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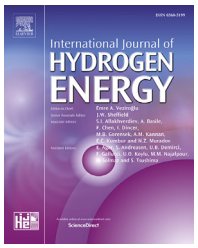

Fischer-Tropsch synthesis using iron based catalyst in a microchannel reactor: Performance evaluation and kinetic modeling

Yong Sun [a,*], Zhe Jia [a], Gang Yang [b,c], Lian Zhang [d], Zhi Sun [e,**]

[a] Edith Cowan University School of Engineering, 270 Joondalup Drive Joondalup WA 6027, Australia
[b] Anpeng High-tech Energy Corp, Beijing, China
[c] National Engineering Laboratory of Acid/base Coupled Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China
[d] Monash University Department of Chemical Engineering, VIC 3800, Australia
[e] National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

Fischer-Tropsch (FT) synthesis was carried out in a microchannel reactor using an iron-based catalyst. The performance of microchannel reactor was evaluated in the aspect of CO conversion versus time on stream, catalyst deactivation, pressure drop and gas hour space velocity. The result indicates an excellent mass and heat transfer in the microchannel reactor. The negative impact of external and internal film diffusional limitation could be avoided in this microchannel reactor at experimental conditions. The effect of reaction temperature, operational pressure, syngas ratio and space velocity upon CO conversion and hydrocarbon selectivity were extensively investigated. The kinetic modeling was conducted and the mechanisms *i.e.* carbide, enlic, alkyl, formate and CO insertion were extensively explored. A mechanism derived from Eley-Rideal-type mechanism was found to be the most statistical and physical relevance at the experimental conditions during FT synthesis using iron-based catalyst in this microchannel reactor.

Introduction

Natural gas, coal, biomass obtained from abundant resources i.e. agricultural, forestry industry etc, and biogas may be converted to fuels and bulk chemicals such as FT (Fischer-Tropsch) synthesis products, methanol/or DME (dimethoxyethane), hydrogen and ammonia, *via* synthesis gas generated by feedstock dependent combination of reforming, oxidation and gasification reaction [1–3]. To realize economics of this type of process, the scale needs to be over certain threshold. For example, the Pearl GTL (gas-to-liquid) operated by Pearl and Qatar petroleum with the productivity reaching 140,000 bpd (barrels per day) is regarded as a successful example of profitable economical scale of GTL processing [4]. However, there are many gas wells that are too small to meet the current

* Corresponding author. Edith Cowan University School of Engineering, 270 Joondalup Drive Joondalup WA 6027 Australia.
** Corresponding author.
E-mail addresses: y.sun@ecu.edu.au, ysunipecas@gmail.com (Y. Sun), sunzhi@ipe.ac.cn (Z. Sun).
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economical productivity demands of industrial scale GTL. In addition, the limitation of transporting biomass to realize its cost-effectiveness calls for the processing scale being less than 500 bpd [5]. These scenario all drive both industries and researchers to pursue the alternative technologies that challenge the dependency of scale. Because of high degree of process intensification in field of strongly endothermic and exothermic reactions [6–9], the microstructured technology is regarded as one of reliable and promising solution for small and medium scale catalytic process, and many research groups and companies such as Velocys, and Micrometrics have been very active and led R&D researches in this area during the last decade [10–13]. As FT synthesis is the one of core technology for GTL and BTL (biomass to liquid), the room left for optimization of reaction system, preparation of high performance catalyst with better selectivity and longer stability still remains big. Because of advantages of utilizing low syngas (H_2/CO) ratio, larger selectivity in petrol, diesel and olefin fractions, and cost-effectiveness in production when it is compared with cobalt based catalyst [14], the iron-based catalyst still shows its obvious attractive advantages in practical applications for high temperature FT synthesis [15–18]. Although the FT synthesis using iron-based catalyst in many different types of conventional reactor system i.e. fixed bed reactor (FBR), micro-fixed bed reactor, slurry phase CSTR (continuous stirred tank reactor) etc have been widely investigated [19–21], the reports of using iron-based catalyst in the microchannel reactor are still very limited. For sake of process intensification, easiness of implementing into BTL process with a low syngas ratio and providing valuable data for comparisons among different reactor systems, the FT synthesis using iron-based catalyst in a microchannel reactor was therefore performed. In this work, the performance (both mass transfer and process parameters) of FT synthesis in microchannel reactor was evaluated, the effects of process parameters *i.e.* reaction temperature, operational pressure, syngas ratio and space velocity upon CO conversion and hydrocarbon selectivity were extensively investigated. In addition, the modeling of CO consumption rate in this microchannel reactor using Langmuir-Hinshelwood and Eley-Rideal mechanistic approach was also deployed to gain some insightful understandings of reaction route during CO initiation.

