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

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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 -Fe₃C 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 H₂ conversion was ~87.5% and 85%, respectively. The C₅₊ 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.

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

1. Introduction

Olefins are one of the most important chemicals and essential raw material in the petrochemical industry [1,2]. Lower olefins (C₂⁻–C₄⁻) such as ethylene, propylene, and butylenes are among the most important feedstock monomers for chemical and polymer industries [3–6]. Higher olefins (C₅₊⁻) 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].

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 ($\text{CO} + \text{H}_2 > 90\%$) 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 $\text{Fe}_x\text{O}_y@\text{C}$ 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 $\text{Fe}_x\text{O}_y@\text{C}$ 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 m²/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(NO₃)₃·9H₂O, Sigma–Aldrich] was added to 100 mL deionized (DI) water and stirred for 30 minutes. 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.

2.2 Carbothermal reduction of iron-impregnated carbon black

Carbothermal reduction of iron-impregnated carbon black samples were conducted in a one-inch quartz tubular reactor placed in a furnace and heated under different purging gases. Fifteen grams of the iron-impregnated carbon black were packed in the middle of the quartz tubular reactor, which was heated by a tubular furnace. The first series of the experiments were carried out at 1000 °C for 1 h under different purging gases, i.e., high purity nitrogen (99.999% purity),

4% H₂/Ar or cleaned biosyngas. The experiments were performed at atmospheric pressure, and the temperature was increased at a rate of 2°C/min to 1000 °C and kept at 1000 °C for 1 h. After that, the furnace was turned off and the samples were cooled to ambient temperature under the purging gas flow. The second test was performed at 1200 °C for 1 h with high purity nitrogen. After cooling down to room temperature under the purging gas, the raw products were collected and weighed. Then the raw products were subjected to the purification procedure to remove all non-encapsulated iron carbide/iron particles. The purification procedure included refluxing the products in 2 M boiling HCl overnight, washing the products with an excess of DI water and ethanol, and drying the products in a vacuum oven at 100 °C for 3 h. The dried products were recovered and weighed. The yield of purified sample was calculated based on Eq. (1), where *A* is the weight of the purified iron-impregnated carbon black after carbothermal reduction, and *B* is the weight of the sample before carbothermal reduction, respectively.

$$X\% = \left(\frac{A}{B}\right) \times 100\% \quad (1)$$

2.3 Catalyst characterizations

XRD patterns of the catalyst samples were measured by using a Rigaku Ultima III X-ray Diffraction System operated at 40 kV and 44 mA using Cu-Kα radiation with a wavelength of 1.5406 Å, from 15° to 80° at a scan rate of 0.02°/s.

The morphology of the samples was investigated with a SEM equipped with energy-dispersive X-ray spectroscopy (EDX) (JEOL JSM-6500F). All samples were pre-coated with gold before being introduced into the vacuum chamber. The system was operated with accelerating voltage of 10 kV.

TEM was performed on a JEOL JEM-100CX II microscope operating at an accelerating voltage of 100 kV. Specimens were prepared by dispersing the catalyst in isopropanol using an

1 ultrasonic bath, then the solution was dispersed on a TEM carbon-coated copper grid and left to
2 air dry. High resolution TEM (HRTEM) analysis was performed on a FEI Tecnai F-20 TEM
3 operated at an accelerating voltage of 200 kV. **Selected area electron diffraction (SAED) – a**
4 **crystallographic experiment technique, was performed inside a TEM to identify the crystallite**
5 **structure of a catalyst.**

6 Measurement of X-ray photoelectron spectra was conducted by using a PHI model 1600
7 XPS instrument, with Mg K α X-ray source ($h\nu = 1253.6$ eV) operating at 300 W and 15 kV. The
8 instrument used a PHI 10-360 spherical capacity energy analyzer and Omni Focus II small-area
9 lens to focus the incident source to an 800 μm diameter surface analysis area. Survey spectra
10 were taken using an average of 10 scans with a pass energy of 46.95 eV in the range of 0–1100
11 eV and a step size of 0.2 eV. High-resolution spectra were obtained **using an average of 15 scans**
12 **with a pass energy of 23.5 eV and a step size of 0.1 eV.** The incident sample angle was held
13 constant at 45°. XPS data were collected and averaged using PHI Surface Analysis software,
14 Version 3.0 (Physical Electronics, Eden Prairie, MN). XPS data were analyzed using Casa XPS
15 software.

16 Raman spectra of the catalyst samples were collected using a Jobin–Yvon spectrometer
17 equipped with a thermoelectrically cooled **charge coupled device (CCD)** detector and
18 holographic super-notch filter. The sample was excited with the 514.5 nm Ar line, and an
19 incident power around 1 mW on a thin surface of a few μm^2 covering dispersed samples. The
20 spectra were recorded in the range between 500 and 3500 cm^{-1} .

21 TPD experiments were performed by heating the iron/carbon black sample in a purging gas
22 with a programmed heating rate (2 °C/min). TPD experiments were carried out in a fixed-bed 1-
23 inch tubular stainless-steel reactor. High purity nitrogen was used as the carrier gas with a flow

rate of 20 mL/min. Volatile species were analyzed using an on-line Agilent 5975C on-line mass spectrometer (MS) during the TPD process. The TPD profiles provide information on the type of species formed from the carbothermal reduction process.

TGA experiments were carried out in a TGA (Shimadzu TGA-50H) through isothermal analyses. The system quantitatively measured the change in mass of a sample as a function of temperature. The change in mass is then related to the changes taking place in the sample during calcination. The high purity N₂ (99.999%) flowed through the TGA at 50 mL/min and the temperature was ramped at 2 °C/min. The assessment of each sample was repeated at least three times.

2.4 Biosyngas preparation and biosyngas cleaning

Biosyngas was produced from loblolly pine wood chips (a moisture content of 8.3–10.8%) in a pilot-scale downdraft gasifier and passed through a cleaning system for impurity removal. The detailed gasification and cleaning processes were described in our previous work [\[13,38,39\]](#).

The pilot-scale downdraft gasifier BioMax 25 was purchased from Community Power Corporation (Littleton, CO). The capability of biosyngas production was about 65 m³/h. The gasifier mainly contained the auger feeding system, the gasifier unit, the heat exchanger, and the filters. To monitor the gasification process, multiple thermocouples and pressure transducers were installed in the system. The automatic gasification system employed a computer installed with LabView software to control the whole gasification process. The LabView program adjusted the air injection rate and wood chip feeding rate based on the setting biosyngas flow rate. The gasifier involved five levels of air injection loops, and each loop had six injection ports that entered the gasifier. This design ensured that the air was distributed into the gasifier at a desired level. The amount and the rate of air injection was controlled and adjusted by the computer based

on the monitored temperatures inside the gasifier. The heat exchanger used ambient air to cool the exiting biosyngas from 500–700 °C to about 110 °C. The biosyngas went through bag filters to remove fine particles and a filter with activated carbon to remove tars. The cool raw biosyngas was then compressed into a storage tank or sent to a burner. The effluent raw biosyngas contained about 47% N₂, 21% CO, 18% H₂, 12% CO₂, 2% CH₄, some water vapor, and trace amount of other gases (e.g., 1% O₂, 107.1 ppm of NO_x (nitrous oxides), 3.5 ppm of NH₃, 20 ppb of sulfurs) [40].

