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Full Length Article

Enhanced catalytic properties of mesoporous mordenite for benzylation of benzene with benzyl alcohol

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ABSTRACT

Zeolite mordenite has been treated with nitric acid at different severities so as to facilitate the framework dealumination and optimization of the textural properties such as acidity and porosity. The samples obtained have been characterized by X-ray diffraction, FTIR, SEM, TEM, surface area, porosity by N_2 adsorption and ammonia TPD. The resultant samples have been evaluated towards the bulky alkylation reaction of benzylation of benzene with benzyl alcohol. The studies indicated the improvement in the textural properties such as surface area, pore volume and acidity of the samples after the acid treatment. While, the phenomenon of enhancement in properties was exhibited by all the acid treated mordenite samples, the highest improvement in properties was observed at a particular condition of acid treatment (SM-2 sample). This particular sample also exhibited highest acidity and the presence of ~10 nm size pores that resulted in the effective catalytic activity towards the bulky alkylation reaction of benzene with benzyl alcohol to produce high yields of di-phenyl methane.

1. Introduction

Acid catalyzed hydrocarbon conversions are major class of reactions used for the wide number of industrial applications related to petroleum, petrochemical, fine chemical and pharmaceuticals. Friedel-crafts alkylation is one of the important acid catalyzed reactions used for the production of large variety of alkylated aromatics [1,2]. The catalysts used for this reaction work under Liquid phase homogenous conditions where metal chlorides such as $ZnCl_2$, $AlCl_3$ in presence of HCl/H_2SO_4 has been traditionally applied for the bulk production of alkylated aromatics [3,4]. Here the liquid acids are very effective for conversion, but they also have drawbacks such as difficulty in separation of the liquid catalyst from the reaction medium, recovery of the liquid catalyst for its reuse, difficulty in handling and disposal of the catalyst, and corrosive and toxic nature of the liquid acids [5]. Zeolites, the microporous crystalline solid acid materials, stand as better alternative catalysts for this purpose. But, the restrictions involved in free entry and diffusion of molecules in the narrow micro pore channels of zeolites limit their catalytic applications for bulky molecular transformations [6]. Creation of mesopores in the microporous zeolites is the advanced concept available to expand their applications to such reactions [7].

Dealumination and desilication are the two important classes of post synthesis methods successfully adopted for the creation of mesopores in the zeolites [8,9]. Dealumination is widely used for low silica zeolites such as zeolite Y, where the dealumination is also observed to give extra stability to the zeolite framework (ultra stable Y) for industrial applications such as Fluid catalytic cracking (FCC), a well known proven refinery process. The purpose of desilication is especially for the creation of mesopores and unlike in dealumination, here the Al/Si ratio related with acidity increases [10]. The desilication method is adoptable for high silica zeolites such as BEA and ZSM-5. Overall, the post synthesis methods not only alter the porosity but also change the number (density of acid sites) and strength (heat of adsorption of individual site) of acid sites in the zeolites. It is interesting to study the combined effects of acidity and porosity of the modified zeolites on in aromatic alkylation reactions.

Benzylation of benzene in one of the important alkylation reactions used for the production of diphenyl methane, an important chemical for the agrochemical, fragrance, dye and polymer industries. Recently, this chemical also find applications as an additive to improve the lubricity and stability of the jet fuel. The wide pore BEA zeolite (Si/Al = 35.8) was reported to produce this compound from alkylation of benzene with benzyl alcohol in a continuous flow reactor [11]. Further improvement in catalytic performance of BEA was observed to occur by desilication of the BEA zeolite. The

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hierarchical Beta prepared by desilication method was observed to have enhanced catalytic activity towards the Friedel crafts alkylation [12]. Most of the studies were conducted on the BEA zeolite due to the presence of relatively wide pores when compared to the other zeolites ZSM-5 and mordenite. However, creation of mesopores can make ZSM-5 and mordenite zeolites suitable for bulky reactions. Recently, Jin et al. **s**tudied the effect of mesoporosity of ZSM-5 on the benzylation of aromatics with benzyl alcohol [13]. The studies indicated the effective formation of alkylated aromatics on mesoporous ZSM-5, whereas, the ZSM-5 without any mesopores encouraged the formation of dibenzyl ether as main product due to diffusion limitations in the narrow micropores.

It is known that for the application of zeolites for the production of diphenyl methane through alkylation reaction demands high acidity on one hand and large space around the active site (acid site) to facilitate bulky reaction. Zeolite mordenite is known to have high acid density and the acid strength due to its structure which made this zeolite suitable for low temperature applications in reactions such as light paraffin isomerization. But, the narrow pores in the side channels (8-membered ring) make it not suitable for bulky reactions. Our previous studies on the dealumination of mordenite through acid leaching resulted in the improvement in the pore system of the zeolite to give enhanced performance in the *n*-hexane isomerization reaction [14]. Surprisingly, the studies on mordenite zeolite for bulky alkylation reactions are scare except a recent report of Leng et al. on hierarchical mordenite [15].

In the present study, we would like to create the mesopores in the mordenite zeolite through acid leaching (dealumination) to see the changes in acidity and porosity aspects of the mordenite and their combined effect on the production of diphenyl methane through benzylation of benzene with benzyl alcohol. The purpose of selecting mordenite is to have high acid strength while the benzyl alcohol (rather than benzyl chloride) as alkylating agent to have environment friendly by product water. The reaction conditions adopted (80 °C) are milder to avoid the occurrence of any further framework dealumination in presence of water.

