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Fischer–Tropsch synthesis over different structured catalysts: The effect of silica coating onto nanoparticles

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ABSTRACT

Core–shell structured catalysts with cobalt nanoparticles coated by the silica shell were prepared by an in situ coating method to explore the dependence of their Fischer–Tropsch synthesis performances on catalyst structures. The reduction degrees of the catalysts were decreased by silica coating as evidenced by H_2-TPR results. However, the catalytic activity was not decreased due to the enhanced and stabilized particle dispersion by the shell. In addition, such core–shell structures gave rise to a higher selectivity toward methane with a lower proportion of C_{19+} fraction as compared with an uncoated sample, which had cobalt particles located outside the silica spheres. It was considered that the shell coating not only resulted in severe diffusion restrictions of reactants but also retarded secondary reactions of olefins, both of which shifted product distribution toward the lighter end. As a result, the shell coating improved the selectivity to middle distillates with a higher percentage of olefins.

1. Introduction

The Fischer–Tropsch synthesis (FTS) is well known as an indirect liquefaction process for producing high quality sulfur-free fuels from coal, natural gas, and biomass-derived syngas. Among group VIII metals, cobalt is widely recommended as a preferable catalyst due to its higher selectivity toward hydrocarbons and lower activity for the water gas shift (WGS) reaction than the iron-based systems and more efficient price than that of ruthenium [1]. Unfortunately, a key challenge within this field is that carbon number distribution of FTS products follows the Anderson–Schultz–Flory (ASF) distribution [2], which means an unselective and wide range. Most researchers currently target at increasing the selectivity toward long-chain hydrocarbons and transforming waxes into branched, liquid fuels by a subsequent hydrocracking process [3]. Compared with this two-stage technology, an alternative single-step strategy to directly produce liquid fuels without hydrocracking would be more promising and energy efficient. Considering the catalytic performances are structure-sensitive to supports, dispersions, metal loadings and preparation methods [1], catalysts with optimal structures should be designed to realize the goal of producing liquid fuels via a single-step process.

For conventionally supported catalysts, the sintering of active phase is proved to be the primary cause of deactivation [4] as suggested by extended X-ray absorption fine structure results [5]. In addition, the support deformation always leads to loss of activity during reaction [6,7]. Both phenomena are the obstacles of long-term operation for catalysts in FTS reactions. Recently, the idea of core–shell morphology has been attracted to many researchers [8–11]. It is proved that shells prevent the possible sintering of the core particles and reveal high thermal stability during catalytic reactions at high temperatures [9,11]. However, the synthetic protocols for generating such a configuration involve stepwise high temperature decomposition and multiple transfers of intermediates before coating the shells [10,11]. Besides, the inert and deaerated atmosphere are required to synthesis the core particles [8,10]. Those harsh preparation conditions block the ways of large-scale synthesis of core–shell catalysts. Moreover, significant challenges still remain in establishing control over the shape and maximizing accessibility of reactants to the cores via porosity of the shell [12].

Wonderful catalytic performances might be obtained by adjusting core and shell properties of core–shell structured catalysts [9]. Tsubaki et al. [13,14] previously synthesized core–shell catalysts with acidic zeolite shell coating onto the Co/Al_2O_3 through hydrothermal method, which completely suppressed the formation of the C_{12+} hydrocarbons due to spatial confinement effect and molecular shape selectivity of zeolite shell. Our group [11] found that the core–shell structured $Co_3O_4@m{-}SiO_2$ presented higher selectivity toward C_5–C_{18} hydrocarbons in FTS than the conventionally supported $Co_3O_4/m{-}SiO_2$, which was prepared by impregnation method. However, previous studies focused on the

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acidic nature of zeolite shell and the mesoporous feature of silica shell. The intrinsic effects of shell coating on the mechanism for modifying hydrocarbon distribution were not clearly understood.

Based on the above discussion, herein we report a facile procedure to prepare core–shell structured catalysts with cobalt nanoparticles coated by porous silica shell. The oxidation of Co(II) to Co_3O_4 nanoparticles was proceeded under ambient atmosphere at the reaction temperature of 333 K, which was the lowest to the present stage of our knowledge. The core–shell catalysts were prepared via an in situ coating method without the prior use of silane coupling agent [15] or ultrasonic dispersion [16]. In the present investigation, a comprehensive correlation between the shell coating in connection with the mass transfers and product distribution is established.

2. Experimental

2.1. Catalyst preparation

All catalysts were prepared according to cobalt loadings of 15 wt% in the as-synthesized catalysts by weight. Cobalt oxide particles with a size of approximately 13 nm were synthesized according to Ref. [17] with some modifications. In a typical process, 0.5 M hexamethylenetetramine (HMT) and 0.02 M $Co(NO_3)_2 \cdot 6H_2O$ aqueous solution were mixed together under ambient atmosphere. Subsequently, a desired amount of polyvinylpyrrolidone (PVP, MW = 1300 kg/mol; mass ratio of $PVP/Co(NO_3)_2 \cdot 6H_2O = 2$) was dissolved in the mixture for 10 min followed by addition of H_2O_2 (3%, mass ratio) under stirring. After that, the whole system was heated to 333 K in a water bath reactor for 12 h. Then tetraethyl orthosilicate (TEOS) was added in situ and reacted for another 48 h. The products were collected by filtration, drying at 333 K and calcination at 823 K in static air to remove organic species. The as-prepared catalyst was designated as Co@SiO_2-PVP.

