Received in revised form 11 September 2013

Accepted 8 October 2013

Available online 17 October 2013

## Keywords:

H/BEA zeolite

Post-synthesis modification

Mesoporosity

Esterification

Ethyl levulinate

## ABSTRACT

A series of bimodal micro–mesoporous H/BEA zeolite derivatives were prepared by the post-synthesis modification of H/BEA zeolite by NaOH (0.05 M–1.2 M) treatment. Samples were characterized by powder XRD, low temperature nitrogen adsorption/desorption, temperature programmed desorption of ammonia and ICP. The mesopore formation was found to play a crucial role in liquid phase esterification of levulinic acid with ethanol. The enhanced catalytic activity of a bimodal micro–mesoporous H/BEA zeolite derivative (H/BEA<sub>0.10</sub>) prepared by treatment with 0.1 M NaOH can be mainly attributed to the high mesoporosity coupled with better preserved crystallinity and acidic properties.

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## 1. Introduction

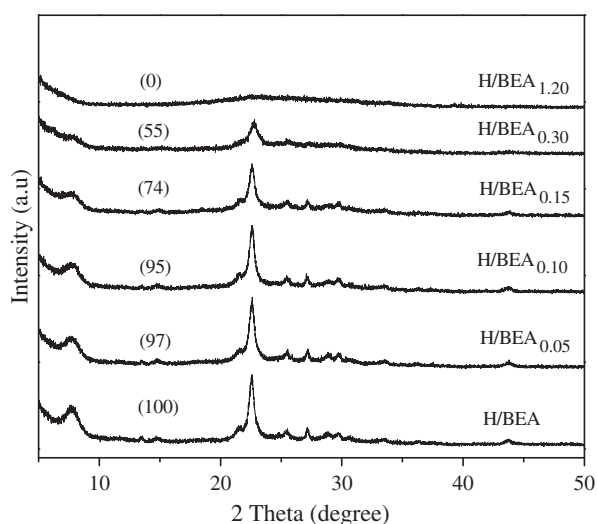
Synthesis of levulinate esters from biomass is one of the avenues where substantial research efforts are being invested with a view to achieve sustainable energy supply and production of value-added chemicals. Ethyl levulinate (EL) is a short-chain fatty ester and possesses unique properties which make it as: a) a very attractive candidate as novel diesel and gasoline miscible biofuel [1,2], b) a chemical feedstock in flavoring and fragrance industries [3] and c) a substrate for various kinds of organic condensation and addition reactions [4]. After realizing the drawbacks of homogeneous catalysts such as mineral acids [4–7], considerable efforts were made to develop environmentally benign heterogeneous catalysts [8–12] which are recyclable and efficient for esterification of levulinic acid (LA). In esterification of LA with ethanol, the performance of non-zeolitic catalysts, in particular, Amberlyst-15 and sulfated oxides was found to depend on the total acidity, whereas, in case of the zeolite catalysts, it depends on the pore structure (large cavities) rather than the total acidity [10]. Heterogeneous catalysts resulted from the effective confinement of H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> (up to 30 wt.%) within the mesoporous channels of SiO<sub>2</sub> mesoporous (H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>–SiO<sub>2</sub>) were also reported as the efficient and recyclable catalysts for the synthesis of methyl and ethyl levulinates [12]. Thus, for improved performance, it is necessary to use the zeolite catalyst with larger cavities to favor the formation of the transition state in esterification of LA with ethanol. Although great progress has been made for the catalytic preparation of EL, still the development of catalysts including efficient reaction systems and establishing the structure–property relationships

of catalysts are some of the challenges that exist for the further improvement in productivity and selectivity [13].

Zeolites are microporous, crystalline aluminosilicates having very regular pore structures of molecular dimensions. By generating the mesoporosity in their matrix, their catalytic performance can be improved on account of increased diffusion rate [14,15]. Post-synthesis treatment with alkaline solution is one of the simple, feasible and highly effective methods to prepare hierarchically structured zeolites with combined advantages of microporous and mesoporous molecular sieves [16–20]. The concentration of the base is one of the process parameters to tailor the characteristics of such bimodal micro–mesoporous zeolite derivatives. Protonic form of the bimodal micro–mesoporous zeolite beta derivative has exhibited catalytic activity in  $\alpha$ -pinene isomerization [21], n-hexane isomerization [22] and selective hydrocracking of heavier hydrocarbons to C<sub>5</sub>–C<sub>11</sub> hydrocarbons [23] because of mesopore formation resulting from the alkaline treatment.

The benefits of protonic form of zeolite beta (H/BEA) and the challenges associated with the further improvement in productivity and selectivity for EL have triggered our interest to prepare and examine the performance of bimodal micro–mesoporous H/BEA zeolite derivatives in the synthesis of EL. In this communication, a series of bimodal micro–mesoporous H/BEA zeolite derivatives were prepared by the post-synthesis modification of H/BEA zeolite by NaOH treatment. The effect of NaOH concentration on the XRD crystallinity, textural and acidic properties, chemical composition and catalytic performance in EL synthesis is investigated. An attempt was made to establish the structure–property–activity relationships. In view of maximizing the EL yield, the reaction parameters such as catalyst loading, LA:ethanol molar ratio and time on stream were optimized using optimum catalyst.

\* Corresponding author. Tel.: +91 20 25902457; fax: +91 20 25902633.  
E-mail address: [pn.joshi@ncl.res.in](mailto:pn.joshi@ncl.res.in) (P.N. Joshi).



**Fig. 1.** Powder XRD patterns for H/BEA and its bimodal micro-mesoporous derivatives (bracketed numbers indicate the % crystallinity).

