



Short Communication

Effective control of α -olefin selectivity during Fischer–Tropsch synthesis over polyethylene-glycol enwrapped porous catalyst

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ABSTRACT

Effective control of α -olefin selectivity during Fischer–Tropsch synthesis (FTS) was achieved through continuously adding a polar solvent, polyethylene glycol (PEG), in a fixed-bed reactor over an industrial Fe-based catalyst under typical FTS reaction conditions. The α -olefin content increased drastically and was independent of carbon number in C_{6+} range, whereas the product carbon-number-distribution changed unobviously. Similar trend was also observed in the results obtained from a continuously stirred tank reactor using PEG as reaction medium. This phenomenon can be explained by the suppressed α -olefin secondary reactions due to the existence of a PEG-membrane on the catalyst surface.

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1. Introduction

Fischer–Tropsch synthesis (FTS) is generally considered as a consecutive reaction giving linear α -olefins as the main primary products [1–5]. These α -olefins can readsorb upon catalyst surface and undergo secondary reactions such as hydrogenation, isomerization, chain growth and/or hydrogenolysis to produce *n*-paraffins, internal olefins, heavier hydrocarbons and/or lighter hydrocarbons as final products. As linear α -olefins are important industrial feedstock for premium lubricating oils, plasticizer, detergent or surfactant, comonomers etc. [6,7], it is of high significance to selectively produce linear α -olefins by suppressing their secondary reactions. However, it is very difficult to realize such target in a traditional FTS process. The catalyst pores under conventional reaction conditions are supposed to be filled with wax formed during FTS reaction [5–8]. This may reduce the diffusion rate of reactive α -olefins in the catalyst pores and consequently increase their probability of secondary reactions. Moreover, this effect would be more pronounced for α -olefin with long chain. As a result, the ratio of α -olefin to *n*-paraffin in conventional FTS product decreases exponentially with the increase of chain length, irrespective of what catalysts used [1–8].

Previous studies [6–8] reported that supercritical Fischer–Tropsch might be a potential approach to promote α -olefin selectivity. By introducing a nonpolar supercritical fluid, such as *n*-hexane [6] or propane [7], into the FTS reaction system, the diffusion ability of α -olefin in catalyst pores could be largely improved, resulting in an enhancement in the α -olefin selectivity. However, this approach is not efficient suppressing the secondary reactions completely, since it might hardly prevent the readsorption of α -olefins. Moreover, the nonpolar solvents applied were miscible with the FTS product, leading to difficult product separation and solvent recycling [8].

To inhibit the α -olefins secondary reactions thoroughly, an efficient method is extracting these α -olefins out of the catalyst pores rapidly while preventing them from readsorption. In this paper, we demonstrate that this objective can be fulfilled through preferentially enwrapping the catalyst particles with a polar solvent. The schematic diagram of this scheme is shown in Fig. 1. Specifically, the porous catalyst particles are enwrapped by a polar solvent, which serves as a liquid membrane. Reactants need to diffuse through this liquid membrane to reach the catalyst surface, where they react and synthesize the intermediate products, mainly α -olefins. These products must leave the catalyst pores immediately due to their negligible dissolvability in the polar solvent, and hardly return to the catalyst surface since the surface is protected by a polar liquid membrane. Therefore, it is expected that the α -olefin selectivity could be greatly enhanced, and the solvent separation from FTS product would become easier.

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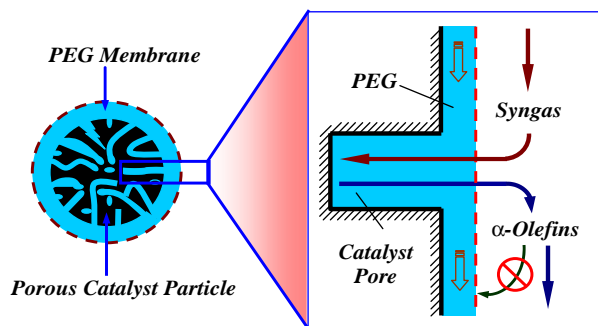


Fig. 1. Principle diagram of the PEG-enwrapped porous catalyst particle during Fischer-Tropsch synthesis.

In order to test the feasibility of this novel scheme in this paper, polar solvent co-feeding experiments were performed in a fixed-bed reactor. The addition of polar substances such as water or oxygenates into FTS system over various catalysts have been reported in the literatures [5,9–17], from which an increase in the α -olefin selectivity was frequently observed. However, these studies mainly focused on exploring FTS reaction mechanisms or kinetics, and paid little attentions to either the origin of this phenomenon or the improvement of this process. Moreover, those polar substances used were the products or possible intermediates (i.e., water, alcohols or acids) of Fischer-Tropsch synthesis and might be unstable in the reaction process, thus were not proper solvent for the proposed scheme in this paper.

Selecting an appropriate polar solvent is crucial to the success of this scheme. Firstly, the solvent should have a high boiling point ensuring it in liquid state under FTS reaction condition. Secondly, its adsorption to the catalyst surface should be stronger than that of hydrocarbons in order to avoid being washed away by the hydrocarbon product. Polyethylene glycol (PEG), as a long chain polymer with a high boiling point, has been frequently utilized as phase transfer solvent in many homogeneous reactions [18,19]. Recently, PEG was also used as the liquid carrier of nano-catalyst in Fischer-Tropsch reaction due to its excellent thermal and chemical stability [20–22]. Therefore, PEG was chosen as the testing solvent in this study.

