



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



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ABSTRACT

The liquid-phase hydrogenation of cinnamionitrile 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 cinnamionitrile conversion but formed only small amounts of cinnamylamine. In contrast, Cu/SiO₂ and Ru/SiO₂ presented low activity for cinnamionitrile 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 cinnamionitrile 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

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 were 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.

Cinnamionitrile 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 cinnamionitrile conversion to primary and higher amines according to [3]. Cinnamionitrile (CN) may be initially hydrogenated in the C=C bond to yield hydrocinnamionitrile (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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