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Unique vapor phase synthesis of 1,2,3,5,6,7-hexahydrodicyclopenta[*b*,*e*]pyridine selectively over Co–Al-MCM-41

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Abstract

Cyclization of cyclopentanone, formaldehyde and ammonia in vapor phase gives 1,2,3,5,6,7-hexahydrodicyclopenta[*b*,*e*]pyridine (HHDCP) and spiro[cyclopentane-1,8′-(1′,2′,3′,5′,6′,7′,8′,8′a) octahydrodicyclopenta[*b*,*e*]]pyridine (SCOHDCP) over zeolites HY, HZSM-5, Hβ and mesoporous Al-MCM-41 molecular sieves. The preliminary screening of catalysts clearly shows that Al-MCM-41 is more suitable for the vapor phase synthesis of HHDCP. As the NH_3-TPD profiles of Al-MCM-41 show wide range distribution of acid sites in the temperature range of 200–600 °C (weak–medium–strong), Al-MCM-41 is further modified with transition metal ions like V(V), Mn(II), Fe(III), Co(III), Cu(II), La(III) and Ce(III) to fine tune the acid sites. Correlation of activity and selectivity of transition metal modified Al-MCM-41 with the NH_3-TPD profiles show that though the conversions are high, selectivity of either HHDCP or SCOHDCP is a preference of acid site strength formed on metal ion modification. Interestingly Co^{2+} ion modification of Al-MCM-41 resulted distinctly into two sets of acid sites with T_{max} around 218 °C (weak–medium) and 673 °C (strong). The reaction is studied on Co–Al-MCM-41 by adsorbing pyridine at 300 °C. The typical acidity available on pyridine adsorbed Co–Al-MCM-41 around 300 °C is showing cyclization activity forming only HHDCP indicating that weak–medium acid sites are responsible for the formation of HHDCP. Based on the product distribution plausible reaction mechanism is proposed.

Keywords: Cyclization; Co–Al-MCM-41; Annulated pyridines; Cyclopentanone

1. Introduction

The drive for green chemistry has led to the synthesis of novel materials with an endure application. Zeolites of different classes, mesoporous molecular sieves and mesoporous oxides are being exploited in developing greener and cleaner technologies [1–3]. The recent trend is designing materials for specific applications.

Annulated pyridines and their derivatives are an important class of organic compounds being fully represented in a plethora of natural products. They provide valuable synthetic templates for the preparation of new compounds with specific biological or material properties. The annulated nitrogen heterocyclics, bearing pyridine constitute a class of biologically active compounds that are potent anti-inflammatory agents [4], anti-bacterial agents [5], inhibitors of gastric acid secretion [6] and calcium channel blockers [7]. Conventionally diannelated pyridines are prepared by partial hydrogenation of isooxazole over Raney nickel catalyst to β-amino acrolein, which on Friedlander condensation with cyclopentanone gives 2,3-fused pyridines [8]. Tabyaoui *et al.* [9] synthesized bis-annulated pyridines from cycloalkane carboxaldehyde which on reaction with NaN_3 gave azides. Further reaction of azides with

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triphenyl posphines gave iminophosphoranes, which on thermolysis gave bis annulated pyridines. Unfortunately most of the methods earlier reported require several steps and the yields are low. Obviously an eco-friendly, single step synthetic method, which allows entry into these annulated systems is highly desirable.

Catalysis division at IICT-Hyderabad has established a specialty in synthesizing important drugs and drug intermediates using zeolites and modified zeolites [10–14]. The present investigation is a part of such on-going activity describing the vapor phase synthesis of 1,2,3,5,6,7-hexahydrodicyclopenta[*b*,*e*]pyridine an important anti-ulcer agent [15] selectively over modified Al-MCM-41.

Vapor phase synthesis using heterogeneous catalysts is gaining importance due to advantages in comparison to homogenous catalysts highlighting continuous production, simplified product recovery, catalyst regenerability, without liquid waste, etc. The present paper is a first report of vapor phase synthesis of HHDCP selectively over a heterogeneous catalyst using cheaper raw materials cyclopentanone, formaldehyde and ammonia in a single step. The cyclization reaction involves the condensation of 2 mol of cyclopentanone and 1 mol of formaldehyde in presence of ammonia forming 1,2,3,5,6,7-hexahydrodicyclopenta[*b*,*e*]pyridine (HHDCP) as a main product and the by-product spiro[cyclopentane-1,8′-(1′,2′,3′,5′,6′,7′,8′,8′a)octahydrodicyclopenta[*b*,*e*]]pyridine (SCOHDCP), as shown in Scheme 1.

