Hierarchical Zeolite Beta: An Efficient and Eco-Friendly Nanocatalyst for the Friedel–Crafts Acylation of Toluene

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P-Methyacetophenone, the acylated product of toluene finds a wide range of applications in the flavors and fragrance industry. It is typically produced on an industrial scale by Friedel–Crafts acylation of toluene with acetic anhydride using homogeneous, corrosive and polluting acid catalysts such as aluminium chloride. The pollution problems related to this process such as the disposal of catalyst and treatment of acidic effluent needs to be replaced by a green process. The current work reports on the activity of hierarchical zeolite Beta in the liquid phase acylation of toluene with acetic anhydride. The liquid phase reactions were carried out in the temperature range of 60–140 °C in an autoclave. The effect of various reaction parameters such as time-on-stream (TOS), mole ratio of reactants, catalyst loading, and reaction temperature on the rates of reaction has been investigated. Under the optimum reaction conditions the performance of hierarchical zeolite Beta was compared with nanocrystalline zeolite Beta. It was found that hierarchical zeolite Beta catalyst exhibit higher activity, which is due to the hierarchical porosity and to the nano size of the Beta zeolite catalyst particles allows faster diffusion of the products out of the catalyst.

Keywords: Zeolite, Beta Zeolite, Hierarchical Zeolite, Nanozeolite, Acylation, Toluene.

RESEARCH ARTICLE

1. INTRODUCTION

Friedel–Crafts acylation reactions are of great importance in the industrial production of aromatic ketones, and are used extensively in the production of fine and specialty chemicals as well as pharmaceuticals.[1, 2] Conventional acylations have been carried out by using homogeneous acid catalysts such as $AlCl_3$, $FeCl_3$, $ZnCl_2$, HF etc.[3] The use of these catalysts leads to many problems concerning handling, safety, corrosion and waste disposal. Indeed the major drawbacks linked with the effective utilization of these catalysts are environmental concerns due to the excessive generation of wastes along with corrosion problems, and the impossibility of regeneration. In addition, the formation of complexes between the acid catalysts and the produced ketone leads to a gradual loss of activity and a separation post-reaction is further needed to recover the formed ketone. Recently, the development and use of solid acid catalysts simplified the purification processes involved; therefore, considerable efforts have been made to develop heterogeneous processes using solid acid catalysts

such as zeolites, clays and heteropolyacids.[4–11] Attempts to replace homogeneous acids with their heterogeneous counterparts in fine-chemicals synthesis has recently been reported by Rhodia, which has established the first industrial application of zeolites for the acylation of anisole and veratrole, with HY and H-β zeolites as catalysts in a fixed bed process.[12–13]

It is evident from the literature that the zeolite catalyzed acylation of phenols and aromatic ethers is carried out with very good yields and selectivitys.[14–16] On the other hand, acylation of low activated aromatic rings like toluene and benzene are poorer using less reactive acylating agents, such as carboxylic acids and their anhydrides on zeolites.[17, 18] Thus, there still exists scope to develop better catalysts which would catalyze the acylation of toluene with excellent conversion and selectivity at comparatively lower temperatures.

Zeolites are currently studied for applications in the synthesis of organic compounds and fine chemicals. Zeolite materials are attractive as catalysts for the acylation reactions due to their acidity, shape selectivity and regenerability properties, etc.[19–21] Zeolite beta (BEA), a large-pore high-silica zeolite with a three dimensional (3-D) pore

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system has been demonstrated to be an active and selective heterogeneous catalyst for several liquid-phase reactions. Unfortunately, slow diffusion of reactants through commercial micro-porous zeolites makes them relatively poor catalysts in liquid phase.

Zeolites with a small particle size have exhibited attractive performances in a series of catalytic reactions such as hydro cracking of crude oil, hydroxylation of phenol, isomerization of xylene, and oligomerization of ethylene.[22–25] The decrease in the crystal size of zeolites can effectively improve their catalytic activity and stability.

