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# The effect of syngas composition on the Fischer Tropsch synthesis over three-dimensionally ordered macro-porous iron based catalyst

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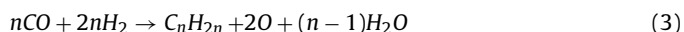
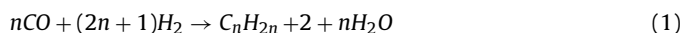
## ABSTRACT

Three-Dimensionally Ordered Macro-porous (3DOM) Fe based catalysts were synthesized via a facile “glyoxylate route” poly (methyl methacrylate) (PMMA) colloidal crystal template (CCT) method. Fischer Tropsch Synthesis (FT) using different biosyngasses over the 3DOM Fe based catalyst for producing the liquid hydrocarbon was studied. The morphology, structure and microstructures of 3DOM Fe based catalysts were characterized by SEM, BET, TPR, HRTEM, XRD, XPS and DRIFTS. The experimental results demonstrated that the hydrogen lean syngas decreased the partial pressure of H<sub>2</sub>/CO, which caused the decrease of the CO conversion rate during FT reaction. Moreover, the addition of CO<sub>2</sub> and CH<sub>4</sub> in the hydrogen lean syngas could well preserve the iron carbide phase in the catalyst, and the CO conversion rate was improved. Lower H<sub>2</sub>/CO ratio syngas would shift the liquid hydrocarbon distribution to higher molecular weight hydrocarbons, and the addition of CO<sub>2</sub> and CH<sub>4</sub> into the syngas further facilitated the shift. Meanwhile, it was also found that the CO conversion rate and C<sup>5+</sup> selectivity were 68.23% and 70.44% respectively during the simulated biosyngas from biomass gasification (the hydrogen lean syngas contained CO<sub>2</sub> and CH<sub>4</sub>) FT over the 3DOM Fe based catalyst, and CO<sub>2</sub> and CH<sub>4</sub> selectivity were 12–26% and 2.67–5.5% respectively.

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## 1. Introduction

With the challenges of diminishing the traditional petroleum reserves and increasing the environmental concerns, the thermochemical conversion of biomass to liquid fuels (BTL) has been regarded as one of the promising routes of producing tomorrow's liquid transportation fuels [1]. Fischer Tropsch (FT) synthesis, as one of the key technologies in the BTL process, has been attracted to more attention in recent years [2]. The syngas is mainly converted into a range of hydrocarbons of various molecular weights according to the following reactions [3]:



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Unfortunately, the biomass-derived syngas is not optimal for the commercial catalysts (Fe and Co based catalysts) because of the low H<sub>2</sub>/CO ratio (0.45–1.03) [4]. Biomass steam-oxygen gasification usually produces the hydrogen lean biosyngas which contains 25–30% H<sub>2</sub> and 43–47% CO [5], and the hydrogen lean biosyngas from the biomass ambient air gasification usually contains 18–20% H<sub>2</sub>, 20–24% CO, 9–12% CO<sub>2</sub>, 1–4% CH<sub>4</sub> and nitrogen as the balance [6]. The relative high level of CO<sub>2</sub> lowered the partial pressures of CO + H<sub>2</sub> and the rate of hydrocarbon formation. Moreover, the active iron carbide phase of catalyst would be oxidized by CO<sub>2</sub> [7]. Hence, enormous efforts have been made to improve the gas utilization efficiency of these H<sub>2</sub>-lean biosyngasses. The activity and selectivity of catalysts could be promoted by adding promoters such as alkali metals, Cu, and the noble metals (Ru, Rh, Pt, etc.) or metal oxides (ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, MnO) [8–12]. The improvement of the structure, textural and morphology of catalysts supports was an alternative method of enhancing the selectivity and activity of catalysts [13,14]. Hou et al. reported that three dimensionally ordered (3DOM) catalysts could significantly improve the catalytic performance for CO oxidation because 3DOM catalysts were beneficial for the reactant species diffusion. At the same time, the existence of the meso-porous and macro-porous may simultaneously provide

the high surface areas and more active sites [15]. Zhang et al. also found that the cobalt catalyst supported on a meso-porous support with larger pore diameter had achieved better activity and C<sub>5+</sub> selectivity [16]. Jung et al. stated that the catalyst supported on a meso-macro pore structure support showed a more stabilized catalytic activity and better heavy hydrocarbon selectivity in the FT reaction compared to other catalysts [17]. However, the syngas from biomass gasification contains 9–12% CO<sub>2</sub>, and the previous researches did not concern FT synthesis using the model biosyngas with CO<sub>2</sub>.

The present work focuses on developing a novel 3DOM Fe based catalyst using PMMA microspheres as templates (no rare-earth metal addition), and converts the model syngas (contain CO<sub>2</sub> and CH<sub>4</sub>) from biomass gasification into the liquid hydrocarbons. The effects of the syngas compositions on the surface carbonaceous species formation, phase transformations and catalytic performance over the 3DOM Fe based catalyst will also be discussed.

## 2. Experimental

### 2.1. Catalyst preparation

In this study, the mono-dispersed PMMA microspheres were synthesized by a modified dual-phase emulsifier-free emulsion polymerization method [18,19]. The batch polymerization reactor for synthesizing Poly(methyl methacrylate) (PMMA) microspheres was shown in SFig. 1. For synthesizing 3DOM Fe based FTS catalyst, 44 ml Ethylene Glycol (EG) and 6 ml methanol were mixed in a 100 ml beaker, then 40 g iron nitrate was added into the EG-methanol mixture. The solution was stirred with a speed of 50 r/min at room temperature for 2.5 h, and the precursor solution was formed. The dried PMMA template was then added into the well-mixed precursor solution for 3 h. The excess precursor was removed by a vacuum filtration, and an impregnated PMMA template was obtained. After drying, the impregnated PMMA template-precursor sample was finally mixed with quartz sand and calcined in a quartz tube reactor at the ramping rate of 1 °C/min from room temperature to 650 °C, and maintained at 650 °C for 3 h. Thus, the 3DOM Fe based FT catalyst was prepared.

