



Catalyst deactivation by carbon formation during CO hydrogenation to hydrocarbons on mesoporous Co_3O_4



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ABSTRACT

Mesoporous cobalt oxide (Co_3O_4) was prepared through the template-replicating method by using the templating material of KIT-6, and its catalytic activity for CO hydrogenation to hydrocarbons by the Fischer–Tropsch (FT) synthesis was investigated and compared with that of precipitated Co_3O_4 . The mesoporous Co_3O_4 showed an enhanced catalytic activity at initial reaction stage by an increased mass-transfer rate of heavier hydrocarbons in large regular pore structures above 6 nm in size and high metallic surface area of cobalt. Different deactivation phenomena were observed during the FT reaction due to collapse of the pore structure and carbon deposition such as formation of graphitic whisker carbon on mesoporous Co_3O_4 and encapsulation of amorphous carbon on precipitated Co_3O_4 . The different catalytic performance and deactivation behavior of the two Co_3O_4 catalysts were mainly due to the variation of surface morphologies and the types of coke formed.

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1. Introduction

Mesoporous materials have recently been received enormous attention in many potential applications for various catalytic reactions. Ordered mesoporous silica materials have attracted great attention due to their relatively higher surface area compared with amorphous silica. Many researchers have reported various results using cobalt-based Fischer–Tropsch (FT) catalysts supported on ordered mesoporous silicas [1–4]. Furthermore, the FT synthesis is a well-known alternative process to produce clean fuels of higher liquid hydrocarbons from syngas which is derived from natural gas or coal through chemical conversion [5].

Synthesized liquid fuels through FT reaction have various product distributions depending on the kinds of active metals such as iron and cobalt. Linear hydrocarbons are known to be dominantly produced over cobalt-based FT catalysts, while branched hydrocarbons and light olefins are main products over iron-based FT catalysts [6]. Although cobalt-based FT catalysts are known to show higher selectivity to long chain paraffins with longer catalyst lifetime and lower water–gas shift activity [6–8] compared with iron-based FT catalysts [5,9,10], wax deposition and aggregation

of cobalt crystallites in catalyst pores are known to be the main deactivation mechanisms [6]. In addition, the catalytic performance of cobalt-based FT catalysts is largely affected by the number of active sites on the surfaces [10,11]. Therefore, in order to obtain higher dispersion of active metallic cobalt with lower wax deposition, hexagonally ordered mesoporous silica supports such as SBA-15 and ordered mesoporous carbon supports have largely been investigated as supporting materials for the FT synthesis because of their larger regular pore diameter and specific surface area, which provide higher metal dispersion with enhanced mass-transfer rate of heavier FT products formed [1,10]. Therefore, synthesis of highly ordered two dimensional or three-dimensional mesoporous metals or metal oxides using mesoporous silicas as the framework or hard templating material has widely been studied for catalytic applications [12–16]. However, few studies have been reported on mesoporous Co_3O_4 for verifying the variation of CO hydrogenation activity with simultaneous consideration of the mass-transfer rate of heavier FT products and deactivation due to filamentous carbon formation.

In the present investigation, two different types of Co_3O_4 catalysts were prepared by employing nano-replicating and precipitation methods to verify the advantages of mesoporosity of Co_3O_4 catalysts. The mesoporous Co_3O_4 synthesized by adopting the nano-replicating method possessed a highly ordered three-dimensional meso-structure and thus showed a good initial

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activity with enhanced mass-transfer rates of heavier FT products. Deactivation phenomena of the two different Co_3O_4 catalysts were explained by investigating the different types of coke deposition and morphology changes after the FT reaction.

2. Experimental

2.1. Synthesis of precipitated and mesoporous Co_3O_4 catalysts

The precipitated Co_3O_4 was prepared by the precipitation method, and it is designated as bulk-Co. To synthesize bulk-Co, cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) precursor was initially dissolved in deionized water at 70 °C. To obtain precipitates, an aqueous sodium carbonate (Na_2CO_3) solution was slowly dropped into the cobalt salt solution, and it was stirred vigorously for 1 h at 70 °C. The resulting mixture was further aged for 1 h at the same temperature, and the final precipitates were filtered, dried for 12 h, and subsequently calcined at 400 °C for 3 h.

The ordered mesoporous KIT-6, which has a three-dimensional hexagonal regular arrangement with uniform mesopores like a honeycomb-shaped structure, was synthesized using an amphiphilic co-polymer as a structure-directing agent as previously described [17–19]. A triblock copolymer, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P123, Aldrich), was used as the structure-directing agent, and tetraethylorthosilicate (TEOS, Aldrich), was used as the silica source. P123 (poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide)) was dissolved completely in deionized water. The viscous cloudy polymer solution was added to a 35 wt% HCl aqueous solution with vigorous stirring at 35 °C. Subsequently, butanol was added and aged for 1 h with stirring. Then, TEOS was added to the mixture solution under stirring in order to form hexagonal array of micelle rods which were covered with silica. The final mixture solution was vigorously stirred for 24 h at 35 °C. The product of milky solution was placed in an autoclave and kept for 24 h at 100 °C under static condition. The hydrothermally-treated white solid product was filtered without washing, and it was subsequently dried at 100 °C for 24 h. To remove the surfactant, an ethanol/HCl solution was used with stirring for about 2 h, and the as-prepared KIT-6 powder was calcined at 550 °C for 6 h.