This suggests that both activity and stability may be improved by using the zeolites of small crystal size and large external surface as catalysts in the acylation reaction. Nevertheless, nanocrystalline zeolite particles provide large external surface areas and shortening of the diffusion distances in the channels of the particles, thereby exposing the active surface for reaction and reducing deactivation. However, the crystals often easily aggregate and the mass transfer to and from the active sites located within the micropores can be slow, depending on diffusivities. It is thus advantageous to introduce meso- and even macropores into the zeolite materials.[26, 27] The introduction of mesopores or macropores into zeolites has recently been achieved using various methods.[28–34] The porosity of hierarchical materials is primarily controlled by varying the size of the nanocrystals. Therefore good control of nanocrystal size is a pre-requisite to control the porosity of the hierarchical materials. The macro pore size of the zeolite material can be flexibly tailored through a rational choice of the macro template.

The current study deals with the acylation of toluene using hierarchical zeolite Beta catalyst under autogenous pressure. The reaction parameters such as, time-on-stream, toluene:acetic anhydride molar ratio, catalyst quantity and reaction temperature were optimized. The influence of hierarchical zeolite Beta pore size on the catalyst performance has been studied.

2. EXPERIMENTAL DETAILS

2.1. Chemicals

Aluminium isopropoxide (AIP), Tetraethoxysilane (TEOS), tetraethylammonium hydroxide (TEAOH, 35% aq), were commercial samples from Merck and were used without further purification. Styrene butadiene rubber latex was purchased from Apar Industries, India.

2.2. Synthesis of Hierarchical Zeolite Beta and Nanocrystalline Zeolite Beta Catalyst

In order to synthesize of hierarchical zeolite Beta and nanocrystalline zeolite Beta, a hydrolysed clear sol of TEAOH-AlP-TEOS-H_2O was prepared at room temperature. The hierarchical zeolite Beta was fabricated using dual

template approach under controlled steaming at 200 °C. Tetraethyl ammoniumhydroxide (TEAOH) was used as a structure directing agent and styrene butadiene rubber (SBR) latex particles was used as macro pore template.

In a typical synthesis, a clear solution of zeolite was prepared by mixing tetraethyl ammonium hydroxide (TEAOH) and aluminium isopropoxide (AIP) and to the clear solution, tetraethylorthosilicate (TEOS), and DI water were added with stirring for 2 hrs. The molar composition of the resulting sol was 0.27 TEAOH/1 TEOS/0.02 AlPO/4 EtOH/15 H_2O. The pH of the final solution was 11.02. The clear sol was concentrated in a rotary evaporator at 80 °C as described in the literature.[32] The concentrated precursor sol was divided into two portions. To one portion of the concentrated sol, 0.3 g of SBR latex solid content was added and dried at room temperature. The other portion of the concentrated sol was dried at room temperature. The samples were steamed at 200 °C for 24 hrs. The steamed samples were calcined in air at 550 °C (5 h, 2 °C/min).

2.3. Characterization

Powder X-ray diffraction patterns were recorded on a Regaku 2000 diffractometer using Cu-Kα radiation from $2\theta = 2.5$ to 50° at a scan rate of 2°/min with a step size of 0.04°. Morphology and particle size of the zeolite nanocrystals were examined with Transmission electron microscopy (TEM; JEM-2010, 200 kV) and scanning electron microscopy (SEM; JEOL JSM-6500f) and. For TEM analysis, a drop of the diluted solution (0.0005 wt% g/water) was placed (placed a drop of ethanol and dried before placing sample) on carbon coated copper grid.

