The 6th International Conference on Applied Energy – ICAE2014

An experimental study on a microchannel reactor for Fischer-Tropsch synthesis

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Abstract

In this study, a stainless steel microchannel reactor was applied in Fischer-Tropsch synthesis. The washcoating of γ-alumina on the stainless steel substrate needed two steps included a primary coating and a washcoating of alumina slurry followed by. Conversion was higher in the microchannel reactor than that in a conventional fixed-bed catalytic test. It was attributed to the enhancement of mass and heat transfer within the micro-device. The results also demonstrated the lower CH₄ selectivity could be achieved during Fischer-Tropsch synthesis owing to the better temperature control of the microchannel technology.

Keywords: Microchannel reactor; Fischer–Tropsch synthesis; Washcoating

1 .Introduction

As the global oil reserves decreases, the Fischer-Tropsch synthesis (FTS) has raised scholars’ interests in the alternative sources for liquid fuels, which is a well-known catalytic process for the conversion of carbon monoxide and hydrogen into liquid hydrocarbons mixtures of variable molecular weight. Both conventional fixed bed and slurry reactor technologies exist several serious drawbacks: the fixed-bed multitubular reactor is suffering from higher cost, insufficient heat removal, diffusion limitations and pressure drop. In addition, the slurry bubble column reactor has problems of liquid products-catalyst separation, highly demanding scaling-up, catalyst deactivation and attrition [1].

Large units are usually preferred while the applications such as offshore production is benefiting from compact and modular conversion technology. Demanding conditions on site as well as restriction in space and weight, needs the highly integrated, compact, portable and safe technology [2]. The microchannel reactor applied in FTS enables isothermal operation of the highly exothermic reaction, as it
has lots of small parallel channels to enhance heat transfer and intensify mass transfer. Recent works in microchannel reactor reported the application of FeCrAlY alloy in the forms of felt [3] or foam [4] as catalyst structured support. Surfaces of FeCrAlY formed a dense layer of native aluminum oxide on high temperature oxidation, which enhanced the adhesion of supported oxide catalyst without degradation. Many other researches were carried out to study the FTS performance on micro-systems. Myrstad et al. [5] investigated FTS in a microstructured fixed-bed reactor. The exothermal heat is removed effectively through oil flowing in cross-flow channels. Cao et al. [6] used a single-channel reactor filled with two different CoRe/Al2O3 catalysts and designed the cooling channel to maintain isothermal conditions during FTS. In this work, AISI316L stainless steel was used for the alternative substrate because of the high price of the FeCrAlY. The microchannel reactor wascoated with the Co/Al2O3 catalyst was tested under several experimental conditions.

2. Experimental

2.1 Microchannel reactor

The reactor was a microchannel plate sandwiched in two cover plates with a bolted connection, shown in Fig. 1a. The channels (depth: 0.5mm; width: 1.5mm; length: 30mm; number of channels: 10) were fabricated on the SS316L plate. Reaction and cooling channels were milled on both sides of the microchannel plate, respectively. The original design of cooling channels is failed to use. Because the amount of heat generated by the low syngas flow in tests was much less than the heat loss of the test section. Therefore it is necessary to use the electrically heating component. The system pressure was controlled by a backpressure regulator. PC and Agilent 34970A Data Logger/Switch Unit were used to form the data acquisition system.

2.2 Catalyst preparation

The washcoating of γ-alumina on the stainless steel substrates needed two steps included a primary coating and a washcoating of alumina slurry followed by. Using boehmite as the precursor of γ-Al2O3 catalyst carrier and HNO3 as the peptizer, a stable aluminum sol was prepared with the moderate mole ratio of H+ and AlOOH. Secondary slurry was prepared with γ-alumina, aluminum sol, AlOOH and PVA. After the two-step procedure, the γ-alumina washcoated on the acid-treated 316L stainless steel surface was prepared. The catalyst was then synthesized by the incipient wetness impregnation method with aqueous solutions of cobalt nitrate hexahydrate.