The raw biosyngas produced from the gasifier was first passed through a pre-cleaning system (a water scrubber followed by a tank containing silica gel desiccant to dry the biosyngas) under 50 psig to remove the majorities of the poisoning or negative components, e.g., ammonia, nitrous oxides, sulfurs, and moisture [40]. The cleaned biosyngas was then compressed to ~2000 psig by using a two-stage pneumatic air pump purchased from Hydraulics International (Chatsworth, CA). In addition, a deep purification process was designed and installed before the Fischer–Tropsch reactor to further eliminate oxygen, sulfur, ammonia, and nitrous oxides under 1500 psig [13,38,39]. The selected catalysts and adsorbents were alumina-supported metal catalysts, molecular sieve 13X, activated carbon, silica gel, and other high surface area materials. These catalysts and adsorbents were loaded into the reactors in series. The deep purification reactor system for cleaning was designed with the controlling parameters of temperature, pressure, and flow rate. The cleaned biosyngas met the basic requirements for the FTS, i.e., total sulfurs (H₂S + COS) < 10 ppb, (NH₃ + NO_x) < 1 ppm, oxygen < 1 ppm, tars < dew point [13,14, 38–40]. The cleaned biosyngas, which contained 47% N₂, 21% CO, 18% H₂, 12% CO₂, and 2% CH₄, was utilized for the catalytic conversion tests.

2.5 Catalytic conversion of biosyngas

The catalytic conversion of cleaned biosyngas was carried out in a continuous flow, half-inch, fixed-bed reactor system. The catalytic reaction experiments were carried out with a 12 mm i.d. stainless steel tubular reactor. For all reaction experiments, three grams of carbon-encapsulated iron carbide/iron nanoparticles catalysts without dilution were loaded in the center of the reactor, where a thermocouple covered with a stainless sleeve was placed to monitor the central temperature of the catalyst bed, i.e., the reaction temperature. The two-ends of catalyst bed were supported by using quartz wool and glass beads (2 mm O.D.). The system was then purged by using a helium flow for 30 min, followed by *in situ* reduction with cleaned biosyngas at 400 °C for 2 h to eliminate the possible adsorption of oxygen or moisture on the CEICINs catalyst surface. Then the cleaned biosyngas was fed into the reactor until reaching the desired pressure. After the desired pressure was reached, the temperature was slowly adjusted to the desired level. Once the reaction temperature was achieved, the FTS reaction was continued for a period of 24 h to ensure steady state of the catalyst activity. The time-on-stream after achieving steady state was 100 h. The FTS reactions were operated under the following conditions: a reaction temperature of 250–350°C, a gas volume hourly space velocity (GHSV) of 1000 to 5000 h⁻¹, and a pressure of 500–1250 psig. The catalytic performances were evaluated for CO and H₂ conversion, and CO₂ and hydrocarbon selectivity. N₂ in the biosyngas was used as an internal standard for CO and H₂ conversion calculations. The CO conversion, H₂ conversion, and product selectivity were calculated via Eqs. (2–4), respectively, where F^0 and F are the total molar flow rates of the inlet biosyngas and effluent gas, respectively; C_i^0 and C_i are the concentrations of component i in the inlet biosyngas and effluent gas, and n is the carbon number in component i . Mass and carbon balances were performed based on the total inlet/outlet flows of a material. The

inlet and effluent mass and composition analysis was carried out to determine the appropriate balance of material.

$$CO \text{ Conversion}(\%) = \frac{F^0 C_{CO}^0 - F C_{CO}}{F^0 C_{CO}^0} = \frac{C_{CO}^0 - C_{N_2}^0 C_{CO} / C_{N_2}}{C_{CO}^0} \times 100\% \quad (2)$$

$$H_2 \text{ Conversion}(\%) = \frac{F^0 C_{H_2}^0 - F C_{H_2}}{F^0 C_{H_2}^0} = \frac{C_{H_2}^0 - C_{N_2}^0 C_{H_2} / C_{N_2}}{C_{H_2}^0} \times 100\% \quad (3)$$

$$Product \text{ selectivity} (\%) = \frac{F n C_i}{F^0 C_{CO}^0 - F C_{CO}} = \frac{C_{N_2}^0 n C_i}{C_{N_2} C_{CO}^0 - C_{N_2}^0 C_{CO}} \times 100\% \quad (4)$$

2.6 Analytical methods

The effluent gas was analyzed by using an on-line Agilent 7890 gas chromatograph equipped with two thermal conductivity detectors (TCD) and one flame ionization detector (FID). Helium and nitrogen were used as the carrier gases. C₁–C₄-ranged alkanes and alkenes were analyzed by using a HP Plot capillary column. H₂, CO, CO₂, CH₄, and N₂ were analyzed by using molecular sieve-packed columns. Liquid products were collected using a condenser kept at 0 °C. Liquid samples were analyzed by using an Agilent 7683B Series Injector coupled to an Agilent 6890 Series gas chromatograph system and a 5973 Mass Selective Detector (i.e. a quadrupole type GC–MS system) as well as a FID detector. An Agilent DB-WAXetr (50 m×0.32 mm I.D., 1.0 μm) capillary column was used as the analytic column. Helium was the carrier gas with a flow rate of 1 mL/min. The temperatures of the injector and detector were both kept at 250 °C. The oven was maintained at 40 °C for 5 min, ramped to 250 °C by 10 °C/min, and then held at this temperature for 10 min. For the MS, temperatures of the transfer line and EI source were 250 °C and 200 °C, respectively.

Detailed hydrocarbon analysis (DHA) was performed over a Perkin Elmer Clarus 680 GC with a FID detector using the PIANO method. PIANO describes the method for determining the amount of paraffins (P), iso-paraffins (I), aromatics (A), naphthenes (N), and olefins (O) within a

sample. This method was based on ASTM test method D 5134-92. A DHA analytical column (100 m $\times$ 0.25 μ m I.D.) was used to separate sample components. Hydrogen was used as a carrier gas with a flow rate of 100 mL/min. The temperature of the GC injector was initially kept at 200 °C for 43.15 min, then ramped to 450 °C at 100 °C/min and held at 450 °C for the rest of entire run. The oven temperature was initially kept at 35 °C for 5 min, and then ramped to 50 °C at 10 °C/min and held at this temperature for 21.5 min, followed by heating to 150 °C with a rate of 3 °C/min and holding at this temperature for 4.67 min. The FID detector temperature was 250 °C.

3 Results and discussion

3.1 Synthesis of CEICINs catalysts by a carbothermal reduction process

The results (Table 1) showed that the highest CEICINs yield was 58.6% for the carbothermal reduction process by using cleaned biosyngas at 1000 °C for 1 h (S1000-biosyngas), while the lowest yield (35.0%) was observed for the carbothermal reduction process by using high purity nitrogen at 1200 °C for 1 h (S1200-N₂). The different yields in CEICINs are possible because more carbon black was consumed as reducing agent for the carbothermal reduction process when using high purity nitrogen as the purging gas, while carbon derived from CO in biosyngas can deposit over iron nanoparticles using the S1000-biosyngas process. In addition, the inclusion of H₂ as reduction gas in the S1000-H₂ and S1000-biosyngas processes facilitated the reduction of iron oxides to metallic iron formation, thereby increasing the CEICINs yields in comparison to the inert N₂ gas used in the S1000-N₂ carbothermal reduction process.

