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Fischer–Tropsch catalysts deposited with size-controlled Co_3O_4 nanocrystals: Effect of Co particle size on catalytic activity and stability

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ABSTRACT

The influences of cobalt particle size on the Fischer–Tropsch reaction have been studied by using pre-synthesized cobalt oxide nanoparticles. Cobalt oxide nanoparticles in the range of 3–16 nm were synthesized by reacting colloidal solution of Co_3O_4 at the different reaction temperatures from 150 to 250 °C and stabilized by capping agent. The nanoparticles were impregnated on γ-Al_2O_3 to prepare 5 wt% Co/Al_2O_3 catalysts and compared with the catalysts prepared by conventional methods. The reduction degree by TPR and O_2-uptake increased with the increase in the cobalt crystal size from 4.8 to 17.5 nm, however H_2-uptake decreased. The rapid growth in the catalytic activity was observed when the cobalt crystal size increased from 4.8 to 9.3 nm and then the activity decreased with further increase in crystal size showing volcano shape in catalytic activity. The catalyst with the cobalt particle size of 9.3 nm showed higher CO conversion, better C_{5+} selectivity and lower methane conversion. These size-defined cobalt catalysts showed considerably higher FTS activity and better TOF (S^{-1}) than conventional catalysts and with the increase in the cobalt particle size, their deactivation rates also decreased as well even after 54 h on stream.

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 acetate 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_2O_3 for fixed bed FT reaction and obtained some interesting results [15]. Lee et al. [16] reported that the impregnation of pre-synthesized Co_3O_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_3O_4 nanocrystals and their subsequent deposition over γ-Al_2O_3. The aim of this investigation is to study the effect of various particle sizes on the efficiency of FTS catalyst. We

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