3. RESULTS AND DISCUSSION

3.1. Morphological and Structural Characterizations

The morphologies of hierarchical zeolite Beta and nanocrytalline zeolite Beta were analyzed by TEM and SEM and results are presented in Figure 1. Figure 1(a) shows the typical TEM image of synthesized nanocrytalline zeolite Beta. It is seen from the TEM images that the nanocrystals are grown in high density and possessing almost spherical shaped morphologies. The sizes for most of the nanocrystals are similar; however some bigger and smaller sized nanocrystals are also seen in the micrograph. The average particle size was found to be around 40 nm. Figures 1(b) and (c) exhibit the typical SEM images of hierarchical zeolite Beta. It is very clear from the SEM image that the zeolite mixed with SBR produced long-range ordered and well distributed macropores along the material (Fig. 1(b)). This was due to the fact that the zeolite precursors possess much silanol groups and they can interact more with the SBR and form a long-range macropore order material. The average size of the
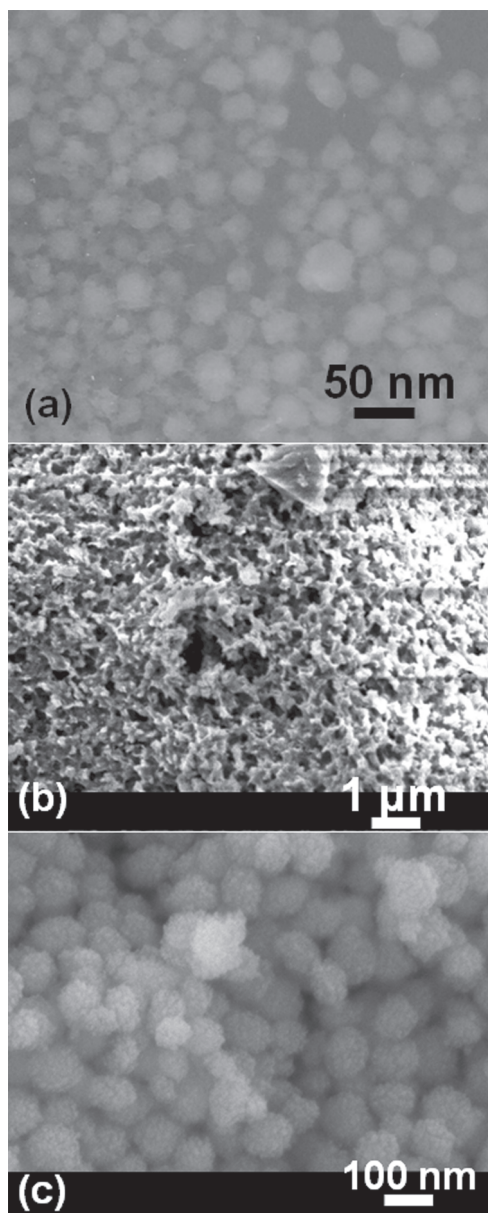
Fig. 1. Typical (a) TEM image of nanocrystalline zeolite Beta and (b) and (c) SEM images of hierarchical zeolite Beta.

Fig. 2. Typical XRD patterns for (a) hierarchical zeolite Beta and (b) nanocrystalline zeolite Beta.

hierarchical zeolite Beta is about 80 nm, which is almost double of nanocrytalline zeolite Beta (Fig. 1(c)).

The crystallinity and crystal phases of prepared hierarchical zeolite Beta and nanocrystalline zeolite Beta was observed by X-ray diffraction (XRD). The XRD analysis results of sample are shown in Figure 2. Figure 2(a) exhibits the typical XRD pattern for hierarchical zeolite Beta while Figure 2(b) shows the XRD pattern for nanocrystalline zeolite Beta. All the diffraction reflections and the interplanar spacings calculated from the XRD patterns are comparable and well matched with the reported values for zeolite Beta.[33] Interestingly, it is seen that the diffraction reflections in the XRD patterns for the prepared materials are broad compared to the diffraction reflections
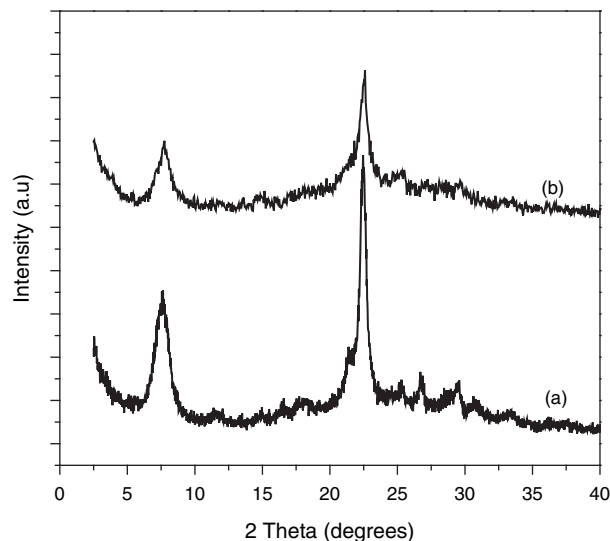
of the micrometric zeolite reported in the literature which provide a clear indication that the crystallites of the prepared crystalline materials are in nanoscale.

