

R4885

ENHANCEMENT OF DISTILLATE SELECTIVITY IN FISCHER-TROPSCH SYNTHESIS BY USING IRON AND COBALT CATALYSTS IN A NOVEL DUAL-BED REACTOR

**Sonia Jam, Masume Ghalbi Ahangary, Ahmad Tavasoli* ,
Kambiz Sadaghiani and Ali Nakhaei Pour**

Research Institute of Petroleum Industry, P.O.Box: 18745-4163, Tehran, Iran

Received March 17, 2006, accepted April 3, 2006

Abstract

An integrated process for producing liquid fuels from synthesis gas *via* a two-stage Fischer-Tropsch (FT) reaction is disclosed. An iron catalyst was used in the first bed of a fixed-bed reactor followed by a ruthenium promoted cobalt catalyst in the second bed. The activity and selectivity of the dual-bed system were assessed and compared with those using catalysts in a single bed system, separately. The methane selectivity in the dual-bed reactor was about 11% less compared to that of the single-bed system. The C₅⁺ selectivity for the dual-bed reactor was 19.7% higher than that of the single-bed system.

Keywords: Fischer-Tropsch, cobalt, iron, dual bed, C₅⁺ selectivity, methane selectivity

INTRODUCTION

In gas to liquid (GTL) technologies, by steam reforming, synthesis gas is produced from natural gas. By FT the synthesis gas is then converted to a mixture of hydrocarbons. Then hydrocarbons undergo further treatment to yield

* Corresponding author. E-mail: tavassolia@ripi.ir

distillates. The selectivity considerations are the key parameters in optimizing the gas conversion plants, so the enhancement of C_5^+ and suppression of CH_4 are quite crucial. Incorporation of olefins has been used as a means of lowering CH_4 and raising C_5^+ hydrocarbons. Once linear α -olefins are formed, they can readsorb and undergo secondary reactions: hydrogenation, isomerization, and re-insertion. The final product can thus have been affected by these secondary reactions. Jordan and Bell by co-feeding of C_2H_4 over a Ru catalyst showed that at C_2H_4 high partial pressures C_3^+ products enhances and CH_4 reduces [1]. Iglesia and Madon showed that by introducing ethylene to the reactor, the CH_4 selectivity decreased from 8.3% to 7.2% and the C_5^+ selectivity increased from 92.9% to 93.9% [2]. Schulz and Claeys showed co-feeding of C_2 - C_{11} α -olefins shifts the curves of formation rates of compounds with carbon numbers higher than the olefin, which had been added [3]. Kibby [4] claimed that combination of iron and cobalt catalysts enhances C_5^+ selectivity. Tavasoli *et al.* by using a dual bed reactor showed 12.3% enhancement of C_5^+ [5]. In this study to affect C_5^+ and CH_4 selectivity, we used iron and cobalt catalyst in a dual bed reactor.

EXPERIMENTAL

Iron catalyst precursor was precipitated at 82°C from a flowing aqueous solution containing iron and copper nitrates at the desired Fe/Cu ratio, using aqueous ammonia. The precipitate was washed with distilled water. Impregnation with SiO_2 was accomplished by addition of reslurried Fe/Cu coprecipitate, at pH to ≤ 6 . Then lanthana was added via an aqueous incipient wetness technique. The catalyst dried at 120°C for 16 h and calcinated at 450°C for 4 h. The composition of the final catalyst is $100Fe_2O_3/5.1CuO/0.1La_2O_3/25SiO_2$. Cobalt catalyst was prepared with 15wt% cobalt on alumina via aqueous impregnation of cobalt nitrate. Then Ru was also added by incipient wetness impregnation of aqueous solutions of ruthenium (III) nitrosyl nitrate. Then the catalyst was dried at 120°C and calcined at 450°C for 3 h. BET surface area of the catalysts was measured by an ASAP-2000 system. XRD measurements were conducted with a Philips PW1840 X-ray diffractometer with monochromatized $Cu/K\alpha$ radiation. The average size of the crystallites of the catalysts was estimated by Scherrer formula. Temperature programmed reduction (TPR) of the catalysts were recorded using a Micromeritics TPD-TPR 290 system. The samples were purged in argon and TPR of 50 mg of samples were performed using 5.1% H_2 in Ar with a flow rate of 40 cm^3/min . The samples were heated from 313 to 1173 K with a heating rate of 10 K/min.

