



Enhanced performance of nano-crystalline ZSM-5 in acetone to gasoline (ATG) reaction

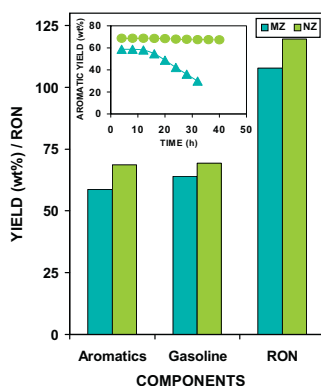
Nagabhatla Viswanadham*, Sandeep K. Saxena

Catalysis and Conversion Process Division, Indian Institute of Petroleum (Council of Scientific and Industrial Research), Dehradun 248 005, India

HIGHLIGHTS

- ▶ Nano-crystalline ZSM-5 (NZ) exhibits a twofold increase in pore volume.
- ▶ Enhanced catalytic performance of NZ in acetone to gasoline reaction.
- ▶ Cracking and remaking based mechanism to form toluene-rich aromatics.
- ▶ As high as 120 RON of product suitable for gasoline blending.
- ▶ Low C₉₊ hydrocarbon formation and enhanced catalyst stability of NZ.

GRAPHICAL ABSTRACT



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ABSTRACT

Two ZSM-5 zeolites exhibiting micro (MZ) and nano (NZ) range crystal size have been synthesized and evaluated for their activity towards acetone to gasoline (ATG) reaction. The NZ possessed comparable acidity with that of MZ, but a significant increase in porosity (twofold increase in pore volume) was observed in case of NZ. The hierarchical pore system in NZ was observed to be responsible for enhanced catalytic activity of this material in terms of higher aromatic yields, higher octane number and increased time-on-stream stability in acetone to gasoline reaction.

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1. Introduction

Recent trends in bio-mass conversion result in production of huge amount of alcohols, poly alcohols and ketones that demand efficient catalysts for their value addition [1–3]. Acetone is one of the important bi-products of bio-mass conversion [4,5] as well as cumene cracking process [6,7]. Aromatics find potential fuel applications due to their high octane number suitable for gasoline

blending that makes the acetone to gasoline (ATG) reaction important [8–11].

The medium pore ZSM-5 zeolite, by virtue of its properties especially acidity and porosity, is known for its activity towards aromatization of paraffins, isoparaffins, olefins and naphthenes present in variety of feedstocks [12–14]. Unlike the traditional dehydrocyclization of paraffins occur on noble metal loaded alumina and mixed oxide supports, the cracking and remaking path of paraffins in ZSM-5 provides opportunity to the production of aromatics even from the shorter hydrocarbons having less than 6 carbon atoms which has resulted in commercial success of

* Corresponding author. Fax: +91 135 2660202.

E-mail address: nvish@iip.res.in (N. Viswanadham).

important M2-forming [15], Cyclar process [16], Platforming process [17] and NTGG processes [18–20].

Synthesis of zeolites with hierarchical porosity such as micro-meso bi-modal, micro-meso-macro tri-modal porosity is of significant importance in recent years for catalytic applications where bulky molecular transformations are involved [21,22]. Though the main reaction occurs in the micropores, the presence of additional meso and macro pores can facilitate facile molecular diffusion. In our earlier studies, the hierarchical porosity created in nano-crystalline ZSM-5 was observed to influence the catalyst performance in cracking and aromatization of *n*-paraffins for the production of LPG and gasoline [23–25]. However, the chemical behavior of carbonyl group containing acetone is not similar to that of the *n*-paraffins as the reaction pathways and intermediates involved in the aromatization of these two reactants are different [26]. In order to check this aspect, in the present study, we considered two ZSM-5 based catalysts, MZ (normal micro range crystalline ZSM-5) and NZ (nano-crystalline ZSM-5) where attempts were made to explore the properties of NZ for ATG reaction. The NZ of present study contains zeolitic micropores (0.6 nm), mesopores (2–50 nm) and macropores (>50 nm). This is not the similar case with that of the large pore zeolites such as BEA and Y where only micropores of large diameter (~0.7 nm) are available. Hence, the NZ with its improved porosity properties is applied to the aromatization of acetone in the present study.

Here we report the improved aromatic yields with improved selectivity to toluene and decreased selectivity to C₉+ hydrocarbons in ATG reaction on NZ catalyst. Since, C₉+ species is known to be the precursor for coke formation, the NZ catalyst is also expected to give decreased coke lay down to improve the stability in activity of the catalyst with reaction time, that is indeed realized through the experimental studies on the NZ.

2. Experimental

2.1. Catalyst preparation

Two ZSM-5 zeolite based catalysts, have been prepared using micro-crystalline ZSM-5 (MZ) and nano-crystalline ZSM-5 (NZ) zeolites exhibiting Si/Al ratio of 30 synthesized in the laboratory.

