Applied Catalysis A: General 493 (2015) 129–141

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Synthesis of industrially important aromatic and heterocyclic ketones using hierarchical ZSM-5 and Beta zeolites

Rajkumar Kore[a], Rajendra Srivastava[a,*], Biswarup Satpati[b]

[a] Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar 140001, India
[b] Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata 700 064, India

ARTICLE INFO

Article history:
Received 17 August 2014
Received in revised form 1 January 2015
Accepted 2 January 2015
Available online 10 January 2015

Keywords:
Hierarchical zeolites
Solid acid catalyst
Acylation
Benzoylation
Aromatic ketones
Heterocyclic ketones

ABSTRACT

Hierarchical ZSM-5 and Beta zeolites were investigated in the synthesis of wide range of industrially important aromatic/heterocyclic ketones by Friedel–Crafts acylation and benzoylation reactions. For comparative study, conventional ZSM-5 and Beta, and amorphous mesoporous Al-MCM-41 were investigated. Hierarchical zeolites were prepared by multi-ammonium structure directing agents whereas conventional zeolites were prepared by mono-ammonium structure directing agents. Among the catalysts investigated in this study, hierarchical Beta exhibited the highest reactant conversion in the acylation and benzoylation reactions. In this study, the systematic assessment of the catalytic activity of acid catalysts for wide range of aromatic and heterocyclic compounds is shown under one umbrella. To the best of our knowledge, these reactions over hierarchical zeolites (ZSM-5 and Beta) are reported here for the first time. Structure activity relationship is explained based on the physico-chemical properties, molecular size, reactivity of reactants, and reaction mechanism. Catalysts can be easily recovered and reused with negligible loss in the catalytic activity.

1. Introduction

Aromatic ketones are synthetic intermediates for the production of fine chemicals, pharmaceuticals, agrochemicals, fragrances, flavors, dyes, etc. [1]. In general, aromatic ketones are synthesized by the Friedel–Crafts acylation reaction using acid catalysts. Friedel–Crafts acylation is considered to be one of the fundamental reactions in chemistry and applied in the preparation of several synthetic intermediates of industrial importance. One such interesting example is the synthesis of the antirheumatic Naproxen, which is produced by the Friedel–Crafts acylation of 2-methoxynaphthalene into 2-acetyl-6-methoxynaphthalene and subsequent Willgerodt–Kindler reaction [1–3]. Acid catalyzed Friedel–Crafts acylation based research articles have been published in wide range of chemistry and chemical engineering journals [4–16]. Initially, conventional homogeneous Lewis acids ($AlCl_3$, $FeCl_3$, BF_3, $ZnCl_2$, $TiCl_4$, etc.) and Brönsted acids (HF, H_2SO_4, etc.) were used [7,8]. These reagents have several disadvantages such as use of excess amount (more than the stoichiometric amount) and corrosiveness. This led to produce a large amount of corrosive waste streams or inorganic salt as a by-product. Moreover, the catalyst was not recyclable. Further, efforts have been made to prepare substances (lanthanide trifluoromethanesulfonates alone, micro-encapsulated on polyacrylonitrile and graphite) that can be used in catalytic amount for this reaction [9–11]. Emphasis was made to develop solid acid based heterogeneous catalysts due to their easy separation and recyclability, which makes the process economical and eco-friendly. A wide range of heterogeneous solid acid catalysts such as zeolites, mesoporous molecular sieves, clays, heteropoly acids, zirconia, Nafion and metal oxides are known [12,13]. Among these materials, zeolites have shown promising activity in the Friedel–Crafts acylation reactions due to their strong acidity [14–17].

Zeolite catalyzed chemical processes solved several obstacles associated with petroleum refinery industry due to the strong acid strength and shape selectivity. For example, in industrial practice, zeolites are used in fluid catalytic cracking [18–20]. However, role of the conventional microporous zeolites is restricted in the reactions requiring large organic molecules due to diffusion constraints. In petroleum/fine chemical industry, deactivation of the catalyst is a serious concern [21–26]. In the recent past, efforts have been made to improve the diffusion in the zeolites by inserting mesoporosity or reducing the zeolite thickness to unit cell dimension [27,28]. Top down and bottom up approaches were made to prepare zeolites with inter/intra-crystalline mesopores [29,30]. Soft and hard templates both were used to prepare mesoporous zeolite [31,32].

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[*] Corresponding author. Tel.: +91 1881 242175; fax: +91 1881 223395.
E-mail address: rajendra@iitrpr.ac.in (R. Srivastava).

http://dx.doi.org/10.1016/j.apcata.2015.01.002

When organosilanes were added in the synthesis composition of conventional zeolites, hierarchical/nanocrystalline zeolites were obtained [27,28,33–35]. Zeolite with structural feature as small as the size of unit cell (≈10 nm) can be prepared with multi-quaternary ammonium based soft-templates [36]. Our research group also developed soft template based synthesis strategies for the preparation of disordered mesoporous zeolites of different framework structures [37–39]. We recently reported the synthesis of ordered zeolite nanosheets using 1,4-diazabicyclo[2.2.2]octane (DABCO) based multi-quaternary structure directing agents (SDA) [40].

An acid catalyst is believed to be a good catalyst if it exhibits good activity in acylation and benzoylation reactions. Several reports are available in the literature, which deals with the acylation of aromatic substrates such as anisole and 2-methoxy naphthalene [14,15,41]. However, to the best of our knowledge, there is no report in the literature, which covers a wide range of substrates investigated under identical reaction conditions. In this study, applications of the hierarchical zeolites (Beta and ZSM-5) were investigated in the acylation and benzoylation reactions for the synthesis of industrially important aromatic and heterocyclic compounds. Catalytic activities of hierarchical zeolites were compared with conventional microporous zeolites (ZSM-5 and Beta) and amorphous mesoporous aluminosilicate (Al-MCM-41). In this study, catalytic activities of hierarchical zeolites are shown for a wide range of aromatic and heterocyclic compounds under one umbrella.