3 g of the Fe catalyst was charged into 1/4" tubular micro-reactor. The reactor was placed in a molten salt bath with a stirrer to ensure a uniform

temperature along the catalyst bed. The temperature of the bath was controlled *via* a PID temperature controller. Separate Brooks 5850 mass flow controllers were used to add H₂, N₂ and CO. Prior to the activity tests, the catalyst was reduced in a flow of H₂ and N₂ (H₂/N₂ = 1/10) at 400°C for 1 h. The flow of N₂ switched off and the temperature was decreased to 270°C. The catalyst was reduced at this temperature for 24 h in a flow of H₂ and CO (H₂/CO = 1). The tests were performed at 320°C, 1 bar and H₂/CO ratios of 1 for a period of 24 h. Online analyses of CO, CO₂ and C₁-C₂₀ hydrocarbons in the effluent were performed *via* a refinery gas analyzer (GC). In the second series of experiments, 1.5 g of the Co catalyst was charged into reactor. The catalyst was reduced in a flow of H₂ at 400°C for 12 h. The experiments were performed at 220°C, 1 bar, and H₂/CO ratios of 2 for a period of 24 h. Online analyses of effluent was performed as the first step.

In the third series of experiments, the dual-bed reactor was adapted by combination of Fe and Co catalysts. 3 g of Fe and 1.5 g of Co catalysts were charged into the first and the second beds of the micro-reactor respectively. The two beds were set in series in such a way that the effluent from the first bed directly went into the second bed. Each bed was placed in separate molten salt bath with a stirrer to ensure a uniform temperature along each catalytic bed. The total length of the beds was about 75 cm. Prior to the activity tests; the catalysts were reduced with above reduction procedures. The temperature of the first bath was set at 320°C and the second one at 220°C. The flow of the syngas was adjusted in such a way that the total feed flow rate equals the sum of two last steps and the condition of 1/1 ratio and 2/1 ratio of H₂/CO in the first and second beds were maintained unchanged. Analyses of CO, CO₂, and C₁-C₂₀ hydrocarbons in the second bed effluent were performed in a GC. Anderson-Schultz-Floury (ASF) was plotted. CO conversion and selectivities were calculated and compared with those using catalysts in a single bed system. CO conversion and selectivities of the single bed system were calculated using the formula: $Y_{\text{single bed}} = X_{\text{Fe}} * y_{\text{Fe}} + X_{\text{Co}} * y_{\text{Co}}$, where X is weight fraction of the specified catalyst and y is selectivity or conversion.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of iron and cobalt catalysts. In the profile of cobalt catalyst, the peaks at 46.1 and 66.5° correspond to γ -alumina, while the other peaks relate to the different crystal planes of Co₃O₄ [5]. Also the average particle size of Co₃O₄ of catalyst was calculated from broadening of the peak at $2\theta = 36.8^\circ$. In the profile of iron catalyst the peak at 23° is attributed to the Fe₂O₃, which is the main iron phase [6]. Figure 2 presents the TPR spectra for the catalysts. In the spectrum of cobalt catalyst, the first peak is typically assigned

