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Chemoselective hydrogenation of unsaturated nitriles to unsaturated primary amines: Conversion of cinnamonitrile on metal-supported catalysts



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ABSTRACT

The liquid-phase hydrogenation of cinnamonitrile to selectively obtain the unsaturated primary amine (cinnamylamine) was studied at 383 K and 13 bar on Ni, Co, Ru and Cu metals supported on a commercial silica. Ni/SiO₂ and Co/SiO₂ were the most active catalysts for cinnamonitrile conversion but formed only small amounts of cinnamylamine. In contrast, Cu/SiO₂ and Ru/SiO₂ presented low activity for cinnamonitrile hydrogenation but formed selectively cinnamylamine in the liquid phase; nevertheless, on both samples the carbon balance was only about 40%. In an attempt of promoting the rate and yield to cinnamylamine, additional catalytic runs were carried out at higher temperatures and H₂ pressures on a highly dispersed Cu(11%)/SiO₂ catalyst prepared by the chemisorption–hydrolysis method. Results showed that when cinnamonitrile hydrogenation was performed at 403 K and 40 bar on Cu(11%)/SiO₂, the yield to cinnamylamine was 74% giving as by-product only the unsaturated secondary amine (dicinnamylamine).

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1. Introduction

The liquid-phase selective hydrogenation of unsaturated nitriles on solid catalysts is an important route to obtain unsaturated primary amines that are valuable intermediates in agrochemical, pharmaceutical, and fine chemicals industries [1,2]. Nevertheless, the selective hydrogenation of the C=N group in unsaturated nitriles is still a challenging objective in heterogeneous catalysis [3]. In general, the hydrogenation of unsaturated nitriles may form three types of products: unsaturated amines (hydrogenation of C=N bond), saturated nitriles (hydrogenation of C=C bond) and saturated amines (hydrogenation of C=C and C≡N bonds). Besides, in order to obtain selectively primary amines the coupling reactions leading to secondary and tertiary amines have to be avoided. Previous works have reported that C=C bonds are more reactive to hydrogenation than the nitrile groups [4,5] and therefore selective C=N hydrogenation in presence of double bonds is difficult to achieve, in particular when both unsaturated groups are conjugated or in close proximity [6]. Most of the few papers dealing with the hydrogenation of unsaturated nitriles on solid catalysts

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have been carried out on Ni and Co-based catalysts [4,5,7,8], probably because both metals are highly active and selective to obtain saturated primary amines from the corresponding saturated nitrile [9-11]. However, in the case of unsaturated nitriles, Raney Ni and Co catalysts promote the preferential hydrogenation to the corresponding saturated nitrile rather than to the unsaturated primary amine [3]. Thus, in an attempt of tuning the Ni(Co) selectivity to the formation of unsaturated primary amines, Cr-doped Raney Ni(Co) catalysts and amorphous Ni(Co)-B alloys were employed, but significant yields to the unsaturated amine where obtained only when alkaline or ammonia solutions were co-fed to the reactor [3,6,12]. Ammonia is often employed to suppress the formation of higher amines by shifting equilibrium to the primary amine since ammonia is released in the coupling reactions leading to secondary and tertiary amines; nevertheless, the addition of ammonia entails concerns related to corrosion and disposal of spent base materials.

Cinnamonitrile has been used as a substrate molecule to study the hydrogenation of α,β -unsaturated nitriles [3,6]. In this compound, the C=C bond is in conjugation with the nitrile as well as with the phenyl group. In Scheme 1 we present a possible reaction network of the cinnamonitrile conversion to primary and higher amines according to [3]. Cinnamonitrile (CN) may be initially hydrogenated in the C=C bond to yield hydrocinnamonitrile (HCN) or in the C=N group producing cinnamylamine (CA), the desired unsaturated primary amine, probably via the formation of an imine intermediate (cinnamylimine). CA may then react with the

