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Enhanced formation of α-olefins by the pulse process between Fischer-Tropsch synthesis and N₂ purging

SHI He-xiang[1,2], LI Zhi-kai[1], LIU Ke-feng[3], XIAO Hai-cheng[3], KONG Fan-hua[3], ZHANG Juan[1], CHEN Jian-gang[1,*]

[1]State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China;

[2]University of Chinese Academy of Sciences, Beijing 100049, China;

[3]Petrochemical Research Institute of Petro China Company Limited, Beijing 100029, China

Abstract: The Fischer-Tropsch synthesis has offered an alternative way to convert coal and biomass into chemicals such as α-olefins via syngas comprised of H_2 and CO. A pulse process switching between Fischer-Tropsch synthesis and N_2 purging was carried out when the Fischer-Tropsch synthesis became stable in the fixed bed reactor. The activity and selectivity over Fe-Co catalyst for α-olefins in Fischer-Tropsch synthesis reaction were measured under the normal conditions of 2.0 MPa, 497 K, 2000 h^{-1} and H_2/CO volume ratio of 2.0. It was found that the olefin to paraffin ratio of C_3 for Fe-Co catalyst purged at 517 K and 0.2 MPa was almost nine times higher than that of the fresh one without purging under the same reaction conditions, and the CH_4 selectivity and CO conversion decreased after purging. Two possible reasons were proposed to explain these phenomena. Moreover, a batch experiment by the pulse process in fixed bed reactor was performed. Notably, a high olefins yield was obtained via the pulse process during the Fischer-Tropsch synthesis.

Keywords: alpha olefins; pulse process; N_2 purging; Fischer-Tropsch synthesis

α-Olefins are valuable products and intermediates, which are used in various kinds of commercial products, including polymers, additives and so on. Especially, α-olefins are key building blocks for the manufacture of plastics, cosmetics, and drugs[1,2]. There are various options which can produce olefins, including: (1) direct conversion of syngas (H_2 and CO) via Fischer-Tropsch synthesis (FTS), (2) steam cracking of crude oil, (3) indirect conversion of syngas via methanol, (4) ethylene oligomerization, and (5) cracking hydrocarbon products from FTS[3–7]. Methods (3), (4) and (5) need at least two conversion steps which have to increase equipment investment and reduce the economy of the process, while methods (2) and (3) are the main ways for producing light olefins. Thus, the direct conversion via FTS is an appropriate technology in production of olefins from syngas derived from the gasification of coal and other carbon-containing materials[8].

The FTS is well known as a technology to produce transportation fuels from syngas. However, it is also a technology to produce specific fine chemicals, since products of FTS are particularly composed of straight chain hydrocarbons and α-olefins[9,10]. It is well accepted that the FTS reaction is a surface-catalyzed polymerization process which uses CH_x monomers formed by the hydrogenation of CO[11]. As the primary α-olefins can readsorb on the active sites and initiate secondary reactions which consume olefins and lower its yield, it is desired to shorten the residence time of α-olefin and thus reduce opportunities of α-olefin secondary reaction in favor of increasing the olefin to paraffin ratio (O/P)[12]. Since the condensed hydrocarbon liquid will accumulate in pore of catalyst pellet, and restrict the diffusion in liquid and instant release of olefins to gaseous phase, it is critical to eliminate the liquid phase to improve the production of α-olefins[13].

In recent years there has been growing interest in the development of bimetallic catalysts to achieve high olefins yield[14–17]. Most studies have focused on a combination of conventional FTs transition metals, namely Co, Ni, Fe and Ru. Among these, Co-Fe catalyst is given special attention[18].

Generally, cobalt based-catalysts have longer catalyst life, but generate less olefins than iron-based catalysts. When a lean hydrogen feed is used, iron-based catalysts is more suitable for olefins formation because of high activity for water-gas shift (WGS) reaction[19]. Accordingly, a range of preparation variables of Fe-Co catalyst were investigated to improve the olefins selectivity[20–24]. Besides, the parameters of process on producing olefins were studied[25]. Linghu et al[13] reported that the purpose of synthesizing higher α-olefins was achieved by utilizing suitable reaction media. The selectivity of α-olefins raised under the supercritical phase reaction via Co catalyst in the fixed bed reactor[26]. It was demonstrated that syngas diluted with N_2 would lead to the decrease in selectivity for C_{1-4} hydrocarbons[27].

