

Characterization of SiO₂ supported Co catalysts synthesized by solution combustion method for Fischer Tropsch synthesis.

Snehesh Shivananda Ail^{1*}, S Dasappa^{1*}
¹Center for Sustainable Technologies, Bangalore – 560012, India
*corresponding author: snehesh.s@gmail.com

Introduction

Escalating energy demands due to depleting petroleum sources has renewed interests in Fischer Tropsch (FT) process and can be used to convert natural gas, coal or biomass to liquid transportation fuel and other useful chemicals[1][2]. Recently, biomass to liquid (BTL) process has gathered immense attention for the production of eco-friendly, carbon neutral diesel from biomass. In this process, biomass is subjected to gasification to generate syngas (mixture of CO and H₂), followed by conversion to higher hydrocarbons (HHC) via the FT process. HHC may be cracked further to produce high quality diesel[3].

In this work, metal dispersion, degree of reduction, cobalt crystallite size and FT selectivity were examined for catalysts synthesized by solution combustion (SC) method. Catalysts synthesized by this method were characterized by percentage metal loading, TPR, XRD, XPS and TEM. 20%Co/SiO₂ (wt.%) catalyst was prepared by incipient wetness impregnation (IWI) and SC method. Changes in the TPR profile and crystallite sizes were examined. The SC synthesis procedure increases the dispersion from 15% to 18%. Smaller crystallite sizes are obtained for SC synthesized cobalt catalysts.

The catalysts prepared by these two methods were further examined with FT reaction conditions in a fixed bed reactor in temperature range of 200-220 °C, at pressures of 30 bar and H₂/CO ratio of 2.3:1.

Materials and Methods

20%Co/SiO₂ (wt.%) catalysts were prepared by single step IWI and single step SC method. Co(NO₃)₂·6H₂O was used as a common precursor for both the synthesis methods. Urea (N₂H₄CO) was used as a fuel for this redox reaction. N₂H₄CO was used in amount corresponding to oxidizer molar ratio (ϕ_c) = 1. This ratio is determined by method as explained by K.C. Patil et al [4]. IWI synthesized catalyst was calcined in a muffle furnace at 350 °C for 5 hours. Similarly, SCM synthesized catalysts were calcined at 200 °C for 0.5 hours till the self-propagating high temperature reactions result in the formation of cobalt oxide.

Synthesized catalysts were subjected to characterization tests. Catalysts were characterized using TPR, XRD, SEM, TEM and XPS. FT experiments were conducted in a fixed bed autoclave reactor in temperature ranges of 200-230 °C. Flow rates to the FT reactor were controlled by a calibrated Brooks mass flow controller. Pressure of 30 bar was maintained in the reactor with the help of electronic back pressure regulator which also enabled the extraction of liquid samples from the condensate trap, at regular intervals for analysis in a GC MS. Gas composition from FT reactor were analyzed using an online gas chromatograph.

Results and Discussion

Figure 1 shows the TPR plot of catalysts synthesized by IWI and SCM. For SCM synthesized catalyst, the reductive decomposition of the nitrate ion occurs in the same

temperature range as in IWI method. However, the consecutive two step reduction to metallic cobalt occurs over a wider temperature range (320-860 °C) with two identifiable peaks occurring at 310 and 370 °C.

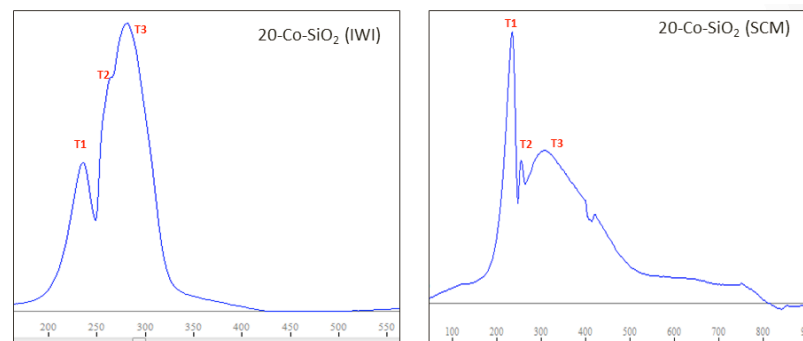


Figure 1. TPR curves for 20-Co-SiO₂ catalysts prepared by IWI and SC process.

Significance

The solution combustion method of preparing catalyst, as discussed in this work, is a comfortable method for synthesizing supported nano-structured cobalt catalysts. This method produces higher dispersion catalysts, as compared to IWI synthesized catalysts. Above all SC catalysts have smaller crystallite size and can be used as an active FT catalyst for the production of HHC products from syngas.

References

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