

Thin-film catalyst concept in Fischer-Tropsch synthesis

Avela Kunene^{1*}, Imane El Arrouji¹, Ali Shan¹, Veroushia Padayachee², Dominic De Oliveira², Mohamed Fadlalla², Micheal Claeys², Rutger Schlattmann¹ and Daniel Amkruetz¹.

¹Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin 141901 (Germany)

²Catalysis Institute, University of Cape Town, Rondebosch, Cape Town 7701 (South Africa)

*avela.kunene@helmholtz-berlin.de

Introduction

Fischer-Tropsch synthesis (FTS) catalytic activity is known to depend on -the availability of surface metal sites for reaction- dispersion.

In powder catalyst systems, enhancing metal dispersion and stability is commonly achieved by supporting active metal particles on stable metal oxides like Al_2O_3 or SiO_2 . Typically, cobalt active metal is supported as nanoparticles on metal oxides, by impregnation onto the support^[1], with cobalt loadings generally in the range of 10-20 wt%.

In thin-film catalysts, however, cobalt is deposited onto a substrate, such as aluminum foil, using methods like magnetron sputtering. The cobalt layer is stabilized onto the substrate by metal oxide layer such as SiO_x , deposited using methods such as plasma enhanced chemical vapour deposition (PECVD). Here, the cobalt loading is determined by the thickness of the deposited layer, although only the surface layer accessible to syngas contributes to the reaction. This makes the overall thickness less critical to catalytic performance. Consequently, cobalt loadings in thin-film catalysts are significantly lower than in powder systems, which may result in low CO conversions, X_{CO} .

This study investigates the FTS catalytic performance of a Co-SiO_x/Al thin-film catalyst (0.07wt-% Co) synthesised through magnetron sputtering and PECVD deposition techniques. The catalyst was evaluated for FTS activity at various weighted hourly space velocities (WHSV) of approximately 840, 3370, and 6736 hr⁻¹.

Materials and Methods

Sample is prepared by depositing a 100 nm layer of SiO_x onto a 10 cm × 10 cm aluminum foil substrate using PECVD, followed by a 25 nm layer deposition of cobalt, using magnetron sputtering, resulting in Co-SiO_x/Al thin film catalyst. The SiO_x acts as buffer, stabilizing the cobalt layer and also inhibit alloy formation. The sample was calcined in a static oven at 350 °C overnight to obtain a *spinel*-Co₃O₄ layer. Prior to FTS catalytic testing, both samples were *in-situ* reduced under flowing H₂ for 16 hours at 350 °C and atmospheric pressure. The prepared thin film catalyst was tested for Fischer-Tropsch synthesis at 220 °C and 20 bar with H₂/CO ratio of 2 at various total gas flow rates.

Results and Discussion

The morphology of the Co-SiO_x/Al thin film was analyzed using SEM. Specifically, Figure 1a presents the catalyst morphology prior to calcination and reduction, while Figure 1b shows the morphology after treatment. Obviously, gas and thermal treatments resulted in a structural reconstruction of the thin-film catalyst. This effect is analogous to particle sintering in powder catalyst systems.

The Co-SiO_x/Al thin film catalyst was evaluated for Fischer-Tropsch synthesis activity at various total gas flow rates of 40, 20, and 5 mL/min. Figure 2 illustrates that CO conversion, as a function of time on stream, increases with decreasing total gas flow rate. This resulted in X_{CO} levels of 0.9%, 1.2%, and 2.7% obtained at 40, 20, and 5 mL/min, respectively;

see Figure 2A. Considering the cobalt metal loading of 0.07wt-%Co in the sample tested, the rate of CO consumption ($-r_{\text{CO}}$) was *ca.* 23, 40, and 61 gco/gco/hr for WHSV of 840, 3370, and 6736 hr⁻¹, respectively.

Figure 1. SEM images of Co-SiO_x/Al thin film catalyst (A) prior and (B) post calcination and reduction treatment.

Additionally, a comparison of the $-r_{\text{CO}}$ between the 0.07wt-% Co-SiO_x/Al thin-film catalyst and 10-20 wt% Co powder catalyst, as shown in Figure 2(B), suggests that Co-SiO_x/Al thin-film catalyst demonstrates a higher $-r_{\text{CO}}$ than the powder system. Therefore, the relatively low CO conversion observed over Co-SiO_x/Al thin film may be attributed to low cobalt metal loading rather than an intrinsically low catalytic activity of the sample.

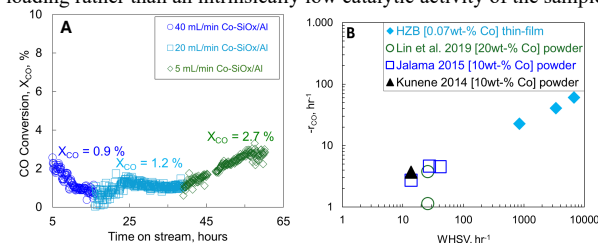


Figure 2. (A) Time-dependent CO conversion levels for the Co-SiO_x/Al thin film catalyst at varying total flow rates, illustrating the effect of flow rate on X_{CO} levels. (B) Comparative analysis of CO reaction rate ($-r_{\text{CO}}$) over the Co-SiO_x/Al thin film catalyst versus conventional powder catalyst systems^[2-4].

Significance

Comparing the $-r_{\text{CO}}$ to powder-based systems, a thin-film based catalyst system performs comparably or even surpass traditional power systems. Addition of Mn as a stability promoter can inhibit restructuring of the cobalt layer during calcination and reduction.

Thus, the thin-film catalyst concept in FTS is a plausible approach for improving catalytic efficiency, potentially reducing material costs, and enabling better control over catalyst structure and performance.

References

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