

Effects of Manganese Oxide Promoter on the CO and H₂ Adsorption Properties of Titania-supported Cobalt Fischer-Tropsch Catalysts

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Introduction

Fischer–Tropsch technology is to play a major role in the expected shift from crude oil to natural gas and biomass as feedstock for chemical industries. An effective way to improve the FT catalytic performances is by adding small amounts of promoters to the catalyst materials. Promoters have been shown to strongly affect the physicochemical and catalytic properties of the cobalt active sites and hence, can be employed to tune the reaction selectivity towards the desired product range distributions. Recently, we have reported on the benefits of using Mn as promoter for Co/TiO₂ catalysts [1]. Addition of small amounts of Mn was shown to largely improve the selectivity and in some cases the activity in the FT reaction. By using advanced characterization techniques (e.g., *in situ* XAFS, STEM-EELS and XPS), new insights into the active site composition and the state and location of the Mn promoter have been gained. In this research, CO and CO/H₂ mixtures have been used to probe the surface of Co/TiO₂ catalysts promoted with different amounts of Mn [2]. By monitoring the position of the absorption bands of surface-bonded CO molecules, we have obtained information on the nature of the surface cobalt sites before and during the FT reaction.

Materials and Methods

Cobalt was deposited onto a TiO₂ support according to the Homogeneous Deposition Precipitation method using cobalt nitrate precursor solutions and urea as the precipitation agent. After filtering the solution and drying the solid overnight, the precursor material was loaded with various amounts of manganese by the Incipient Wetness Impregnation method. Finally, the samples were calcined in an air flow to obtain the oxidized catalyst precursors. DRIFTS experiments were carried out using a Perkin Elmer FTIR 2000 series infrared spectrometer. The spectrometer was equipped with a Harrick “Praying Mantis” DRIFTS accessory combined with a reactor cell with CaF₂ windows. Catalysts were tested at 1 bar and 220 °C using CO/H₂ (1/2 v/v) after reduction treatments in H₂ at 350 °C for 2 h. Product analysis (C₁–C₂₀) was carried out on-line using a Varian CP-3800 gas chromatograph equipped with a FID detector and fitted with a 50 m CP-Sil 5 CB column. Other characterization techniques involved include XAFS, XPS, TEM and STEM-EELS.

Results and Discussion

The adsorption properties of Mn-promoted Co/TiO₂ catalysts were investigated by DRIFTS and H₂ sorption experiments. Three effects on the CO band pattern can be distinguished. The first one is a decrease in total CO adsorption at higher Mn loadings. This indicates that less Co surface sites are available for binding CO. Similar to the IR results, a drop in H₂ uptake and FT activity at the highest Mn loadings also pointed to a masking effect. The second effect is the disappearance of bridge bonded CO species on increasing Mn amounts. This can be ascribed to an increasing Lewis acidity as result of an electronic effect of Mn²⁺ in the MnO phase on the active Co⁰ phase. According to literature, a measure for the

Lewis acidity of cations is the Kamlet–Taft parameter. A high value corresponds to a strong Lewis acid character. Mn²⁺, with a Kamlet–Taft value of 4.28, is a strong Lewis acid and can thus withdraw electron density from the Co⁰ phase. As a result less bridge bonded CO species are observed. The third effect of the increasing Mn contents is a change in intensity ratio of the linearly bonded CO bands at 2030 cm⁻¹ and 2050 cm⁻¹. This effect cannot be readily explained as an electronic or structural effect. From the donation-back donation model, one would expect some blue-shift of the C=O stretching vibration upon lowering the electron density of the cobalt metal phase, but hardly any frequency effect is observed. Possibly, this effect is related to the observation of increased H₂ uptake and catalytic activity in the sense that relatively more 2030 cm⁻¹ cobalt adsorption sites become available as the SMSI interactions are reduced and the dispersion of the catalyst is increased. Hence, it can be considered as a structural effect of the MnO. Alternatively, MnO species might interact directly with the adsorbed CO molecules in the catalyst with higher Mn loadings, thereby weakening the C-O bond. In this case it could be considered as an electronic interaction between MnO and the cobalt phase.

DRIFTS was also applied to study the catalysts under FT test conditions. Two main spectral regions were evaluated: the CO absorption carbonate absorption region. The CO stretching region between 2250 and 1700 cm⁻¹ shows a broad peak centered around 2020 cm⁻¹ which can be assigned to CO linearly adsorbed to Co. The band maximum shifts from 2012 cm⁻¹ to 2031 cm⁻¹ with increasing manganese loading. This blue-shift is in accordance with the earlier described model that the presence of Mn²⁺ at the surface of the Co⁰ particles lowers its electronic density. Consequently, the C≡O bond gains strength, leading to the observed higher vibrational frequency. In contrast with the CO adsorption experiments, none of the catalysts displayed any bridged-bonded CO bands. Hence, it is proposed that in the presence of hydrogen the bridge bonded CO species are very rapidly hydrogenated to hydrocarbons. The region between 1700 and 1300 cm⁻¹ reveals the presence of two major bands around 1590 and 1375 cm⁻¹, which can be assigned to CO₃²⁻ groups bonded to the titania support oxygen atoms. Thus, the formation of carbonate species is promoted by the presence of manganese. As the formation of surface carbonates requires the presence of CO₂, this result indicates that Mn plays a role in catalyzing the conversion of CO to CO₂.

Significance

Besides the *structural* and *synergistic* (water-gas shift activity) promotion effects observed when Mn is added to the catalyst material, the use of in-situ DRIFTS in combination with CO and CO/H₂ has demonstrated that Mn remains closely associated to the cobalt particles during the FT reaction, acting as an *electronic* promoter on the Co⁰ surface sites. Based on these findings, new catalysts with pre-defined catalytic properties can be designed.

References

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