Effect of Fluoridation on DRIFTS measurements in bimetallic Cu/ZnO-systems for methanol synthesis

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Abstract: In this work, we present an fluoridated bimetallic (F)Cu/ZnO-catalysts for carbon dioxide hydrogenation to methanol. The fluorine exposed catalysts exhibit changes in physical properties to the non-fluoridated catalyst. Conducted DRIFTS experiments (diffuse reflectance infrared fourier transform spectroscopy) on both *in-situ* reduced catalysts (non-fluoridated and fluoridated) show varying behavior during CO_2 exposure. The fluoridated catalyst show no carbonates on the surface up to 30 bar of pure carbon dioxide at different temperatures, but further experiments are still pending.

Keywords: Methanol Synthesis, Heterogeneous Catalysis, DRIFTS.

1. Introduction

The utilization of carbon dioxide for a sustainable energy environment is of increasing interest. Energy sources such as solar- and wind power generate seasonally fluctuating amounts of energy. One possible solution to store excess power could be the production of hydrogen from water electrolysis and subsequent hydrogenation of carbon dioxide to methanol (Power-to-Liquid) or methane (Power-to-Gas).

Alternatively, carbon dioxide is an interesting C1 source for the production of valuable secondary products, like formaldehyde or oxymethylene ether (OMEs). Thermodynamic stability is one of the main problems in the usage of carbon dioxide as starting reagent. This results in a high activation energy barrier and the use of highly active catalysts.

Industrially, methanol synthesis by CO/CO_2 hydrogenation is conducted over $Cu/ZnO/Al_2O_3$ catalyst at 250-300 °C with pressures of 50-100 bar.[1] Therefore, the interface between Cu and ZnO provides multiple active sites, which implement multiple possible reaction pathways. The type and amount of intermediates on the surface of the catalysts like Formate, *HCOO, Carboxyl, *HOCO, or Methoxy, $*H_3CO$, can help for a superior understanding of the active sites to design more efficient catalysts.[2]

2. Experimental

Pre-catalysts, CuO/ZnO, were prepared by a co-precipitation method to form hydroxy-carbonates followed by its calcination to the oxides, analogous to the industrial synthesis.[3] To prepare the fluoridated bimetallic (F)Cu/ZnO, the pre-catalysts were exposed to low specific amounts of elemental fluorine, F_2.

In-situ DRIFTS measurements were performed to detect and characterize surface adsorbates and reaction intermediates over both catalyst under reaction conditions. At first, the diluted catalyst in the reaction chamber was reduced *in-situ* in a hydrogen/nitrogen mixture (5 % H_2) with a temperature ramp of 1 K min^{-1} up to 240 °C, and then purged with N_2 at 240 °C. After, the reaction chamber was switched to a defined temperature and gas composition like CO_2, CO, H_2 or 3 H_2/CO_2. Following Spectra were acquired on a Tensor II spectrometer (Bruker) with a narrow-band MCT (mercury cadmium telluride) detector.

3. Results and discussion

As a result of the fluoridation, superficial oxygen of bimetallic CuO/ZnO is formally exchanged by a small part of fluoride. These modified catalysts exhibit changes in physical properties such as higher methanol selectivities to the non-fluoridated catalysts despite smaller surface areas (copper, SA_{cu}, and total surface, BET).[4,5]

Following DRIFTS experiments on both catalysts (non-fluoridated and fluoridated) show entirely different intermediates during CO_2 exposure (Figure 1). Fluoridation of CuO/ZnO leads to the absence of any surface species in the range between 2500-750 cm^{-1}. Although some of the peaks are caused by the reaction of CO_2 with the reduced copper surface. For example gaseous carbon monoxide (2076 cm^{-1}) is formed by reverse water-gas shift reaction on reduced copper ($CO_2 + Cu^0 \rightarrow CO + CuO$).

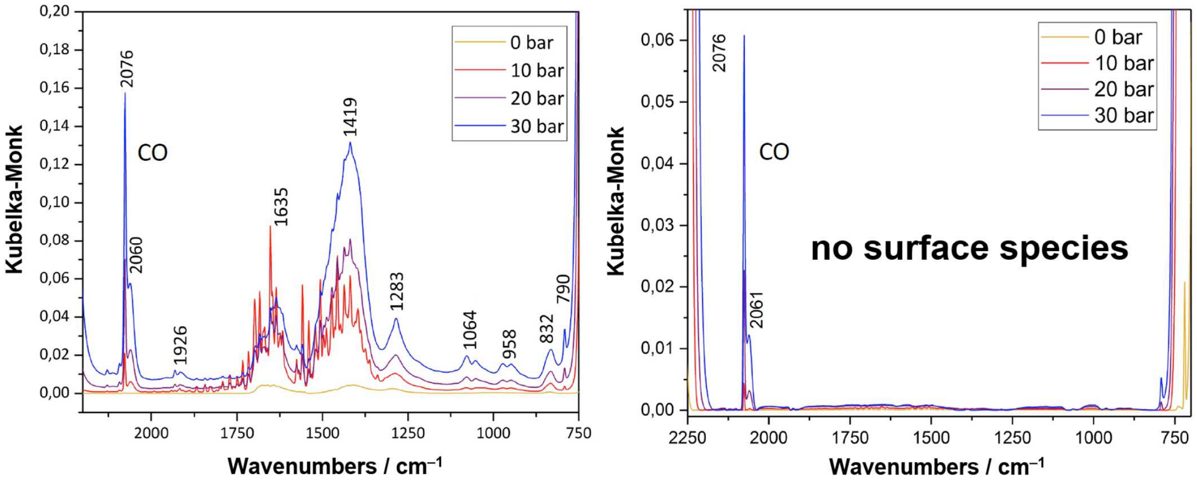

Figure 1. In-situ DRIFT spectra after CO_2 absorption on non-fluoridated Cu/ZnO (left) and fluoridated (F)Cu/ZnO (right, treated with 500 mbar F_2) in the regions 2500-750 cm^{-1} (Reaction conditions: 100 % CO_2, 1-30 bar, RT).

4. Conclusion

Through the fluoridation of CuO/ZnO the methanol selectivities are slightly increased to the non-fluoridated catalysts despite smaller copper surface and total surface. In addition, fluoridated (F)Cu/ZnO-catalyst reveal no carbonates on the surface in pure carbon dioxide at different temperatures and pressures. Further work covers investigation of the influence of fluorine on bimetallic Cu/ZnO-systems relating to intermediates on the surface during hydrogenation of carbon dioxide to methanol.

References

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