



Cobalt supported on Graphene – A promising novel Fischer–Tropsch synthesis catalyst



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ABSTRACT

Graphene and CNTs-supported cobalt catalyst, is introduced for Fischer–Tropsch synthesis (FTS). The catalysts were prepared using wet impregnation method with cobalt loading of 15.0 wt%. The catalysts were characterized by TGA, BET, XRD, XPS, H₂ chemisorption, TPR, and TEM techniques. The activity, selectivity and stability of the catalysts in FTS were assessed in a fixed-bed micro-reactor, and the results were compared with each other. Comparing TEM images showed dispersion of cobalt clusters in graphene-supported catalyst is higher and the average clusters size decreased from 7.5 to about 6.0 nm. Graphene as the support shifted the reduction temperature of cobalt oxide species to lower temperatures. Degree of CO conversion increased from 61 to 74%, FT synthesis rate increased by about 22%; the product distribution shifted to the higher molecular weight hydrocarbons, compared to CNTs-supported catalyst. On the graphene-supported cobalt catalyst, 480 h continuous FT synthesis decreased 22% of the initial CO conversion. However, at the same time for CNTs-supported catalyst the CO conversion decreased 34%.

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1. Introduction

Fischer–Tropsch synthesis involves the catalytic conversion of synthesis gas (H₂ and CO) into fuel hydrocarbons, such as diesel, gasoline, and naphtha. Cobalt catalysts are the preferred catalysts for FTS based on natural gas because of high activity, selectivity to linear hydrocarbons, low activity for the water–gas shift (WGS) reaction, more stability toward deactivation by water (a by-product of the FTS reaction), and low cost compared to ruthenium-based catalysts [1–14].

In FT synthesis, decreasing formation rate of low molecular weight hydrocarbons (especially methane) and also increasing formation rate of long-chain hydrocarbons (C₅⁺ production) is considered as a big challenge. This subject is an important goal on developing new FTS catalysts [15–21].

The use of carbon nano-materials as supports in catalysis has been increased during the last 25 years. They are one class of materials, which are used either as support or as metal-free catalysts.

This is mainly due to their unique structure and intrinsic properties, including high specific surface areas, chemical and electrochemical inertness and easy surface modification [22–24].

On our previous studies, we extensively reported the good performance of CNTs as support for the iron- and cobalt-based catalysts to produce mid-distillates [25,26]. However, the activity and product selectivity of the CNTs-supported catalyst depends largely on where the active phase is deposited, inside or outside of the nanotubes.

Metal nanoparticles deposited on the inner surface of the CNTs are more active than ones on the outer surface. Also, metals particles deposited on the outer surface of the CNTs are more sensitive to sintering. Besides, the catalyst performance is largely dependent on the diameter of the tubes. Moreover, carbon nanotubes are very expensive [27]. These problems provide enough motivation for developing new catalysts.

Recently, graphene has shown unique properties and remarkable tunability in supporting a variety of metallic and bimetallic nanoparticle catalysts in heterogeneous catalysis [22]. Ideally, graphene is a single-layer material, but graphene samples with two or more layers are being investigated with equal interest. Graphene possesses unique electronic, optical, thermal, and mechanical properties. In addition, having large specific surface area, good bio-compatibility and high adsorption capacity, graphene and its

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derivatives may be used as valuable substrates to interact with various species [22].

In this study, the properties of 15 wt% Co/graphene catalyst prepared by the incipient wetness impregnation method are presented. The physico-chemical characteristics, performance and stability of the catalyst are evaluated, and the results are compared with the results of a CNTs-supported cobalt catalyst with the same cobalt loading.

2. Experimental

2.1. Catalyst preparation

Purified CNTs (purity >99.5%) and graphene (purity >99.5%) were purchased from Research Institute of Petroleum Industries, Tehran, Iran. These materials were used as support for the preparation of cobalt FTS catalysts. Prior to catalyst preparation, supports were treated with 30% HNO₃ refluxed at 120 °C overnight, washed with distilled water several times and dried at 120 °C for 6 h. Graphene-supported cobalt catalyst was prepared with cobalt loading of 15.0 wt%. The catalysts were prepared using an aqueous solution of cobalt nitrate (Co(NO₃)₂·6H₂O 99.0% Merck). Furthermore, the control catalyst with the same cobalt loading was prepared on CNTs support. After impregnation step, catalysts were dried at 120 °C and calcined under argon (Ar) flow at 450 °C for 3 h with a heating rate of 10 °C/min. The samples were carefully passivated at 150 °C using 1:200 (v/v) flow of O₂/Ar gas mixture, during the cooling step. Also one γ -alumina-supported (Condea Vista Catalox B γ -alumina) cobalt catalyst with cobalt loading of 15.0 wt% was prepared just for comparison purpose. This catalyst was dried at 120 °C and calcined at 450 °C for 3 h with a heating rate of 1 °C/min.

2.2. Characterization

The Raman shift of the support materials were measured on a Confocal Raman Microscope System with a laser source of 785 nm.

PerkinElmer TG/DTA thermogravimetric differential thermal analyzer was used to measure weight changes of the sample when heated under a flow of argon (flow rate of 40 mL/min) at a constant heating rate of 10 °C/min.

