



# Microfibrinous entrapped hybrid iron-based catalysts for Fischer–Tropsch synthesis



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## ABSTRACT

Fischer–Tropsch synthesis (FTS) is a highly exothermic reaction, and a FTS reactor must have an efficient heat transfer mechanism in order to maintain a stable reaction temperature. Copper microfibrinous entrapped catalyst (Cu MFEC) has demonstrated an excellent intra-bed heat transfer ability for FTS thermal management. The porous structure of Cu MFEC can entrap any pre-manufactured catalyst particles, while its counterpart approaches such as metallic foams or monolith reactor structures are typically based on washcoating process and require the details about catalyst formulation and preparation procedure to proceed. In this investigation, a highly active and stable iron-based FTS (Fe-FTS) catalyst, i.e. iron supported on  $\gamma$ -alumina and promoted with copper and potassium, has been developed. The apparent reaction rate constant of Fe-FTS and its productivity at 27.7% of CO conversion are 167 mmol ( $H_2 + CO$ )/g<sub>cat</sub>/h and 0.30 gC<sub>5+</sub>/g<sub>cat</sub>/h, respectively, which are comparable to the most active unsupported Fe-based catalyst. When Fe-FTS was physically mixed with equal mass of mesoporous aluminosilicate (MAS) loaded with 0.3 wt% Pt, a hybrid catalyst was formed. This hybrid catalyst demonstrated an extremely low CO<sub>2</sub> selectivity (27.7 C%) and a very high selectivity (38.1 C%) to liquid products (C<sub>5</sub>–C<sub>20</sub>). The result suggested that FTS and hydrocracking process simultaneously took place within a single reactor. Furthermore, FTS was carried out in a larger tubular reactor (34.0 mm I.D.) packed with Cu MFEC. It demonstrated a radial temperature gradient less than 5 °C and similar reactivity and product selectivity as those obtained in a small FTS reactor (9.5 mm I.D.). While with the same catalyst loading density and the same test conditions, the comparative packed bed (34.0 mm I.D.) reached radial temperature gradient around 54 °C. It was also found that the FTS based Cu MFEC required negligible amount of time to reach its steady state compared with the packed bed. With these attributes and advantages, Cu MFEC approach is a promising alternative to the traditional packed bed for exothermic reactions such as FTS.

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## 1. Introduction

Fischer–Tropsch synthesis (FTS) is a well-known Gas-to-Liquid technique for converting natural gas or syngas into liquid fuels. However, FTS is a highly exothermic reaction which causes many heat transfer issues for FTS intensification since FTS was established in 1920s [1]. First of all, the reaction temperature is easy to run away due to extensive heat generation, which can lead to some severe quality and even safety problems. More importantly, FTS is a temperature sensitive reaction, and its product distribution is strongly dependent on the reaction temperature. Undesirable gaseous products like methane, ethane, etc. will be produced at

high temperatures. For the maximum selectivity to desired liquid products, the FTS reactor should be well controlled at a single stable temperature for entire reactor. In addition, the high reaction temperature could deactivate the catalysts by sintering its active metal sites. As a result, an efficient heat transfer is the key to solve FTS related issues.

In the past, researchers put tremendous efforts to develop various heat transfer structures for FTS in order to avoid reaction temperature overshoot and formation of hot spots. The major representative works are fluidized reactor and slurry reactor. Both of them have been successfully used in research and industrial areas [2–7]. For other types of reactors, including metallic foams and metal monolith catalyst structures, some successful applications also existed in their infant stage [8–12]. However, they all have disadvantages. For instance, fluidized reactors require catalysts with good mechanical strength and complicated downstream

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recovery processes [3]. The serious issues for slurry reactor are back-mixing of the gas phase, catalyst attrition and separation from the liquid and wax products [13]. For metallic foams and monolith reactor structures, catalysts need to be prepared either directly on the reactor structure or on a washcoating process to load catalytic components [14,15]. Hence, these two kinds of reactor structures are not suitable for pre-manufactured catalysts. Through persistent efforts, our group developed a novel catalyst structure called microfibrillar entrapped catalyst (MFEC) structure which is now commercially available at IntraMicron Inc. MFEC is a structured catalyst and it consists of a highly porous network structure made of micron-sized metal, glass, or polymer fibers with small catalyst particles entrapped inside [16–20]. One of the biggest advantages of MFEC when compared with metallic foams or monolith reactor structures is that MFEC can be used for pre-manufactured catalyst particles. This unique advantage greatly extends the applications of MFEC on many heterogeneous reactions by using the original optimized catalyst recipes, instead of seeking a new recipe for washcoating support [21–23]. Previous efforts have found out that MFEC demonstrates high void volume, which significantly reduces pressure drop compared with packed bed. Moreover, intra-particle heat transfer and mass transfer are enhanced in MFEC structure, since small particles are used and acceptable uniform particle distribution are achieved. This unique catalyst structure has been widely used in various fields. For instance, Yang et al. studied the effects of microfibrillar media on external mass transfer in desulfurization [24,25]. Zhu et al. discussed the electrical conductivity of metal microfibrillar in fuel cell [26,27]. Gu et al. built a Computational Fluid Dynamics pressure drop model for MFEC filter [28]. Sheng et al. investigated and simulated the thermal properties of MFEC and applied to FTS reaction [29–31]. According to Sheng et al.'s investigation, copper MFEC can significantly enhance intra-bed heat transfer and maintain a stable reaction temperature for highly exothermic reaction like FTS.

