Fuel 193 (2017) 369–384

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Fischer–Tropsch synthesis of olefin-rich liquid hydrocarbons from biomass-derived syngas over carbon-encapsulated iron carbide/iron nanoparticles catalyst

Yongwu Lu [a], Qiangu Yan [a], Jun Han [b], Baobao Cao [c], Jason Street [d], Fei Yu [a,*]

[a] *Department of Agricultural and Biological Engineering, Mississippi State University, Mississippi State, MS 39762, USA*
[b] *College of Resources and Environment Engineering, Wuhan University of Science and Technology, Wuhan 430081, Hubei, PR China*
[c] *School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu, Sichuan 610031, PR China*
[d] *Department of Sustainable Bioproducts, Mississippi State University, Mississippi State, MS 39762, USA*

HIGHLIGHTS

- Direct conversion of biosyngas to olefin-rich liquid hydrocarbons was reported.
- Carbon-encapsulated iron carbide/iron catalyst showed high selectivity to olefins.
- The formation mechanism of carbon-encapsulated iron carbide/iron was proposed.
- The iron carbide/iron core of catalyst consisted of α-Fe, θ-Fe_3C, and $Fe_{15.1}C$.

ARTICLE INFO

Article history:
Received 9 September 2016
Received in revised form 9 December 2016
Accepted 18 December 2016
Available online 31 December 2016

Keywords:
Fischer–Tropsch synthesis
Olefins
Biomass-derived syngas
Carbon-encapsulated iron carbide/iron nanoparticles

ABSTRACT

Olefins are extensively used in the chemical industry as building blocks for manufacturing a wide range of products such as polymers, drugs, cosmetics, solvents, and detergents. Traditionally, olefins have been produced from thermal or catalytic cracking of petroleum-derived hydrocarbons, but environmental and economic concerns are urging exploration of alternative routes for their production from renewable sources. Herein, we report the synthesis of olefin-rich liquid hydrocarbons from biomass-derived syngas (biosyngas) via Fischer–Tropsch reaction by using carbon-encapsulated iron carbide/iron nanoparticles (CEICINs) catalysts. The CEICINs core-shell nanostructured catalysts typically constituted iron carbide/iron-core diameters of 6–30 nm and graphite-shell thickness of 2–5 nm, where the iron carbide/iron-core consisted of α-Fe, θ-Fe_3C and $Fe_{15.1}C$. The catalytic performance over CEICINs at mild reaction conditions (310 °C, 1000 psig, 3000 h^{-1}) showed that CO and H_2 conversion was ~87.5% and 85%, respectively. The C_{5+} liquid hydrocarbon selectivity was ~65%, ~44.8% of which was olefins. The liquid product formation rate was 0.12 g/(g_{cat} h) during the time-on-stream of 100 h after achieving steady state. The volume percent of the oil phase in the liquid product was ~60%. The higher reaction temperature led to the higher selectivity towards olefins, while the effect of biosyngas pressure was not a significant factor concerning olefin selectivity. Gas hourly space velocity (GHSV) had a negative effect on the formation of olefins due to the short-time contact of the reactant gas with the CEICINs catalyst. This work demonstrated the technical feasibility of the direct synthesis of olefin-rich liquid hydrocarbons by utilizing CEICINs catalysts from biosyngas via biomass gasification, biosyngas cleaning, and Fischer–Tropsch synthesis technology.

1. Introduction

Olefins are one of the most important chemicals and essential raw material in the petrochemical industry [1,2]. Lower olefins ($C_2^=$—$C_4^=$) such as ethylene, propylene, and butylenes are among the most important feedstock monomers for chemical and polymer industries [3–6]. Higher olefins ($C_{5+}^=$) are reactive intermediates for manufacturing products that can be used as high-octane gasoline, lubricating oil additives, detergents, surfactants, detergents, agricultural chemicals, coatings, and corrosion inhibitors [7,8].

---

[*] Corresponding author.
E-mail address: fyu@abe.msstate.edu (F. Yu).

http://dx.doi.org/10.1016/j.fuel.2016.12.061
0016-2361/

Olefins are mainly produced from thermal or catalytic cracking of hydrocarbons such as ethane, propane, butane, liquefied petroleum gas, light naphtha, heavy naphtha, gasoil, and vacuum gas oils [3,4,9,10]. The synthesis of olefins from syngas has attracted eminent interest in the recent decade because it provides alternative routes for olefin production from coal, natural gas, or biomass rather than from non-renewable petroleum sources [3–7]. Generally, two strategies are being explored to synthesize olefins from syngas that includes indirect and direct routes. The methanol-to-olefins (MTO) process is the indirect approach to produce olefins from syngas [11]. Syngas can also be directly converted to olefins using Fischer–Tropsch synthesis (FTS) catalysts [3–7,12]. Direct olefin production from syngas is of great importance for both academic research and industrial applications. Syngas to olefin technologies typically use high concentrated syngas ($CO + H_2 > 90\%$) derived from natural gas and coal [6,7]. Direct catalytic conversion of biosyngas to olefins is a renewable alternative to creating olefins from petroleum, and this synthetic route can reduce greenhouse gas emissions, improve air quality, and increase the national energy security. However, biosyngas produced using air as oxidation agent in the biomass gasification process will significantly increase the amount of undesired gases and lower the amount of H_2 in the overall composition of the syngas (e.g., CO_2 and N_2, and low H_2/CO ratio) [13,14]. These issues may lead to a low conversion efficiency of biosyngas as well as decreased activity of FTS catalysts. Therefore, developing a novel catalyst which can still perform satisfactorily in this environment plays a pivotal role in converting low quality biosyngas to olefin-rich liquid hydrocarbons.