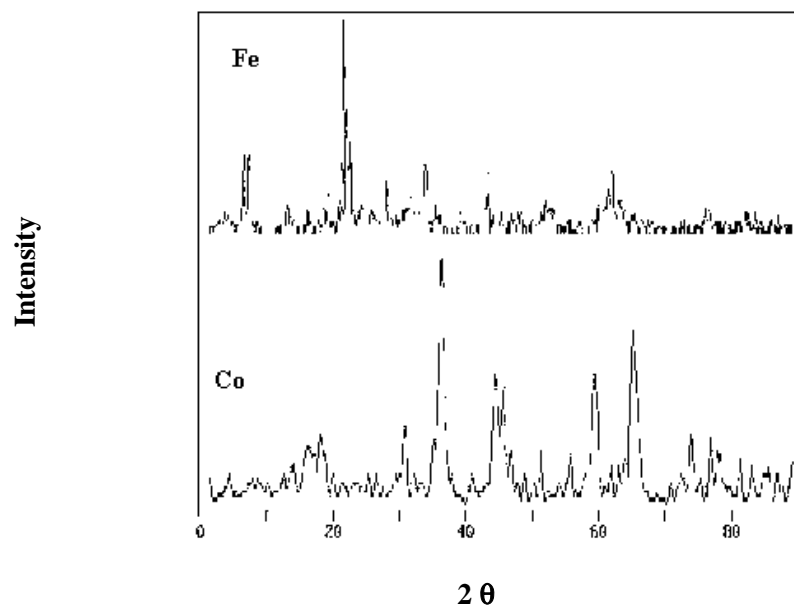


Fig. 1. XRD spectra of the catalysts

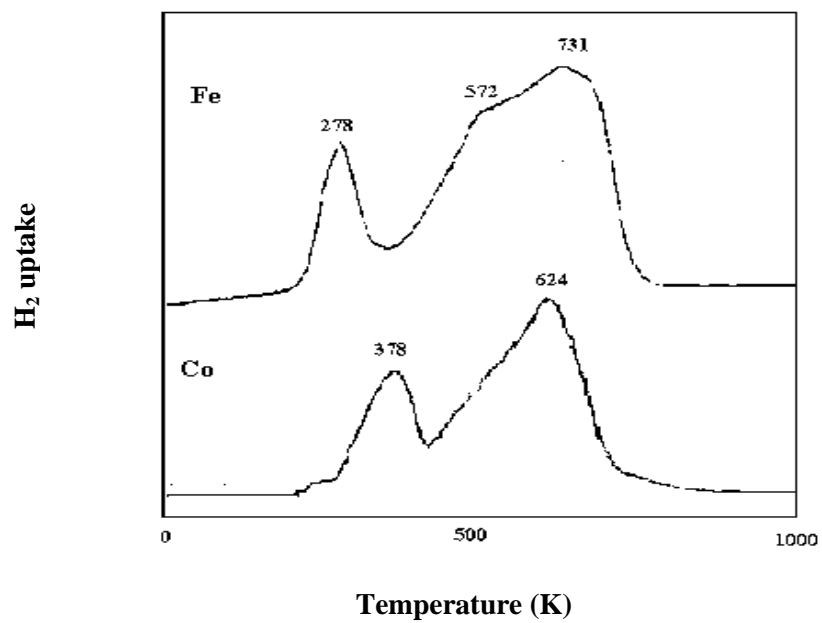


Fig. 2. TPR spectra of the catalysts

to the reduction of Co_3O_4 to CoO , although a fraction of the peak likely comprise the reduction of the larger bulk-like CoO species to Co^0 . The second broader peak is mainly assigned to the second step reduction, which is mainly reduction of CoO to Co^0 . It also includes the reduction of cobalt species that interact with the support [5], which extends the TPR spectra to higher temperatures. In the spectrum of iron catalyst the first peak is reduction of CuO to Cu^0 . The second peak is reduction of Fe_2O_3 to Fe_3O_4 . And finally the high temperature peak is attributed to the reduction of Fe_3O_4 to Fe^0 [6]. Table 1 shows the average particle size and BET surface area of the catalysts.

