



Controlling hydrogenation of C=O and C=C bonds in cinnamaldehyde using silica supported Co-Pt and Cu-Pt bimetallic catalysts

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ABSTRACT

Liquid phase hydrogenation of cinnamaldehyde was evaluated over SiO₂ supported Co-Pt and Cu-Pt bimetallic and Co, Cu, Pt monometallic catalysts in a batch reactor. H₂-temperature-programmed reduction (H₂-TPR) was utilized to characterize the reduction behavior and pulse CO chemisorption measurement was performed to characterize the number of active sites of the catalysts. Transmission electron microscopy (TEM) analysis was used to characterize metallic particle size distribution and extended X-ray absorption structure (EXAFS) measurements were performed to verify the bimetallic bond formation. The reactor evaluation results show that Co-Pt and Cu-Pt bimetallic catalysts exhibit much higher hydrogenation activity than the corresponding monometallic catalysts, and Co-Pt shows much higher selectivity toward C=O bond hydrogenation than Cu-Pt. The trend of hydrogenation activity and selectivity is consistent with previous studies of the hydrogenation of unsaturated aldehydes on model bimetallic surfaces.

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1. Introduction

Selective hydrogenation of α,β -unsaturated aldehydes to the corresponding allylic alcohols has received considerable attention because of its industrial applications [1–3]. The competing hydrogenation pathways of α,β -unsaturated aldehydes can occur through the C=C bond to produce the saturated aldehydes and the carbonyl group to produce unsaturated alcohols. Hydrogenation of the C=C bond is thermodynamically more favorable, and hence research efforts have been directed at improving the selectivity to the more desirable unsaturated alcohols [4]. Many attempts have been made to promote the selective hydrogenation of α,β -unsaturated aldehydes by taking advantage of the synergistic effects of bimetallic catalysts [5–17], such as Co-Pt [5–8], Fe-Pt [9], Ru-Pt [10,11], and Sn-Pt [12]. The catalytic activity and selectivity are influenced by several factors, including reaction conditions and operation mode (e.g. gas or liquid phase hydrogenation), electronic and geometric structures of the metal catalysts, type of catalyst supports, and catalyst preparation and activation procedures.

In order to better understand the hydrogenation pathways of α,β -unsaturated aldehydes on bimetallic catalysts, fundamental studies on Pt single crystal and Pt-based bimetallic surfaces have been performed by adding a 3d-metal, such as Fe, Co, Ni and Cu, to Pt(1 1 1) [18,19]. The 3d-Pt bimetallic catalysts often show properties that differ distinctly from those of their parent metals, offering the opportunity to obtain novel catalysts with enhanced activity and/or selectivity [20–22]. For example, it has been demonstrated under ultra-high vacuum (UHV) conditions that a Pt-terminated Pt-Co-Pt(1 1 1) surface, which represents a subsurface bimetallic structure with Pt on the top-most surface layer and Co residing in the subsurface region, promoted the selective hydrogenation of acrolein (CH₂=CH–CH=O) toward the corresponding unsaturated alcohol [19]. The combined experimental and DFT results suggested that the presence of weakly adsorbed acrolein through a di- σ -C–O configuration appeared to be responsible for this desired hydrogenation pathway [19].

More recently, these surface science results have been extended to γ -Al₂O₃ supported Co-Pt bimetallic catalysts, which exhibit significantly higher activity than monometallic Co and Pt catalysts for the hydrogenation of C=O bonds in two probe molecules, acetone and acetaldehyde [23]. In the current work we extended the hydrogenation of monocarbonyl compounds to that of α,β -unsaturated aldehydes on silica supported Co-Pt bimetallic catalysts. In addition, Cu-Pt catalysts were also evaluated due

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