The interaction of hydrogen with alumina-supported copper catalysts: 
A temperature-programmed adsorption/temperature-programmed 
desorption/isotopic exchange reaction study

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Abstract

The interaction of hydrogen with a series of copper catalysts (Cu/Al2O3, Cu/ZnO, and Cu/ZnO/Al2O3) was studied by combining temperature-programmed (TP) techniques and the isotopic exchange reaction of H2 and D2 with microkinetic modeling. Various TP experiments (TP desorption, TP adsorption) were carried out, resulting in a set of kinetic parameters for a quantitative description. Only small differences in the kinetics of the ZnO-containing Cu catalysts and Cu/Al2O3 were observed, suggesting that the interaction of H2 with the Cu surface is therefore only slightly influenced by the presence of zinc oxide, and alumina seems to act only as a structural promoter. Significant changes in the results were found when the treatment prior to the actual experiments was altered. From these observations and further supporting experiments it was deduced that a change in the morphology of the metallic Cu particles and surface alloying occur under more severe reducing conditions. These dynamical changes seem to be highly relevant for methanol synthesis.

Keywords: Hydrogen; Cu catalysts; Microkinetics; Adsorption; Desorption; H2 TPD; H2 TPA; IER; Methanol synthesis

1. Introduction

Copper has received considerable attention as a model system to study the interaction of hydrogen with metal surfaces in detail [1,2]. However, this is a subject not only of great complexity, but also of enduring controversy. Beginning with the pioneering work of Balooch et al. [3], extensive research on different single crystal surfaces has been carried out by numerous research groups in recent decades [4–15] to obtain a deeper understanding of the kinetics of adsorption and desorption. It is now generally accepted that the adsorption process of hydrogen on Cu is activated [4,5,8–12,14]. The dynamics and energetics of the adsorption of H2 on Cu(110) were probed by Hayden et al. [8,9,11] and by Campbell and Campbell [12] in detail. Their results provided experimental evidence that the chemisorption of hydrogen occurs by a direct dissociative mechanism which was found to be activated with an Arrhenius activation energy of about 57 kJ mol⁻¹. Similar values were found by Rasmussen et al. [14] from sticking probability measurements of H2 and D2 on Cu(100). The temperature-programmed desorption (TPD) of hydrogen from Cu single crystal surface measurements was studied in detail by Anger et al. [10]. While the desorption follows ideal second order on Cu(111), hydrogen causes restructuring of the Cu surface on Cu(100) and Cu(110). These observations were confirmed by several research groups [7,11,16,17].

Metallic Cu was found to be the active component in Cu-based catalysts for methanol synthesis. Nowadays, Cu/ZnO/Al2O3 catalysts are employed commercially in the low-pressure low-temperature methanol synthesis process and in the low-temperature water–gas shift reaction [18,19]. Recently, the kinetics of desorption of hydrogen from ternary Cu catalysts were obtained independently by different research groups [20–22] in detail bridging the pressure and material gaps between surface science and catalysis under relevant reaction conditions. Furthermore, Tabatabaei et al. [23] applied hydrogen-reactive frontal chromatography to study the kinetics of adsorption on Cu/Al2O3. They de-