Table 1. Effect of operational variables on the carbon-encapsulated iron carbide/iron nanoparticles yield.

Experiment	Temperature (°C)	Type of carrier gas	Initial mass of samples (g)	Mass of products (g)	Purification yield (%)
1 (S1000-N ₂)	1000	High purity N ₂	15.0	6.23	41.5
2 (S1200-N ₂)	1200	High purity N ₂	15.0	5.25	35.0
3 (S1000-H ₂)	1000	4% H ₂ in Argon	15.0	7.55	50.3
4 (S1000-biosyngas)	1000	Cleaned biosyngas	15.0	8.79	58.6

3.2 Catalyst characterizations

3.2.1 XRD

The crystallite structures of the samples were characterized by XRD as shown in Fig. 1. Fig. 1a shows XRD pattern of the iron nitrate-impregnated carbon black without calcination. It was difficult to find iron diffraction peaks for the dried sample (Fig.1a). Iron most likely existed as Fe(NO₃)₃ or in the amorphous iron phase. Moreover, no graphite peaks appeared from the XRD pattern of the dried iron nitrate impregnated carbon black. This is because carbon black generally is a non-graphite carbon, which consists of amorphous carbon fragments and small amounts of polycyclic aromatic hydrocarbons [34]. The crystallites inside the particles of carbon black are randomly arranged with intrusions of amorphous carbon. Therefore, it is hard to detect the XRD peaks of the raw carbon black.

Fig. 1. XRD patterns of iron-impregnated carbon black samples: (a) dried at 150 °C overnight, (b) calcined at 300 °C, (c) S1000-N₂, (d) S1200-N₂, (e) S1000-H₂, and (f) S1000-biosyngas.

XRD pattern of the iron nitrate impregnated carbon black sample calcined at 300 °C (Fig.1b) shows several diffraction peaks at 2θ ° of 30.10, 35.42, 37.05, 43.05, 53.40, 56.95, 62.51, and 73.95, which are ascribed to Fe₃O₄ (JCPDS#65-3107) [41], corresponding to the following crystallographic planes: (220), (311), (222), (400), (422), (511), (440) and (533), respectively. The XRD pattern of the thermal-treatment at 1000°C (S1000-N₂) and 1200°C (S1200-N₂) with nitrogen flow for 1 h of the calcined sample is shown in Figs.1c and 1d, respectively.

Fig. 1e shows XRD pattern of thermal-treatment at 1000°C with 4% H₂/Ar for 1 h of the calcined sample (S1000-H₂). Fig. 1f displays XRD pattern of thermal-treatment at 1000°C with cleaned biosyngas for 1 h of the sample (S1000-biosyngas), which is very similar to the XRD pattern of the sample (S1000-H₂). Two diffraction peaks at 2θ ° of 44.68 and 65.03 that corresponded to the body-centered cubic (bcc) α -Fe (110) and (200) planes (JCPDS#06-0696),

respectively, which confirmed the formation of α -Fe during the carbothermal reduction process. The diffraction peak at 2θ of 26.55 corresponded to (002) plane of graphite (JCPDS#41-1487), which indicated that the iron-impregnated carbon black was partially graphited after the thermal annealing treatment. The diffraction peaks at 2θ of 37.63, 37.75, 39.80, 40.70, 42.60, 43.75, 44.56, 44.94, 45.86, 48.40, 49.12, 51.82, 54.40, 57.89, 70.90, 77.90 and 78.60 are assigned to cementite, θ -Fe₃C (JCPDS#35-0772), corresponding to the crystallographic planes of (121), (210), (002), (201), (211), (102), (220), (031), (112), (131), (221), (122), (230), (301), (123), (401), and (133), respectively. The diffraction peaks at 2θ of 43.28, 50.40, and 74.05, which are ascribed to Fe_{15.1}C (JCPDS#52-0512), corresponding to the crystallographic planes of (111), (200), and (220), respectively. The diffraction peaks of α -Fe, θ -Fe₃C and Fe_{15.1}C proved that iron oxide was reduced after carbothermal reduction [24,42].

3.2.2 SEM

The SEM image of catalyst sample (S1000-N₂) is shown in Fig. 2a. Spherically shaped carbon black particles with a uniform particle size range of 20–50 nm was observed. As shown in Fig. 2b, the morphology of catalyst sample (S1200-N₂) is similar to the (S1000-N₂) catalyst sample, except larger particles were observed. The morphology of the products of hydrogen and cleaned biosyngas samples (S1000-H₂ and S1000-biosyngas) (Figs. 2c and 2d) is generally similar when compared to the samples obtained in nitrogen flow at 1000 °C. The regular iron particles are randomly distributed within carbon black matrix (Fig. 2a).

Fig. 2. SEM images of carbon-encapsulated iron carbide/iron nanoparticles samples: (a) S1000-N₂, (b) S1200-N₂, (c) S1000-H₂, and (d) S1000-biosyngas.

3.2.3 TEM

The TEM image of the iron-impregnated carbon black sample dried at 150°C overnight is shown in Fig. 3a. Because iron most likely exists as Fe(NO₃)₃ or amorphous iron phase, the fresh iron-impregnated carbon black shows the significant characteristic feature of the carbon black particle with an average diameter of 20–50 nm, combined in chains and aggregates. Fig. 3b shows the TEM image of the iron-impregnated carbon black after carbothermal reduction at 1000°C with nitrogen flow for 1 h (S1000-N₂). The product obtained from this process is mainly composed of well crystallized CEICINs with small amounts of carbon black particles (Fig. 3b). It can be observed that most of the products were spherical particles with diameters of 10–60 nm

after carbothermal reduction. The carbothermal reduction process is mainly limited by diffusion processes because it is a solid-state reaction. Increasing the temperature can accelerate the carbothermal reduction reaction.

Fig. 3. TEM images of samples: (a) iron nitrate impregnated with carbon black, dried at 150 °C overnight, (b) S1000-N₂, (c) S1200-N₂, (d) S1000-H₂, (e,f) S1000-biosyngas and particle size distribution.

Fig. 3c illustrates the TEM image of the carbothermal sample at 1200°C under a nitrogen flow for 1 h (S1200-N₂). The S1200-N₂ sample is similar with the S1000-N₂ sample (Fig. 3b) in morphology and particle size except there were fewer carbon black particles and a great amount of CEICINs were formed. Figs. 3d and 3e show TEM images of iron-impregnated carbon black after thermal treatment at 1000°C under 4% H₂/Ar for 1 h (S1000-H₂) and thermal treatment at

1 1000°C under cleaned biosyngas for 1 h (S1000-biosyngas), respectively. The CEICINs (S1000-
2 biosyngas) have particle diameters ranging between 6 and 30 nm with an average particle size of
3 18.6 nm (Fig. 3f).

4 The HRTEM image of carbon black sample (Fig. 4a) reveals that carbon black materials
5 is in an amorphous structure [43]. Figs. 4b and 4c show the HRTEM images of the CEICINs
6 sample (S1000-biosyngas). These nanoparticles had a spherical shape and dark cores enveloped
7 by concentric shells. The nanoparticles showed core diameters of ~30 nm and shell thickness of
8 ~5 nm (Fig. 4c). These core-shell nanoparticles can be interpreted as iron carbide/iron
9 nanoparticles core encapsulated by a multilayer of graphite shells [44].

