



Efficient hierarchically structured composites containing cobalt catalyst for clean synthetic fuel production from Fischer–Tropsch synthesis



Yuefeng Liu ^{a,*}, Jingjie Luo ^b, Maria Girleanu ^b, Ovidiu Ersen ^b, Cuong Pham-Huu ^{a,*}, Christian Meny ^b

^a Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), UMR 7515 CNRS-University of Strasbourg, ECPM, 25, rue Becquerel, 67087 Strasbourg Cedex 02, France

^b Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 CNRS-University of Strasbourg, 23, rue du Loess, 67034 Strasbourg Cedex 02, France

ARTICLE INFO

Article history:

Received 17 February 2014

Revised 8 August 2014

Accepted 9 August 2014

Available online 3 September 2014

Keywords:

Fischer–Tropsch synthesis

Clean fuel

Hierarchical structure

Titanium dioxide

Cobalt nanoparticles

Carbon nanotubes

⁵⁹Co zero field NMR

ABSTRACT

We report a straightforward preparation method to synthesize hierarchical composite consisting of TiO₂-coated multi-walled carbon nanotubes (CNTs) decorating a macroscopic host structure of α-Al₂O₃. The obtained composite possesses moderate specific surface area and very open porous structure, as well as moderate interaction with active sites, which significantly improve the cobalt nanoparticles dispersion and the mass diffusion during the reaction. The Co/TiO₂/CNT-α-Al₂O₃ (CoTiCNTA) catalyst is then used in the Fischer–Tropsch synthesis (FTS) process. This hierarchical catalyst achieves a FTS rate to C₅₊ of 0.80 g_{C₅₊} g_{cat}⁻¹ h⁻¹ along with a long-chain hydrocarbons (C₅₊) selectivity of 85%, which can be pointed out as the most outstanding noble promoter-free catalyst for the FTS process. The as-synthesized catalyst also exhibits an extremely high stability as a function of time on stream which is also one of the prerequisites for the development of future FTS catalysts, especially for the Biomass-to-Liquids process where trace amount of impurities and/or moisture could have an impact on the catalyst stability. The present work also introduces a new investigation methodology based on the use of zero field ⁵⁹Co NMR, which allows one to map in a precise manner the cobalt active phase distribution and to correlate it with the FTS performance. It is expected that such technique would be extremely helpful for the understanding of the catalyst structure–performance relationship and for future optimization in the FTS process as well as in other fields of investigation where cobalt particles are involved.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

The demands for energy and goods did increase sharply during the last decades due to the fast industrial growth of the emergent countries like China and India and also to the increase of the world population. In the same time, the oil reserves are decreasing and their production rate is close to reaching its maximum before facing a decline [1,2]. Thus, sustainable and environment friendly energy production and consumption are becoming key challenges of this century. The new developments of promoting low-CO₂ footprint technologies need to consider the alternative feedstock, such as natural gas, charcoal and biomass [3,4]. It is worth noting that no pressure will come from natural gas and coal in the near future as large resources of these raw materials still exist. The Fischer–Tropsch synthesis (FTS) is a key technology in the more global X-To-Liquids (XTL) processes which allow the transformation of

synthesis gas (2H₂ + CO) into liquid hydrocarbons followed by a hydrocracking of the heavy fraction into useful compounds such as naphtha, diesel, jet fuel, and lubricant [5–10]. The liquid fuels produced by FTS are aromatic, nitrogen, and sulfur-free which will greatly contribute to reduction of the pollution resulting from the transportation sector. In addition, FTS could allow the development of a more environmental friendly process such as the Biomass-to-Liquids (BTL) in regard to reduction of the carbon footprint [11].

According to earlier studies, FTS activity and selectivity are influenced by the support physical properties like specific surface area, pore volume, and pore size distribution in addition to the support material itself [12,13]. The nature of the support plays a crucial role in the properties of the final Fischer–Tropsch catalyst; indeed, the activity is indirectly affected by the support nature. Moreover, under conditions favoring chain growth, site-time yields and stability on supported cobalt catalysts are traditionally considered to be independent of cobalt dispersion and support identity [14–20]. The selectivity of long-chain hydrocarbons (C₅₊) depends significantly on the reactor temperature profile, and thus, the

* Corresponding authors. Fax: +33 3 68 85 26 74.

