



Effect of catalyst pre-reduction temperature on the reaction of 1,2-dichloroethane and H₂ catalyzed by SiO₂-supported PtCu bimetallics

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ABSTRACT

A combination of reaction kinetics experiments, temperature-programmed investigations and FTIR CO adsorption studies were used to understand the effect of catalyst pretreatment on the reaction of 1,2-dichloroethane and H₂ catalyzed by SiO₂ supported PtCu bimetallics prepared from metal chloride precursors. Higher initial and steady-state selectivities towards ethylene were obtained for catalysts with a Cu to Pt atomic ratio of 1, 2, and 3 after pre-reduction at 220 °C than after pre-reduction at 500 °C. For catalysts with a Cu to Pt atomic ratio of 4 and 5, the initial ethylene selectivity was higher after the 220 °C pre-reduction, but the steady-state ethylene selectivities were essentially the same. Based on the catalyst characterization results, the low temperature pre-reduction yields supported particles with Pt-rich cores covered with Cu-rich layers that are still well-chlorinated, whereas the high temperature pre-reduction yields particles both more metallic and with surfaces richer in Pt. The factors governing the evolution of the catalysts during the two different pretreatments are discussed as well as the impact catalyst pretreatment has on the macroscopic performance behavior.

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1. Introduction

Catalysis by bimetallics continues to be an active field of research. Combinations of a Group VIII metal, such as Pt, and a Group IB metal, such as Cu, have been extensively studied using reactions such as reforming, hydrogenation, and hydrogenolysis [1–4]. The role of the Group IB metal in altering the catalytic performance has been attributed to an electronic effect that modifies the Group VIII metal reaction sites [5–7], to an alteration in the geometric size of the Group VIII metal reaction sites [4–7], and to participation as an active site for one or more elementary reaction steps of the overall reaction [6,8,9].

For the reaction of 1,2-dichloroethane and H₂ catalyzed by PtCu bimetallics, it has been suggested that Cu participants as an active site for the formation of ethylene, as the selectivity towards ethylene increases at the expense of ethane when the concentration of Cu atoms is increased [10–15]. In mechanistic terms, it is proposed that at sufficiently high surface concentrations of Cu, the ensembles of Pt are smaller than the size required to catalyze the dissociative adsorption of the 1,2-dichloroethane, but still large enough to dissociate H₂ and provide by spillover the H atoms that react with Cl to regenerate the Cu sites [10]. The dissociative adsorption of the 1,2-dichloroethane then occurs on the large surface ensembles of Cu atoms, forming an ethyl surface species and two surface Cl species.

Unlike on Pt, the ethyl species on Cu is unstable and readily rearranges to ethylene. And again unlike on Pt, the interaction strength of ethylene with Cu is very weak and thus the ethylene desorbs without undergoing further reaction. In short, by forcing the 1,2-dichloroethane to react on Cu, the strongly adsorbed alkyl species on Pt that ultimately yield ethane are prevented from forming.

This investigation centers on the effect of catalyst pretreatment on the reaction of 1,2-dichloroethane and H₂ catalyzed by Pt–Cu/SiO₂. Of particular interest is the relationship between the pre-reduction temperature and the genesis of catalysts with varying Cu to Pt atomic ratio. Temperature-programmed desorption and reduction experiments were conducted to puzzle out the evolution of the catalysts from impregnation to reaction start, and FTIR spectroscopy of adsorbed CO was used to probe the surface composition of the metal particles. The impact catalyst pretreatment on reaction performance was ascertained through chemical reaction kinetics investigations.

2. Experimental

2.1. Catalysts preparation

Silica powder (Aldrich, 99+%, 60–100 mesh, 300 m²/g, 150 Å) was used as the catalyst support. The silica was calcined in air at 500 °C for 12 h prior to the impregnation of the metal precursors using a 0.1 N HCl aqueous solution of H₂PtCl₆·6H₂O (Alfa, 99.9%) and/or a 0.1 N HCl aqueous solution CuCl₂·2H₂O (MCB Manufacturing Chemist, 99.5%). The concentrations of the metals in the

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