10 The selected area electron diffraction (SAED) pattern of Fig. 4c consists of eight rings
11 (Fig. 4d). One of the internal dim diffuse rings originated from the graphite, and the other seven
12 rings were from the crystalline iron carbide/iron-core. The internal dim diffusion ring was
13 assigned to the graphitic carbon shell (002) since the outer carbon shells of these nanostructures
14 were in an amorphous state. Three of the rings attributed to α -Fe (JCPDS#06-0696) of the
15 encapsulated iron-core nanoparticle (Fig.4c). The diffraction rings belonged to the (110), (200)
16 and (211) planes of bcc α -iron. Besides the α -iron, two diffraction spot rings from the crystalline
17 iron carbide core were assigned to orthorhombic θ -Fe₃C (JCPDS#35-0772), which ascribed from
18 the diffraction of (121) and (301) planes, respectively. The rest of the two diffraction spot rings
19 originated from the crystalline iron carbide core and were assigned to Fe_{15.1}C (JCPDS#52-0512),
20 which stemmed from the diffraction of (200) and (220) planes, respectively.

Fig. 4. HRTEM images of (a) carbon black, (b) and (c) carbon-encapsulated iron carbide/iron nanoparticles (S1000-biosyngas), and (d) selected area electron diffraction pattern of Fig. 4c.

3.2.4 XPS

The XPS spectra were obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escaped from the top 0 to ~5 nm of the materials being analyzed. XPS was utilized to study the surface-sensitive elementary information of the CEICINs sample (S1000-biosyngas) (Fig. 5). In the survey spectrum (Fig. 5a), the three peaks attributing to the binding energies of C 1s, O 1s, and N1s

were observed. It is interesting to notice that no peaks related to iron species were detected in the sample. This may be due to the iron carbide/iron nanoparticles being encapsulated in carbon shells (~5 nm), which made it difficult to detect iron species peaks in the high-resolution Fe 2p spectrum. However, a deconvoluted weak carbon peak at 283.5 eV ascribed from iron carbide can be speculated in the high-resolution C1s spectrum (Fig. 5b). The presence of O 1s peak indicated that oxidation of the sample took place after exposure to the atmosphere (Fig. 5a). The quantification of the XPS peaks showed that the ratio of elements on the surface C:O:N:Fe is 86.8%:10.3%:2.9%:0%, indicating that iron carbide/iron core nanoparticles were encapsulated in carbon shells.

In addition, the C 1s spectrum (Fig. 5b) can be deconvoluted into three peaks, indicating that carbon atoms were presented in different bonding states. The three components were located at 283.5, 284.6, and 287.4 eV in binding energy. The strong peak at 284.6 eV can be assigned to graphite carbon, while the relative weak peak at 283.5 eV was the evidence of the formation of iron carbides [45,46]. This was consistent with the XRD analysis of iron carbide in Fig. 1. The presence of a peak at 287.4 eV associated to C=O bonds were in accordance with the oxygen contamination of the surface observed in the survey spectrum (Fig. 5a). It is interesting that the N 1s peak was observed in the XPS spectra (Fig. 5c), which may be attributed to the formation of surface carbon nitride species on the sample by thermal treatment of the sample at high temperature in biosyngas containing 47% N₂. Besides, the N 1s spectrum (Fig. 5c) can be deconvoluted into three components of C–N, C=N, and N–O at 398.8, 400.6, and 403.8 eV, respectively [47].

Fig. 5. XPS spectra of the carbon-encapsulated iron carbide/iron nanoparticles sample (S1000-biosyngas): (a) survey spectrum, (b, c) high-resolution C 1s, and N 1s spectra, respectively.

3.2.5 Raman spectra

The Raman spectra provided further information on carbon structures of the carbon black samples. The D-band at a shift of 1368 cm^{-1} and G-band at a shift of 1600 cm^{-1} represented a stretching vibration mode of amorphous carbon and graphite C=C bonds, respectively [48]. The G-band was related to the vibration of sp^2 hybridized carbon in the two-dimensional graphite for ordered carbon species [49]. The D-band was highly sensitive to disorders in the carbon materials [50]. The peak ratio of A_D/A_G of carbon black was 2 and decreased to 1.5 after thermal treatment (Figs. 6a and 6b). Dried iron-impregnated carbon black had A_D/A_G close to that of pure carbon black (Fig. 6c), while thermal treated iron-impregnated carbon black (S1000-biosyngas) possessed the lowest A_D/A_G of 1.25 (Fig. 6d). The change in Raman spectra of different carbon black samples suggested that thermal treatment increased the graphite degree in the carbon black with iron further promoting graphitization of the amorphous carbon in carbon black.

Fig. 6. Raman spectra of (a) carbon black, (b) thermal treatment of carbon black at 1000°C with nitrogen flow for 1 h, (c) iron-impregnated carbon black, (d) carbon-encapsulated iron carbide/iron nanoparticles (S1000-biosyngas).

3.2.6 TPD

The reactivity of the carbon materials is related to the surface functional groups presented on the surface. The TPD result of carbon black heated to 1000 °C at a heating rate of 2 °C/min with a nitrogen purging gas rate of 20 mL/min is presented in Fig. 7a. Fig. 7a shows one weak and broad CO₂ peak between 100 and 260°C, two sharp CO₂ peaks between 260 and 850°C with the concentration level of 0.3–0.85 % in the purging gas. The low-temperature peak (100–260°C) was assigned to the decomposition of carboxylic acids [51], while the high-temperature CO₂ evolution peaks were attributed to the decomposition of carboxylic anhydrides (260–430°C) and lactones (430–850°C) [52]. Fig. 7a shows two distinct CO desorption peaks at 680 °C and 850 °C, which corresponded to ether structures (680°C) [53], and phenols, quinone groups (800–1000°C), respectively [53,54]. The peak concentrations of CO in the carrier gas were 0.75% (680°C) and 0.8 % (850°C). Fig. 7a displays that hydrogen desorption began at 800 °C, and increased to 0.3% at 1000°C.

The TPD result of iron-impregnated carbon black heated to 1000 °C at a heating rate of 2 °C/min and with a nitrogen purging gas rate of 20 ml/min is shown in Fig. 7b. It demonstrated that most of the oxygen-containing functional groups were eliminated after heating treatment to a temperature of 1000 °C. Trace amounts of hydrogen in carbon black were chemically bonded to carbon through C–H bonds. The C–H bond was very stable but could break at high temperature. Nevertheless, the complete desorption of hydrogen did not happen at temperatures below 1200°C. The heat treatment in an inert nitrogen atmosphere eliminated part of the hydrogen via surface reduction. An expansive CO₂ peak between 100°C and 800°C can be deconvoluted to four peaks that corresponded to the steps of carbothermal process of the iron-impregnated carbon black sample. As a catalyst precursor, the iron nitrate-impregnated carbon black sample first

decomposed into ferric oxide between 100–150°C via Eq. (5). Simultaneously, oxygen generated from the decomposition of iron nitrate reacted with amorphous carbon, and CO₂ was released via Eq. (6). This release corresponded with the CO₂ peak found at 100–250 °C. Because only a few surface functional groups existed on the carbon black (Fig.7a), solid phase carbon atoms should play a key role when the reactions occurred during the carbothermal reduction process. As the temperature increased, ferric oxide (Fe₂O₃) was gradually reduced to Fe₃O₄, FeO, and Fe⁰ via Eqs. (7–9) [55,56]. Each reaction would respond to one CO₂ peak in Fig. 7b as follows: Eq. (7) represented the peak between 250 and 450°C, Eq. (8) represented the peak at 620°C, and Eq. (9) corresponded to the peak at 750°C.