Table 1
Characterization data of fresh catalysts

| Catalyst | Fe | Co |
|---|----------------------|-----------|
| BET Specific Area (m^2/g) | 47 | 154 |
| d_p (XRD) | 60 (μm) | 14.4 (nm) |

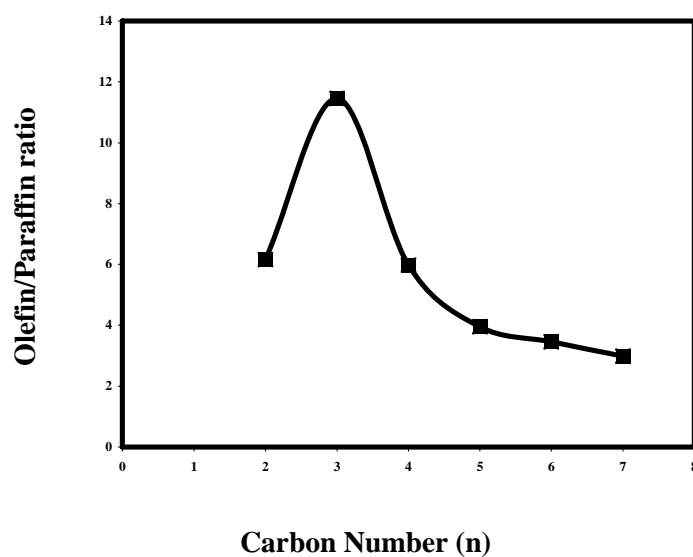


Fig. 3. α -olefin/ n -paraffin ratio of Fe

Figure 3 demonstrates the olefin to paraffin ratio in the products of Fe catalyst at 320°C , 1 bar and H_2/CO of 1. As shown in Fig. 3, Fe catalyst is highly olefin selective. Studies on iron catalysts indicated at low H_2/CO

ratios, the mobility of H₂ was significantly restricted by blocking the low-coordination edge and corner sites for dissociative adsorption of hydrogen [7,8]. The reduced H₂ mobilities as well as reduced hydrogen adsorption rates could qualitatively explain the decrease in hydrogenation of alkenes to alkanes and as a result the increased olefin/paraffin ratios. The CO conversion and different products selectivities of the iron and cobalt catalysts are listed in Table 2. As shown in Table 2 the products of cobalt are heavier than the products of iron catalyst. Selectivity towards light gases, *i.e.*, C₂-C₄ in the products of iron catalyst is higher than that of the cobalt catalyst. Also CO conversion per gram of catalyst is higher when cobalt was used.

Table 2

CO conversion and products hydrocarbon selectivities of the iron and cobalt

| Catalyst | Fe | Co |
|--------------------------------|-------|-------|
| CO conversion | 18.4 | 19.89 |
| CO conversion/g cat | 6.13 | 13.26 |
| C ₁ | 27.38 | 19.23 |
| C ₂ -C ₄ | 36.47 | 25.35 |
| C ₅ ⁺ | 36.15 | 55.42 |

