

Vapour phase hydrogenation of cinnamaldehyde over silica supported transition metal-based bimetallic catalysts

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Received 22 September 2005; received in revised form 10 November 2005; accepted 16 November 2005

Available online 22 December 2005

Abstract

A series of silica supported transition metal-based bimetallic catalysts $M-M^1/SiO_2$ ($M=Co, Ni, \text{ and } Cu; M^1=Ni, Cu, \text{ and } Co$) were prepared by deposition–precipitation method. Nitrate salts of the corresponding transition metals and colloidal silica were used as the precursors. The physicochemical characteristics of the prepared catalysts were investigated by means of X-ray powder diffraction, thermogravimetry, FT-infrared, scanning electron microscopy-energy dispersive X-ray analysis, and BET surface area techniques. These catalysts were evaluated for selective hydrogenation of cinnamaldehyde to cinnamyl alcohol in the vapour phase at normal atmospheric pressure. Among the various catalysts investigated, the $Cu-Co/SiO_2$ combination catalyst exhibited very promising results for the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol, whereas $Co-Ni/SiO_2$ and $Ni-Cu/SiO_2$ bimetallic catalysts provided good yields of hydrocinnamaldehyde.

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Keywords: Bimetallic catalysts; $Co-Ni/SiO_2$; $Ni-Cu/SiO_2$; $Cu-Co/SiO_2$; Selective hydrogenation; Cinnamaldehyde; Cinnamyl alcohol; Hydrocinnamaldehyde

1. Introduction

Research in heterogeneous catalysis is increasingly focused on the chemo- and regio-selective catalytic hydrogenation of α,β -unsaturated carbonyl compounds to produce fine chemicals [1,2]. The selective hydrogenation of α,β -unsaturated carbonyls is a key step in the manufacture of pharmaceuticals, flavors and fragrances [3–7]. The hydrogenation of $C=C$ bond to yield saturated carbonyls is thermodynamically favored and can be readily achieved with high selectivity. However, the selective hydrogenation of $C=O$ bond to provide unsaturated alcohols is much more difficult to achieve [3]. Cinnamaldehyde selective hydrogenation is one such important commercial reaction, which gives cinnamyl alcohol, hydrocinnamaldehyde and phenyl propanol as products. Cinnamyl alcohol is a valuable chemical in the perfumery industry for its odour and fixative properties. It is, also, used as an intermediate in the pharmaceuticals for the synthesis of antibiotic-chloromycetin [8,9]. Recently, hydrocinnamaldehyde has been found to be an important intermediate in the preparation of pharmaceuticals used in the treatment of HIV [10,11].

Although various attempts have been made in the literature to develop a suitable catalytic system for selective hydrogenation of cinnamaldehyde to cinnamyl alcohol or hydrocinnamaldehyde, the selectivity is still an important issue [12,13]. Industrial relevance of unsaturated alcohols in conjunction with economically constraining methods based on chemical reduction of unsaturated carbonyl compounds calls for the development of new catalysts for selective preparation of unsaturated alcohols [14].

A few articles can be found in the literature on the use of group VIII metals deposited over oxidic supports for selective hydrogenation of α,β -unsaturated aldehydes [3,15–17]. Conventional catalysts based on metals such as nickel, palladium or rhodium are almost unselective towards unsaturated alcohols [3]. Although, ruthenium itself is just moderately selective, and similar or better selectivities can be achieved with osmium, iridium or platinum catalysts [18]. Palladium catalyst is known to be effective for the selective hydrogenation of α,β -unsaturated aldehydes to saturated aldehydes. However, such selective reactions are quite problematic when the carbon–carbon double bond

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of an unsaturated aldehyde is conjugated both to a carbonyl group and an aromatic ring [12,19]. The high costs of precious metals, their limited availability, sensitivity to sulfur poisoning, and the decrease of selectivity at high temperatures have long been motivated the search for better substitute catalysts [20]. Additionally, it was found that the catalyst deactivation rate in monometallic catalysts is significant and hence the low stability predominates [21]. Therefore, in the field of hydrogenation bimetallic catalysts are often used in order to improve selectivity and stability of a single component catalyst [22].