3.2. Catalyst Activity

Acylation of toluene by acetic anhydride was studied systematically using the synthesized hierarchical zeolite Beta samples as catalyst. The catalyst sample was activated before the reaction by heating for 3 h at 200 °C under N_2. The acylation of toluene catalyzed by hierarchical zeolite Beta catalysts were carried out in a Teflon autoclave under autogeneous pressure at 120 °C for 100 min. A mixture of 200 mmol of toluene and 10 mmol of acetic anhydride was added. The freshly activated catalyst (0.5 g) was added in an autoclave. The autoclave was placed in air oven and the contents were heated at a constant temperature at 120 °C. The products were analyzed by gas chromatographic analysis (Hewlett Packard 5890), using OV-101 column (2 m length, 1/8 inch dia) and FID detector. The major product of acylation of toluene was found to be *p*-Methylacetophenone (MAP) and only 1 to 3% of the ortho-substituted product was formed. Scheme 1 represents the reaction pathway of the acylation of toluene with acetic anhydride. The effect of various reaction parameters such as time-on-stream (TOS), mole ratio of reactants, catalyst loading, and reaction temperature on the rates of reaction has been investigated. Under the optimum reaction conditions the performance of hierarchical zeolite Beta was compared with nanocrystalline zeolite Beta.

3.2.1. Effect of Time on Stream on Catalytic Activity (TOS)

In the first step the influence of time-on-stream (TOS) on the conversion was studied using the catalyst hierarchical
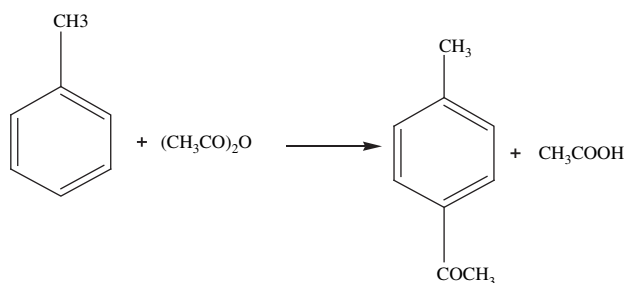
Scheme 1. Acylation of toluene with acetic anhydride.

zeolite Beta. Figure 3 shows the conversion of acetic anhydride converted into the acylated product with the reaction temperature at a time on stream (TOS) of 140 min. It was found that the conversion first increases with increasing TOS but remains practically constant after 100 min. Hence all further experiments were carried out for 100 min.