In order to prepare mesoporous Co_3O_4 , cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) precursor was dissolved in deionized water, and the solution was impregnated into the pores of KIT-6 by homogenous mixing. The well-mixed gel of cobalt precursor solution with KIT-6 powder was dried in an oven at 80 °C overnight and calcined at 550 °C for 3 h. Finally, KIT-6, used as a template of mesoporous Co_3O_4 , was removed by washing with 2 M NaOH solution to obtain template-free mesoporous Co_3O_4 metal oxides [16], and it is denoted as meso-Co.

2.2. Catalytic activity test and characterizations

Catalytic activity test on as-prepared two types of Co_3O_4 was conducted in a stainless steel fixed bed tubular reactor with an outer diameter of 12.7 mm. Fifty milligram of the Co_3O_4 catalyst was mixed with 150 mg of gamma- Al_2O_3 powder as a diluting material for ensuring an even temperature profile in the catalyst-bed. Prior to reaction, Co_3O_4 was reduced in situ under a flow of 5% H_2 gas balanced with N_2 at a relatively low temperature of 350 °C for 6 h to minimize the structure collapse of Co_3O_4 mesopores during phase transformation of Co_3O_4 to metallic cobalt. The catalytic performance was evaluated for around 25 h under the following reaction conditions: $T = 230$ °C, $P = 2.0$ MPa, weight hourly space velocity (WHSV) = 16,000 L(mixed gas)/kg_{cat}/h, and feed gas composition of $\text{H}_2/\text{N}_2/\text{CO} = 62.84/5.60/31.56$, as reported in our previous work [20]. The effluent gas from the reactor was

analyzed by using an online gas chromatograph (YoungLin Acme 6000, GC) equipped with two columns in parallel: one is a GS-GAS-PRO capillary column connected to a flame ionization detector (FID) for the analysis of C_1 – C_5 hydrocarbons, and the other is a Porapak Q packed column connected to a thermal conductivity detector (TCD) for the analysis of H_2 , CO, CO_2 and CH_4 . Based on the results of GC analyses, the amount of C_5+ was calculated by using the carbon material balance.

The powder X-ray diffraction (XRD) patterns on the calcined bulk-Co and meso-Co were obtained using the Rigaku D/MAX-2200V diffractometer operated at 40 kV and 40 mA with Cu- $K\alpha$ radiation of 1.5406 Å and a scanning rate of 5°/min. The crystallite size of Co_3O_4 was also calculated by using X-ray line broadening values with the help of the Debye–Scherrer equation; the values of full width at half maximum (FWHM) were obtained for the peak of Co_3O_4 at $2\theta = 36.8^\circ$ on both catalysts.

The Brunauer–Emmett–Teller (BET) surface area, pore volume and average pore diameter of as-prepared two Co_3O_4 catalysts were also analyzed through the nitrogen desorption isotherm branch obtained at –196 °C using the Micromeritics ASAP 2000 instrument equipped with a high vacuum pump which provided 10^{-6} Pa. The pore size distributions of Co_3O_4 catalysts were also calculated using the BJH (Barrett–Joyner–Halenda) model from the desorption branch of the nitrogen isotherm. The surface areas of metallic cobalt crystallites in meso-Co and bulk-Co were measured by H_2 chemisorption at 100 °C under static condition using the Micromeritics ASAP 2000. Prior to adsorption measurements, the calcined fresh 0.5 g sample was reduced in situ at 400 °C for 12 h under a flow of 5 vol% H_2 balanced with N_2 . The surface area of metallic cobalt was calculated by assuming the H/Co stoichiometry of 1.0.

The temperature-programmed reduction (TPR) experiment was carried out to determine the reducibility of Co_3O_4 crystallites. Prior to the TPR experiment, the Co_3O_4 catalyst was pretreated in He flow at 350 °C and maintained for 2 h to remove adsorbed water and other contaminants, followed by cooling to 50 °C. The reducing gas containing 5% H_2 /He mixture was passed over the sample at a flow rate of 30 ml/min with a heating rate of 10 °C/min from 100 to 900 °C. The effluent gas was passed over a molecular sieve trap to remove the water formed during TPR, and then analyzed by the GC equipped with TCD.

To confirm the types of deposited carbons on the used Co_3O_4 catalysts, Fourier-transformed infrared (FT-IR) analysis was carried out by using the samples pelletized with potassium bromide powder. Surface morphologies of as-prepared two different Co_3O_4 catalysts and used ones, which were previously washed with hexane solvent to remove adsorbed soluble wax components on the Co_3O_4 surfaces, were also characterized by transmission electron microscopy (TEM) using a TECNAI G2 instrument operated at 200 kV. Dispersive Raman spectroscopy analysis was conducted under ambient condition using Bruker FRA106/S with the excitation laser of Nd:YAG (wavelength of 1064 nm) and optical power of 300 mW at the sample position.

3. Results and discussions

3.1. Physicochemical properties of Co_3O_4 catalysts

The powder XRD patterns of bulk-Co and meso-Co catalysts before FT reaction are displayed in Fig. 1. The crystalline phases of cobalt oxides were obviously observed with the characteristic peaks of Co_3O_4 planes appearing at 2θ values of 31.2°, 36.8°, 38.5°, 44.8°, 55.7°, 59.3° and 65.2°. The larger peak intensity of bulk-Co catalyst is responsible for formation of larger size Co_3O_4 crystallites. The calculated crystallite sizes of bulk-Co and meso-Co using the most

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