In general, supported bimetallic catalysts are very interesting materials because one metal can tune and/or modify the catalytic properties of the other metal as a result of both electronic and structural effects [22]. Bimetallic catalysts supported on high surface area carriers, such as, silica and alumina, have attracted considerable attention recently because of their better performance in catalytic reactions which differs significantly from that of the corresponding monometallic counterparts [21]. Additionally, the preparation of supported bimetallic catalysts (by deposition–precipitation) may lead to catalysts with new characteristics, where a specific interaction between the two metals could produce a hybrid catalyst whose behavior may differ from that of the catalysts prepared by conventional methods. In order to achieve absolute selectivity towards unsaturated alcohols, the promotion of either the C=O double-bond polarization and/or the inhibition of the α,β -unsaturated aldehyde adsorption through the C=C bond is necessary and this could be achieved by the presence of two metals in a given catalytic system. So far several reports have appeared on the liquid phase hydrogenation of cinnamaldehyde under different reaction conditions [6–22]. Nevertheless, a few studies have been realized in the gas phase with well-defined metal surfaces. Hydrogenation of crotonaldehyde and methyl crotonaldehyde (prenal) have been studied over Pt(1 1 1) and PtFe(1 1 1) single crystals [23,24]. However, no such attempts can be found in the literature on the vapour phase hydrogenation of cinnamaldehyde. In the present study, a series of transition metal-based bimetallic M–M¹/SiO₂ (M = Co, Ni, and Cu; M¹ = Ni, Cu, and Co) catalysts were prepared by deposition–precipitation method, characterized by TGA, BET SA, XRD, FT-IR and SEM-EDX techniques, and evaluated for hydrogenation of cinnamaldehyde to cinnamyl alcohol in the vapour phase at normal atmospheric pressure.

2. Experimental

2.1. Catalyst preparation

A series of silica supported transition metal-based bimetallic catalysts M–M¹/SiO₂ (M = Co, Ni, Cu and M¹ = Ni, Cu, Co) were prepared by deposition–precipitation method. Both the metals (M–M¹) were loaded in 1:1 mole ratio (based on metals) keeping the loading amount constant at 20 wt.% w.r.t. SiO₂. In a typical preparation, the requisite quantities of the respective nitrate precursor salts were dissolved in deionized water and mixed together. To this mixture solution, required quantity of colloidal silica was added and the resulting slurry was stirred for several hours to obtain homogeneity. Subsequently,

the homogenized slurry was titrated with aqueous ammonia until pH 8.5. Thus, precipitated gel was filtered, washed several times and dried at 393 K before subjecting to calcination treatment at 723 K for 4 h. A small portion of the above catalyst was further calcined at 873 K for 4 h to evaluate the thermal stability.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of various samples were recorded on a Siemens D-5000 diffractometer, using Ni-filtered Cu K α (0.15418 nm) radiation source. Crystalline phases were identified by comparison with the reference data from International Centre for Diffraction Data (ICDD) files. The BET surface areas were measured by N₂ adsorption using a Micromeritics Gemini 2360 instrument. Prior to analysis, samples were oven dried at 393 K for 12 h and flushed with Argon gas for 2 h. The FT-IR spectra were recorded on a Nicolet 740 FTIR spectrometer at ambient conditions, using KBr disks, with a normal resolution of 4 cm⁻¹ and averaging 100 spectra. Scanning electron microscopy analyses were carried out with a Jeol JSM 5410 microscope, operating with an accelerating voltage of 15 kV. SEM micrographs were taken after coating by gold sputtering. Elemental analysis was carried out on a Kevelex, Sigma KS3 EDX instrument operating at a detector resolution of 137 eV. The DTA–TGA measurements were made on a Mettler Toledo TG-SDTA apparatus. Sample was heated from ambient to 1273 K under nitrogen flow and the heating rate was 10 K min⁻¹.

2.3. Catalyst evaluation

The vapour phase selective hydrogenation of cinnamaldehyde was carried out in a down flow vertical fixed bed differential quartz micro-reactor (i.d. 10 mm) at normal atmospheric pressure. In a typical experiment, ca. 0.3 g of catalyst with twice the amount of quartz was secured between two plugs of quartz wool. Ceramic beads were filled above the catalyst bed, which act as preheating zone. The reactor was placed vertically inside a tubular furnace, which was heated electrically. The reactor temperature was monitored by a k-type thermocouple with its tip located near the catalyst bed and connected to a temperature-indicator-controller. Prior to reaction, the catalyst was pre-reduced in flowing H₂ for 3 h. Cinnamaldehyde was fed (1–3 ml h⁻¹) from a motorized syringe pump (Perfusor Secura FT, Germany) into the vapourizer where it was allowed to mix uniformly with H₂ gas (20 ml min⁻¹) before entering the preheating zone of the reactor. The liquid products collected through spiral condensers in ice-cooled freezing traps were analyzed by a gas chromatograph using SE-30 packed column and FID detector. The activity data were collected under steady-state conditions. The conversion, selectivity, and yield were calculated as per the procedure described elsewhere [25].

3. Results and discussion

The N₂ BET surface areas of various bimetallic catalysts prepared in this investigation and calcined at 723 and 873 K

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