2.3 Activity test

Prior to reaction the catalyst was in situ activated at 673K during 12h under pure H2 (240ml/min). After the reduction, the catalyst was cooled to 453K. The reactor was pressurized with pure H2 and switched to premixed syngas at a H2/CO ratio of 2:1 with nitrogen as the internal standard. The temperature was then slowly ramped to the desired temperature. Gaseous products were analyzed online by GC9790, using a FID for light hydrocarbons until C4 and a TCD to analyze H2, CO, CO2, N2, H2O, CH4. The CO conversion \(X_{\text{CO}}\) and the methane selectivity \(S_{\text{CH4}}\) were calculated with Eqs. (1) and (2), where \(R\) is the peak area ratio of species CO or CH4 and N2 and \(f\) is a specific calibration factor [7].

\[
X_{\text{CO}} = \frac{R_{\text{CO,n}} - R_{\text{CO}}}{R_{\text{CO,n}}} \tag{1}
\]

\[
S_{\text{CH4}} = \frac{R_{\text{CH4}}}{R_{\text{CO,n}}} \tag{2}
\]
3. Results and discussion

3.1 Characterization

The appearance feature and phase composition of the catalyst support were characterized by scanning electron microscope (SEM) (Fig. 1b), X-Ray diffraction (XRD) (Fig. 1c) and Brunauer Emmett Teller (BET) (Fig 2). The adhesion between the stainless steel substrate and the support was tested by ultrasonic vibration. The mass-loss rate of the support was only 1.24%. The results show that the acid treatment and two sintering processes could effectively improve the adhesion. The main pore size was between 30 Å and 100 Å which matched with commonly used carriers for catalyst. The carrier grew smoothly and evenly with no cracks, and possessed with extensive specific surface area, 234 m²/g, and good pore connectivity.

3.2 Catalytic performance

Fig 3 shows the FTS performance of the catalyst washcoated on the microchannel reactor. The temperature was maintained at 493 K and the pressure at 2 MPa. By varying gas hourly space velocity (GHSV) from 6950 h⁻¹ to 20850 h⁻¹, CO conversion decreased from 89.9% to 67.5% and CH₄ selectivity rose at a high GHSV. The CH₄ selectivity at lower GHSV could not be detected owing to the limited instrumental sensitivity. The effects of the reaction temperature on CO conversion and CH₄ selectivity were also studied. By varying the temperature from 493 to 543 K at same syngas flow, the increment trend of CO conversion and CH₄ selectivity was found. It could be explained by the different diffusivities of H₂ and CO and the effect of the water–gas shift (WGS) reaction. In fact, when increasing CO conversion produces more reactants and products throughout the liquid filling the catalyst pores, the resistance to the diffusion of the reactants is enhanced. Owing to the higher diffusivity of H₂, the H₂/CO ratio on the catalytic sites is raising [1]. From Table 1 it can be seen that the washcoated microchannel reactor is better than the fixed bed and the microstructure reactor (micro-fixed reactor) at similar condition. This can be considered as an indication of the excellent heat transfer properties of the washcoated microchannel reactor which can be operated at severe conditions without temperature runaways in the catalyst.

\[ S_{\text{CH}_4} = f \left( \frac{R_{\text{CH}_4}}{R_{\text{CO}_2}} \right) \]

Fig. 1. (a) Exploded diagram of the test section; (b) SEM image of fresh catalysts; (c) XRD patterns of fresh catalysts

Fig. 2. BET of fresh catalysts (a) isotherm linear plot; (b) pore size distribution

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Table 1. Conversion and selectivity in present work compared with reference [5]

<table>
<thead>
<tr>
<th>Catalyst(Reactor)</th>
<th>Temperature(K)</th>
<th>Pressure(bar)</th>
<th>GHSV(h⁻¹)</th>
<th>X_{CO}</th>
<th>S_{CH4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed-bed reactor</td>
<td>498</td>
<td>20</td>
<td>14400</td>
<td>69</td>
<td>9</td>
</tr>
<tr>
<td>Microstructure reactor</td>
<td>498</td>
<td>20</td>
<td>16200</td>
<td>72</td>
<td>9</td>
</tr>
<tr>
<td>Present work</td>
<td>493</td>
<td>20</td>
<td>13900</td>
<td>84</td>
<td>cannot be detected</td>
</tr>
</tbody>
</table>

4. Conclusions

In this paper, a washcoated stainless steel microchannel reactor was investigated for Fischer-Tropsch synthesis. Conversion was higher in the microchannel reactor than that in a conventional fixed-bed catalytic test. This was attributed to enhancement of mass and heat transfer within the micro-device. The results also demonstrated the lower CH₄ selectivity could be achieved during Fischer-Tropsch synthesis owing to the better temperature control of the microchannel technology.

References


Biography

Xiang Ying is a doctoral candidate from East China University of Science and Technology. He is also a Research Assistant in Engineering Center of Efficient Green Process Equipment and Energy Conservation, Ministry of Education. His research focuses on microreactor technology for Fischer-Tropsch synthesis.