

On the catalytic performance in isopropylation of benzene over H/ β zeolite catalysts: Influence of binder

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Abstract

A largely unsolved problem in environmentally detrimental waste products is utilization of flyash. Zeolite beta is synthesized using flyash as a source of silica and alumina. Isopropylation of benzene has been used as a probe reaction to evaluate the quality of flyash-based zeolite beta. Influence of the different percentages of alumina binder and formulations on the catalytic performance in isopropylation of benzene reaction over protonic forms of flyash zeolite beta (H/ β) has been investigated. It is also shown that, flyash based zeolite beta synthesis opens new possibilities for commercialization of environmentally detrimental product to cost-effective and eco-friendly catalyst of commercial interest.

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1. Introduction

New applications of flyash and recognizing new methods of recycling are very important. Elaboration of methods of transformation of flyash into zeolite catalysts is important because of the broad spectrum of industrial applications of zeolites.

Isopropylation of benzene is an industrially important petrochemical process as cumene is used as an intermediate for the production of phenol. In recent times cumene plants are being retrofitted using zeolite catalysts to avoid drawbacks from corrosion, handling, safety and environmental problems by replacing earlier Fridel-Crafts catalysts or solid phosphoric acid catalysts. Although several zeolites are reported to be active catalyst for cumene synthesis [1–5], zeolite beta was found to be quite valuable solid acid catalyst in various hydrocarbon conversion reactions on account of its unique structure, thermal stability, acidity and shape selective property [6–10]. However for commer-

cial applications, most of the zeolite catalysts have to be formulated by embedding zeolitic phase in a matrix especially in a suitable binder to provide enough mechanical strength in order to resist the attrition loss. Moreover, binder-zeolite interactions may lead to alterations in the overall performance of the catalyst. Although the use of a suitable binder in optimized quantity may provide an appropriate mechanical strength, it is crucial to monitor adequately the activity and selectivity of the catalyst depending on its formulation in suitable shape. Thus, it is a basic necessity to maximize the products yields and selectivity through judicious choice of suitable binder and shape of the final catalyst for developing an industrial zeolite catalyst. Correlations between catalyst composition with different percentages of alumina binders along with the shape of the final composite catalyst and the performance in isopropylation of benzene reaction need to be studied in detail. In this communication, such correlations are studied on the basis of evaluation of catalytic performance of catalyst composite materials containing flyash based zeolite H-beta and different percentages of alumina binder such as in the isopropylation of benzene reaction.

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Similarly, by varying the quantity of alumina binder, the formulation in different shapes such as pellets and extrudates were obtained and their influence on the catalytic performance in isopropylation of benzene using isopropanol as alkylating agent was also studied.

2. Experimental

2.1. Materials

The flyash beta samples were synthesized by using the procedure described earlier [11]. After completion of the crystallization the autoclave was taken out of the oven one by one and quenched to room temperature. The solid products were separated by suction filtration or by centrifugation, washed thoroughly with deionised water and then dried at 120 °C in a static air oven for 12 h. The crystallinity was evaluated by powder XRD profiles. The fully crystalline (100%), pure zeolite beta was obtained after a crystallization period of 96 h. In order to remove organic template, as-synthesized sample was then calcined at 550 °C for 10 h under flowing air. The temperature was increased from room temperature to 550 °C with the rate of 1 °C/min. The calcined sample thus obtained was further subjected for repetitive ion-exchange (three times) using 1 M ammonium chloride solution (in the proportion 15 ml per gm of solid) at 80 °C for 6 h. Excess salt was washed by deionised water until there was no detectable chloride ions, followed by drying at 120 °C in a static air oven overnight. These samples were further subjected to calcinations at 550 °C for 6 h under flowing air for converting them into protonic forms. The 100% crystalline beta phase was designated as parent sample. After converting in protonic forms the binder was added to the sample with the proportions of dry weight ratio of sample to binder ratio 90:10 designated as catalyst A, 80:20 designated as catalyst B, 70:30 designated as catalyst C, 60:40 designated as catalyst D and 50:50 designated as catalyst E. The final catalyst composite material was prepared by following several steps such as (1) preparation of 10 wt% slurry of binder and Parent zeolite separately by keeping it stirred for 1 h, (2) addition of slurry containing binder to the slurry containing Parent zeolite under vigorous stirring, (3) continuation of stirring for 2 h, (4) filtration, (5) washing and finally (6) drying at 120 °C in a static air oven overnight. The dried powder was then formulated into self-bonded pellet and then broken into pieces from which 10–20 mesh granules were collected for loading into the reactor.

The catalyst composite was also shaped in the extrudates form. The extrudates were prepared by mixing Parent sample and alumina as a binder keeping the proportion constant as mentioned above on dry weight basis. Acetic acid (3%) was added to this mixture till it formed a homogeneous paste. It was further peptized till the required consistency was achieved. This was then subjected to extrusion

using hand extrusion machine having 1.2 mm dia disc. The extrudates were dried and then calcined at 550 °C for 10 h in air atmosphere.

2.2. Methods

The phase purity and crystallinity of the samples were determined by powder X-ray diffraction (Rigaku D Max III VC, Japan) using Ni-filtered CuK α radiations. The % crystallinity of the sample was calculated by comparing the integrated area of the peak at $2\theta = 22.6^\circ$ to that of the most crystalline and pure Parent H-beta. The powder XRD patterns of phases in protonic forms were also collected to confirm whether any change/ structural damage has occurred during ion exchange and calcination processes. The morphologies were determined by scanning electron microscopy (JEOL, JSM-5200). Prior to the SEM measurements, the sample was mounted on a carrier made from glass carbon and coated with a film of gold. ^{27}Al MASNMR spectra were obtained from a Bruker MSL-300 NMR spectrometer with commercial MAS probe. The rotor was spun at 3 kHz. Chemical shifts were referred to external $\text{Al}(\text{H}_2\text{O})_6^{3+}$ in AlCl_3 aqueous solution. Typically 4000 free induction decays were accumulated with intervals of 1 s.

Isopropylation of benzene was carried out in a continuous, down-flow, fixed bed reactor at atmospheric pressure. 2.0 g catalyst was loaded in the reactor. Before the start of the reaction run, the catalyst was activated at 450 °C, for 8 h in air to drive off moisture and adsorbed organic material, if any. The reactant (benzene and isopropyl alcohol) was fed through a syringe pump (ISCO, USA) into the reactor at the desired reaction temperature. The analytical grade benzene and isopropyl alcohol (Merck India Ltd.) were used in this study. The products of benzene isopropylation were analyzed in a Shimadzu Gas Chromatograph (Model GC 15 A), fitted with Apiezone L (B.P. 1/1) column, using a flame ionization detector. The column employed was of 0.0032 m id \times 50 m length. The product distribution as a function of time on stream over all the H/beta catalysts was investigated at 210 °C with weight hour space velocity (WHSV) of 2.5 h $^{-1}$ and Feed (benzene: isopropanol) molar ratio of 6.5:1. Quantification of various products was accomplished using response factors of typical standard mixtures and the liquid mass balance was of the order of 98%.

3. Results and discussion

3.1. Characterization

3.1.1. Powder X-ray diffraction

The powder XRD pattern, Fig. 1, of the as-prepared parent sample matches well with the reported [12] confirming the well crystalline zeolite beta phase with no other impurity. The powder XRD patterns of the protonic forms of the parent and sample A after post-synthesis treatment

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