



# Hierarchical K/LTL zeolites: Synthesis by alkali treatment, characterization and catalytic performance in Knoevenagel condensation reaction



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## ABSTRACT

The hierarchical K/LTL zeolites prepared by post-synthesis modification with aqueous 1.5 M KOH solution by varying alkali volume to K/LTL zeolite (10–70 ml/g) ratios, were examined in Knoevenagel condensation. The physico-chemical properties of the catalysts were thoroughly evaluated by PXRD, FTIR, ICP, CO<sub>2</sub>-TPD, XPS, N<sub>2</sub> adsorption/desorption and <sup>29</sup>Si and <sup>27</sup>Al MAS-NMR. Among all the samples, hierarchical K/LTL prepared by treating K/LTL with 50 ml aqueous 1.5 M KOH solution per gram of K/LTL displayed about 1.5 fold higher catalytic activity as compared to parent K/LTL, presumably because of combined effect of enhanced basicity and molecular diffusion through pore channels.

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## Introduction

The base catalyzed condensation and addition reactions have gained attention considerably in the synthesis of a wide range of organic compounds, including novel sources for the effective production of fine chemicals and pharmaceuticals. Considering the emerging trend for the development of an environmental benign processes or sustainable technologies for the chemical industry, the adverse effects of homogeneous catalysts in particular liquid bases such as the difficulties in the separation, recovery, and their reusability can be overcome by the use of heterogeneous solid bases [1,2]. The heterogeneous catalysis resulted in the improved performance in terms of remarkable selectivity and product yield by the suppression of the side reactions including self-condensation and oligomerization, and additionally, the beneficial economic downstream separation and purification processes.

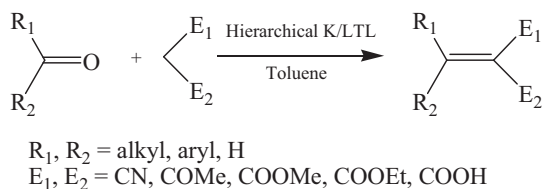
Knoevenagel condensation of aldehyde or ketone with active methylene group compounds to form bulky unsaturated products (Scheme 1) is one of the most important base catalyzed reactions involving C–C bond formation and plays a vital role in the synthesis of fine chemical [3–5]. It is also employed as a probe reaction for

the characterization of the basic catalysts [6,7]. The homogeneous Knoevenagel condensation reaction is catalyzed by using various liquid bases such as piperidine, amines, ammonia, and ammonium salts [8]. However, the requirement of the stoichiometric amount of catalyst, contamination of the products, and the corrosive nature of the catalysts limit their applications from industrial point of view. In this context, several studies have been focused on heterogeneous base catalysts for the Knoevenagel condensation reaction, for instance, hydrotalcites [9], alkali earth oxides on alumina support [10], hydroxyapatite encapsulated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles [11], MCM 41 [12], etc. Other heterogeneous catalysts such as basic zeolites and zeolites exchanged using organic and inorganic cations were also found capable of catalyzing the Knoevenagel condensation reaction under mild reaction conditions [13–16].

Hierarchical zeolites, a family of crystalline zeolite materials featuring the interconnected secondary mesopores in the microporous framework have been reported to circumvent diffusion limitations [17–19]. The zeolite having hierarchical structure provides the accessibility of active sites on the internal surfaces which greatly influence the catalytic performance [20]. Several attempts were made in order to modify zeolite structure to generate mesoporosity in the microporous framework [21–24]. Desilication is one of the promising post-synthesis modification techniques by which the hierarchically structured zeolites with

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**Scheme 1.** Knoevenagel condensation reaction using the hierarchical K/LTL catalyst.

intracrystalline mesoporosity can be synthesized owing to its versatile, effective, scalable and green synthetic approach. The scientific investigations have been increasingly focused on desilication which involves the study of the hierarchically structured zeolites [25–27]. The post-synthetic treatment parameters such as Si/Al ratio, concentration and volume of alkali solution, exposure time and temperature were found to influence the nature of secondary mesoporous network in the microporous zeolite. Thus, the viability of the zeolite catalyzed reactions can be enhanced distinctly by the application of hierarchically structured zeolites in the catalysis. The micropores provide the reactive sites for the catalytic conversion and the interconnected mesopores result in the enhanced molecular transport on account of improved diffusion rate. The hierarchical zeolite-based porous materials with combined micro-mesoporosity have proved to be promising candidates for the liquid phase Knoevenagel condensation [28].

Linde type L zeolite (LTL), a member of large pore zeolite family, is known to exhibit interesting sorption and base catalyzed properties [29]. Structurally, it comprises cancrinite cages and double six-membered rings [30], whereas compositionally, its framework is defined by the Si/Al ratio of about  $3.05 \pm 0.45$ . Zeolite LTL with  $\text{K}^+$  as an extra-framework charge balancing cation (K/LTL) is conventionally prepared by hydrothermal crystallization of  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  gel system [31]. Its compositional and related properties can be modified by the post-synthesis modifications such as ion exchange, dealumination and combination thereof [32,33]. Although there have been many reports about synthesizing micro-mesoporous zeolites by post-synthesis treatment, the studies on the synthesis of hierarchical K/LTL zeolite by using different volume of aqueous KOH solution have been seldom reported. Herein, we describe the synthesis of hierarchical K/LTL zeolite by post-synthesis modification by varying the alkali volume used per gram of zeolite. The catalytic performance of the hierarchical K/LTL zeolites was investigated in the liquid phase Knoevenagel condensation reaction of benzaldehyde and malononitrile using toluene as solvent.