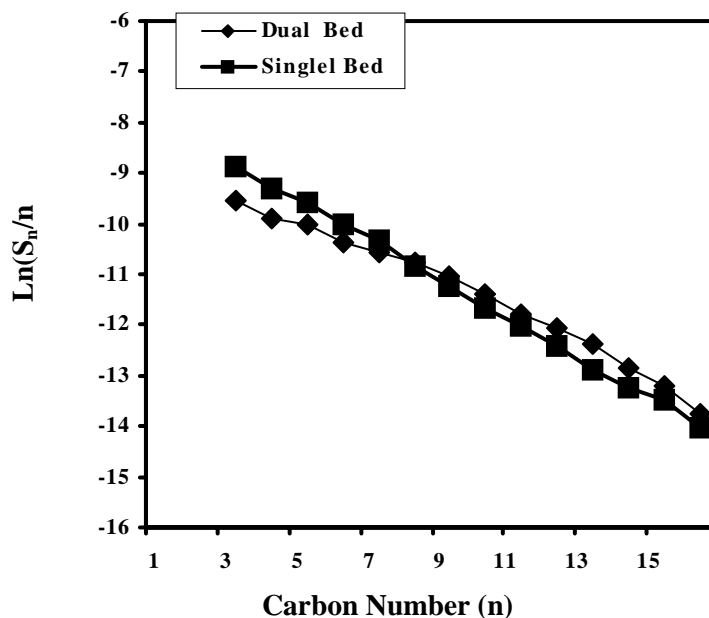


Fig. 4. ASF of the two systems

It is well known that adding one or more types of olefins to the feed increases liquid C_5^+ yield in the FTS [3,9]. Preferred olefins useful in the process are α -olefins of the type $R-CH=CH_2$ wherein R is hydrogen or an alkyl group having about 1 to 10 carbon atoms [10]. These α -olefins can compete with carbon monoxide and heavier olefins for readsorption and chain initiation. Also they can add directly to the growing chains. These secondary reactions can strongly influence product selectivity. So using a dual bed reactor with the first bed packed with a catalyst with high 1-alkenes selectivities and the second bed using a catalyst with an appropriate activity and selectivity leads to high distillate yield and low CH_4 selectivity. So Fe catalyst was chosen for this purpose and charged to the first bed of the reactor in series with the second bed packed with Co. Figure 4 compares the ASF plots of the dual-bed reactor packed with Fe and Co catalysts (3 g of Fe and 1.5 g of Co) and single reactor. Operating conditions were as follows, $T = 320^\circ C$, $P = 1$ bar and $H_2/CO = 1$ at the first bed and $T = 220^\circ C$, $P = 1$ bar and $H_2/CO = 2$ at the second catalytic bed. As is shown in Fig. 4 the dual-bed reactor serves to increase the average carbon number of the products produced during the FT synthesis. The high chain growth may be attributed to the effective participation of α -olefins to the carbon-carbon chain propagation [1,3,9].

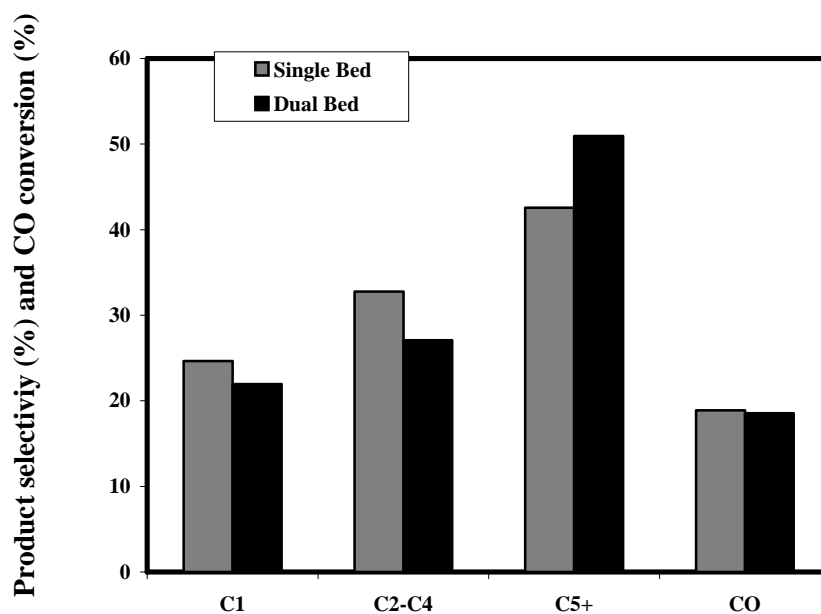


Fig. 5. Product selectivity and CO conversion of the two systems

Figure 5 compares the product selectivity and CO conversion for the dual-bed and the single-bed reactors. As shown, CH_4 selectivity in the dual-bed reactor is about 11% less compared to that of the single-bed reactor. The C_5^+ selectivity for the dual-bed reactor is about 19.7% more than that of the single-bed reactor. Also $\text{C}_2\text{-C}_4$ in the dual-bed reactor is about 21.2% less compared to that of the single-bed reactor. In the dual-bed system C_2^+ olefins produced in the first bed can readsorb and act as chain starters in the second bed of the reactor, and by this way modify the product distributions. The decrease in CH_4 in the dual-bed system is attributed to the increasing formation rates of compounds with high carbon numbers due to olefin readsorption. Interestingly CO conversion is about the same for both single bed and dual-bed reactors.