Experimental

Catalyst preparation

The catalyst in this work was prepared by the wet co-precipitation method [22,23]. About 10 g of $Fe(NO_3)_3{\cdot}9H_2O$ and $Cu(NO_3)_2{\cdot}5H_2O$ was firstly dissolved in 500 ml ultrapure water in a glass flask, after which a certain amount of silica solution was added and mixed well. Afterwards, 100 ml ammonia solution was added to this 500 ml mixture in flask with good agitation. During co-precipitation, the flask was placed in a 333 K thermostatic water-bath and the pH value of co-precipitated slurry was maintained at 9.0. After the co-precipitation, the slurry was filtered and the filter cake was washed by de-ionized water until the pH value of slurry reached 7.0. After filtration, the K_2CO_3 (10 wt%) solution was mixed with the filter cake and the mixture was agitated in an ultrasonic bath for sake of better mixing. The obtained slurry was repeatedly filtered and washed and dried under 393 K for 36 h and then calcined at 723 K for 4 h with flow rate of air at 2.5 $L.g_{cat}^{-1}.h^{-1}$. The prepared catalyst was then sieved to obtain the particle range of 37–75 μm. To test metal loading, the prepared catalyst was digested and the metal concentration was determined by ICP-OES (induced coupled plasma-optical emission spectrometer) using a microwave digestion method. The detailed property of the prepared catalyst is shown in Table 1.

Characterization of catalyst

XRD (X-ray powder diffraction): Philips X-Pert diffractometer using Co Kα radiation at a wavelength of $\lambda = 0.15406$ nm with 2θ changing from 10 to 90° at speed of 3 $deg.min^{-1}$.

SEM morphology: JSM-7001F + INCA X-MAX Field emission electron microscope.

Specific surface area and porosity: Micromeritics ASAP 2020 automated gas sorption system using N_2 adsorption at 77 K at a saturation pressure of 0.1 MPa. BET (Brunauer-Emmett-Teller) specific surface area was assessed within the range of relative pressure from 0.05 to 0.3. The porosity was measured by mercury porosimeter (Auto Pore IV 9500, Micromeritics, USA).

Elemental analysis: ICP-OES (OPTIMA 7100DV, Perkin Elmer, USA) with the aid of microwave, the detailed sample digestion procedures could be found from prior report [24].

Configuration of microchannel reactor and FT synthesis

The FT synthesis was carried out in a microchannel reactor system. The schematic diagram of the system and the configuration of microchannel reactor are shown in Fig. 1. The dimension of stainless steel metal plate and a channel are 80 × 80 mm and 1 × 1 × 40 mm (depth × width × length), respectively. The D_h (hydraulic diameter) of the channel is 1 mm. The total volume of the channels is about 0.32 ml. The heater was inserted into both the top and bottom plates to keep

Table 1 – Physical properties of catalyst and reactor system.

Property	Value	ICP-OES	Composition (wt %)
Bulk density/$kg.m^{-3}$	1300	Fe	40.3
Porosity/-	0.65	Cu	4.33
Surface area/$m^2.g^{-1}$	85	K	8.57
Volume of reactor/ml	0.32	Si	2.01
Mass of catalyst/g	0.25	O*	44.79
Average diameter/μm	40		
Tortuosity factor/-	2 [47]		
CO diffusivity in wax/$m^2.s^{-1}$	1.2×10^{-8}		

* represents by difference.