E-mail addresses: yuefeng.liu@unistra.fr (Y. Liu), cuong.pham-huu@unistra.fr (C. Pham-Huu).

selection for appropriate catalysts and carriers should obey several rules: good thermal conductivity of the support [21]; low pressure drop along the catalyst bed [22,23]; effective utilization of all active sites present in the catalyst, along with appropriate macroscopic structure of the support that favors the evacuation of the products and provides high accessibility to the reactants [22]. Previous results revealed that the opened porous structure of the nanofibrous γ - Al_2O_3 could enhance the specific activity and stability in FTS reaction by providing high metallic cobalt dispersion and enhancing the CO diffusion to the active sites [24,25]. Thus, it is of interest to develop new type of carbon-based support with high accessibility and good thermal conductivity in the highly exothermic Fischer–Tropsch synthesis. Chin et al. [26] explored the Fe–CrAlY foam covered with aligned multiwall carbon nanotube arrays as microchannel support containing Co–Re active sites for FTS. The catalyst with such structure, especially resulting from the hierarchical CNT, provided larger surface area for anchoring active sites, high thermal conductivity and enhanced mass transfer by the larger interstitials. Many studies have also demonstrated that the growth of carbon nanotubes/nanofibers on macroporous host structures could provide efficient contact between active sites and reactants, improving thermal conductivity along with better mass transfer throughout the catalyst body [27–30]. The carbon nanofibers were grown onto carbon-felts (FB–CNF/carbon-felt) host structure synthesized by Zarubova et al. [29] using the method of chemical vapor deposition (CVD) leading to the formation of carbon composite support with high BET surface area ($>280\text{ m}^2/\text{g}$) and unique hierarchical structure. The cobalt supported on this kind of composite (Co/FB–CNF/carbon-felt) showed a very uniform reaction temperature during the FTS reaction [29]. This type of composites were even coated by a layer of SiO_2 , presenting a relatively uniform temperature through the reactor and stable catalytic activity [31].

We have previously found that thermally conductive support (β -SiC) matrix doped with TiO_2 exhibits a medium metal–support interaction with cobalt nanoparticles and leads to the formation of small cobalt particles with enhanced FTS activity compared to the same catalyst supported on undoped SiC support [32]. It is expected that the TiO_2 phase not only participates in the increase of the cobalt dispersion [32–34], but also interacts with the active phase to prevent the motion of the nanoparticles or even the deactivation by sintering during FTS test [35,36]. However, to date, there has been no reports on the utilization of TiO_2 promoted hierarchically structured composite for the FTS reaction. Herein, we explore an efficient strategy based on the use of hierarchically structured composites promoted with TiO_2 in order to combine high mass transfer and good thermal conductivity with highly dispersed cobalt catalyst. The FTS results obtained have shown that the catalyst exhibits a relatively high FTS activity along with a high selectivity toward long-chain hydrocarbons and also displays an extremely high resistance toward deactivation.

2. Experimental section

2.1. Synthesis of hierarchically structured composites

The α -alumina support (Sasol) was crushed and sieved, and a fraction of 150–400 μm was retained for catalyst preparation. The catalyst was prepared using an aqueous solution of Fe ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldrich) and Co ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aldrich) precursor, respectively. The various metal mass loadings of either iron or cobalt can be found in Table 1 to adjust the CNT growth yield. The wet solid was dried in an oven at 110 $^\circ\text{C}$ and then calcined in air at 350 $^\circ\text{C}$ for 2 h. The carbon nanotubes (CNTs) were synthesized by a chemical vapor deposition (CVD) method [37,38]. The

residual catalyst was expected to be completely encapsulated within a graphene overlayers according to our previous work [37] and is no longer accessible to the reactants during the FTS experiments.