The Co@SiO_2-NP was prepared by identical steps without PVP addition.

An uncoated sample with nanoparticles located outside silica spheres was also synthesized for comparison. Cobalt oxide particles were synthesized similarly to the above steps without PVP addition. Then ammonium citrate tribasic (ACT), which was equal weight to PVP, was added and dissolved under ultrasonic vibration for 30 min. Addition of TEOS and latter operations were proceeded above. The obtained catalyst was designated as Co/SiO_2-ACT.

2.2. Characterizations

The as-prepared samples were observed by transmission electron microscopy (TEM) using a JEOL: JEM·2010FEF microscope operated at 200 kV. Before microscopy observation, the samples were suspended in ethanol and dispersed by ultrasonic vibration for 10 min. Afterwards, a drop of the suspension was extracted from the top side and placed on a carbon-coated copper grid (200 mesh). In order to investigate the real dispersion of core particles in the as-synthesized colloid, a drop of the colloid was directly extracted without further ultrasonic dispersion. X-ray diffraction (XRD) patterns of the samples were received on a DX-2700 diffractometer using a Cu Kα radiation ($\lambda = 0.154184$ nm). The spectra were scanned at a rate of $2^\circ \min^{-1}$ in the range $2\theta = 5$–80°. Prior to the nitrogen physisorption experiment on a Micromeritics Tristar 3000 sorptometer, the samples were outgassed at 473 K for 24 h. The BET surface area and pore volume of the catalysts were derived from the corresponding nitrogen adsorption isotherms conducted at 77 K. The adsorption average pore diameter was determined by the BJH method. 30 mg of catalyst was used for hydrogen temperature programmed reduction (H_2-TPR) analysis, which was carried out on TP-5080 multi-purpose automatic adsorption instrument by heating at the ramp rate of 10 K $\min^{-1}$ with a H_2/N_2 (5 vol%) flow. The hydrogen consumption rate was monitored in a thermal conductivity detector (TCD) calibrated previously using the reduction of CuO as standard [18].

2.3. Catalyst test

The as-prepared catalysts were tableted and sieved to obtain 60–80 mesh. 2 mL of catalysts were mixed with the equal volume of quartz sands and evaluated in a stainless-steel fixed-bed reactor (I.D. = 10 mm). After reduction at 673 K for 6 h and cooling to room temperature, syngas with a H_2/CO mole ratio of 2.0 was switched. Wax and liquid products were collected by hot trap and cold trap, respectively. The exhaust gases were analyzed on-line using Carbosieve-packed column with thermal conductivity detector (TCD) and Porapack-Q column with flame ionization detector (FID). Oil and wax were analyzed off-line in a GC-920 chromatograph which was equipped with a 35 m OV-101 capillary column and FID. N_2 with a volume ratio of 4% was blended in the syngas as an internal standard. To ensure reliability of data, results were started to collect after time on stream (TOS) of 24 h with nitrogen balance, oxygen balance, carbon balance and total mass balance in the range of $100 \pm 5\%$.

3. Results and discussion

3.1. Catalyst morphologies, phases and textures

The TEM images of pure cobalt oxide particles and all the composites are presented in Fig. 1. The particles show a uniform diameter of approximately 13 nm (Fig. 1a) as determined using more than 200 particles from several imaged areas. Without PVP addition, nanoparticles tend to aggregate into large clusters due to strong forces, such as van der Waals forces and magnetic dipole interactions [19]. Bulky core–shell structures are attained when direct coating silica shell onto large aggregate of cores (Fig. 1b). PVP leads to a much higher particle dispersion (Fig. 1c) because the amphiphilic character, which derives from the presence of highly polar amide group and apolar organic groups, enables its adsorption onto many surfaces [20]. Highly dispersed core–shell structures are formed with coating silica shell onto the monodispersed nanoparticles (Fig. 1d). The silica coating may be considered as a seeded growth process [20], in which TEOS tends to polymerize around particle surfaces rather than nucleate independently. ACT addition cannot disperse the core particles (Fig. 1e). Clusters of uncoated particles and self-seeded silica beads appear after TEOS addition (Fig. 1f: discerning from particle sizes, the larger particles are silica spheres and the smaller ones are cobalt oxide nanoparticles), indicating ACT is not beneficial for silica growth onto the outer surface of the particles. This result is consistent with that reported by Graf who failed to coat citrate-stabilized gold particles by silica [20]. It is known that SiO^- species dominate on silica surface when the pH value is higher than 5 [21], thus the self-seeded behavior of silica is probably attributed to the electrostatic repulsion between negatively charged citrate ions and SiO^- species (pH = 7.2). By contrast, the cobalt particle size of Co/SiO_2-ACT increases evidently after TOS of 240 h (Fig. 1i) as compared with that of reaction before, indicating serious sintering revealed. However, the core–shell catalysts exert strong ability to resist sintering and the original structures are well preserved (Fig. 1g and h).

Fig. 2 shows the XRD patterns of the calcined catalysts. All the diffraction peaks are indexed according to the JCPDS card (NO. 42-1467) for cobalt oxide having a cubic spinel structure [17],