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Scheme 1. Probable reaction network of cinnamonitrile conversion reactions

imine intermediate to form by deamination the unsaturated secondary amine dicinnamylamine (DiCA) and partially unsaturated secondary amine hydrocinnamyl-cinnamylamine (HCCA). Otherwise, CA may be hydrogenated to the saturated primary amine (hydrocinnamylamine, HCA). Similarly, in parallel pathways, HCN may be hydrogenated to HCA or it may react with the imine intermediate (hydrocinnamylimine) to produce by deamination the saturated secondary amine (dihydrocinnamylamine, DiHCA) and partially unsaturated secondary amine HCCA. According to bibliography, the highest yields to CA (\approx 70%) from cinnamonitrile hydrogenation have been obtained on Cr-doped Raney cobalt catalysts at 373 K, using 14% NH₃ in methanol and 80 bar H₂ [3].

In this work, we investigate the selective hydrogenation of cinnamonitrile to CA on silica-supported Co, Ni, Ru and Cu metals. In our catalytic tests, we detected and identified all the compounds depicted in Scheme 1, excepting the highly reactive imine intermediates. The goal of our work was twofold: (i) to establish the effect of the nature of the metal on the catalyst activity and selectivity for selectively obtaining CA from cinnamonitrile hydrogenation; (ii) to achieve high CA yields from cinnamonitrile conversion by selecting efficient metal-supported catalysts and optimizing reaction operating conditions, without using ammonia in the reaction media. Results will show that Cu/SiO₂ catalyst remarkably promotes the selective formation of CA from cinnamonitrile, thereby yielding 74% of CA at 403 K and 40 bar H₂, in absence of ammonia.

2. Experimental

2.1. Catalyst preparation

Co/SiO₂, Ni/SiO₂, Cu/SiO₂ and Ru/SiO₂ catalysts were prepared by supporting Co, Ni, Cu, or Ru on a SiO₂ powder (Sigma–Aldrich G62, 60–200 mesh, $300 \text{ m}^2/\text{g}$) by incipient-wetness impregnation at 303 K. Metal nitrate solutions $[Co(NO_3)_2 \cdot 6H_2O \text{ Aldrich 98\%}, Ni(NO_3)_2 \cdot 6H_2O \text{ Fluka 98\%}, Cu(NO_3)_2 \cdot 3H_2O \text{ Anedra 98\%}]$ were used for impregnating Co, Ni, and Cu while Ru/SiO₂ was prepared by using RuCl₃·H₂O (Aldrich 99.98\%). The impregnated samples were dried overnight at 373 K, then heated in air at 5 K/min to 673 K and kept at this temperature for 2 h. Cu/SiO₂-I and Cu/SiO₂-II catalysts were obtained by supporting Cu on Grace Davison Davisil (grade 634, 320 m²/g) and Merck (chromatographic, 366 m²/g) silicas, respectively, using the chemisorption–hydrolysis method as detailed elsewhere [13]. The support was added to a solution containing $[Cu(NH_3)_4]^{2+}$ and the slurry was slowly diluted with water. Then, solids were separated by filtration, washed with water, dried overnight at 383 K and calcined in air at 623 K for 4 h.

2.2. Catalyst characterization

BET surface areas (S_g) were measured by N₂ physisorption at its boiling point in a Micromeritics Accusorb 2100E sorptometer. Elemental compositions were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES), using a Perkin-Elmer Optima 2100 unit. Powder X-ray diffraction (XRD) patterns were collected in the range of $2\theta = 10-70^{\circ}$ using a Shimadzu XD-D1 diffractometer and Ni-filtered Cu K α radiation. Oxide crystallite sizes were calculated using the Debye–Scherrer equation.

The temperature programmed reduction (TPR) experiments were performed in a Micromeritics AutoChem II 2920, using 5% H₂/Ar gaseous mixture at $60 \, \mathrm{cm^3/min}$ STP. The sample size was 150 mg. Samples were heated from 298 to 973 K at 10 K/min.

The metal dispersions (D_M , surface M atoms/total M atoms) of Ni/SiO₂ and Ru/SiO₂ were determined by H₂ chemisorption. Volumetric adsorption experiments were performed at 298 K in

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