Fig. 7. Hydrogen, carbon monoxide, and carbon dioxide evolution for the temperature-programmed thermal treatment of (a) carbon black, (b) iron-impregnated carbon black heated to 1000 °C at a heating rate of 2 °C/min and with a nitrogen purging gas rate of 20 mL/min, and (c) iron-impregnated carbon black heated to 1000 °C at a heating rate of 2 °C/min and with 20 mL/min 4% H_2 /Ar.

The TPD result of iron-impregnated carbon black heated to 1000 °C at a heating rate of 2 °C/min and with a 4% H₂/Ar purging gas rate of 20 mL/min is shown in Fig. 7c. The results showed that the carbothermal hydrogen reduction reaction proceeded in three stages within the temperature range studied. First, there was a considerable amount of hydrogen consumption at about 430 °C. Meanwhile, both CO₂ and CO reached a peak concentration of 7.0% and 1.8% in the purging gas, respectively. This stage was attributed to the reduction of Fe₂O₃ to Fe₃O₄ according to Eqs. (7), (10), and (11). Second, a hydrogen consumption peak and the formation of CO and CO₂ peaks appeared when the temperature was increased to 512 °C. This stage corresponded to the reduction of Fe₃O₄ to FeO based on Eqs. (8) and (12). Third, one significant CO formation peak, one CO₂ formation peak, and one H₂ consumption peak emerged at the temperature of 680 °C. These peaks were assigned to the reduction of FeO to Fe⁰ according to Eqs. (9) and (13). Hydrogen concentration increased with increasing temperature, and it reached 4.0% at 800°C and gradually increased to 4.5% at 1000°C. Although the C–H bonds were very stable, the existing of transitional metal iron would catalytically promote the decomposition of C–H bonds in the carbon black. Therefore, the inclusion of H₂ into carbothermal reduction facilitated the reduction of iron oxides and the formation of metallic iron.

3.2.7 TGA

The TGA experiments were employed to examine the reaction process of iron-impregnated carbon black (Fig. 8). Fig. 8a shows the TG and derivative thermogravimetric (DTG) curves of carbon black heated at a rate of 2 °C/min in N₂ atmosphere. Two possible steps of weight loss existed for the carbon black sample. The initial weight loss corresponded to the loss of physically adsorbed water and occurred between RT and 120 °C. This step indicated that ~1wt.% moisture existed in the carbon black sample, followed by a plateau region from 120 to

730°C. The second mass loss happened at 730 to 1000 °C. In this zone, the mass loss (~3wt.%) was mainly attributed to the decomposition of surface functional groups of C–H bonds, phenols and quinone [53,54], which emitted CO and H₂ as the main products.

Fig. 8b shows the TG and DTG curves of iron-impregnated carbon black heated at a rate of 2 °C/min in N₂ atmosphere, which was significantly different from that of the carbon black (Fig. 8a). The first-stage mass loss of iron-impregnated carbon black occurred in the temperature range from RT to 110 °C, which was due to the escape of physical adsorbed water from the sample. There was about 2 wt.% moisture in the sample. The second-stage mass loss occurred in the temperature range of 110–370 °C. The mass loss was 12 wt.%, and one reaction involved in this step was that ferric oxide (Fe₂O₃) was slowly reduced to Fe₃O₄ according to Eq. (7), and part of amorphous carbon was consumed and generated CO₂. The TPD results (Fig. 7b) also demonstrated the reduction reaction in the iron-impregnated carbon black sample since the CO₂ peak was detected. The third-stage mass loss occurred in the temperature range of 370–650 °C, where Fe₃O₄ was reduced to FeO according to Eq. (8), and the mass loss was about 4 wt.%. The fourth-stage mass loss of the sample occurred in the temperature range of 680–790 °C with a peak temperature of 756 °C, where the mass loss was ~10 wt.%. CO was the main product in the gas phase, which suggested that C reduced FeO to form Fe⁰ via Eq. (9). Finally, in the temperature range of 800–1000°C, the mass of the sample gradually decreased due to the decomposition of C–H bonds, phenols and quinone [53,54], and released CO and H₂ as the main products.

Fig. 8. TGA and DTG curves of (a) carbon black, (b) iron-impregnated carbon black heated at a rate of 2°C/min in N₂ atmosphere and (c) the iron-impregnated carbon black heated at a rate of 2 °C/min in 4% H₂/Ar atmosphere.

Fig. 8c displays the TGA and DTG results of the iron-impregnated carbon black heated at a rate of 2 °C/min in 4% H₂/Ar atmosphere. The first-stage mass loss of the sample occurred in the temperature range from RT to 125°C, which resulted from the desorption of physically adsorbed water from the sample. The second-stage mass loss occurred in the temperature range of 150–250°C, which can be assigned to the decomposition of iron nitrate impregnated carbon black according to Eq. (5). The third- and fourth-stages mass losses occurred in the temperature range of 300–350 °C and 450–570 °C, respectively. Two reactions were involved in these mass losses. Ferric oxide (Fe₂O₃) was slowly reduced to Fe₃O₄ via Eqs. (7) and (11), and then Fe₃O₄ was reduced to FeO by both solid carbon and hydrogen via Eq. (8) and (12), respectively. The highest mass loss (27.5wt.%) occurred in the range of 680–720°C with a peak temperature of 700°C, and FeO reduced to Fe⁰ in this stage via Eqs. (9) and (13).

3.3 Formation of carbon-encapsulated iron carbide/iron nanoparticles

The above-mentioned characterization results clearly display that the formation of CEICINs could be explained by the solid carbothermal reduction and chemical vapor deposition processes. In the fresh iron-impregnated carbon black sample, iron ions distributed uniformly in the carbon black matrix. At elevated temperatures, the iron nitrate impregnated carbon black sample first decomposed into ferric oxide (Fe₂O₃) in the temperature range of 100–150 °C via Eq. (7). Then the ferric oxide (Fe₂O₃) was reduced to Fe₃O₄, FeO, and Fe⁰ by solid carbon. The metallic Fe nanoparticles were generated in this step. The reduced iron nanoparticles were able to agglomerate with each other to form larger particles or be encapsulated in the carbon shells. Transition metals like iron or nickel were excellent catalysts for cleaving C–C and C–H bonds and rearranging free carbon atoms or fragments over their surfaces [57]. In addition, the transition metals were also superior for promoting the graphitization of carbon materials [57].