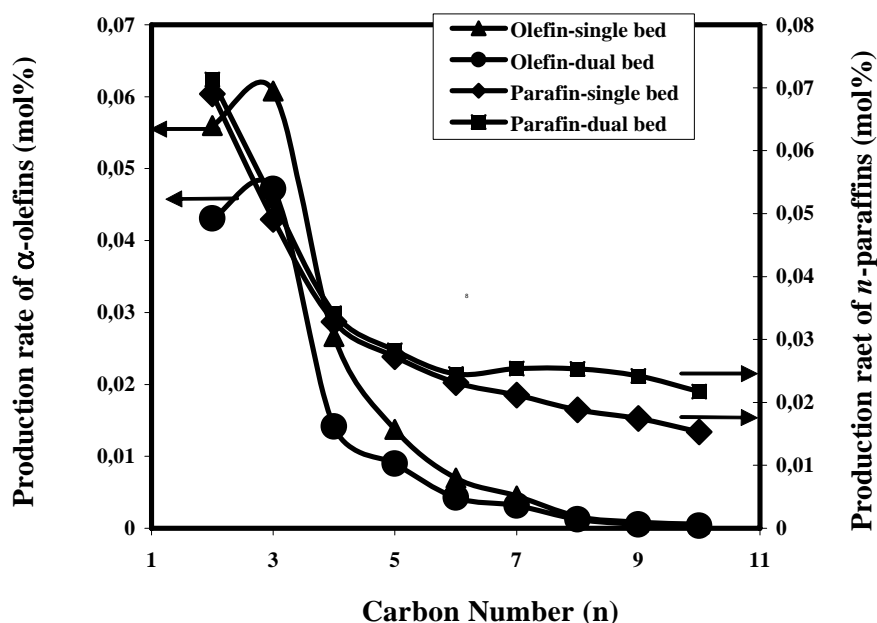


Fig. 6. Production rates of n -paraffins and α -olefins of the two systems

Figure 6 presents the formation rates of $\text{C}_2\text{-C}_{10}$ n -paraffins and α -olefins for both single bed and dual bed systems. As may be seen the paraffin content in the products of single bed reactor decreases as carbon number increases. The same trend can be seen for α -olefins except C_3 . Comparing the production rates of α -olefins in the two systems, the mol% of α -olefins in the products of the dual bed reactor is about 35-50% less than that of single bed reactor. The

paraffins in the products of the dual bed reactor is the same for both systems in the range of C₂-C₆, but the production rate of the paraffins with carbon numbers larger than 6, increases significantly in the dual bed system. The results clearly show that the increasing paraffin content arises predominantly from the net disappearance of C₂-C₆ α -olefins and not from their direct hydrogenation to the corresponding *n*-paraffin. C₂-C₆ α -olefins production rate decreases in the dual bed system without a corresponding increase in C₂-C₆ *n*-paraffins, leading to a net increase in the fraction of the converted CO that appears as C₇⁺ paraffins. The observed increase in the C₇⁺ *n*-paraffins actually results from the effects of enhanced readsorption of C₂-C₆ α -olefins in the dual bed system.

REFERENCES

1. D.S. Jordan, A.T. Bell: *J. Phys. Chem.*, **90**, 4797 (1986).
2. E. Iglesia, S.C. Reyes, R.J. Madon: *J. Catal.*, **129**, 238 (1991).
3. H. Schulz, M. Claeys: *Appl. Catal.*, **186**, 71 (1999).
4. C.L. Kibby: U.S. Patent 6331573 (2001).
5. A. Tavasoli, A. Khodadadi, K. Sadaghiani: *Int. J. Chem. Chem. Eng.*, **24**, 3 (2005).
6. D. Bukur, X. Lang, D. Mukesh: *Ind. Eng. Chem. Res.*, **29**, 1588 (1990).
7. D.O. Uner, M. Pruski, B.C. Gerstein, T.S. King: *J. Catal.*, **146**, 530 (1994).
8. D.O. Uner: *Ind. Eng. Chem. Res.*, **37**, 2239 (1998).
9. E. Iglesia, R. Madon: U.S. Patent 4754092, (1998).
10. E.W. Kuipers, I.H. Vinkenburg, H. Osterbeek: *J. Catal.*, **152**, 137 (1995).