Selective liquid-phase hydrogenation of acetophenone and 1indanone over Cu-based catalysts

Nicolás M. Bertero, Carlos R. Apesteguía, Alberto J. Marchi*

Grupo de Investigación en Ciencias e Ingeniería Catalíticas (GICIC) – Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE) – Facultad de Ingeniería Química – Universidad Nacional del Litoral (UNL) - CONICET, Santiago del Estero 2654, (3000) Santa Fe, Argentina.e-mail: amarchi@fiq.unl.edu.ar

Introduction

Aromatic alcohols are important intermediates in the synthesis of pharmaceuticals and fine chemicals. In particular, 1-phenylethanol and 1-indanol are of industrial importance because they are used in the production of medicines, agrochemicals, perfumes, catalysts, etc. [1,2]. These alcohols can be produced in high yield by reduction of the C=O group of the ketones using complex metal halides such as NaBH₄, LiAlH₄ y KBH₄ [3]. However, these homogeneous processes are environmentally unfriendly due to the production of a high amount



of toxic, polluting and corrosive wastes. In this sense, the liquid-phase hydrogenation of acetophenone and 1-indanone (Figure 1) over Cu-based catalysts is proposed as an eco-compatible alternative for producing 1-phenylethanol and 1-indanol.

Figure 1. Reaction scheme for the hydrogenation of 1-indanone.

Experimental

Cu/SiO₂ catalyst was prepared by incipient wetness impregnation using aqueous solutions of 0.57 M Cu(NO₃)₂ and a commercial silica [1]. Cu-Zn-Al catalyst was prepared by coprecipitation at pH=7, as described elsewhere [4]. Samples characterization was performed by employing XRD, TPR, N₂ physisorption at 77 K and H₂ chemisorption. Catalytic tests were carried out in liquid phase at 363 K and 10 bar, in a 600 ml batch reactor, using 1 g of catalyst, 0.025 mol of acetophenone/1-indanone and 150 ml of cyclohexane as solvent. Reaction products were analyzed ex-situ by gas chromatography using a capillary column and FID.

Results/Discussion

Characterization results show that the catalysts have different physicochemical properties (see Table 1). Cu/SiO_2 contains large metal particles with low metal-support interaction and low

capacity for H_2 chemisorption. On the contrary, Cu-Zn-Al sample has small metal particles interacting strongly with the spinel phase with high capacity for H_2 chemisorption [4].

 Table 1. Characterization results for the Cu-based catalysts.

Catalyst	Metal load (%)	Phase XRD	L _{CuO} (Å)	$\frac{S_g}{(\mathbf{m}^2/\mathbf{g})}$	V_P (cm ³ /g)	T _{MAX} TPR (K)	$\frac{V_{H2}}{(\text{cm}^3/\text{g})}$
Cu/SiO ₂	8.0	CuO	190	230	1.10	536	0.32
Cu-Zn-Al	11.8	Spinel	-	221	0.46	575	1.51

Catalytic tests indicate that 1-indanone hydrogenation is faster than acetophenone hydrogenation over both catalysts. The time for total ketone (ONE) conversion is lower with the Cu-Zn-Al than with Cu/SiO_2 (Figure 2). In addition, an induction period is clearly seen for the ONE hydrogenation over Cu-Zn-Al catalyst. It is likely that ONE adsorption over small Cu



particles is much slower than over large ones. Then, initially, the C=O hydrogenation is delayed in the case of Cu-Zn-Al. Respect to the product distribution, it is observed that the alcohol (NOL) yield depends stronger on the reactant molecule than on the Cu-based catalyst. In the acetophenone hydrogenation, NOL was the only product over both catalysts. However, in the case of 1-indanone hydrogenation, minor quantities of indane (ANE) were detected due to hydrogenolysis of NOL. Nevertheless, both Cu/SiO₂ and Cu-Zn-Al are highly selective to the alcohol, showing NOL vields between 85 and 97%.

Figure 2. Hydrogenation of acetophenone (a,b) and 1-indanone (c,d) over Cu/SiO₂ (a,c) and Cu-Zn-Al (b,d) catalysts.

In summary, acetophenone and 1-indanone are selectively hydrogenated in liquid phase to the alcohol over Cu/SiO_2 and Cu-Zn-Al catalysts using mild conditions, being Cu-Zn-Al more active. This reveals the potential of these eco-friendly catalysts for producing fine chemicals.

References.

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