In this work, it was attempted to obtain high O/P over Fe-Co catalysts by purging off the liquid filled in pore of catalyst with inert gas (nitrogen), thus promoting the release of olefins from liquid to gas phase and minimizing its secondary reaction. The effect of various purging conditions was investigated and the possible explanations were proposed. The objective of this study was to design a pulse process to acquire as much olefins as possible based on the optimum operation of the pulse reaction unit.

1　Experimental

1.1　Catalyst preparation

A precipitated Fe-Co catalyst with BET area of 100 m^2/g and average pore diameter of 6 nm was applied in the experiments. The method for preparation of catalyst was as follows. Firstly, the precipitate was gelled at 300 K in a container by slowly adding basic solution into $Fe(NO_3)_3$ and $Co(NO_3)_2$ mixed solution and subsequently stirred for 2 h. Secondly, the slurry after filtering was dried and calcined at 700 K to obtain the catalyst.

1.2　Fischer-Tropsch synthesis

Approximately 3 g of the prepared iron-cobalt catalyst diluted with quartz sand of the same particle size was loaded into a fixed-bed reactor. The volume ratio of catalyst to quartz sand was 1:3. The reactor was a 1000 mm long stainless tube with 14 mm internal diameter and heated with a salt bath. The experimental setup is presented in Figure 1. The outlet of the reactor was connected with two traps. The hot trap was maintained at 500 K and the temperature of cold trap was 273 K. The uncondensed gas was conveyed to a sampler of online gas chromatograph (GC). The condensed products collected from the hot and cold traps were analyzed through off-line GC.

The online GC included a thermal conductivity detector

(TCD) with Ar carrier for analyzing H_2, N_2, CH_4 and CO on 1.5 m × 3 mm i.d. 13X molecular sieve packed column, and the flame ionization detector (FID) for analyzing C_{1-6} hydrocarbons in gas phase with N_2 carrier. The oil product from the cold trap was analyzed on 60 m×0.25 mm i.d. OV-101 capillary column, FID, N_2 carrier with temperature programmed (3 K/min) to 563 K. The wax product from the hot trap was analyzed on 15 m×0.53 mm i.d. OV-101 capillary column, FID, N_2 carrier with temperature programmed (1 K/min) from 343 to 570 K.

Before reaction, the catalyst was reduced with H_2 (99.999% in purity) at 2000 h^{-1} at 0.2 MPa. The gas space velocity was based on the total mass of the unreduced catalyst. The temperature was programmed (1 K/min) to 673 K and eventually remained steadily at 673 K for 12 h. After reduction the temperature decreased at a speed of 1 K/min to 497 K, and then N_2 (99.999% in purity) was switched from H_2 before the reaction began until H_2 was replaced by N_2. Once the FTS started, the syngas (15% N_2/27% CO/58% H_2 for mole ratio) replaced nitrogen. The flow rate of syngas, nitrogen and hydrogen were controlled by Brooks 5850 Mass Flow Controller. The parameters of FTS were 2.0 MPa, 497 K and 2000 h^{-1}. Since this report focused on olefins, propane and propylene were chosen as index regardless of changes of oil and wax.

1.3　Pulse process in a fixed bed reactor

The purpose of purging operation is to reduce the deposit of liquid in the catalyst during the FT reaction and the purging process continued for 48 h in our experiment. After the state of reaction became steady (time of reaction was longer than 6 h), the feedstock was switched from syngas to nitrogen (purging gas). The purging temperature was chosen 497, 507 and 517 K respectively, and the purging pressure was set to a sequence of 0.2, 1.0 and 2.0 MPa respectively. The space velocity of nitrogen was the same as that of syngas. The rate of temperature change was 1 K/min.
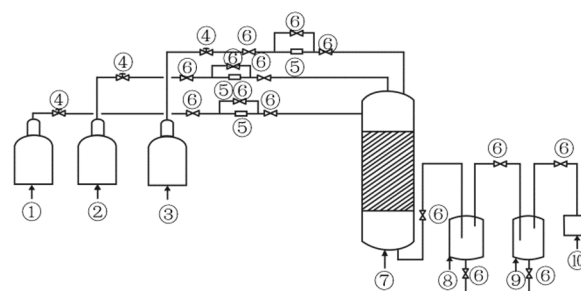

Fig. 1　Experiment setup of the FTS

①: H_2 cylinder; ②: N_2 cylinder; ③: syngas cylinder; ④: regulators;
⑤: mass flow controllers; ⑥: shut-off valves; ⑦: fixed bed reactor;
⑧: hot trap; ⑨: cold trap; ⑩: gas chromatograph