The work involves mainly three aspects: (1) identifying a material with suitable acidity and acid site strength for cyclization to proceed, (2) optimization of various reaction parameters (3) further shaping the catalysts (like metal modification) to achieve high selectivity and (4) proposing a mechanism based on product distribution. The above aspects are investigated to develop a catalyst for the selective synthesis of HHDCP.

2. Experimental

2.1. Preparation of catalysts

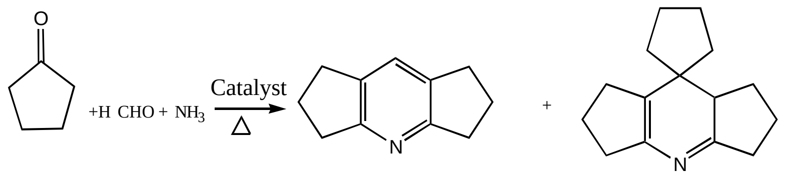
HY (2.6) zeolite was obtained from PQ Corporation USA. The HZSM-5 (30) zeolite was supplied by the Conteka Sweden. Hβ (20) was obtained from Sud-Chemie, India. Al-MCM-41 molecular sieves were prepared with varying Si/Al ratio (∼15.5–150) in the laboratory, as described earlier [12]. An aqueous solution of aluminum isopropoxide (0.76 g) and sodium hydroxide were taken in a 50 ml beaker and stirred while heating till a clear solution appeared. Then 9.4 ml of tetra ethyl ammonium hydroxide (TEAOH) was added to the solution while cooling under stirring (solution A). Simultaneously the required amount of tetraethylorthosilicate was taken in another beaker in 50-ml water (solution B) and then solution A was added slowly to solution B with stirring. After stirring for 2 h, hexadecyltrimethyl ammonium bromide (HDTAB) 10.55 g was added slowly to the above mixture. Finally the gel mixture having the molar composition of $SiO_2{:}xAl_2O_3{:}2.2HDTAB{:}3.16TEAOH{:}1.89Na_2O{:}615H_2O$ (x varies with Si/Al ratio) was transferred in to an autoclave and heated at 100 °C for 24 h. The recovered product was calcined at 500 °C in air for 12 h to expel the imprisoned template.

The Al-MCM-41 is modified by metal ions like V(V), Mn(II), Fe(III), Co(III), Cu(II), La(III) and Ce(III) during synthesis to increase the number of Bronsted protons (acidity) by incorporating metal ions in the framework as the acidity of the molecular sieve plays a crucial role in shaping the activity. Corresponding nitrate or acetate salts of the metals are taken as precursors. The $Si/M = 50$ is maintained in all the M-Al-MCM-41 catalysts. The method of preparation is similar to that of Al-MCM-41 except that the metal precursor is dissolved in NaOH and aluminum isopropoxide solution before adding TEAOH. All the catalysts were characterized by various techniques like XRD, BET-surface area, NH_3-TPD and UV–Vis DRS techniques.

2.2. Characterization

The diffraction patterns of the Al-MCM-41 and modified Al-MCM-41 catalysts were recorded with Siemens D-5000 X-ray diffractometer using Cu Kα radiation. UV–Vis-diffuse reflectance spectroscopy with a sphere reflectance measurements were recorded on Cintra 10_e spectrometer using pellets of 50 mg sample ground with 2.5 g of KBr. BET surface areas were measured in all glass high vacuum system by N_2 adsorption at 77 K.

Temperature programmed desorption studies were also conducted on Auto Chem 2910 (Micromeritics USA) instrument. In a typical experiment for NH_3-TPD studies about 300 mg of oven dried sample (dried at 383 K for over night) was taken in a U-shaped quartz sample tube. Prior to TPD studies, the catalyst was pretreated at 473 K for



1,2,3,5,6,7-hexahydrodicyclopenta[b, e] pyridine (HHDCP)

Spiro[cyclopentane-1,8'-(1',2',3',5',6' 7',8',8'a-octahydrodicyclopenta[b, e]pyridine (SCOHDCP)

Scheme 1.