FISCHER-TROPSCH SYNTHESIS USING $H_2/CO/CO_2$ SYNGAS MIXTURES OVER A COBALT CATALYST

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Summary

The effect of CO_2 on Fischer－Tropsch synthesis on a cobalt catalyst had been investigated in a fixed-bed micro reactor. Two feed gases, $H_2:CO:CO_2$ = 2:1:0 and $H_2:CO:CO_2$ = 3:0:1, were mixed in various proportions thus varying the ratio of CO, CO_2 and H_2 stoichiometrically. The product distribution, olefin/paraffin ratio and catalyst activity and selectivity were measured and compared. It was shown that there was a large variation in the performance of the catalyst for the different feed gas mixtures and there was an opportunity to optimize catalyst performance by choice of the correct operating partial pressures of CO, CO_2 and H_2.

Keywords

CO_2 utilization and sequestration, Clean coal/heavy oil/frontier resources/biomass processing technologies.

Introduction

Fischer-Tropsch Synthesis(FTS) is a catalyzed chemical reaction in which synthesis gas, usually a mixture of carbon monoxide and hydrogen, is converted into liquid hydrocarbons[1]. Due to their good activity and selectivity, supported Cobalt catalysts are often the choice for CO hydrogenation to hydrocarbons in the low-temperature Fischer Tropsch synthesis (FTS) [2]. The synthesis gas can be produced from coal, natural gas or biomass [3]. In some cases, CO_2 may be a significant component in the synthesis gas [4]. Although the need for CO_2 separation before using the synthesis gas in FTS is mentioned in the patent literature for some cases, recent process development studies with biomass derived synthesis gas discuss a potential cost advantage if CO_2 is not removed before the synthesis step [5]. It is therefore interesting to investigate the effect of carbon dioxide on a cobalt catalyst under low temperature FTS conditions.

In addition, fixation of carbon dioxide has become of greater interest in recent years, primarily because of its impact on the environment through the greenhouse effect. There have been various attempts to transform carbon dioxide into hydrocarbons, mainly using those catalysts that have been proved active in the FTS, such as Co, Fe, Ni, Ru [6].

Experimental Method

The Co/TiO_2 catalyst used in this study was prepared by impregnation of TiO_2 with a cobalt nitrate solution. The Co loading was around 10%w/w, calcination temperature was 400℃ and the particle diameter of the catalyst was in the range of 0.5 mm to 1mm.

FTS experiments over the Co/TiO_2 catalyst with synthesis gas of varying proportions of CO, CO_2 and H_2 have been carried out in a fixed-bed micro reactor. They were conducted at a constant total synthesis pressure of 20bar, flow rate of 60ml/min/g.cat and temperature of 473K.

Two feed gases, one of composition $H_2:CO:CO_2$ = 3:0:1 and the other of $H_2:CO:CO_2$ = 2:1:0 were fed to the reactor and the reactions monitored. Mixtures of various proportions of the two feed gases were also fed to the reactor and the catalyst selectivity and activity were measured. In particular the impact of the partial pressures of CO, CO_2 and H_2 on the product distribution and selectivity and olefin/paraffin ratio were discussed. It is shown that there is potential to optimize the ratio of CO

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and CO_2 in the feed gas, and varying the objective, will vary the optimal feed ratios.

Results and Discussion

Fig.1 shows that CO_2 rich feeds produce products that are mainly methane while CO rich feeds shift the product composition to a Fischer–Tropsch type (mainly higher hydrocarbons) product; similar results were reported by [7]. It is however quite interesting when looking at the data more closely to see that the CH_4 rate or the CH_{2+} rate can be maximised by controlling the feed gas composition. In this case the CH_4 rate is maximized at a feed gas composition of H_2:CO:CO_2 =73.1%: 6.5%: 20.4%; and the CH_{2+} rate is maximized at a feed gas composition of H_2:CO:CO_2 =70.0%: 20.0%: 10.0%. Thus there are opportunities to firstly optimize the FT reaction as well as to consume CO_2 in the FTS reaction.

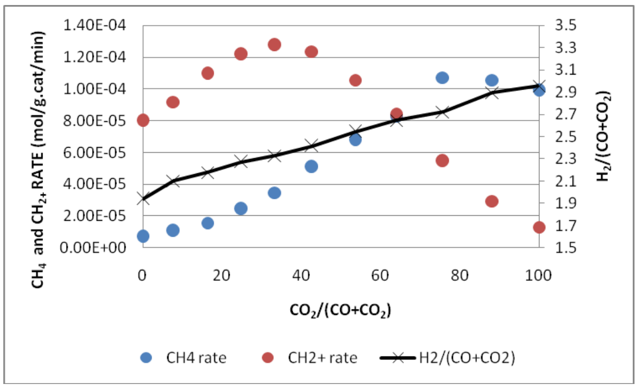

Fig. 1: The reaction rates of organic product as a function of synthesis gas composition. Reaction conditions: 473K, 60 ml syngas/min/g. cat and 20bar.

Conclusions

Carbon dioxide and carbon monoxide mixtures can be used as feeds to a cobalt catalyst. This is in spite of the fact that cobalt catalysts are not water gas shift active. It is shown the rate of hydrocarbon production is maximized at a composition that is a mixture of carbon dioxide and carbon monoxide. This result could have implications for the need to remove carbon dioxide from synthesis gas in FTS.

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