The attraction force of the unpaired electrons between 2p of C and 3d of Fe may play an important role in the self-assembly formation of carbon shells. Under carbothermal reaction conditions, the carbon atoms bound to the iron nanoparticles would evolve into the lowest energetic configuration, i.e., carbon atoms precipitated over the metallic iron particle surface and thereby reduce their surface energy. Iron carbides, i.e., θ -Fe₃C and Fe_{15.1}C were formed by the reaction of iron nanoparticles with surrounding carbon to form the molten iron–carbon alloy at a high temperature based on Eqs. (14–15), which transferred into iron carbides during cooling [39].

A growing carbon shield gradually encapsulated the iron carbide/iron nanoparticle to form the iron carbide/iron-core carbon-shell structure (Fig. 4). At high temperature (>1000°C), carbon black can be transferred to carbon atoms C_s, or CH_{xs} or smaller molecules of CO and CH₄, and deposited directly on the iron nanoparticle surface. The extended sp² carbon network, including hexagons and pentagons, would expand along the direction tangential to the surface of a nanoparticle, and accumulate through a graphite shell. This can facilitate further crystallization and growth of the graphite layer. Consequently, a growing carbon shell gradually encapsulated the iron carbide/iron nanoparticles to form the CEICINs core-shell nanostructure. The surface energy of the metal nanoparticles played a dominant role in the formation of carbon shells and stabilization of the nanoparticles [23,58]. The heating of iron nanoparticles supported on amorphous carbon resulted in the graphitization and encapsulation of iron nanoparticles, and has been observed by *in situ* TEM [59]. The results of the present work showed that high purity CEICINs are generated (Fig. 4). This observation suggested that the majorities of the iron carbide/iron nanoparticles were encapsulated in the carbon layers to form core-shell nanostructures.

3.4 Catalytic performances of CEICINs

The catalytic performances of the CEICINs were investigated from 250 to 350°C, reaction pressure from 500 to 1250 psig, and GHSV from 1000 to 5000 h⁻¹. Three grams of the catalyst sample (S1000-biosyngas) was used in each run. The time-on-stream after achieving steady state for each run was 100 h.

Fig. 9. Effect of reaction temperature on (a) CO and H₂ conversion, CO₂ and hydrocarbons selectivity, (b) hydrocarbons distribution, and (c) liquid fuels distribution. Reaction conditions: 3 g carbon-encapsulated iron carbide/iron nanoparticles catalyst (S1000-biosyngas), biosyngas, P = 1000 psig, GHSV = 3000 h⁻¹, time-on-stream after achieving steady state is 100 h.

3.4.1 Effect of reaction temperature on the catalytic performance

The effect of reaction temperature on the catalytic performance of the CEICINs (S1000-biosyngas) at $P = 1000$ psig, $GHSV = 3000 \text{ h}^{-1}$, time-on-stream (after achieving steady state) of 100 h is depicted in Fig. 9. Fig. 9a shows the CO conversion, hydrocarbon and CO_2 selectivity for different temperature levels. When the reaction temperature increased from 250 to 350 °C, CO conversion increased from 80.1% to 93.5%, and H_2 conversion increased from 77.2% to 91.6%. This was ascribed from the mobility of the H atom on the CEICINs catalyst surface facilitated at higher temperatures. However, C_{5+} hydrocarbon selectivity decreased from 70.0% to 61.5% (Fig. 9b). The formation of the light hydrocarbons ($\text{C}_1\text{--C}_4$) were favored at the elevated temperatures (Fig. 9b), which may be attributed to higher temperatures lowering the average carbon-chain length of products [60].

Fig. 9c shows the liquid fuel distribution of paraffins, iso-paraffins, aromatics, naphthenes, olefins, and oxygenates. The results indicated that as the temperature increased from 250°C to 350°C, paraffins decreased from 27.1% to 13.7%, and oxygenates decreased from 6.0% to 2.3%; while iso-paraffins increased from 9.9% to 11.6%, olefins increased from 41.3% to 47.1%, naphthenes increased from 5.5% to 7.1%, and aromatics increased from 10.2% to 18.2%. Olefins consisted of about 47.1% of the liquid hydrocarbon products at 350°C. The C_7 , C_6 , C_5 , C_9 and C_4 hydrocarbons were the main olefin components created. Fig. 9d shows the olefin distribution between C_2 and C_{11} . The amounts of C_4 and C_5 olefins increased with the increasing temperature, while the amounts of C_6 and C_7 olefins decreased with increasing temperature. The ratio of olefin-to-paraffin (O/P) increased from 1.12 to 1.81 between 250 °C and 350 °C. Dictor et al. [61] also observed an increase of the olefin to paraffin ratio on potassium-promoted precipitated iron catalysts with increasing temperature.

Fig. 10. Effect of biosyngas pressure on (a) CO and H₂ conversion, CO₂ and hydrocarbons selectivity, (b) hydrocarbons distribution, and (c) liquid fuel distribution. Reaction conditions: 3 g carbon-encapsulated iron/carbide iron nanoparticles catalyst (S1000-biosyngas), biosyngas, T = 310 °C, GHSV of 3000 h⁻¹, time-on-stream after achieving steady state is 100 h.

3.4.2 Effect of biosyngas pressure on the catalytic performance

The influence of biosyngas pressure on the catalytic performance of the CEICINs is presented in Fig. 10. The experiments were carried out under biosyngas pressures of 500–1250 psig. The other operating conditions were as follows: 3 g CEICINs catalyst (S1000-biosyngas), biosyngas, T = 310 °C, GHSV of 3000 h⁻¹, time-on-stream (after achieving steady state) of 100 h. As reaction pressure increased from 500 to 1250 psig, CO conversion increased from 85.1 %

to 91.5 % (Fig. 10a), C_5^+ hydrocarbon selectivity increased from 59.3% to 68.9% (Fig. 10b), while CH_4 selectivity decreased from 12.7% to 7.7% (Fig. 10b), and light hydrocarbon (C_2 – C_3) selectivity did not significantly change with the increasing reaction pressure (Fig. 10b). Hence, the increase in biosyngas pressure favored the formation of C_5^+ hydrocarbons.

Fig. 10c shows the liquid fuel distribution. The results indicated that with the increase of the biosyngas pressure, paraffins, iso-paraffins, aromatics, naphthenes and olefins were almost unchanged except that the oxygenate distribution increased from 2% to 6.3% as the pressure increased. Dictor et al. [61] also showed that the product selectivity shifted to heavier products and oxygenate compounds with increasing total reaction pressure. The synthesis rates for both alcohols and hydrocarbons were dependent on the biosyngas pressure over the CEICINs catalyst. Therefore, increasing biosyngas pressure resulted in an increased productivity of almost all products except CO_2 , which was not affected by the change in biosyngas pressure. Fig. 10d shows that the olefin selectivity shifted toward heavier products with increasing pressure.

