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Effect of method of preparation on the activity and selectivity of iron phosphate catalyst in the ammoxidation of 2-methyl pyrazine

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Abstract

Ammoxidation of methylpyrazine (MP) to cyanopyrazine (CP) was performed at 633–693 K over iron phosphate catalysts having a P/Fe ratio of 1.2, obtained by adopting different methods of catalyst preparation. The catalysts were characterized by XRD, FTIR, UV-DRS, laser-Raman spectroscopy, TPR, TEM, XPS, acidity by Potentiometric titration and TPD of NH_3. XRD and Raman data suggested predominant formation of quartz phase of iron phosphate. The structure and texture of the catalysts varied with the nature of starting material as well as the preparation method. The catalytic activity depended on the extent of quartz phase formation. Precipitation in the basic medium improved quartz phase formation and enhanced the activity. However, the decreased acid strength caused reduction in nitrile selectivity. A judicious combination of the redox and acid strength properties is required for obtaining maximum yield of CP.

Keywords: Iron phosphate; Ammoxidation; 2-Methyl pyrazine; 2-Cyano pyrazine

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1. Introduction

The heterogeneously catalyzed vapor phase ammoxidation of alkyl aromatics and hetero alkyl aromatics to their corresponding nitriles is an industrially important reaction. The products are valuable intermediates in the synthesis of several dyestuffs, pesticides and pharmaceuticals [1]. Amidopyrazine, often referred to as pyrazinamide, is an important anti-tubercular drug. It is conventionally prepared by a non-catalytic multi-step process which is economically as well as environmentally disadvantageous [2]. Vapor phase processes are advantageous compared to liquid phase reactions in terms of continuous processing, easy catalyst handling, homogeneity of the reaction mixture and environmental acceptability [3]. Ammoxidation refers to the interaction of ammonia with reducible organic material (alkyl aromatics or heteroalkyl aromatics, Scheme 1) in the presence of oxygen [4]. For this reaction the catalyst should possess both acidic and redox functionalities [5]. Even though, iron phosphate possesses both acidic and redox properties as molybdenum and vanadium phosphates, it has received less attention [6,7] for ammoxidation. Very few references exist on its characterization and catalytic application. An adsorption–desorption study by Gadgil and Kulshreshtha [8] reveals that both Bronsted and Lewis acid sites are present in $FePO_4$ catalyst. Ai et al. [9–12] have reported the effects of method of preparation of iron phosphate catalyst and its unique catalytic performance at a P/Fe atomic ratio of 1.15–1.2 for oxidative dehydrogenation reactions.

As a part of our on going study on ammoxidation of methylpyrazine (MP), we have recently reported [13] the activity and selectivity functionalities of iron phosphate prepared with different P/Fe atomic ratios ranging from 1 to 1.6, and revealed that the $FePO_4$ with a P/Fe atomic ratio of 1.2 offers highest selectivity towards cyanopyrazine (CP) (98%). The aim of the present study is to explore a suitable method of preparation by means of which the conversion could be enhanced, still retaining the superior selectivity. Iron phosphate catalysts with a fixed P/Fe atomic ratio of 1.2, prepared by different methods have been examined in order to establish the structure-activity relationship.

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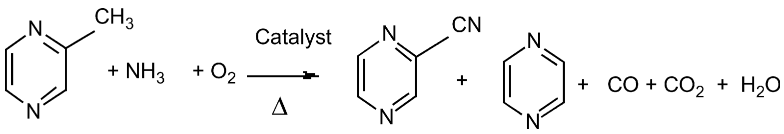

Scheme 1.

2. Experimental

2.1. Preparation of catalysts

Iron phosphate catalysts, with a constant P/Fe atomic ratio of 1.2, were prepared by the following methods:

2.1.1. Method A

$Fe(NO_3)_3{\bullet}9H_2O$ was dissolved in water and dilute urea solution was added to precipitate iron hydroxide gel. The precipitate was filtered and the gel was mixed with desired amount of 85% H_3PO_4. The mixture was boiled slowly for 1–2 h and then the excess water was evaporated to yield a paste.

