Support Effects in Catalytic Methanol Synthesis

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Introduction
Methanol synthesis is a large-scale process, where H₂ and CO₂ react over a Cu/ZnO/Al₂O₃ (CZnA) catalyst and form methanol. Despite more than 50 years of research, the origin of CZnA’s active sites is still intensely debated. Several studies report a linear relation between the methanol rate (g₃,000cat/g Cu) and the specific Cu surface area (m² Cu/g cat) for different Cu-oxide catalysts [1,2]. However, the slope of the linear relationship, which corresponds to the turnover frequency (TOF: rate per Cu surface atom) also depends strongly on the underlying support. Mechanistic investigations indicate that the methanol synthesis proceeds via formate (HCOO) on the metal surface [3], and it is therefore important to quantify the coverage of formate (θHCOO) at working conditions. This work seeks to evaluate θHCOO on supported copper catalysts at working conditions and to investigate if interactions with the support can influence θHCOO. The evaluation of θHCOO involves development of methods for quantifying θHCOO on catalysts operating at the high-pressure working conditions as well as spectroscopic investigations of metal-support interactions, which can modify the coverage of adsorbate species on the metallic surface of the working catalyst.

Materials and Methods
Oxide-supported Cu catalysts are characterized by various methods after pre-reduction. Cu surface areas are determined by oxidizing the surface with dilute N₂O, and these results allow determination of the methanol TOF at reaction conditions (H₂/CO₂ = 68/29/3 at 250°C, 50 bar) by gas chromatography (GC) followed by quantification of θHCOO by TPD and mass spectrometry. Characteristic IR frequencies of HCOO during desorption from Cu and the stretching frequency of CO bonded to Cu (νCO) are evaluated by Diffuse Reflectance IR (DRIFTS).

Results and Discussion
The surface coverage of formate (θHCOO) on the Cu surface of Cu/oxide catalysts after methanol synthesis at high temperature and pressure conditions is quantified by the amount of CO₂ desorbed in a subsequent temperature programmed desorption (TPD) experiment. The first step is to measure the methanol TOF at reaction conditions followed by rapid cooling using liquid N₂ to preserve the θHCOO at reaction conditions. Integrating the amount of desorbed CO₂ and H₂ in a subsequent TPD experiment is a way to quantify θHCOO. Significant H₂ desorption from the oxide necessitates that quantification of the apparent θHCOO is based on desorbed CO₂. Figure 1 shows, that at the characteristic desorption temperature for HCOO bonded to Cu (around 140°C [4]), Raney Cu and Cu/ZnO catalysts yield relatively sharp CO₂ desorption profiles, which indicate a relation between the apparent θHCOO and the TOF.

Figure 1: Methanol TOF (250°C, 50 bar in syngas) as function of apparent θHCOO based on integration of desorbed CO₂ post methanol synthesis.

Figure 2: Combined MS and DRIFTS during TPD on Cu/ZnO with a partially HCOO-covered surface demonstrate concurrent CO₂ and HCOO desorption and decreasing νCO-HCOO.

Validation of the quantitative method, where desorbed CO₂ is assigned to HCOO desorption, is provided by DRIFTS. After formate synthesis in syngas at around 100°C (1 atm.), the catalysts are cooled and flushed with He prior to a TPD experiment. Figure 2 shows, for a Cu/ZnO catalyst, how the relative intensity (IL) of characteristic frequencies for HCOO on Cu (νCO-HCOO) at 1600 and 2850 cm⁻¹ [4,5] (blue and red curves) and evolution of CO₂ (green curve) vary, as the HCOO covered surface is heated. Concurrent CO₂ and decreasing νCO-HCOO in the temperature range characteristic for HCOO desorption from Cu validates the θHCOO quantification method of integrating the CO₂ desorption. However, for other catalysts including Cu/Al₂O₃ and Cu/SiO₂ ill-defined CO₂ desorption profiles are obtained and higher than expected θHCOO’s (ΔθHCOO) are measured as shown in Figure 1. CO₂ desorbed from oxide(s) and other surface species may explain ΔθHCOO and ongoing work are designed to resolve the CO₂ desorption profiles and θHCOO’s for such catalysts.

Further work include evaluation of the support effect through investigations of support reducibility by N₂O titration and changes in the electron donor ability of the catalytic surface using infrared analysis of adsorbed CO.

Significance
Understanding the support effect provides both industrial value in terms of optimizing methanol catalysts and important fundamental insight into, how support directs the behavior of a catalytic reactions.

References