

Isolation of Promotional Effects of Manganese in Cobalt-Based CO₂ Hydrogenation Catalysts

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Introduction

In the era of energy transition with the goal to overcome the impact on climate changes, the utilization of CO₂ poses as a key potential solution in all sectors. Coupled with H₂ 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 Mn²⁺ on the edge of manganese oxide structure, which interacts with adsorbed carbon monoxide species [2], an intermediate product in the CO₂ hydrogenation. In the closely related Fischer-Tropsch (FT) synthesis, the rate of CO consumption was enhanced by Mn promotion with a molar Mn/Co ratio of 0.15 [3]. 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 various metal ratios [4]. Subsequent deposition of these nanoparticles on various support materials yield model catalysts [5], which are thoroughly characterized and tested under CO₂ hydrogenation conditions to gain fundamental insight.

Experimental

Cobalt oxide and cobalt manganese oxide nanoparticles were synthesized via surfactant-free heat treatment of dissolving cobalt acetate tetrahydrate and manganese acetate tetrahydrate in benzyl alcohol [4]. 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 to obtain the model catalyst [5]. Synthesized nanoparticles and model catalysts were characterised with X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES), transmission electron microscopy (TEM), temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD). Additional catalytic activity testing at 300 °C and 20 bar was conducted in fixed-bed reactor.

Results

The synthesized cobalt oxide and cobalt manganese oxide nanoparticle sizes range from 7 to 14 nm in spinel structure according to analysis by means of XRD and TEM. With the support of Rietveld refinement, XRD data shows a maximum Mn incorporation in the spinel structure at a Mn:Co molar ratio of 0.2, which results in the largest crystal lattice expansion. TPR confirmed a retarded reduction of cobalt oxide due to Mn promotion. Partial and early reduction of the mixed-oxide was observed. Catalytic activity testing of the various manganese-promoted cobalt catalyst was conducted for CO₂ 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 catalysts.

The research is part of the CARE-O-SENE [6] project that connects German and South African partners for the development of optimized catalyst to produce sustainable aviation fuel. Synthesis and preparation of nanoparticles and model catalyst are core element of the project to provide fundamental understanding of Mn-promoted Co-based FT catalysts. This work is supported by the German Federal Ministry of Education and Research (BMBF) within the CARE-O-SENE project (03SF0673B). Additional financial funding is provided by the Baden-Württemberg Stipendium.

Reference

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