2.1.2. Method B

In this method $FePO_4$ was synthesized from a mixture of $Fe(NO_3)_3{\bullet}9H_2O$ and $NH_4H_2PO_4$. Aqueous solutions of iron nitrate and ammonium dihydrogen phosphate, in appropriate quantities were mixed and the solution was evaporated at 363 K.

2.1.3. Method C

Appropriate quantities of $Fe(NO_3)_3{\bullet}9H_2O$ and 85% H_3PO_4 were mixed in water and the excess water was subsequently evaporated.

2.1.4. Method D

The preparation was similar to Method B. However, $(NH_4)_2HPO_4$ was used instead of $NH_4H_2PO_4$.

2.1.5. Method E

In this method ammonia was used instead of urea for the precipitation and the rest of the procedure was the same as in Method A. The catalyst masses were subjected to air-drying at 393 K for 12 h before calcination in air at 823 K for 4 h. The finished catalysts were named correspondingly as catalysts A, B, C, D and E based on the method of preparation.

The Fe concentration in the catalysts, as determined by the AAS analysis, agreed well with that of the amount of iron taken in the solution for preparation. (295 mg/l in the solution vs. 286 ± 5 mg/l of the finished catalysts.)

2.2. Characterization of fresh catalysts

BET surface areas of the catalysts were determined on a Micromeritics (Auto Chem-2910) instrument with nitrogen physisorption at 77 K, taking 0.169 nm^2 as the cross sectional area of dinitrogen. XRD patterns of the catalysts were obtained with a Rigaku Miniflex diffractometer, using Cu Kα radiation (1.5405 Å) at 30 kV and 150 mA.The average crystallite size was determined from the XRD patterns using the Scherrer equation [14]. The extent of quartz phase formation, as represented by the area of the peak at $2\theta = 25.8$ Å in the X-ray difractogram, was calculated as reported by Nagaraju et al. [13]. FTIR spectra were recorded on a DIGILAB (USA) spectrometer, with a resolution of 1 cm^{-1} using KBr disc method. The iron content was determined by atomic absorption spectroscopy using a Perkin–Elmer Analyst 300 double beam spectrometer. The powders were first dissolved in acidic solution (aquaregia) and diluted to concentrations within the detection range of the instrument.

Diffuse reflectance spectra of the catalysts samples were recorded in the UV–vis region (200–800 nm) with GBC Cintra 10_e spectrometer with a slit width of 1.5 nm and a scan speed of 400 nm/min. The Raman spectra of the samples were collected on a UV–vis Raman spectrometer system (Horiba-Jobin Yvon LabRam-HR) equipped with a confocal microscope, 2400/900 grooves/mm gratings, and a notch filter.

Transmission electron microscope (TEM) photographs were obtained using Tecnai-12 FEI instrument operating at 120 kV. Temperature programmed reduction (TPR) of the catalysts was carried out in a flow of 10% H_2/Ar mixture gas at a flow rate of 30 ml/min with a temperature ramp of 10 K/min. Before the TPR run the catalysts were pretreated with Ar at 523 K for 2 h. The hydrogen consumption was monitored using a thermal conductivity detector.

XPS measurements of the catalysts were conducted on a Kratos axis 165 apparatus equipped with a dual anode (Mg and Al) using the Mg Kα source. The carbon 1s binding energy of 284.6 eV was used as a reference for determining the binding energies.

The acid strength of the solid samples was measured by the potentiometric titration method [15,16]. Temperature programmed desorption of ammonia (TPD) was performed using 100 mg of catalyst after pretreatment at 573 K under a dry He flow (50 cm^3/min). The catalyst was exposed to NH_3 from a gas mixture containing 10% NH_3 in He for 45 min at 373 K and the excess NH_3 was removed under a He flow (50 cm^3/min). The temperature of the sample was raised at a rate of 10 K/min up to 1073 K, and the desorbed gas was monitored by using a gas chromatograph with a TCD detector.

2.3. Catalytic reaction

The ammoxidation was carried out in a fixed-bed flow reactor under vapor phase at atmospheric pressure in the temperature range of 633–693 K, with a molar ratio of MP:water:ammonia:air = 1:13:17:38 using 3 g of catalyst and an MP flow rate of 2 ml/h. The detailed procedure is available elsewhere [13].