2. Experimental

2.1. Catalyst preparation

The mordenite powder (SAR = 16) obtained from Sud-chemie India Ltd., was used as parent H-mordenite sample (SM). The Nitric acid was used for the framework dealumination of the parent H-mordenite, where; the degree of dealumination is varied by varying the concentration on of nitric acid (1N, 2N and 3N) for the treatment of mordenite. The reaction was carried out in a round bottom flask, where 20 g H-mordenite powder was mixed with 200 ml nitric acid and refluxed at 100 °C for 1 h. During acid leaching water at room temperature was circulated through a condenser and the reaction temperature was maintained by heating mantel and controller. Washing with distilled water is needed because it replaces the mother liquor (nitric acid) present in zeolite pores and interparticular voids with pure water. Drying of the wet zeolite cake was conducted by allowing it at room temperature (25 °C) for 8 h and further dried at 100 °C for 7 h followed by calcination at 500 °C. The catalysts are named on the basis of the concentration of nitric acid used for the treatment of the mordenite, where SM-1, SM-2 and SM-3 represent the mordenite treated with 1N, 2N and 3N nitric acid respectively.

2.2. Physico-chemical characterization

X-ray powder diffraction (XRD) patterns were measured on PANalytical, Xpert PRO instrument, USA equipped with rotating anode and Cu Kα radiations. The measurements were conducted in continuous θ/2θ scan refraction mode. The anode was operated at 30 KV and 15 mA the 2θ angles were measured 5°–60° at the rate of 2°/min. The Scanning Electron Microscope (SEM) images were recorded for obtaining particle morphology on JEOL JSM-7900F instrument Japan. Transmission Electron Microscopy (TEM) images were recorded on JEOL, JSM-2100F instrument, Japan. The sample preparation involves the dispersion of the mordenite powder in the drops of ethanol (sonicate the sample in ethanol about 30 min for good dispersion) on a lacey carbon Formvar coated Cu grid and allow them to dry at room temperature (25 °C) overnight (12 h). The analysis carefully carried out and measurements were taken at low power (200 kV) so as to avoid any damage to the sample from the high energy electron beam.

The Fourier Transform Infrared (FTIR) spectra of the zeolite samples were recorded on Perkin-Elmer Frontier FTIR spectrometer USA, where, approximately 0.001 g of solid sample is well mixed into 0.1 g of Potassium Bromide (KBr) powder and pulverized the contents in the mortar well with a pestle to obtain a fine mixture. The resultant powder was pelletized using a pellet-forming die to obtain a transparent pellet. Degassing is performed to eliminate air and moisture from the KBr powder. Before forming the KBr powder into pellets, pulverize it to 200 mesh and then dry at approximately 110 °C for 2–3 h. The FTIR spectrum was recorded from 400 to 4000 cm^{-1} at 4 cm^{-1} resolution averaging over 100 scans. Background measurements on a pellet holder with a pellet of KBr only, that contains no sample, were taken to correct infrared light scattering losses in the pellet and for moisture adsorbed on the KBr.

The BET surface area, pore size and pore volume measurements of all the zeolite based catalysts were carried out using a standard adsorption equipment (ASAP 2020, Micromeritics Instruments Inc., Norcross, GA, USA) using N_2 gas (99.995% pure). For measuring above characteristics, 0.2 g of the sample is taken in a specially designed sample tube and degassed at 573 K under vacuum of 1.3×10^{-6} bar for 4 h A frit is attached to the mouth of the sample tube, so that when the sample tube is removed from the preparation mode, it does not allow the sample to expose in atmosphere. The sample is cooled to room temperature under vacuum and the sample tube is removed from the preparation port and attached to the analysis port of the instrument. For all the samples, N_2 adsorption desorption isotherms were obtained at 77 K and the temperature was maintained constant by using liquid nitrogen, whereas helium gas was used for measuring the dead space. The surface area, pore volume and pore size distribution were obtained by measuring the volume adsorbed at different P/P_0 values and by applying different methods. Total pore volume was estimated by measuring the volume of gas adsorbed at P/P_0 of 0.99 whereas, t-plot method was used to calculate the micro pore surface area (0–20 Å) using the Harkins-Jura equation [16]. The total micro pore volume (0–20 Å) and the micro pore size distribution were obtained by applying the Horvath-Kawazoe method (H-K). The acidity of the catalyst was measured by temperature programmed desorption of NH_3 (NH_3-TPD) using a Micromeritics chemisorbs 2750 pulse system. 0.1 g sample was used for each TPD experiment. It was carried out after of the catalyst sample was dehydrated at 500 °C in helium gas (30 cm^3 min^{-1}) for 1 h. The temperature was decreased to 100 °C and NH_3 was adsorbed by exposing sample treated in this manner to a stream containing 10% NH_3 in helium for 1 h at 100 °C. It was then flushed with helium for another 1 h to remove physicosorbed NH_3. The desorption of NH_3 was carried out in helium gas flow (30 cm^3 min^{-1}) by increasing the temperature upto 950 °C at 10 °C min^{-1} heating rate, measuring NH_3 desorption using TCD detector. The Si/Al wt% ratio of all the samples were measured by ICP-MS (DRE, PS-3000UV, LEEMAN LABS, INC.,USA) and SEM-EDX method.