The 10 wt.% TiO_2 nanoparticles loaded on the structured materials were prepared by pore volume impregnation. Typically, 5 g of as-synthesized materials were impregnated with 5 mL absolute ethanol containing 1.97 g $\text{Ti}(\text{iOC}_3\text{H}_7)_4$ (Aldrich). After impregnation, the samples were allowed to dry at room temperature for 4 h and then dried in an oven at 110 $^\circ\text{C}$ in air for 8 h. The transformation of the precursor into TiO_2 crystalline phase was performed in argon at 600 $^\circ\text{C}$ for 5 h with a heating rate of 2 $^\circ\text{C}/\text{min}$.

2.2. Catalyst preparation

The cobalt loading was set at 10 wt.% for all catalysts. The real cobalt mass content was analyzed by inductively coupled plasma (ICP) technique and the results can be found in Table 2. In this process, the cobalt phase was deposited onto the supports via pore volume impregnation method using an ethanol–water (50:50 v:v) solution containing cobalt nitrate. The as-prepared materials (typically 5 g), either with TiO_2 or not, were impregnated by 7 mL of ethanol–water solution to which 2.74 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added. After impregnation, the solid was allowed to dry at room temperature for 2 h and then oven-dried at 110 $^\circ\text{C}$ for 8 h. The solid was calcined in air at 300 $^\circ\text{C}$ for 2 h in order to decompose the nitrate into its corresponding oxide. The oxide form was further reduced in flowing hydrogen (30 mL $\text{g}_{\text{cat}}^{-1}\text{ min}^{-1}$) at 350 $^\circ\text{C}$ for 6 h. In order to prevent excessive air oxidation during the exposure of the catalyst, a passivation process was performed before discharging of the catalyst (surface passivation was carried out with a mixture of 1 vol.% O_2 diluted in helium at room temperature). The obtained reduced catalysts are noted as CoTiCNTA and CoCNTA for the one supported on the TiO_2 -promoted and TiO_2 -free hierarchical structure of alumina decorated with carbon nanotubes, respectively, and CoTiA and CoA for the one supported on alumina promoted with TiO_2 or pure alumina, respectively.

2.3. Characterization techniques

Thermogravimetric analysis (TGA) was carried out on a Setaram apparatus with an air flow rate of 25 mL min^{-1} and a heating rate of 10 $^\circ\text{C min}^{-1}$, from room temperature to 1000 $^\circ\text{C}$. The textural properties of materials were characterized on a Tristar Micromeritics sorptometer using nitrogen as adsorbent at $-196\text{ }^\circ\text{C}$. The morphology of the solid was examined by scanning electron microscopy (SEM) on a JEOL 6700-FEG microscope. X-ray diffraction (XRD) measurements were carried out on a Bruker D-8 Advance diffractometer ($2\theta = 10\text{--}80^\circ$) with a Cu $K\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) measurements of the support were performed on a MULTILAB 2000 (THERMO VG) spectrometer equipped with Al $K\alpha$ anode ($h\nu = 1486.6\text{ eV}$) with 10 min of acquisition. Temperature-programed reduction (TPR) profiles were carried out at atmospheric pressure in a U-shaped tubular quartz reactor in an Autochem II (Micromeritics). The calcined catalysts (100 mg) were exposed to a diluted hydrogen flow (5 vol.% H_2 in argon) with a heating rate of 10 $^\circ\text{C min}^{-1}$ from room temperature to 900 $^\circ\text{C}$.

Conventional and scanning transmission electron microscopy analyses were performed on a JEOL 2100 F (S)TEM electron microscope operating at 200 kV beam voltage and equipped with a Cs-corrected condenser allowing to reach a resolution of 0.11 nm in STEM. The STEM mode is based on scanning a sample by a focused electron probe and detecting high-angle scattered electrons using an annular dark-field detector (HAADF) [39]. Indeed, in the HAADF–STEM technique, the proportionality between the intensity

Download English Version:

<https://daneshyari.com/en/article/61073>

Download Persian Version:

<https://daneshyari.com/article/61073>

[Daneshyari.com](https://daneshyari.com)