Iron-based catalysts have been widely used in the commercial FTS plants mainly because of their low cost, low H_2/CO usage ratio (~0.7), and high selectivity for olefin production [4,7,12]. One major problem for the use of iron- or cobalt-based catalysts is the serious attrition which occurs during FTS reactions [12,15]. Controlling the metal particle size can dramatically improve the catalyst activity and selectivity [12]. However, the fine catalyst particles can cause fouling of downstream equipment and make the separation of the catalyst from long chain hydrocarbons (e.g., wax) extremely difficult. Additionally, the nanoparticle agglomerations and sintering limit the use of the nanoparticle catalysts at high temperature operations [12,16,17]. Many studies have been performed to improve the long-time stability of metal-supported catalysts by creating strong metal–support interactions (SMSI) between the metal and support [18], or encapsulating metal particles with a carbon support [19].

Carbon-encapsulated metal nanoparticles (CEMNs) typically have a core-shell nanostructure of metal cores surrounded by a multilayer of carbon shells that have an average interplanar distance of 0.34 nm [13]. CEMNs have potential valuable applications in catalysis, magnetic data storage, xerography, electronics, and drug delivery. These applications are attributed to their unique magnetic and electrical properties and their high thermal, mechanical, and chemical stabilities [19–23]. There are several routes to fabricate CEMNs. High temperature processes [22,23] are the most selective methods that can be used for fabrication of transitional metal carbon nanostructures, including high-temperature annealing (HTA) [24,25], arc discharge or modified arc discharge [26,27], chemical vapor deposition [28,29], electron beam irradiation [30], pyrolysis of organometallic compounds [31], microwave arcing [22], and explosion or detonation [32]. Among these methods, HTA is regarded as a simple and efficient method for high-yield production of CEMNs [33]. Carbonaceous material has been employed in the HTA method for the synthesis of CEMNs that includes graphite, pitch, diamond nanoparticles, carbon-containing polymers, and biochar [13,33]. Carbon black usually exists in the form of colloidal amorphous carbon particles, and it can be a good candidate carbonaceous material for the fabrication of CEMNs because of its low cost and high surface area [34–37]. Carbon black is generally produced from the incomplete combustion or thermal decomposition of gaseous [34], liquid hydrocarbons [35], polymers [36] or coal tar [37], etc. under controlled conditions.

Recently, CEMNs have gained attention as a new type of core-shell nanostructured catalyst for the FTS process because of their high mechanical, thermal, and chemical stabilities [13,19,21]. Yu et al. [19] demonstrated a facile and efficient one-pot route for the fabrication of Fe_xO_y@C spheres by hydrothermal treatment of a glucose solution containing iron nitrate. The catalytic study revealed the remarkable stability and selectivity (46.2% C_{5+} hydrocarbons) of the reduced Fe_xO_y@C in the FTS reaction. This result clearly illustrates the confinement effect of the carbonaceous matter on the encapsulated nanoparticles imparted by the unique microstructure [19]. The surrounding carbonaceous matter facilitated the formation of iron carbides during H_2 activation, which is beneficial for the formation of C_{5+} hydrocarbons, and it also inhibited the aggregation of the iron carbide nanoparticles during the activation and reaction processes [19]. Tu et al. [21] reported a novel carbon-encapsulated Fe_3O_4 nanocatalyst synthesized by a simple one-step solvothermal method without calcination. The catalyst exhibited excellent catalytic activity and higher selectivity for C_{5-12} gasoline range hydrocarbons (45.25%), which is close to the maximum value from the Anderson–Schulz–Flory distribution [21]. However, it is still of great industrial interest to develop high-performance catalysts for direct synthesis of high-selectivity olefin-rich liquid hydrocarbons from biosyngas.

Our previous studies have demonstrated the feasibility to synthesize liquid hydrocarbon fuels from biosyngas using various Fe-based FTS catalysts [13,38,39]. This study aims to develop high purity carbon-encapsulated iron carbide/iron nanoparticles (CEICINs) catalysts by using carbon black as raw materials through a simple and cost-effective thermal-treatment method for the direct catalytic conversion of biosyngas to olefin-rich liquid hydrocarbons. The catalysts were characterized by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD), and thermogravimetric analysis (TGA). The formation mechanism of CEICINs catalyst was proposed based on the catalyst characterization results. The effects of operating conditions including the reaction temperature, pressure, and gas hourly space velocity (GHSV) on the catalytic performance of the CEICINs catalysts were studied in a continuous flow, half-inch, fixed-bed reactor.

2. Experimental

2.1. Iron-impregnated carbon black

Vulcan XC-72 carbon black from Cabot (Billerica, MA) with an average particle size of 50 nm and a surface area of 254 m^2/g was used as the catalyst support in this work. Iron-impregnated carbon black was prepared by using an incipient impregnation method. First, 40 g of carbon black was weighed as the support. Second, 73.4 g iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$, Sigma–Aldrich] was added to 100 mL deionized (DI) water and stirred for 30 min. Finally, the carbon black was added to the iron nitrate solution and a black paste was obtained. The obtained carbon black paste was kept at room temperature for 24 h, and then transferred to an oven and dried at 150 °C overnight.