

A SSITKA study to understand the cobalt particle size effect in Fischer-Tropsch catalysis

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Introduction

In the Fischer-Tropsch (FT) reaction CO and H₂ are converted into hydrocarbons, using for example a supported cobalt catalyst. It has been shown earlier that the site-specific FT activity and selectivity is sensitive to the cobalt particle size. For small Co particles (<6 nm) a lower surface-specific activity or Turn Over Frequency (TOF) is observed compared to larger ones. [1] To study the origin of this cobalt particle size effect Steady State Isotopic Transient Kinetic Analysis (SSITKA) experiments have been conducted. [2] These experiments showed that the residence time of reversibly bonded CH_x species increases with decreasing cobalt particle size (< 6 nm). Based on this, it was suggested that small Co particles bind CH_x intermediates too strong, thereby causing a lower TOF. However, the role of surface OH_x and H intermediates was not considered at that time, which made reaction rate and methane selectivity modeling unfeasible.

The current study provides a better understanding for the lower TOF for cobalt catalysts with a smaller (<6 nm) particle size. First, a kinetic study was performed in which the apparent activation energy was determined as function of cobalt particle size. Second, Steady State Isotopic Transient Kinetic Analysis (SSITKA) was used to study the coverage (θ) and surface residence times (τ) of CH_x, OH_x, H and CO as function of the cobalt particle size, using labeled gases. [2] Also the presence of irreversibly bonded CO species was investigated.

Materials and Methods

The carbon nanofiber support (fishbone-type) with a fiber diameter of about 30 nm was obtained as described before [1]. Cobalt catalysts with different particle sizes (2.6 – 27 nm) were obtained by varying cobalt loading (1 – 22 wt%), cobalt salt (cobalt nitrate and cobalt acetate) or solvent (water and ethanol). [1] The catalysts were analyzed with TEM, H₂-chemisorption and XPS in order to determine the cobalt particle size.

All SSITKA experiments were performed as described elsewhere. [3] Typically 100 mg catalyst was diluted with 200 mg SiC and loaded in a plugflow microreactor. The experiments were performed at 210 °C, with an H₂/CO ratio of 10. During steady-state FT isotopic switches were performed. Three different switches were performed, viz. from H₂/Ar/¹²CO to H₂/Kr/¹³CO, H₂/Ar/C¹⁸O to H₂/Kr/C¹⁸O and H₂/Ar/¹²CO to D₂/Kr/¹²CO. The transients of labeled reactants and products (e.g. ¹³CH₄) were monitored with a mass spectrometer. The surface residence times and coverage of CO, CH_x, OH_x and H intermediates

could be estimated based on those transients. Gas chromatography was used to determine the CO conversion.

Results and Discussion

From the SSITKA experiments at 210 °C, a constant residence time τ for CH_x, OH_x and CO species of 10, 40 and 12 s respectively was found for cobalt particles larger than 6 nm. Also the surface coverage of the mentioned species was constant. However, for smaller particles (< 6 nm), the residence times of CH_x and OH_x increased by a factor two. This probably points towards an increase in Co-C and Co-O bond strength with decreasing cobalt size. In contrast, the residence time of CO decreased for those smaller cobalt sizes. The surface coverage of all involved reactants and intermediates also decreased for small particles. It was also shown that small particles have a significant amount of irreversibly bonded CO, in contrast to large Co particles.

The SSITKA data on coverages and surface residence times of the FT intermediate species were used to describe the TOF and C₁ selectivity as function of the cobalt particle size. For this purpose, models based on elementary reaction steps were used. To calculate the TOF

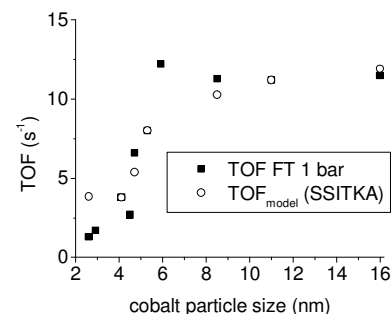


Figure 1. Comparison measured and modeled TOF.

Significance

Present work shows the surface coverage and residence time of FT reaction intermediates for a Co/CNF catalyst based on *in-situ* experiments. Using this data a *quantitative* description of the cobalt particle size effect in FT synthesis is provided. This implies a significant step in the understanding of the particle size effect.

References

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