FTS produces a broad spectrum of products including gas, liquid and wax [32,33]. In order to maximize amount of hydrocarbons in the range of liquid fuels, a suitable operational conditions are required. For example, cobalt based catalyst typically requires 220 °C and 20 bar to produce hydrocarbon liquids with the maximum selectivity. In order to further enhance hydrocarbon liquid fraction, paraffinic wax formed during FTS is hydrocracked to form more liquids. Traditionally, the complicated and expensive process of hydrocracking is performed downstream in a separate reactor. However, by physical mixing of an FTS catalyst with an acidic zeolite component, the FTS and hydrocracking process can simultaneously occur in a single reactor [34–36]. The common FTS catalysts used in the industry are cobalt and iron based catalysts [37,38]. Iron-based catalysts are more favorable to produce long chain hydrocarbons from coal or biomass (low H<sub>2</sub>/CO ratio) due to their high water-gas shift activity, low cost and low methane selectivity [5]. Typically, unsupported iron catalysts promoted with copper and potassium are used in the industry. These catalysts provide high activity and selectivity to hydrocarbons. However, the unsupported Fe-based catalysts are generally lack of physical strength and durability. In contrast, alumina-supported Fe-based catalysts although providing low activity and high methane selectivity, are stronger and more attrition resistant than unsupported Fe-based catalysts [39].

In the current investigation, a highly active and stable  $\gamma$ -alumina supported Fe-based catalyst was prepared and tested for FTS, and a mesoporous aluminosilicate (MAS) was synthesized as hydrocracking catalyst. A hybrid FTS catalyst that physically combined these two components together, has been developed to be applied on FTS and hydrocracking reactions simultaneously within a single reactor. The results revealed that this type of hybrid catalyst can produce wax-free liquid fuels (C<sub>23</sub>+ less than 5 wt%), but the C<sub>5</sub>–C<sub>20</sub> selectivity was relative low and the selectivity of light hydrocarbons

(C<sub>1</sub>–C<sub>4</sub>) was significantly high. Recently, the addition of 0.3 wt% of Pt to the MAS for formation of a new hybrid FTS catalyst greatly enhanced C<sub>5</sub>–C<sub>20</sub> selectivity and reduced the selectivities to CO<sub>2</sub> and the light hydrocarbons (C<sub>1</sub>–C<sub>4</sub>).

Typical tubular reactors filled of active FTS catalysts will experience thermal runaway at a large reactor diameter due to inefficient radial heat transfer through the packed bed. However, the Cu MFEC structure successfully scaled up the FTS reaction to this larger degree without losing catalyst activity and major product selectivity, by significantly enhancing heat transfer and maintaining a stable reaction temperature. In order to demonstrate the benefits of the MFEC structure, a tubular reactor with a large inside diameter (I.D.) of 34.0 mm I.D. has been designed and tested for FTS using hybrid FTS catalysts.

## 2. Experimental

### 2.1. MFEC structure and catalyst preparation

#### 2.1.1. Fabrication of Cu MFEC

A traditional paper-making technique was developed to prepare MFEC by Auburn University. The detailed process can be found in the literature [31]. Briefly, micro-sized copper fibers and cellulose fibers were dispersed in an aqueous suspension. Then, the resulting mixture was cast into a paper-making model and formed a preformed sheet by removing the water. A two-sided sheet can be fabricated by stacking two pieces of performed sheets together, which were made by copper microfibers with different diameters. The top layer was made by 12  $\mu$ m diameter copper microfibers, and the bottom layer was 4  $\mu$ m diameter copper microfibers (IntraMicron, Auburn, AL, USA). After drying these two layers, a self-supporting two-sided sheet has been created. Subsequently, this preformed sheet was pre-oxidized in a flowing air at 500 °C for 30 min in order to remove the bulk of cellulose. Then, the pre-oxidized sheet was sintered in a flow of hydrogen at 700 °C for 60 min to form fiber-fiber junctions. These junctions can form a sinter-locked network through the fiber media, which greatly enhanced heat transfer on this media. The final step was loading catalyst particles with certain sizes into this porous microfiber media. Actually, after sintering, the top layer of media became very fluffy, and bottom layer was much compact since it was made by fibers with smaller diameter. Hence, the catalyst particles can be easily load into the top layer of this microfiber media, and the bottom layer was aimed to prevent the catalyst particles from leaking or moving out from the microfiber media.

#### 2.1.2. Preparation of Fe-based FTS catalyst

The Fe-based FTS catalyst was supported on a commercial gamma-alumina (Alfa Aesar,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> #43832). The metal precursors were iron(III) nitrate nonahydrate (Alfa Aesar, ACS grade, 98.0–101.0 wt%), copper(II) nitrate hemipentahydrate (Alfa Aesar, ACS grade, 98.0–102.0 wt%), and potassium hydrogen carbonate (Alfa Aesar, ACS grade, 99.7–100.5 wt% dried basis). In a typical procedure,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were grounded and sieved to 60–80 mesh (177–250  $\mu$ m), and then calcined in static air at 750 °C for 5 h to remove the hydroxyl groups on the surface. Then, 9.3 g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 2.555 g Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O, and 0.954 g KHCO<sub>3</sub> were dissolved in 36.0 mL deionized water. An excess solution impregnation method was used to load the metal solution on 3.0 g calcined  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in three steps [40,41]. In each step, one third of the above metal solution was added to the support while kept it on a shaker and dried it slowly in atmosphere. After drying, the sample was calcined at 300 °C for 5 h in static air. Then, the previous steps were repeated two times in order to load the leftover metal solution. It must be noted that each time of loading followed by calcination.

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