2. Experimental

2.1. Material preparation

Three different ZSM-5 materials with Si/Al = 50 were prepared. DABCO based multi-quaternary SDA (represented as SDA-1, Fig. 2) was used to synthesize nanosheet hierarchical ZSM-5 (hereafter represented as Hier-ZSM-5 (A)) by following our reported procedure [40]. Another type of hierarchical ZSM-5 (hereafter represented as Hier-ZSM-5 (B)) was prepared using tetrapropyl ammonium hydroxide (TPAOH) as a SDA but in the presence of propyltriethoxy silane as an additive by following the reported procedure [28]. Conventional ZSM-5 (hereafter represented as ZSM-5) was prepared by following the reported procedure using tetrapropyl ammonium bromide (TPABr) [42]. Two different Beta materials, hierarchical Beta and conventional Beta with Si/Al = 20 were prepared. Hierarchical Beta (hereafter represented as Hier-Beta) was prepared using piperidine based di-quaternary SDA (represented as SDA-2, Fig. 2) by following our reported procedure [37]. For comparative catalytic activity, conventional Beta (represented as Beta) was prepared using tetraethylammonium bromide (TEABr) [43].

For comparative catalytic investigations, amorphous mesoporous aluminosilicate, Al-MCM-41 with Si/Al = 50 was prepared by following the reported procedure using cetyltrimethylammonium bromide as SDA [44].

For catalytic investigations, calcined Na-form of material (2 g) was ion-exchanged (thrice) into the NH_4-form by using 1 M aqueous NH_4NO_3 solution (100 mL) at 353 K for 4 h. H-form of material was obtained by the calcination of NH_4-form of material at 823 K for 6 h.

2.2. Material characterization

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–50° (0.5°/min for ZSM-5 samples and 2°/min for other samples) for wide angle and 0.5–5° for low angle (scan speed = 1°/min) on a PANalytical X'PERT PRO diffractometer using Cu Kα radiation ($\lambda = 0.1542$ nm, 40 kV, 40 mA) and a proportional counter detector. N_2-adsorption measurements were performed at 77 K by Quantachrome Instruments Autosorb-IQ volumetric adsorption analyzer. The specific surface area of zeolites was calculated from the adsorption data points obtained at P/P_0 between 0.05 and 0.3 using the Brunauer–Emmett–Teller (BET) equation. The pore diameter was estimated using the Barret–Joyner–Halenda (BJH) method. Scanning electron microscopy (SEM) measurements were carried out on a JEOL JSM-6610LV to investigate the morphology of the zeolites. The detailed TEM structural analysis of the developed morphologies were carried out using FEI, Tecnai G^2 F30, S-Twin microscope operating at 300 kV equipped with a GATAN Orius CCD camera. The sample was dispersed in ethanol using ultrasonic bath, mounted on a carbon coated Cu grid, dried, and used for TEM measurements. Acidity was examined by temperature-programmed desorption (TPD) with ammonia. Before TPD experiments, catalyst was pre-treated in He (50 mL/min) at 873 K for 1 h. After cooling down to 343 K, a mixture of NH_3 in He (10:90) was passed (75 mL/min) at 343 K for 1 h. Then, the sample was subsequently flushed by He stream (50 cm^3/min) at 373 K for 1 h to remove physisorbed ammonia. The TPD experiments were carried out in the range of 373–973 K at a heating rate of 10 K/min. The ammonia concentration in the effluent was monitored with a gold-plated, filament thermal conductivity detector.

2.3. Procedure for catalytic reactions

2.3.1. Acylation reaction

In a typical acylation reaction, substrate, acetic anhydride and catalyst (activated at 473 K) were mixed in a 25 mL round bottom flask. Reactions were conducted at a desired temperature for a stipulated time period. The reaction mixture was analyzed using gas chromatography (GC) (Yonglin 6100; BP-5; 30 m × 0.25 mm × 0.25 μm). Reactant conversion and product selectivity were obtained using GC. Products were confirmed using GC–MS (Schimadzu GCMS-QP 2010 Ultra; Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 μm). In most of the cases, products were also confirmed by the authentic samples obtained from Aldrich (based on the retention time of the authentic sample in the GC analysis). In the case of indole acylation, products were also confirmed using NMR.

2.3.2. Benzoylation reaction

In a typical benzoylation reaction, substrate, benzoylating agent (benzoic acid or benzoyl chloride) and catalyst (activated at 473 K) were mixed in a 25 mL round bottom flask. Reactions were conducted at a desired temperature for a stipulated time period in solvent/neat condition. The reaction mixture was analyzed using GC. Reactant conversion and product selectivity were obtained using GC. Products were confirmed using GC–MS. In most of the cases, products were also confirmed by the authentic samples obtained from Aldrich (based on the retention time of the authentic sample in the GC analysis).

3. Results and discussion

3.1. Catalyst characterization

Wide angle XRD patterns of Hier-ZSM-5 (A), Hier-ZSM-5 (B), and ZSM-5 show diffraction patterns corresponding to the MFI framework structure (Fig. 1a). XRD diffraction peaks were broad for Hier-ZSM-5 (A) and Hier-ZSM-5 (B) when compared to ZSM-5, which confirms that the materials are nanocrystalline in nature [40,42,43]. One could clearly observe the doublet at approx 45° (2θ) in the ZSM-5 and Hier-ZSM-5 materials. Furthermore, three