Fischer–Tropsch catalysts deposited with size-controlled Co$_3$O$_4$ nanocrystals: Effect of Co particle size on catalytic activity and stability

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1. Introduction

Fischer–Tropsch synthesis (FTS) has been a promising process for the conversion of coal and natural gas to liquid fuel since its commercialization. Certain transition metals such as Co, Fe, Ni, Ru, etc. are the most recommended catalysts for FT synthesis. Cobalt catalyst is preferred due to its high selectivity to heavy hydrocarbons, low activity for the water–gas shift (WGS) reaction, produce less oxygenates than the iron-based systems and price efficient than ruthenium [1,2]. The activity of the cobalt catalysts in FTS depends upon the number of active sites on the surface. The number of active sites determined by the cobalt crystal size, loading amount, reduction degree and support-cobalt interaction [1–8]. Iglesia [9] reported a large increase in the FTS activity when the cobalt particle size was decreased from 200 to 9 nm. On the other hand small metal particles on the support are highly prone to metal-support interaction, leading to the formation of difficultly reducible cobalt species [10]. Hence the synthesis of catalyst with the uniform size and homogeneous distribution of metal is important for the higher FTS activity.

Sun et al. [11] reported the preparation of Co/SiO$_2$ catalyst with high cobalt dispersion using the mixture of cobalt nitrate and cobalt nitrate precursors and showed that the catalyst performance depends on the number of active sites. Bezemer et al. [12] studied the effect of cobalt particles of various sizes on the carbon nanofiber support where he observed the turnover frequency (TOF) is constant for Co particles larger than 5–6 nm. However, there is possibility of catalyst deactivation during time on stream which makes the catalyst less promising [13]. Martinez and Prieto [14] reported ex-carrier synthesis of cobalt nanoparticles in the core of reverse micelles and their subsequent deposition on the surface protected delaminated all-silica zeolite. However the particle diameter was 4 nm, thus the TOF was very low than that of the impregnated catalysts.

Hence a new approach to prepare size-controlled cobalt nanoparticles followed by deposition on the support is needed in order to decrease metal–support interaction and to design the catalyst with high degree of reducibility. In this regard we have previously reported the synthesis of size-controlled iron oxide nanoparticles and their impregnation on δ-Al$_2$O$_3$ for fixed bed FT reaction and obtained some interesting results [15]. Lee et al. [16] reported that the impregnation of pre-synthesized Co$_3$O$_4$ nanocrystals on the alumina support resulted in the higher CO conversion and reducibility than conventional methods (impregnation and precipitation method).

In the present investigation, we are going a new step forward to design size-defined Co$_3$O$_4$ nanocrystals and their subsequent deposition over γ-Al$_2$O$_3$. The aim of this investigation is to study the effect of various particle sizes on the efficiency of FTS catalyst.