3.2.2. Effect of Mole Ratio

The effect of toluene to acetic anhydride mole ratio was studied at 10:1, 15:1, 20:1, 25:1 and 30:1 by keeping the total volume constant (Fig. 4). The conversion of toluene was found to increase till the toluene to acetic anhydride mole ratio was 20:1 and thereafter remained constant. This is probably due to the inhibiting effect of methylacetophenone, which can be strongly adsorbed on the catalyst.[18] The increasing conversion of acetic anhydride is attributed to the easy desorption methylacetophenone formed through the zeolite pores by the excess toluene. Further increase in molar ratio has no appreciable effect in Ac_2O conversion. Therefore, all reactions were studied by using a toluene to acetic anhydride mole ratio of 20:1.
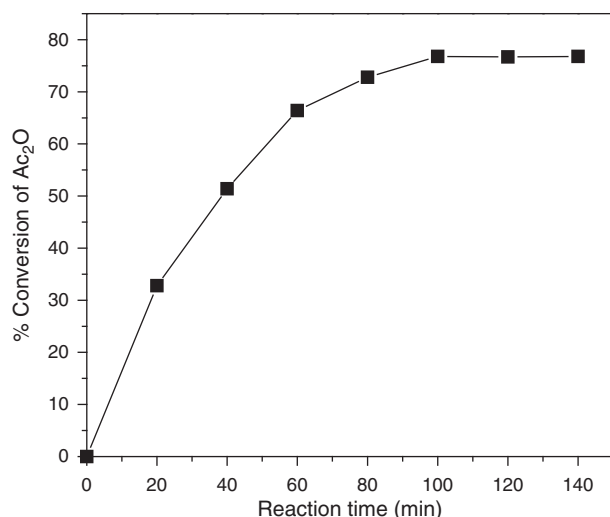

Fig. 4. Effect of catalyst quantity on catalytic activity of toluene with acetic anhydride (Ac_2O) over hierarchical zeolite Beta (TOS, 100 min; molar ratio of toluene: Ac_2O, 20:1; reaction temperature, 120 °C).

3.2.3. Effect of Catalyst Quantity

The effect of catalyst quantity was studied over a range of 0.1–0.7 g for acylation of toluene at 100 °C (Fig. 5). The conversion of acetic anhydride was found to increase with increase in catalyst amount, which is due to the proportional increase in the number of active sites and the 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 and so the conversion of acetic anhydride does not increase much. Hence all further experiments were carried out using 0.5 g catalysts.

3.2.4. Effect of Reaction Temperature

The effect of temperature was studied under otherwise similar reaction conditions in the range of 60–140 °C

Fig. 3. Effect of time-on–stream (TOS) on catalytic activity of toluene with acetic anhydride (Ac_2O) over hierarchical zeolite Beta (reaction temperature, 120 °C; catalyst, 0.5 g of hierarchical zeolite Beta; molar ratio of toluene: Ac_2O, 20:1).
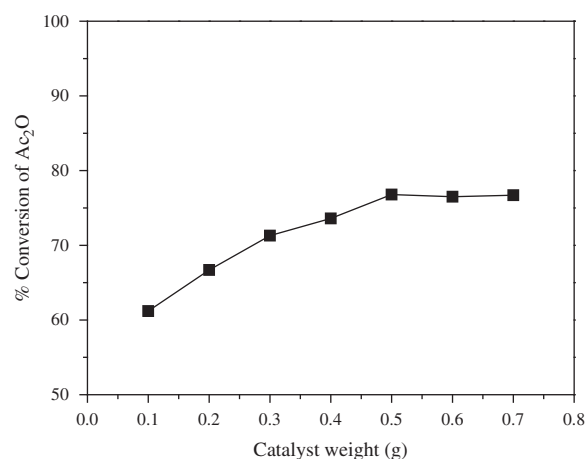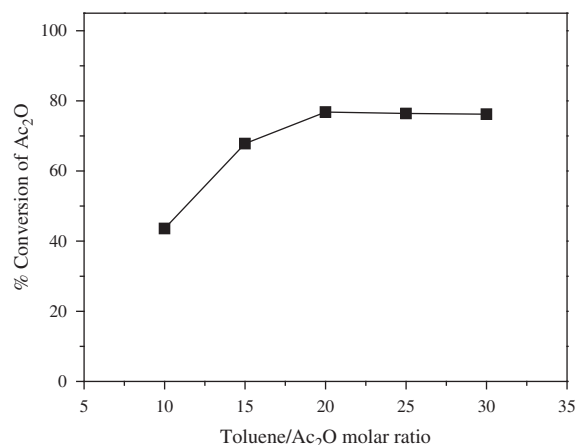