### 2.2. Catalyst characterization

The morphology of PMMA was characterized by Field Emission Scanning Electron Microscope (JEOL JSM-6500F, JEOL USA, Inc., Waterford, VA) with an operating voltage of 5 kV. The morphology of 3DOM iron based catalyst was also characterized by Zeiss SUPRA 40 FEG-SEM system (Thornwood, NY) with an operating voltage of 10 kV. Moreover, High Resolution Transmission Electron Microscopy (HRTEM) images were obtained through JEOL 2100 electron microscope (JEOL, Japan). The structure properties (the specific surface area, average pore diameter, and pore volume) of 3DOM Fe based catalysts were determined using Quantachrome Autosorb-1C instrument (Boynton Beach, FL). Temperature Programmed Reduction (TPR) profile of the fresh catalyst was recorded using a Quantachrome ChemBET PULSAR apparatus (Boynton Beach, FL) equipped with a thermal conductivity detector (TCD). The phase composition and crystalline structure of the catalysts were determined using an Ultima III X-ray diffractometer (Rigaku Americas, The Woodlands, TX). X-ray Photoelectron Spectroscopy (XPS) spectra were taken by a PHI 1600 XPS surface Analysis System (Physical Electronics, Eden Prairie, MN). DRIFTS spectra were obtained using a Bruker FTIR Tensor 27 with a MCT detector in conjunction with Praying Mantis™ Diffuse Reflection Accessory (Billerica, MA).

**Table 1**

Three types of syngas used in the tests.

Gas Composition	H <sub>2</sub> (%)	CO (%)	CO <sub>2</sub> (%)	CH <sub>4</sub> (%)	N <sub>2</sub> (%)
SG21	64	32	0	0	4
SG11	48	48	0	0	4
SB	19	20	12	2	47

**Table 2**

Textural property of 3DOM Fe catalyst at different stages.

3DOM Fe catalyst	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
Fresh	33	0.20	25
Reduced	116	0.67	23
Spent (SG21)	92	0.44	19
Spent (SG11)	15	0.04	14
Spent (SB)	17	0.07	11

### 2.3. Reactor system and operation procedure

The catalytic performance tests were carried out in a micro tubular fixed bed reactor system. The detailed configuration and description of the reactor system can be found in our previous paper [20]. Before each run, 0.125 g 3DOM Fe based FT catalyst was uniformly mixed with the glass beads (the diameter was about 2 mm) to form 10 vol.% catalyst mixture, then 3DOM Fe based FTS catalyst mixture was loaded into the reactor tube and reduced by the syngas (50% H<sub>2</sub> and 50% CO) at 350 °C, 0.35 MPa, and 1000 h<sup>-1</sup> of Gas Hourly Space Velocity (GHSV) for 24 h. After the reduction, the feed gas was switched to the predetermined reactant gas, and the operation parameters were gradually increased to the predetermined parameters (List in Table 3) for FT reaction. GHSV was fixed at 3600 h<sup>-1</sup> in all the tests, while other parameters such as the temperature (270–310 °C) and pressure (2.14–3.79 MPa) were varied. Three types of syngas were used in the tests, as summarized in Table 1 (SG21 mean the syngas with 2.0H<sub>2</sub>/CO ratio; SG11 mean the syngas with 1.0H<sub>2</sub>/CO ratio; SB mean the simulated biosyngas from biomass gasification, which contains 12% CO<sub>2</sub> and 2% CH<sub>4</sub>). The gas at the outlet of the reactor was analyzed using an online Agilent 7890 Gas Chromatography (Santa Clara, CA) with helium and nitrogen as carrier gases. A HP Plot capillary column was used to analyze the gaseous hydrocarbons (C<sub>1</sub>–C<sub>4</sub> ranged alkanes and alkenes) with a Flame Ionization Detector (FID) and a molecular sieve-packed column was used to analyze CO, CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> with a Thermal Conductivity Detector (TCD). The liquid hydrocarbons collected from the condenser were analyzed via a Detailed Hydrocarbon Analyzer (NARL 6560 MODEL 4060, Waltham, MA), which was composed of a Perkin Elmer Clarus 680 GC with a FID detector.

Nitrogen in the syngas was assumed as inert during the reaction. CO and H<sub>2</sub> conversion rates were defined as the mole percentage of carbon monoxide and hydrogen reacted during FT reaction, as shown in Eqs. (4) and (5), respectively. Product selectivity was defined as the mole percentage of CO converted into the specific product during FT reaction, as shown in Eq. (6)–(8):

$$\text{CO conversion rate (mol\%)} = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100 \quad (4)$$

$$H_2 \text{ conversion rate (mol\%)} = \frac{H_2 \text{ in} - H_2 \text{ out}}{H_2 \text{ in}} \times 100 \quad (5)$$

$$CO_2 \text{ selectivity (mol\%)} = \frac{\text{number of CO converted to } CO_2}{\text{total number of CO converted}} \times 100 \quad (6)$$

$$C_{1-4} \text{ selectivity (mol\%)} = \frac{\text{number of CO converted to } C_1 - C_4}{\text{total number of CO converted}} \times 100 \quad (7)$$

$$C^{5+} \text{ selectivity (mol\%)} = 100 - CO_2 \text{ selectivity} - C_{1-4} \text{ selectivity} \quad (8)$$

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