

Characterization of Cu in Methanol Steam Reforming Catalysts by CO Adsorption and IR Spectroscopy

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Introduction

Supported Cu systems are suitable catalysts for methanol synthesis and methanol steam reforming. Cu/ZrO₂ is emerging as a highly selective material for the steam reforming reaction [1,2]. Little is known about the surface state of Cu on zirconia and the interaction of Cu with this support, particularly in comparison to conventional Cu/ZnO systems. Goal of this work was to identify the nature of Cu surface sites on Cu/ZrO₂ catalysts, and to compare to the Cu/ZnO system. Different preparative methods ensure a variety of zirconia morphologies and a range of Cu particle sizes and microstructures. The conditions at start-up and intermittent oxidizing treatments are known to affect the catalytic performance. Hence, the samples were subjected to oxidizing or reducing treatments prior to analysis. To probe the sites, CO was adsorbed at 298 K and the carbonyl species were analyzed by IR spectroscopy.

Experimental

Cu/ZrO₂ catalysts were prepared in three different ways: Cu/ZrO₂ nanopowders by precipitation of Cu(NO₃)₂, mesoporous CuO/ZrO₂ by using copper acetate and a block copolymer as templating agent, and macroporous CuO/ZrO₂ by using a polymer gel templating technique and copper acetylacetonate. Zirconium propylate was employed as zirconia precursor. The materials were calcined at 723–773 K. Copper contents were 6 to 15 at % [3]. Transmission IR spectra, with the samples pressed into self-supporting wafers, were recorded using a PerkinElmer S 2000. After treatments, the cell was evacuated and CO was dosed. For diffuse reflectance IR spectroscopy, a Graseby Specac "Selector" attachment with environmental chamber was placed in a Bruker IFS 66. CO was diluted with He to achieve the desired partial pressure and then admitted to the cell for 15 min. Spectra were recorded after purging gas phase CO species from the cell. All treatments were performed in flow, with either 2% or 15% H₂, or 20% O₂ (balance of He).

Results and Discussion

For some samples, it was not possible to observe adsorption of CO due to lack in

transmittance. These samples were investigated in diffuse reflection. A test sample was selected for analysis in both, transmission and reflection, modes. Satisfactory agreement between the data was achieved. The spectra taken of the various samples after first activation in H₂ differed in the OH-group and carbonate vibrations. Several CO species could be distinguished (Figs. 1 & 2). A band at ≈ 2185 cm⁻¹ was occasionally observed and is assigned to CO adsorption on coordinatively unsaturated Zr⁴⁺ ions. The species belonging to a band at ≈ 2112 cm⁻¹ were fairly stable after removal of CO from the gas phase and thus according to the literature classify as CO attached to Cu⁺. A distinct band at ≈ 2094 cm⁻¹ was detected, and after the initial reduction this band always showed an extended shoulder towards lower wavenumbers. The Cu/ZnO sample exhibited a conspicuously narrow band at 2097 cm⁻¹ and a pronounced band at 2065 cm⁻¹. The species generating bands below ≈ 2100 cm⁻¹ are weakly adsorbed and most likely arise from adsorption on reduced Cu in different environments. After oxidation these species disappear (Fig. 1). Bulk methods indicate CuO after oxidation, but Cu²⁺ cannot be probed by CO at 298 K.

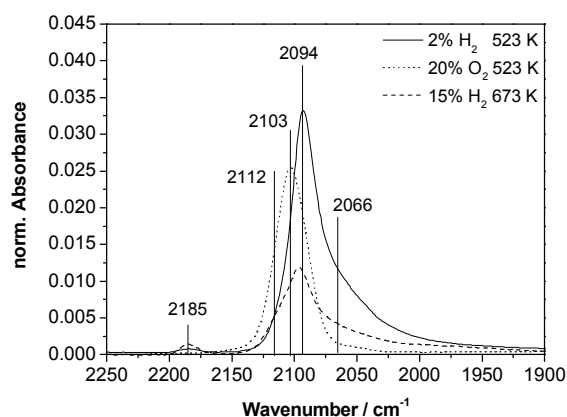


Figure 1: Adsorption of 95 hPa CO at RT on Cu/ZrO₂ after different treatments. Spectra normalized to wafer area weight.

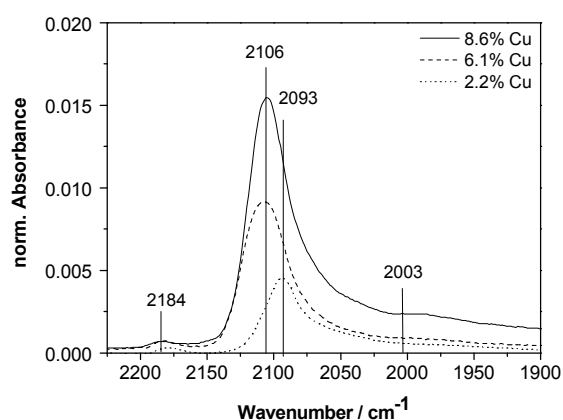


Figure 2: Adsorption of 95 hPa CO at RT on Cu/ZrO₂ series with different Cu dispersions after pretreatment in H₂ at 523 K. Spectra normalized to wafer area weight.

The investigations demonstrate that a number of different surface sites are available on supported Cu catalysts. The results show that a tuning of the electronic nature of the Cu species can be achieved through variation of the support, preparation procedure, post-calcination treatments (Fig. 1), or copper content (Fig. 2).

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