Preparation of model catalyst systems to optimize sustainable aviation fuel (SAF) production via Fischer-Tropsch synthesis

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Introduction

In the era of energy transition with the goal to overcome the impact on climate changes, the utilization of CO_2 poses as a key potential solution in all sectors. Coupled with H_2 produced from renewable sources, catalytic hydrogenation to hydrocarbons may provide alternative non-fossil fuels and chemicals.[1] In the presented work, we investigate supported Co-Mn catalysts while focusing on the interaction of Mn with the active Co phase.

The efficiency of catalysts largely depends on the physico-chemical properties of the surface of the catalysts. Manganese promotion of cobalt-based catalysts may result in Mn^{2+} on the edge of manganese oxide structure, which interacts with adsorbed carbon monoxide species,[2] an intermediate product in the CO_2 hydrogenation. In the closely related Fischer-Tropsch synthesis, the rate of CO consumption was enhanced by Mn promotion with a molar Mn/Co ratio of 0.15.[3] In general, deactivation of cobalt-based catalysts via formation of metal-support compounds (MSCs), represents another challenge when operating at high conversation rates.[4,5] In the present study, we investigate the role of manganese promotion in cobalt model catalysts. Cobalt oxide and mixed cobalt oxide nanoparticles are precisely synthesized separately via surfactant-free benzyl alcohol route at desired various ratio.[6] Subsequent deposition of these nanoparticles on various support materials yield model catalysts, which are thoroughly characterized and tested under CO_2 hydrogenation conditions to gain fundamental insight.

Materials and Methods

Cobalt oxide and cobalt manganese oxide nanoparticles were synthesized via surfactant-free heat treatment of dissolved cobalt acetate tetrahydrate and manganese acetate tetrahydrate in benzyl alcohol.[6] After the precursors were completely dissolved, ammonia solution was added to adjust the pH of the solution to provide optimal reaction condition. The solution was flash heated in an oil bath to complete the synthesis. After cool-down and repetitive washing, the nanoparticles were collected. The mixed metal cobalt oxide nanoparticles were deposited on various support materials, such as alumina, titania, and silica, to obtain series of model catalysts.[4] Synthesized nanoparticles and model catalysts were characterized with X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES), transmission electron microscopy (TEM), temperature-programmed desorption (TPD) and X-ray absorption spectroscopy (XAS). The reduction behavior of selected model catalysts and unsupported nanoparticles was studied by temperature-programmed reduction (TPR) and *in situ* XAS at the CAT-ACT beamline[7] at the KIT Light Source. Additional catalytic activity testing was conducted in fixed-bed reactors.

Results and Discussion

The synthesized cobalt oxide nanoparticle sizes range from 9 nm to 14 nm in spinel structure according to analysis by the means of XRD and TEM (Figure 1). The synthesized cobalt manganese oxide was also identified as spinel structure suggesting incorporation of Mn. Further investigation towards the formation of cobalt manganese oxide targeted composition of manganese-to-cobalt (Mn/Co) molar ratio from 0 to 0.5. A maximum Mn incorporation at a Mn/Co ratio of 0.2, which results in the largest crystal lattice expansion (Figure 1). For higher ratios, a separate hausmannite structure was identified.

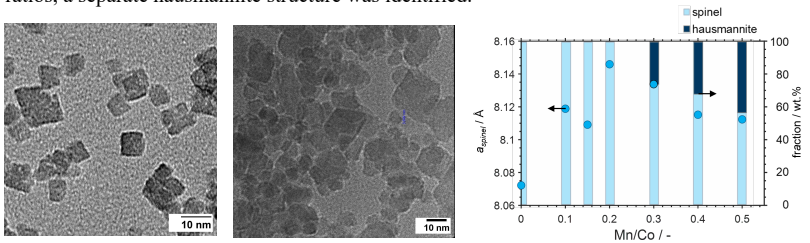

Figure 1. TEM image of cobalt oxide nanoparticles (left) and manganese oxide nanoparticles (center). Crystal lattice expansion of Co_3O_4 due to Mn incorporation according to XRD (right).

TPR confirms a retarded reduction of cobalt oxide due to Mn promotion. The evolution of the (mixed) metal oxides was further studied using *in situ* XAS. Here, the major identified phases in the synthesized mixed oxide nanoparticles before and after reduction were Co_3O_4 and metallic Co with MnO, respectively. Partial and early reduction of the mixed-oxide was observed at low temperature with formation of large amount of metallic Co.

In addition to the detailed characterization, catalytic activity testing of the various manganese-promoted cobalt catalyst was conducted for CO_2 hydrogenation to provide further insight into the working mode of the model catalysts. Variation of the support material in combination with separate synthesis of mixed oxide nanoparticles with a range of Mn/Co ratios provides valuable insight into the effect of Mn promotion of Co-based catlaysts.

Significance

The research is part of the CARE-O-SENE[8] project that connects German and South African partners for the development of optimized catalyst to produce green kerosene. The goal of the research project is to provide a competitive green alternative for the aviation sector. Synthesis and preparation of nanoparticles and model catalyst are core element of the project to provide fundamental understanding of Mn promoted Co Fischer Tropsch catalysts.

References

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