The X-ray photoelectron spectroscopy (XPS) spectra was recorded on a Physical Electronics PHI-5800 spectrometer with a monochromatized Al K α source (1486.6 eV). The C 1s line (284.6 eV) was taken as a reference to correct the electrostatic charging. XPS was employed to detect the nature of cobalt nanoparticles in the targeted samples.

The cobalt loadings of the calcined catalysts were measured by an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) system. The surface area, pore volume, and average pore radius of the two supports and catalysts were measured by an ASAP-2010 system from Micromeritics. The samples were degassed at 200 °C for 4 h under 50 mTorr vacuum and their BET area, pore volume, and average pore radius were determined.

The morphology of the supports and calcined catalysts was characterized by transmission electron microscopy (TEM). Sample specimens for TEM studies were prepared by ultrasonic dispersion of the catalysts in ethanol, and the suspensions were dropped onto a carbon-coated copper grid. TEM images were taken by a Philips CM20 (100 kV) transmission electron microscope equipped with an NARON energy-dispersive spectrometer with a germanium detector.

XRD measurements were conducted with a Philips PW1840 X-ray diffractometer with monochromatized Cu K α radiation. Using

the Scherrer equation, the average size of the Co₃O₄ crystallites was estimated from the line broadening of a Co₃O₄ at 2θ of 36.8°.

Temperature programmed reduction (TPR) spectra of the calcined catalysts was recorded using a Micromeritics TPD-TPR 290 system, equipped with a thermal conductivity detector. The catalyst samples were first purged in a flow of argon at 400 °C, to remove traces of water vapor and other adsorbates, and then cooled to 40 °C. The TPR of 50 mg of each sample was performed using 5.1% hydrogen in argon gas mixture at a flow rate of 40 cm³/min. The samples were heated from 40 to 900 °C with a linear rate of 10 °C/min.

The amount of chemisorbed hydrogen was measured using the Micromeritics TPD-TPR 290 system. 0.20 g of fresh and used catalysts were reduced at 400 °C for 12 h and then cooled to 100 °C under hydrogen flow. The flow of hydrogen was switched to argon at the same temperature, which lasted about 30 min in order to remove weakly adsorbed hydrogen. Afterwards, the temperature programmed desorption (TPD) of the samples was obtained by increasing the temperature of the samples, with a ramp rate of 10 °C/min, to 400 °C under argon flow.

The TPD spectrum was used to determine the cobalt dispersion and its average active surface area. After the TPD of hydrogen, the sample was re-oxidized at 400 °C by pulses of 10% oxygen in helium to determine the extent of reduction. It is noted that during re-oxidation of the catalysts, no CO₂ peak is observed indicating that graphene and CNTs as supports of the catalysts have not reacted with oxygen. It is assumed that Co⁰ is oxidized to Co₃O₄. The calculations are summarized below. The calculated dispersion and diameter are corrected by the percentage reduction [11].

$$\% \text{Dispersion} = \frac{\text{number of Co}^0 \text{ atoms on surface}}{\text{number of Co atoms in sample}} \times 100 \quad (1)$$

$$\text{Fraction reduced} = \frac{\text{O}_2 \text{ uptake} \times (2/3) \times \text{atomic weight}}{\text{percentage metal}} \quad (2)$$

$$\text{Diameter (nm)} = \frac{6000''}{\text{density} \times \text{maximum area} \times \text{dispersion}} \quad (3)$$

2.3. Reaction setup and experimental outline

The catalysts were evaluated in terms of FTS activity (gCH/(g cat·h)), selectivity (the percentage of the converted CO that appears as hydrocarbon products) and stability in a fixed bed down-flow micro-reactor. The reactor temperature was controlled via a PID temperature controller. Brooks 5850 mass flow controllers were used to add H₂ and CO at desired flow rates into the reactor. Prior to the tests, the catalysts activation was conducted according to the following procedure. 0.6 g (0.44 mm, 325 STM mesh) catalyst was placed in the reactor, and pure hydrogen was introduced at a flow rate of 30 mL/min. For this particle size, it can be seen that the CO conversion becomes independent of the external diffusion [28]. The reactor was heated from room temperature to 400 °C at a rate of 2 °C/min. It was maintained on the condition for 20 h and so, the catalyst was reduced in situ. After the reduction and activation period, the reactor temperature was cooled down to 180 °C under flowing hydrogen. The mixed gases entered from the top of the reactor. Synthesis gas at a flow rate of 45 mL/min (H₂/CO molar ratio of 2) was introduced, and the reactor pressure was increased to 1.8 MPa. The reactor temperature was then increased to 220 °C at a rate of 2 °C/min. Synthesis was carried out for a period of 480 h. Products were continuously removed from the reactor and passed through two traps, one maintained at 100 °C (hot trap) and the other at 0 °C (cold trap). The uncondensed vapor stream was reduced to atmospheric pressure through a back pressure regulator. The outlet flow was measured with a bubble-meter, and its composition quantified using an on-line Varian 3800 gas chromatograph. The contents of

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