3.4.3 Effect of GHSV on the catalytic performance

The influence of GHSV on the catalytic performance of the CEICINs is presented in Fig. 11. The experiments were carried out under GHSV of 1000–5000 h^{-1} . The other operating conditions were as follows: 3 g CEICINs catalyst (S1000-biosyngas), biosyngas, $P = 1000$ psig, $T = 310$ °C, time-on-stream of 100 h (after achieving steady state). Fig. 11a shows that increasing the GHSV from 1000 to 5000 h^{-1} shortened the contact time between biosyngas and catalyst surface, which led to a decrease in CO conversion from 92.4 % to 83.8 %. As GHSV increased from 1000 to 5000 h^{-1} , CO_2 selectivity slightly increased from 10.5% to 13.3%, while hydrocarbon selectivity slightly decreased from 89.5% to 86.7% (Fig. 11a), and C_5^+ hydrocarbon selectivity decreased from 68.9% to 59.4% (Fig. 11b). Fig. 11c shows the liquid fuel distribution,

with an increase of GHSV from 1000 to 5000 h^{-1} , olefins decreased from 49.2% to 39.5%, and aromatics decreased from 18.3% to 9.8%, while paraffins increased from 15.2% to 27.9%.

Fig. 11. Effect of GHSV on (a) CO and H₂ conversion, CO₂ and hydrocarbons selectivity, (b) hydrocarbons distribution, and (c) liquid fuels distribution. Reaction conditions: 3 g carbon-encapsulated iron carbide/iron nanoparticles catalyst (S1000-biosyngas), biosyngas, P = 1000 psig, T = 310 °C, time-on-stream after achieving steady state is 100 h.

3.4.4 The stability of the CEICINs catalyst

The stability of CEICINs catalyst was tested at 310 °C, 1000 psig, GHSV of 3000 h^{-1} with cleaned biosyngas. Fig. 12a shows CO and H₂ conversions decreased in the first 5 h and then increased steadily during the first 24 h at 310 °C, and then stabilized at 87.5% and 85%, respectively. After achieving the steady state, the total hydrocarbons selectivity was 88.3%, 65%

of which was C₅₊ hydrocarbons (Fig. 12b). The olefin selectivity within C₅₊ liquid hydrocarbons was 44.8%. The CEICINs catalyst (S1000-biosyngas) was found to be stable at 310 °C for a period of 100 h while undergoing FTS reaction after achieving steady state. For context, we compared the catalytic performances of CEICINs reported herein with other iron on carbon catalyst systems reported in the literature (Table 2). Liquid samples (both the oil phase and the aqueous phase) were collected from condenser during the FTS run over CEICINs catalyst (S1000-biosyngas) at 310 °C, 1000 psig, GHSV of 3000 h⁻¹, and time-on-stream of 100 h after achieving steady state. The liquid product formation rate was 0.07 g/(g_{cat}·h) during the first 24 h. After achieving steady state, the liquid product formation rate increased to 0.12 g/(g_{cat}·h) during the time-on-stream of 100 h. The volume percent of the oil phase in the liquid product was approximately 60%.

Fig. 12. The time-on-stream plots of Fischer–Tropsch synthesis over carbon-encapsulated iron carbide/iron nanoparticles catalyst (S1000-biosyngas) at 310 °C, 1000 psig, GHSV of 3000 h⁻¹ with cleaned biosyngas. (a) CO and H₂ conversions, (b) Hydrocarbons, C₅₊ liquid hydrocarbons, olefins within C₅₊ liquid hydrocarbons, and CO₂ selectivity.

Table 2. Survey of catalytic performances of Fe on carbon catalyst in FTS reaction.

Catalyst	Reaction condition	CO conversion (%)	Hydrocarbons Selectivity (%)	C ₅₊ hydrocarbons selectivity (%)	Olefins within C ₅₊ hydrocarbons (%)	Reference
CEICINs	T = 310°C, P = 1000 psig, H ₂ /CO ^a = 0.9, TOS = 100 h	87.5	88.3	65	44.8	This work
Reduced Fe _x O _y @C	T = 270°C, P = 290 psig, H ₂ /CO = 1, TOS = 108 h	76	77	60	N.A.	Yu <i>et al.</i> [19]
Fe ₃ O ₄ @C	T = 280°C, P = 290 psig, H ₂ /CO = 1, TOS = 48 h	87.8	64.8	55.5	N.A.	Tu <i>et al.</i> [21]
Fe/CNF	T = 340°C, P = 290 psig, H ₂ /CO = 1, TOS = 64 h	88	58	18	N.A.	Torres Galvis <i>et al.</i> [7]
Fe-in-CNT	T = 270°C, P = 739 psig, H ₂ /CO = 2, TOS = 24 h	40	82	35	N.A.	Chen <i>et al.</i> [62]
Fe/CNT	T = 300°C, P = 290 psig, H ₂ /CO = 2.1, TOS = 60 h	85.4	70	55.9	N.A.	Cheng <i>et al.</i> [63]
Fe/AC	T = 300°C, P = 290 psig, H ₂ /CO = 2.1, TOS = 60 h	64	65.9	53.7	N.A.	Cheng <i>et al.</i> [63]
Fe/AC	T = 270°C, P = 739 psig, H ₂ /CO = 2, TOS = 24 h	17	95	9.5	N.A.	Chen <i>et al.</i> [62]

Note: ^aBiosyngas was used for FTS reaction in this work while commercial syngas was used in all cited works. TOS: time-on-stream; CNF: carbon nanofiber; CNT: carbon nanotube; AC: activated carbon.

Fig. 13. GC–MS spectra of liquid products synthesis from cleaned biosyngas over carbon-encapsulated iron carbide/iron nanoparticles catalyst (S1000-biosyngas) at 310 °C, 1000 psig, and GHSV of 3000 h⁻¹. (a) oil phase, (b) aqueous phase.

The typical GC–MS spectrum of the oil phase is shown in Fig. 13a. The GC–MS oil phase product distribution can be separated into three zones. A retention time of 1.2 to 3.8 minutes, includes C₄–C₇ products, where olefins, iso-paraffins, paraffins, and naphthenes were

the main species; oxygenates were also observed in this zone. A retention time zone of 3.9–7.9 minutes, included C₇–C₈ hydrocarbons, and the main products were olefins, aromatics, iso-paraffins, and naphthenes. The third zone was retention time between 8.0 and 18 minutes, and C₈₊ products were included in this zone. These products were mainly comprised of C₉ and C₁₀ aromatics, naphthenes, and long-chain paraffins and iso-paraffins. There was about 10% oxygenates in the aqueous phase, and a typical GC–MS spectrum of the aqueous phase product is displayed in Fig. 13b. The oxygenates mainly consisted of C₁–C₄ alcohols, acetone, 2-butanone and 2-pentanone.

4. Conclusion

Fischer–Tropsch synthesis (FTS) of olefin-rich liquid hydrocarbons from biomass-derived syngas (biosyngas) was investigated by utilizing carbon-encapsulated iron carbide/iron nanoparticles (CEICINs) catalysts. The CEICINs core-shell nanostructured catalysts typically consisted of the iron carbide/iron-core diameters of 6–30 nm and graphite-shell thickness of 2–5 nm, in which the iron carbide/iron-core were composed of α -Fe, θ -Fe₃C and Fe_{15.1}C. The FTS catalytic performance on CEICINs at mild reaction conditions (310 °C, 1000 psig, 3000 h⁻¹) showed that CO and H₂ conversion was ~87.5% and 85%, respectively. The C₅₊ 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 higher selectivity towards olefins in liquid hydrocarbons, while the effect of biosyngas pressure was not a significant factor concerning olefin selectivity. GHSV possessed a negative effect on the formation of olefins because of the short-time contact of the reactant gas with the CEICINs catalyst. This work demonstrated the technical feasibility of the direct manufacture of

olefin-rich liquid hydrocarbons by using CEICINs catalyst from biosyngas via biomass gasification, biosyngas cleaning and FTS technology.

