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Hydrogen-Assisted 1,2-Dichloroethane Dechlorination Catalyzed by Pt-Cu/SiO_2: Insights into the Nature of Ethylene-Selective Active Sites

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Differently pretreated silica-supported Pt, Cu, and Pt-Cu catalysts with Cu to Pt atomic ratio of 1 to 6 have been investigated by a combination of reaction kinetics and FTIR spectroscopic studies in order to understand the factors that control the selectivity toward ethylene and ethane in the CH_2ClCH_2Cl+H_2 reaction. Carbon monoxide adsorption was used to probe the electronic modification of Pt and Cu as well as the nature of ethylene-selective active sites. It was shown that there is a very limited, if any, electronic interaction between Pt and Cu in the bimetallic catalysts reduced at 493 K. However, the Pt-Cu catalysts, for which no dipole-dipole coupling shift was observed in the IR spectra of adsorbed CO suggesting extremely small Pt ensembles on the catalyst surface, demonstrated high ethylene selectivity in the 1,2-dichloroethane dechlorination. Electronic interactions between Pt and Cu have been discovered for the Pt-Cu/SiO_2 catalysts reduced at 773 K. The interactions manifested themselves by a higher stability of Cu^0-CO adsorption complexes in vacuum and by an increase in intensity of the Pt-CO band in the FTIR spectra upon evacuation of CO from the gas phase suggesting the formation of Pt-Cu solid solutions. The higher temperature reduction resulted in the dipole-dipole coupling shift of 6 to 19 cm^{-1} in the FTIR spectra of adsorbed CO. The initial ethylene selectivity of the catalysts was inversely proportional to the dipole-dipole coupling shift. The observations are consistent with the idea that the nature of the Pt-Cu species, viz., alloy particles as opposed to Cu/Pt overlayers, does not control the reaction selectivity, which is a function of the Pt ensemble size on the surface of Pt-Cu moieties.

Keywords: hydrogen-assisted dechlorination, 1,2-dichlorothane, ethylene, Pt-Cu catalysts, infrared spectroscopy, singleton frequency, dipole-dipole coupling.

Introduction

It has been discovered a decade ago that a combination of Pt or Pd with another metal deposited on a solid support catalyzes hydrodechlorination of vicinal dichloroalkanes such as 1,2-dichloroethane and 1,2-dichloropropane toward the formation of the corresponding alkene, viz., ethylene or propylene [1-3]. Such a chemistry looks surprising because any catalyst that activates H_2 should also hydrogenate the product olefin. As chloroalkanes are common environmental pollutants and alkenes

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