## 2. Experimental

### 2.1. Synthesis and characterization

The overall procedure employed to prepare the parent sample (H/BEA) and characterization techniques used are similar to that of described earlier [24]. Details regarding the procedure followed for the post-synthesis modification of H/BEA zeolite by NaOH (0.05 M–1.20 M) treatment and characterization of the bimodal micro-mesoporous H/BEA zeolite derivatives are described in the supplementary information. The protonic form obtained after NaOH treatment was designated as H/BEA<sub>x,yz</sub>, where x,yz is the concentration of NaOH with which H/BEA was treated.

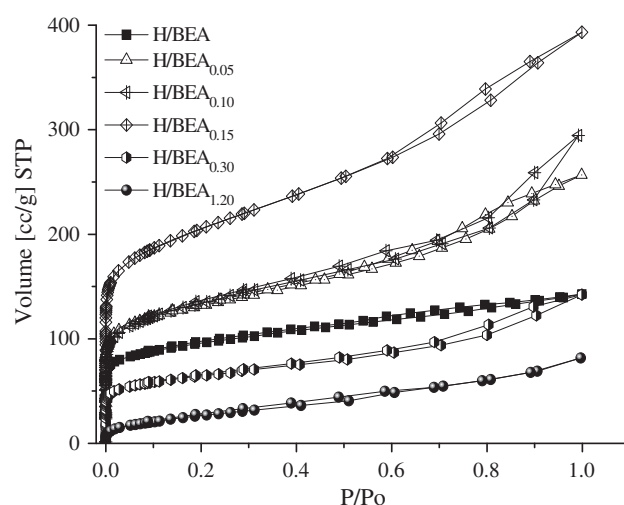
### 2.2. Synthesis of EL

Catalytic liquid phase esterification of levulinic acid with ethanol and analysis of the reactants and products were carried out as per the details provided in the supplementary information.

## 3. Results and discussion

### 3.1. Characterization

Fig. 1 shows powder X-ray diffraction (XRD) patterns of H/BEA and its bimodal micro-mesoporous derivatives obtained by NaOH treatments with different concentrations. H/BEA has shown the characteristic peaks of zeolite BEA [24] with no contribution due to other crystalline or amorphous phase/s. H/BEA sample was treated as a reference sample with 100% crystallinity and the relative crystallinities of different derivatives were estimated and shown as bracketed figures



**Fig. 2.** Low temperature nitrogen adsorption-desorption isotherms of H/BEA and its bimodal micro-mesoporous derivatives.

on corresponding XRD patterns. Although, % crystallinity was dropped with an increase in the NaOH concentration, the zeolitic structure was practically preserved with a negligible drop in crystallinity from 100% to 95% up to 0.10 M NaOH concentration. Further increase in the concentration resulted in the decrease in crystallinity and a completely XRD amorphous sample was obtained with 1.20 M NaOH. It is also evident from Table 1 that, the molar Si/Al ratio decreases with the increase in alkali concentration. The N<sub>2</sub> adsorption-desorption isotherms and the textural parameters of H/BEA and its bimodal micro-mesoporous derivatives are presented in Fig. 2 and in Table 1 respectively. Microporous character of H/BEA has been well reflected in its isotherm type-I with plateau at higher relative pressures. It also showed a small hysteresis loop which might be associated with the presence of the interparticle voids [21]. The type of the isotherm and hysteresis loop showed by the NaOH-treated samples indicated their bimodal micro-mesoporous nature. With increase in the NaOH concentration, the contribution of micropore surface area in total surface area was found to drop and it reached to a minimum value of 89 m<sup>2</sup>/g in XRD amorphous sample. As a result of an introduction of hierarchical mesopores, samples have shown the decreasing trend in the mesopore volume as: H/BEA<sub>1.20</sub> > H/BEA<sub>0.30</sub> > H/BEA<sub>0.15</sub> > H/BEA<sub>0.10</sub> > H/BEA<sub>0.05</sub> > H/BEA. The acidic properties of H/BEA and its bimodal micro-mesoporous derivatives were investigated by NH<sub>3</sub>-TPD and the results based on high temperature peak are summarized in Table 1. An acid amount was found to increase with an increase in the NaOH concentration up to 0.10 M and then decreases with the further increase in the NaOH concentration. The use of NaOH with concentration >0.10 M has resulted in the decrease in % crystallinity which might be contributing to the decrease in an acid amount. In the samples possessing % crystallinity in the range of 100–95, the increase in the acid amount may be attributed to the increased number of strong acid due to the lowering of Si/Al ratio

**Table 1**  
Chemical composition, acidic and textural properties of H/BEA and its bimodal micro-mesoporous derivatives.

Sample	Acid amount (NH <sub>3</sub> mmol desorbed g <sup>-1</sup> )	Si/Al ratio	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	S <sub>micro</sub> <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	S <sub>meso</sub> <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	
						V <sub>micro</sub> <sup>a</sup>	V <sub>meso</sub> <sup>b</sup>
H/BEA	0.53	14	580	529	51	0.22	0.18
H/BEA <sub>0.05</sub>	0.59	12	597	473	124	0.16	0.28
H/BEA <sub>0.10</sub>	0.69	10	620	350	270	0.16	0.32
H/BEA <sub>0.15</sub>	0.45	8	678	329	349	0.14	0.39
H/BEA <sub>0.30</sub>	0.27	5	507	203	304	0.09	0.57
H/BEA <sub>1.20</sub>	0.19	3	303	89	214	0.01	0.79

<sup>a</sup> By t-plot.

<sup>b</sup> By BJH method.

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