Fig. 5. Effect of molar ratio of toluene: Ac_2O on catalytic activity of toluene with acetic anhydride (Ac_2O) over hierarchical zeolite Beta (catalyst, 0.5 g of hierarchical zeolite Beta; TOS, 100 min; reaction temperature, 120 °C).
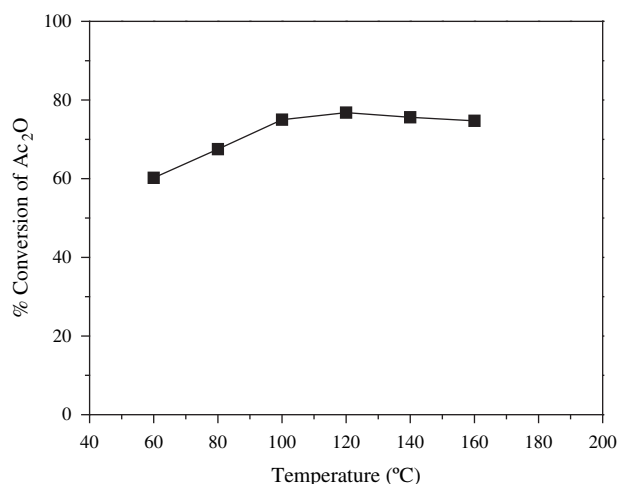
Fig. 6. Effect of temperature on catalytic activity of toluene with acetic anhydride (Ac_2O) over hierarchical zeolite Beta (TOS, 100 min; catalyst, 0.5 g of hierarchical zeolite Beta; molar ratio of toluene: Ac_2O, 20:1).

(Fig. 6). The conversion had been found to increase significantly with increasing temperature till 120 °C and afterwards a slight decrease in conversion of acetic anhydride was noticed due to the inhibiting effects of methylacetophenone which can be strongly adsorbed on the catalyst at higher temperature. 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.[18] Thus, 120 °C was found an optimum temperature.

3.2.5. Influence of Zeolite Properties

Table I compares the performance of two Beta catalysts having different particle sizes and pore sizes in the conversion of acetic anhydride for acylation of toluene. Although the particle size of the nanocrystalline zeolite Beta is smaller than that of the hierarchical zeolite Beta, the later exhibited higher catalytic activity for acylation of toluene. This can be explained on the basis of the macropore present in the nanocrystalline zeolite Beta catalyst.

It has been demonstrated that the hierarchical zeolites as catalysts exhibit excellent catalytic performances for many organic reactions.[34–37] This behavior of hierarchical zeolite Beta here can be ascribed to the improved efficiency by facilitating diffusion of reactants and as a result of better accessibility and less diffusion limitation.[26, 27] Further with zeolites of small particle sizes combined with macro pores as catalysts, the heavy products and ketones produced from

Table I. Influence of zeolite Beta particle and pore size on acylation of toluene with acetic anhydride.

S. no.	Catalyst	Ac_2O conversion (%)
1	Nanocrystalline zeolite beta	54.8
2	Hierarchical zeolite beta	76.8

the acylation of toluene can escape from the macro pores of zeolites much more easily and prevents the heavy products from occupying the active sites.

4. CONCLUSIONS

The present work covers the use of hierarchical zeolite Beta and nano-sized zeolite Beta catalysts for acylation of toluene with acetic anhydride. The catalysts were characterized for their structure by XRD, TEM and SEM. The effects of various parameters were studied on the conversion of acetic anhydride under otherwise similar conditions. The small crystal size of nano-sized zeolites may bring on more accessible active sites and then enhance the catalytic activity. Catalytic activity is strongly influenced by the pore size of the crystal too. The best catalyst for toluene acylation under study is hierarchical zeolite Beta catalyst. It can be concluded from the present investigations that the exposed pore openings in nano-sized zeolites allow a fast desorption of heavy products from the catalyst and can then reduce the occupancy of active sites by the adsorption of products. The present study shows that of hierarchical zeolite Beta catalysts has a potential replacement for conventional Lewis acid or mineral acid catalysts in a number of reactions.

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