2.1.1. Synthesis of microZSM-5 (MZ) sample

In this synthesis, sodium silicate (Merck) was used as silica source and sodium hydroxide was slowly added to this solution, followed by the addition of aluminum nitrate and tetrapropyl ammonium hydroxide (TPAOH, Merck). The components were mixed with constant stirring at room temperature. The pH of the resulting gel was then adjusted to 10.5 by adding 1:1 H₂SO₄ solution before charging it in Teflon lined autoclave for hydrothermal synthesis at 180 °C for 3 days [27].

2.1.2. Synthesis of nanoZSM-5(NZ) sample

In this synthesis method, the crystal size of the ZSM-5 is controlled by controlling the formation of silica and alumina precursors from their chemical sources, where aluminum nitrate solution is slowly added to the pre-cooled TPAOH solution (40%, Merck), followed by the drop-wise addition of Tetra ethyl orthosilicate (TEOS, Merck) with constant stirring. After adding all the ingredients, the solution was left to hydrolyze at room temperature for 41 h. The gel thus obtained was heated at 80 °C to evaporate water and ethanol formed during the hydrolysis of TEOS. The concentrated gel thus obtained was charged in a Teflon lined autoclave for hydrothermal synthesis at 170 °C for duration of 48 h [28].

All the synthesized samples were filtered and washed with deionized water, followed by drying at 100 °C and calcination at 500 °C for 4 h under vacuum. The powder forms of zeolites are converted into extrudates form by mixing with 40wt% of pseudo boehmite (neutral) alumina binder in powder form obtained from Sasol, Germany, followed by drying at 100 °C and calcination at 500 °C before using them for reaction [29,30].

2.2. Physico-chemical characterization

X-ray powder diffraction (XRD) patterns were measured on Rigaku Dmax III B equipped with rotating anode and Cu K α radiations. The measurements were conducted in continuous $\theta/2\theta$ scan refraction mode with 2θ angles 5–60° at the rate of 2°/min. The N₂ adsorption-desorption isotherms were measured at 77 K on ASAP (Model 2010) Micrometrics USA instrument. The BET surface area was calculated from linear part of plot according to IUPAC recommendations [31]. The Scanning Electron Microscope (SEM) pictures were recorded on Hitachi-S250 instrument. The acidity of the catalyst were measured by temperature programmed desorption of NH₃ (NH₃-TPD) using a Micromeritics chemisorb 2750 pulse system.

2.3. Catalyst evaluation studies

The acetone aromatization reactions are conducted in a fixed bed down flow reactor by loading 5.0 g of catalyst in the center of the reactor. Extrudates of α -alumina were loaded above and below the catalyst bed. The feed was introduced with WHSV of 2.3 h⁻¹ in a continuous flow using N₂ as carrier gas. The reactions were conducted at atmospheric pressure and 400–450 °C temperature. The product obtained at the end of the reactor was cooled using water circulator and the gas and liquid forms of products thus obtained were analyzed using Varian capillary column, CP Al₂O₃/KCl (50 m \times 0.53 mm \times 10 μ m) and Petrocal DH, 100% dimethyl polysiloxane as stationary phase (100 m \times 0.25 mm \times 0.5 μ m) respectively.

3. Results and discussion

The XRD patterns of both MZ and NZ illustrate the formation of well crystalline ZSM-5 (Fig. 1A). The SEM images of the samples (Fig. 1B and C) confirm the formation of nanometer range (~30 nm) crystals in NZ when compared to the micro range obtained in MZ. The sample NZ exhibited very high pore volume and surface area that is significantly contributed by the presence of mesopores and macropores (Table 1 and Fig 2A). In the adsorption/desorption isotherms, a loop formation observed between 0.5 and 1.0 of P/P_0 in case of MZ, while there is a steep jump with a big desorption loop appeared in case of NZ. The hysteresis loop of NZ appears at a high relative pressure ($P/P_0 = 0.9 - 1.0$) representing the presence of inter-crystalline voids created by the packing order of nanocrystals (Fig. 2A). The quantity of nitrogen gas adsorbed is also increased more than three fold in case of NZ. It is well known in the literature that the hierarchical porosity in zeolites can be created either through intra-crystalline pores as observed in case of carbon templating synthesis procedures or through the inter-crystalline pores obtain as in case of nano-crystalline materials due to the systematic ordering of the packing of nanocrystals that create voids among the crystals [22]. In the present study, the detailed pore size distribution of the samples are derived from Horvath-Kawazoe (HK) method (up to 20 Å) and BJH methods (20 to >500 Å). The comprehensive pore size distribution data indicate the increase in volume in the entire range of micro, meso and macro pores of NZ, starting from <10 Å to > 500 Å (Table 1). However, the major increase is observed in the pores with

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