



Liquid phase selective hydrogenation of cinnamaldehyde over copper supported catalysts

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ABSTRACT

The selective hydrogenation of cinnamaldehyde is carried out in a batch reactor, at 100 °C and 1 MPa of H₂ using isopropyl alcohol as the solvent, over a series of copper supported catalysts: Cu/Al₂O₃, Cu/SiO₂, Cu/MCM-48, Cu/CeO₂ and Cu/ α -Fe₂O₃. The selectivity of the samples is compared with that corresponding to Pt/SiO₂. Reduced Cu/Al₂O₃ and Cu/SiO₂ showed lower selectivity to the cinnamyl alcohol (16–22%) than Pt/SiO₂ (35%), at 15% of conversion. Following a calcination at 300 °C both, activity and selectivity of copper catalysts were increased. The calcined surface would hydrogenate C=O bond by hydrogen transfer from the solvent. TPR, XRD and FTIR of adsorbed CO showed that Cu (I) species are stabilized on the mesoporous structure of MCM-48. This particular feature renders Cu/MCM-48 a selective catalyst, reaching high selectivity values (51%, at 15% of conversion). Cu/CeO₂ and Cu/ α -Fe₂O₃ showed higher selectivity than Pt based catalyst due to a promotion of the catalytic properties of copper by reduced support species.

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1. Introduction

The selective hydrogenation of α,β -unsaturated compounds is a reaction of paramount importance in the field of organic synthesis. The most important product is the unsaturated alcohol which is employed in the synthesis of cosmetic, pharmaceutical and fine chemicals. Metal hydrides have been employed to carry out this reaction for industrial purpose [1]. However due to environmental, economical and technical considerations, heterogeneous catalysts should be preferred. Traditionally, supported noble metal catalysts have been employed due to their relative high selectivity [1–6].

Supported copper catalysts are an interesting option to perform selective hydrogenation reactions due to the low cost of the metal combined with advantageous catalytic properties of copper for selective hydrogenation reactions [7–12]. From kinetic studies performed over Pt, Cu and Pd catalysts supported on silica, Pham et al. clearly observed that the hydrogenation of C=O bond is faster than that of C=C bond over Cu/SiO₂ catalysts than over Pd/SiO₂ or Pt/SiO₂ for the hydrogenation of 2-methyl-2-pentenal, though this effect is masked for high conversion level [11]. On the other hand, Marchi et al. [13] concluded that Cu/SiO₂ and binary Cu–Al catalysts were unselective toward the hydrogenation of carbonyl bonds,

producing predominantly hydro-cinnamaldehyde during the liquid phase hydrogenation of cinnamaldehyde on Cu-based catalysts. In the same work the author observed that ternary Cu–Zn–Al and quaternary Cu–Ni(Co)–Zn catalysts were more selective than Cu/SiO₂. Cationic species of the promoter (Zn, Ni, Co) were considered to be the responsible for the creation of selective sites for the hydrogenation of C=O. In the same sense, the group of Hutchings concluded that Cu/Al₂O₃ preferentially hydrogenates carbon–carbon double bond, though the modification by sulfur compounds leads to a selective catalyst. The creation of selective Cu⁰–S and Cu⁺ sites is the origin of the high selectivity [7,8].

The present study investigates a series of copper supported catalysts for the selective hydrogenation of α,β -unsaturated aldehydes. Inert support (SiO₂, γ -Al₂O₃ and MCM-48) as well as supports possessing redox properties (CeO₂ and α -Fe₂O₃) was selected for supporting copper. It is speculated that the very different nature of the support would lead to different copper species, from morphological and from chemical aspects.

The most part of the chemical catalytic reactions that are particularly important in the preparation of pharmaceutical or fine chemicals are performed in the liquid phase, under constant H₂ pressure. For this reason the catalysts are tested for the hydrogenation of cinnamaldehyde and crotonaldehyde, in a batch reactor using H₂ as the reductant and isopropanol as the solvent. The selectivity to the unsaturated alcohol (the desired product) as well as the activity of the different samples is measured. The catalytic results are discussed in the light of the characterization results, obtained

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