Co-Mn catalysts for Fischer-Tropsch production of light olefins

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Introduction

Alternative routes towards the production of light olefins have a large industrial and academic interest. Among these routes is the modified Fischer-Tropsch process one of the most promising. The idea is to obtain a high yield of light olefins through the right combination of catalyst tailoring and operating conditions.

Manganese is in both Co- and Fe-based Fischer-Tropsch routinely reported as an important promoter for increasing selectivity towards light olefins. The nature of the promotion is under debate, and the effect of Mn on catalyst performance is reportedly depending on the catalyst preparation method [1]. Under relevant operation conditions, Mn can inhabit several oxidation states, including +2 and +4, and can also enter the Co3O4 spinel structure [2,3].

Materials and Methods

Mn-promoted Co catalysts (Mn:Co = 1:4 w/w) were prepared by the incipient-wetness impregnation (IWI) method using metal nitrates in aqu. solution and γ-Al2O3 (168 m2/g) as support. The effect of co-impregnation vs. sequential impregnation and the order of the components were investigated.

All catalysts were characterized by BET N2 adsorption, temperature programmed reduction (TPR), H2 chemisorption and X-ray photoelectron spectroscopy (XPS). Activity measurements were performed at 240-270 °C, 5 bar and H2 : CO = 2.25. GHSV was varied to compare selectivity at 20-50% CO conv.

Periodic, self-consistent density functional theory (DFT) calculations have been performed using the Vienna Ab-initio Package (VASP) [4,5]. The calculations have been performed to test the effect of Mn addition on Co and the adsorption and dissociation of CO, H2 and CH4 species. The theoretical investigations will be compared with experimental results.

Results and Discussion

The different impregnation methods resulted in differences in the catalyst reducibility, where the catalyst produced using the co-impregnation synthesis route had the largest negative effect. This is likely due to stronger Co-Mn interaction caused by Mn incorporation in the Co particles. The XPS analysis revealed differences in the Co/Mn ratio dependent on preparation method and subtle changes in the electronic structure.

The activity measurements showed that Mn promotion increased initial specific activity (Site-time yield, STY) independently on catalyst preparation method compared to pure Co. Moreover, the Mn promoted catalysts exhibited higher selectivity towards C2-4 olefins and decreased selectivity towards methane across all reaction conditions independently on preparation method, as presented in Fig. 1. Increased selectivity towards C3+, species were also detected with Mn promotion.

Figure 1. Selectivity data taken at differing CO conv. levels at 240 °C (left) and at differing temperatures at CO conv. ~50 % (right). Co = Co reference, Co+Mn = co-impregnated, Co→Mn = sequentially impregnated, Co first. Mn→Co = sequential, Mn first.

Complementary DFT calculations predict that Mn addition alters the adsorption energetics, where relevant species generally bind stronger to the catalyst surfaces containing Mn. Calculated activation barriers towards olefin production are also modified, in agreement with the experimental results.

Significance

The work explores the potential of an alternative production route towards key industrial intermediates. The route represents a potential economic as well as environmental advantage compared to existing routes due to the possibility of utilizing biomass derived synthesis gas.

References