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Table 1. Effect of operational variables on the carbon-encapsulated iron carbide/iron nanoparticles yield.

Table 2. Survey of catalytic performances of Fe on carbon catalyst in FTS reaction.

Table 1. Effect of operational variables on the carbon-encapsulated iron carbide/iron nanoparticles yield.

Experiment	Temperature (°C)	Type of carrier gas	Initial mass of samples (g)	Mass of products (g)	Purification yield (%)
1 (S1000-N ₂)	1000	High purity N ₂	15.0	6.23	41.5
2 (S1200-N ₂)	1200	High purity N ₂	15.0	5.25	35.0
3 (S1000-H ₂)	1000	4% H ₂ in Argon	15.0	7.55	50.3
4 (S1000-biosyngas)	1000	Cleaned biosyngas	15.0	8.79	58.6

Table 2. Survey of catalytic performances of Fe on carbon catalyst in FTS reaction.

Catalyst	Reaction condition	CO conversion (%)	Hydrocarbons Selectivity (%)	C ₅₊ hydrocarbons selectivity (%)	Olefins within C ₅₊ hydrocarbons (%)	Reference
CEICINs	T = 310°C, P = 1000 psig, H ₂ /CO ^a = 0.9, TOS = 100 h	87.5	88.3	65	44.8	This work
Reduced Fe ₃ O ₄ @C	T = 270°C, P = 290 psig, H ₂ /CO = 1, TOS = 108 h	76	77	60	N.A.	Yu <i>et al.</i> [19]
Fe ₃ O ₄ @C	T = 280°C, P = 290 psig, H ₂ /CO = 1, TOS = 48 h	87.8	64.8	55.5	N.A.	Tu <i>et al.</i> [21]
Fe/CNF	T = 340°C, P = 290 psig, H ₂ /CO = 1, TOS = 64 h	88	58	18	N.A.	Torres Galvis <i>et al.</i> [7]
Fe-in-CNT	T = 270°C, P = 739 psig, H ₂ /CO = 2, TOS = 24 h	40	82	35	N.A.	Chen <i>et al.</i> [62]
Fe/CNT	T = 300°C, P = 290 psig, H ₂ /CO = 2.1, TOS = 60 h	85.4	70	55.9	N.A.	Cheng <i>et al.</i> [63]
Fe/AC	T = 300°C, P = 290 psig, H ₂ /CO = 2.1, TOS = 60 h	64	65.9	53.7	N.A.	Cheng <i>et al.</i> [63]
Fe/AC	T = 270°C, P = 739 psig, H ₂ /CO = 2, TOS = 24 h	17	95	9.5	N.A.	Chen <i>et al.</i> [62]

Note: ^aBiosyngas was used for FTS reaction in this work while commercial syngas was used in all cited works. TOS: time-on-stream; CNF: carbon nanofiber; CNT: carbon nanotube; AC: activated carbon.

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Fig. 1. XRD patterns of iron-impregnated carbon black samples: (a) dried at 150 °C overnight, (b) calcined at 300 °C, (c) S1000-N₂, (d) S1200-N₂, (e) S1000-H₂, and (f) S1000-biosyngas.

Fig. 2. SEM images of carbon-encapsulated iron carbide/iron nanoparticles samples: (a) S1000-N₂, (b) S1200-N₂, (c) S1000-H₂, and (d) S1000-biosyngas.

Fig. 3. TEM images of samples: (a) iron nitrate impregnated with carbon black, dried at 150 °C overnight, (b) S1000-N₂, (c) S1200-N₂, (d) S1000-H₂, (e,f) S1000-biosyngas and particle size distribution.

Fig. 4. HRTEM images of (a) carbon black, (b) and (c) carbon-encapsulated iron carbide/iron nanoparticles (S1000-biosyngas), and (d) selected area electron diffraction pattern of Fig. 4c.

Fig. 5. XPS spectra of the carbon-encapsulated iron carbide/iron nanoparticles sample (S1000-biosyngas): (a) survey spectrum, (b, c) high-resolution C 1s, and N 1s spectra, respectively.

Fig. 6. Raman spectra of (a) carbon black, (b) thermal treatment of carbon black at 1000°C with nitrogen flow for 1 h, (c) iron-impregnated carbon black, (d) carbon-encapsulated iron carbide/iron nanoparticles (S1000-biosyngas).

Fig. 7. Hydrogen, carbon monoxide, and carbon dioxide evolution for the temperature-programmed thermal treatment of (a) carbon black, (b) iron-impregnated carbon black heated to 1000 °C at a heating rate of 2 °C/min and with a nitrogen purging gas rate of 20 mL/min, and (c) iron-impregnated carbon black heated to 1000 °C at a heating rate of 2 °C/min and with 20 mL/min 4% H₂/Ar.

Fig. 8. TGA and DTG curves of (a) carbon black, (b) iron-impregnated carbon black heated at a rate of 2°C/min in N₂ atmosphere and (c) the iron-impregnated carbon black heated at a rate of 2 °C/min in 4% H₂/Ar atmosphere.

Fig. 9. Effect of reaction temperature on (a) CO and H₂ conversion, CO₂ and hydrocarbons selectivity, (b) hydrocarbons distribution, and (c) liquid fuels distribution. Reaction conditions: 3 g carbon-encapsulated iron carbide/iron nanoparticles catalyst (S1000-biosyngas), biosyngas, P = 1000 psig, GHSV = 3000 h⁻¹, time-on-stream after achieving steady state is 100 h.

Fig. 10. Effect of biosyngas pressure on (a) CO and H₂ conversion, CO₂ and hydrocarbons selectivity, (b) hydrocarbons distribution, and (c) liquid fuel distribution. Reaction conditions: 3 g carbon-encapsulated iron/carbide iron nanoparticles catalyst (S1000-biosyngas), biosyngas, T = 310 °C, GHSV of 3000 h⁻¹, time-on-stream after achieving steady state is 100 h.

Fig. 11. Effect of GHSV on (a) CO and H₂ conversion, CO₂ and hydrocarbons selectivity, (b) hydrocarbons distribution, and (c) liquid fuels distribution. Reaction conditions: 3 g carbon-encapsulated iron carbide/iron nanoparticles catalyst (S1000-biosyngas), biosyngas, P = 1000 psig, T = 310 °C, time-on-stream after achieving steady state is 100 h.

Fig. 12. The time-on-stream plots of Fischer–Tropsch synthesis over carbon-encapsulated iron carbide/iron nanoparticles catalyst (S1000-biosyngas) at 310 °C, 1000 psig, GHSV of 3000 h⁻¹ with cleaned biosyngas. (a) CO and H₂ conversions, (b) Hydrocarbons, C₅₊ liquid hydrocarbons, olefins within C₅₊ liquid hydrocarbons, and CO₂ selectivity.

Fig. 13. GC–MS spectra of liquid products synthesis from cleaned biosyngas over carbon-encapsulated iron carbide/iron nanoparticles catalyst (S1000-biosyngas) at 310 °C, 1000 psig, and GHSV of 3000 h⁻¹. (a) oil phase, (b) aqueous phase.

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