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 (gMeOH/gcat/h) and the specific Cu surface area (m² Cu/gcat) for different Cu-oxide catalysts [1,2]. The ratio between the rate and surface area corresponds to the turnover frequency (TOF: rate per Cu surface atom), which depends strongly on the support. Mechanistic investigations indicate, that the methanol synthesis proceeds via formate (HCOO) on the metal surface [3]. Consequently, it is of great interest to quantify the coverage of formate (θ_{HCOO}) at working conditions. This work seeks to evaluate θ_{HCOO} on supported Cu catalysts and examine potential support effects on θ_{HCOO}. The evaluation of θ_{HCOO} involves development of methods for quantifying θ_{HCOO} 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 obtained by surface oxidation using dilute N₂O, and the results enable the methanol TOF at reaction conditions (H₂/CO/CO₂ = 68/29/3 at 250°C, 50 bar) to be measured by gas chromatography (GC) with subsequent quantification of θ_{HCOO} by temperature programmed desorption (TPD) and mass spectrometry (MS). Characteristic IR frequencies of HCOO during desorption from Cu and the stretching frequency of CO bonded to Cu (ν_{CO}) are evaluated by Diffuse Reflectance IR Fourier Transform Spectroscopy (DRIFTS).

Results and Discussion

Quantification of θ_{HCOO} on the Cu surface of Cu/oxide catalysts after methanol synthesis at high temperature and pressure conditions is based on the amount of desorbed CO₂ in a TPD experiment after quenching at reaction conditions. First, the methanol TOF at reaction conditions is measured and followed by rapid cooling with liquid N₂ to preserve θ_{HCOO} obtained at reaction conditions. Integrating the amount of
desorbed CO\textsubscript{2} and H\textsubscript{2} in a subsequent TPD experiment is a way to quantify $\theta_{\text{HCOO}}$. Significant H\textsubscript{2} desorption from the oxide necessitates the use of desorbed CO\textsubscript{2} for quantifying $\theta_{\text{HCOO}}$. The characteristic desorption temperature for HCOO bonded to Cu is around 140°C [4]. Raney Cu and Cu/ZnO catalysts yield relatively sharp CO\textsubscript{2} desorption profiles, and Figure 1 shows, how these catalysts indicate a relation between the apparent $\theta_{\text{HCOO}}$ and the TOF.

**Figure 1:** Methanol TOF (250°C, 50 bar in syngas) as function of apparent $\theta_{\text{HCOO}}$ based on integration of desorbed CO\textsubscript{2} post methanol synthesis.

DRIFTS provides validation for the method of relating desorbed CO\textsubscript{2} to $\theta_{\text{HCOO}}$ by performing a TPD experiment after HCOO synthesis in syngas at 100°C (1 atm.). Figure 2 shows, for a Cu/ZnO catalyst, how the relative intensity (I/I\textsubscript{0}) of characteristic frequencies for HCOO on Cu ($v_{\text{Cu-HCOO}}$) at 1600 and 2850 cm\textsuperscript{-1} [4,5] (blue and red curves) and evolution of CO\textsubscript{2} (green curve) vary, as $\theta_{\text{HCOO}}$ desorps upon heating. Concurrent CO\textsubscript{2} and decreasing $v_{\text{Cu-HCOO}}$ at around 140°C validates the quantitative method of integrating the CO\textsubscript{2} desorption. However, other catalysts (Cu/Al\textsubscript{2}O\textsubscript{3} and Cu/SiO\textsubscript{2}) yield ill-defined CO\textsubscript{2} desorption profiles and higher than expected $\theta_{\text{HCOO}}$’s ($\Delta \theta_{\text{HCOO}}$) as shown in Figure 1. CO\textsubscript{2} desorbed from oxide(s) and other surface species may explain $\Delta \theta_{\text{HCOO}}$ and ongoing work is designed to examine this further. Further work includes CO adsorption by IR to evaluate the electron donor ability.

**References**