## Experimental

### Materials

The materials used were silica sol (40%  $\text{SiO}_2$ , V. P. Chemicals, India), pseudoboehmite (70%  $\text{Al}_2\text{O}_3$ , Condea, Germany), potassium hydroxide (85%, Merck, India), benzaldehyde (99.0%, S.D. Fine-Chem Ltd., India), malononitrile (98.0%, S.D. Fine-Chem Ltd., India), toluene (99.5%, Loba Chemie) and de-ionized water.

### Preparation of K/LTL zeolite

K/LTL zeolite was synthesized hydrothermally from the gel having molar composition of  $8\text{K}_2\text{O}:\text{Al}_2\text{O}_3:20\text{SiO}_2:200\text{H}_2\text{O}$ . The overall procedure followed was reported elsewhere [31]. In typical procedure, the requisite amount of pseudoboehmite was dissolved in the aqueous KOH solution followed by the addition of silica sol with vigorous stirring. After stirring for 1 h, the hydro-gel was

transferred to the autoclave for hydrothermal crystallization at  $170^\circ\text{C}$  for 8 h. The solid product was obtained by filtration, followed by the washing with a copious amount of de-ionized water, and finally dried at  $100^\circ\text{C}$  for 12 h. The final product was designated as K/LTL.

### Post-synthesis modification

The hierarchical K/LTL zeolites were prepared following the post-synthesis modification by treating pre-synthesised K/LTL zeolite (ranging from 10 to 70 ml/g) ratios. The aqueous KOH solution was chosen in order to overcome the pronounced effect of other cations such as  $\text{Na}^+$  in NaOH, over catalysis process. In typical alkaline post-synthesis modification, 10 g zeolite was mixed in a requisite volume of aqueous 1.5 M KOH solution and heated at a temperature of  $70^\circ\text{C}$  for 1 h. Then the slurry was cooled to room temperature and the solid product was separated by filtration. It was then washed with de-ionized water and dried in an air-oven at  $100^\circ\text{C}$  for 12 h. The samples obtained by post-synthesis treatment were designated as MMKLX, where X = ml of aqueous KOH solution used per gram of zeolite/10 (Table 1).

### Characterization

The phase identification and purity of samples were determined by powder X-ray diffraction (PXRD). The XRD patterns were recorded using a PAnalytical PXRD system (Model XPert-PRO-1712) with monochromated  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ). The measurements were carried out in the  $2\theta$  range of  $5-70^\circ$  at a scanning rate of  $2^\circ \text{ min}^{-1}$ . The degree of crystallinity of sample was calculated by taking the ratio of the summation of integrated areas under the prominent peaks ( $2\theta = 5.5, 19.2, 22.5, 25.5, 27.8, 30.6^\circ$ ) of the hierarchical zeolites to that of parent K/LTL. The Si and Al content of samples were determined by Perkin-Elmer Optima 3000DV inductive coupled plasma-atomic emission spectroscopy (ICP-AES). Fourier transform infrared spectroscopic (FTIR) analysis of the samples was carried out using Perkin Elmer Spectrum-1 spectrometer. The spectra were recorded in the  $900-450 \text{ cm}^{-1}$  spectral range. The low temperature nitrogen adsorption and desorption isotherms were performed at  $-196^\circ\text{C}$  on the Autosorb-1-Quantachrome instrument. Prior to the measurements, the samples were outgassed at  $250^\circ\text{C}$  for 10 h.  $^{29}\text{Si}$  and  $^{27}\text{Al}$  magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) spectra were recorded on a JEOL ECX-400 spectrometer at resonance frequencies of 79.5 and 104.3 MHz for  $^{29}\text{Si}$  and  $^{27}\text{Al}$ , respectively. Temperature programmed desorption of  $\text{CO}_2$  ( $\text{CO}_2$ -TPD) was carried out in Micromeritics, AutoChem 2910 instrument. The basicity of samples was analyzed by X-ray photoelectron spectroscopy (XPS) using ESCA-3000 (V.G. Scientific Ltd., UK) with the pressure of  $1.3 \times 10^{-7} \text{ Pa}$ . The  $\text{Mg K}\alpha$  radiation (1253.6 eV) was used as an X-ray source and operated at 150 W. For the analysis of the XPS peaks, the charging effects were corrected by setting the position of the C1s at a binding energy of 284.6 eV. Transmission electron microscopy (TEM) was done using FEI Tecnai TF-30 instrument.

### Catalytic activity

The Knoevenagel condensation of benzaldehyde with malononitrile over the parent and hierarchical K/LTL zeolites was carried out in two-necked round bottom flask, equipped with a reflux condenser and magnetic stirrer in the liquid phase using toluene as solvent. In a typical experiment, the requisite amount of catalyst (3–15 wt% with respect to the substrate) was added to the equimolar mixture of benzaldehyde (4.8 mmol) and malononitrile

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