2. Experimental

A stable Fe-based catalyst, prepared by Synfuels China Co. Ltd. for industrial slurry-phase reactor, was used in this study. The fixed-bed reactor used here was a stainless steel tube (I.D. = 10 mm, length = 0.8 m) that was immersed in a salt bath for accurate temperature control and was connected to a hot trap (200 °C) and a cold trap (2–4 °C) for product collection. Solvent PEG 400 (average molecular weight) was added continuously into the inlet line of reactor by a high-pressure liquid pump at a flowrate of 0.05 ml/min that was far smaller than that needed for supercritical FTS (≥ 1.0 ml/min) [6,8].

Initially, the catalyst (20–40 mesh, 3.75 g loaded) was reduced in-situ and passed an induction period of more than 200 h on stream. Then, a series of conventional FTS experiments was conducted for comparison. At about 350 h on stream, the solvent addition experiments under various reaction conditions started. Every experiment at each reaction condition was conducted for at least 48 h, in which the first 24 h was for the reaction system to reach steady state and the following hours for material balance. All PEG in the outflow was gathered in hot trap and could be separated conveniently from wax (the F-T product in hot trap) by a separatory funnel. As a result, the FTS products, consisting of wax, oil, aqueous-phase and tail gas, could be analyzed accurately by the standard gas chromatogram (GC) procedures established in our laboratory. Unfortunately, the compo-

sition of PEG after reaction has still not been analyzed in detail due to the lack of appropriate chromatogram procedure. Detailed description of the experiment was supplied in the supplementary data.

The α -olefin content or selectivity used in this paper was defined as α -olefin/total hydrocarbon $\times 100\%$, where the total hydrocarbon represented all hydrocarbon products with the same carbon number as α -olefin.

3. Results and discussion

3.1. Tests in fixed-bed reactor

In conventional FTS reaction (without PEG addition, See Fig. 2(a)), the total hydrocarbon distribution presented a typical double- α Anderson-Schulz-Flory (ASF) pattern [2] with a turning point at C_6 . Besides, the α -olefin content decreased linearly with the increase of carbon number (Fig. 2(b)). In contrast, when PEG was added under the otherwise identical reaction condition, although no measurable variation was found in the total hydrocarbon distribution (Fig. 2(a)), the α -olefin content changed drastically (Fig. 2(b)). In other words, the α -olefin content in C_{6+} range increased significantly and became almost independent of carbon number (The α -olefin content in C_{30+} range was not provided due to the detection limitation of GC). In addition, as shown in Table 1 (A-1 and A-2), the chain growth probability (α) and the selectivity towards C_{5+} hydrocarbon rose slightly, whereas the CO conversion dropped sharply. The decrease in CO conversion with the addition of PEG might be attributed to the low solubility of H_2 in the polar solvent [23], since the reaction rate of FTS is generally considered an approximate first-order dependency in H_2 partial pressure [24,25]. It was worth mentioning that PEG might be inert to the FTS polymerization reaction since no obvious differences were observed in the total hydrocarbon distributions as shown in Fig. 2(a) (also see GC spectrums in supplementary data for details).

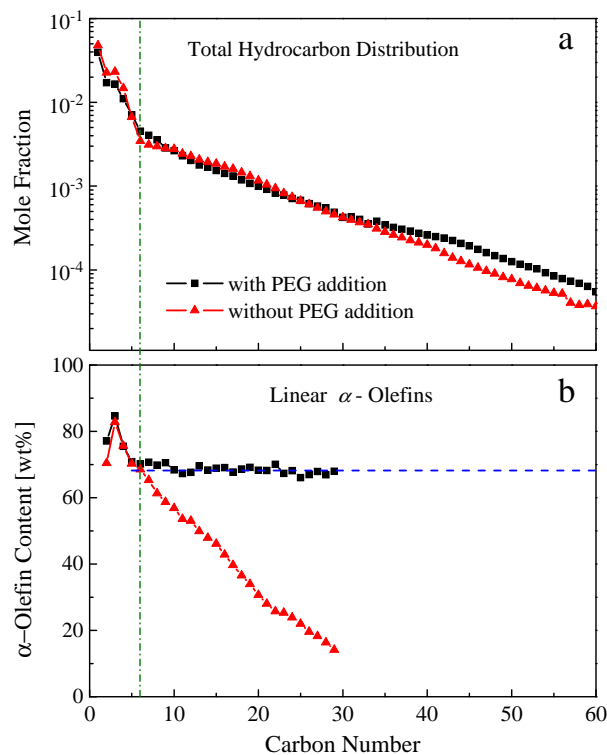


Fig. 2. Effect of PEG addition on the (a) total hydrocarbon Anderson-Schulz-Flory distribution and (b) α -olefin content of Fischer-Tropsch synthesis. Reaction conditions: 270 °C, 4035 ml(STP) $\cdot g_{cat}^{-1} \cdot h^{-1}$, 3.00 MPa, feed H_2/CO molar ratio = 0.67, iron-based catalyst, fixed-bed reactor, corresponding to entries A-1 and A-2 in Table 1.

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