



Redox properties of supported copper catalysts studied in liquid and gas phase by *in situ* ATR-IR and XAS

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ABSTRACT

The redox behavior of copper-based catalysts plays a prominent role in several important chemical processes. So far relatively little is known about how this behavior is affected by the medium (liquid or gas phase) in which the copper particles are immersed. In this study, we have investigated the redox properties of copper nanoparticles supported on Al₂O₃, TiO₂ and SiO₂ in the liquid (presence of solvent) and gas phase by means of *in situ* Attenuated Total Reflection Infrared spectroscopy (ATR-IR) and *in situ* X-ray absorption spectroscopy (XAS) in combination with CO adsorption. Using CO and H₂ as a reducing agent, the presence of the solvent was found to facilitate reduction of the copper constituent at lower temperatures than in the gas phase. Furthermore, the nature of the support strongly affected the extent of the reduction of the copper constituent. Copper was spontaneously reduced in the presence of CO-saturated solvent to an extent increasing in the order Cu/SiO₂ < Cu/Al₂O₃ < Cu/TiO₂. In the gas phase, reduction of the copper constituent in Cu/Al₂O₃ was more difficult than that in Cu/SiO₂. The reduction behavior measured in the presence of the solvent was found to be correlated to the activity of the catalysts in the anaerobic oxidation of 3-octanol.

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1. Introduction

Supported metal particles play a key role in heterogeneous catalysis. The majority of the catalytic processes is based on the unique features of surface metallic aggregates, which interact with reactant molecules, thus favoring bond scission and formation. The nano-character of supported metal particles confers peculiar electronic and geometric properties that often account for improved catalytic performances. Therefore, many efforts have been undertaken in the past years to discover innovative synthetic routes, leading to finely dispersed nanoparticles [1–4]. The electronic properties of the metal experience strong variation in the transition from the continuous energy band in the bulk metal to the discrete energy levels of the isolated surface atoms. This may for instance reflect in modified redox properties. Additionally, it has been very often observed that catalytic performances and stability of the metal-based catalysts are strongly dependent, for example, on the nature of the support, on the preparation method, and on the

activation procedure of the material [5–10]. It is therefore important to determine the oxidation state of the metal at the different stages of its use, since this factor critically influences its catalytic performance.

Among the wide variety of metals successfully employed in catalytic oxidation or reduction reactions, copper plays a prominent role. Methanol synthesis, steam reforming, oxychlorination and selective reduction of NO constitute important applications of copper catalysts in gas-phase processes [11–17]. Copper dispersion and morphology has been shown to be one of the key factors influencing the catalytic activity in these reactions [18–21]. Prominent copper-catalyzed liquid-phase reactions include both selective hydrogenations of carbonyl compounds and oxidation of alcohols [22–31], as well as hydrogenolysis of esters [32], and amination of alcohols [33], just to name a few. The requirement of reductive pretreatments prior to application of these catalysts has proven to be crucial for the majority of catalyzed redox processes occurring in liquid phase, because oxidized Cu species can be totally inactive. Supported nano-sized copper particles prepared by a chemisorption-hydrolysis method [34] have recently been shown to possess remarkable activity in the anaerobic oxidation of non-activated alcohols [35,36]. Still, appreciable differences in performance have been observed depending on the type of support employed.

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