

Effect of Space Velocity on Fischer-Tropsch Reaction over Co/TiO₂ Catalyst

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Abstract— The effect of space velocity on FT reaction has been evaluated over a 10%Co/TiO₂ catalyst prepared by incipient wetness impregnation method. The catalyst was tested in a fixed-bed reactor at 220°C, 20 bar and various feed gas space velocities (20, 40 and 60 Nml/gCat/min). The CO consumption rate, olefin to paraffin ratio, C₅₊ selectivity and the chain growth probability (alpha) were found to increase with an increase in feed gas flow rate. The results were explained in terms of reactants partial pressures and mass transfer in the reactor as function of CO conversion levels.

Index Terms— Co/TiO₂, Fischer-Tropsch, Space velocity

I. INTRODUCTION

FISCHER-TROPSCH (FT) reaction consists of converting synthesis gas into hydrocarbons. The synthesis gas can be derived from coal, biomass or natural gas. Where the synthesis gas is produced from coal, the technology is referred to as Coal to Liquid (CTL) and Gas to Liquid (GTL) when the synthesis gas is derived from natural gas. Biomass to Liquid (BTL) technologies are not as significantly developed as CTL and GTL but also now receive more attention as processes for renewable fuels production. A solid catalyst is required for the FT reaction to occur. Cobalt- and iron-based catalysts are the most used for commercial applications [1]. The reaction is also affected by a number of operating conditions such as temperature, pressure, feed gas composition and flow rates. In this study, the effect of feed gas space velocity on CO conversion rate and product selectivity during FT reaction over a cobalt-based catalyst has been evaluated.

II. EXPERIMENTAL DETAILS

A. Catalyst Preparation

The catalyst was prepared using the procedure described in an earlier study [2]. The support was first prepared by mixing titania (TiO₂) powder (Degussa P25) with an equal amount (weight-based) of water and drying at 120°C for 1 hour. The dried support was calcined in air at 400°C for 16 h, cooled, crushed and sieved to retain particles between 0.1 and 0.5 mm. Cobalt was introduced in the support by incipient wetness impregnation method where a cobalt nitrate solution was added to the support in

order to achieve ca. 10% cobalt loading. The cobalt nitrate-impregnated support was subsequently dried at 120°C in air overnight and calcined at 400°C in air for 6 hours to obtain a fresh catalyst.

B. Catalyst Testing

The catalyst was tested in a fixed-bed reactor where 0.5g of fresh catalyst and an appropriate amount of stainless steel balls (3 mm in diameter) were loaded. Two layers of quartz wool separated the catalyst bed from the stainless steel balls as shown in fig. 1.

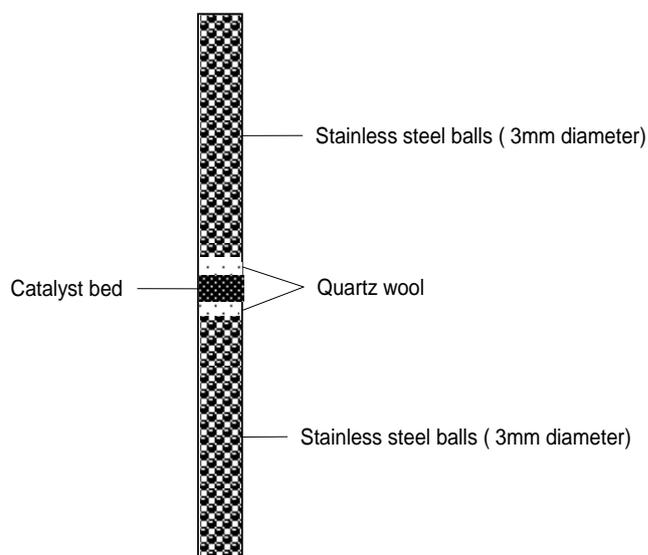


Fig. 1 Details on catalyst loading in the FT reactor

After the calcination process, the fresh catalyst contained cobalt in an oxide form. An activation process that usually consists of catalyst reduction in a hydrogen flow between 250 and 400°C is required prior to the FT reaction [1]. Studies that used other reducing agents such as CO-containing gas mixtures have also been reported in literature [2-9]. In this study, the catalyst was activated using a gas containing 5% H₂ in Ar (30 Nml/min) at 350°C for 14 hours around atmospheric pressure. The reactor was cooled to room temperature, then synthesis gas (30% CO, 60% H₂, balance N₂) was introduced and the pressure was built up to 20 bar using a back pressure regulator placed downstream the reactor. An appropriate feed gas flow rate was set on an Aalborg mass flow controller and the temperature of the reactor was raised to 220°C to perform the FT reaction. A hot pot was mounted at the bottom of the reactor for wax collection followed by a cold pot for water and light oil collection. The gas product was analyzed on-line using a gas chromatograph. An excel spreadsheet was developed to

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calculate the CO conversion, CO conversion rate and product selectivities.

III. RESULTS AND DISCUSSION

%CO conversion, rate of CO conversion and CH₄ selectivity as function of space velocity are reported in fig. 2. The CO conversion decreased with an increase space velocity. Values of ca. 19.9, 16.9 and 16.5 were respectively measured at 20, 40 and 60 Nml/gCat/min. This was expected since an increase in feed gas flow rate decreases the residence time of reactants in the reactor. However, the rate for CO conversion linearly increased with an increase in feed gas flow rate. A CO conversion rate of ca. 3.3 mmol/gCat/h was measured at 20 Nml/gCat/min compared to ca. 8.3 mmol/gCat/h at 60 Nml/gCat/min. On the other hand, the CH₄ selectivity was found to decrease with an increase in space velocity. About 19.4, 13.7 and 10.7% CH₄ selectivity were respectively measured at 20, 40 and 60 Nml/gCat/min.

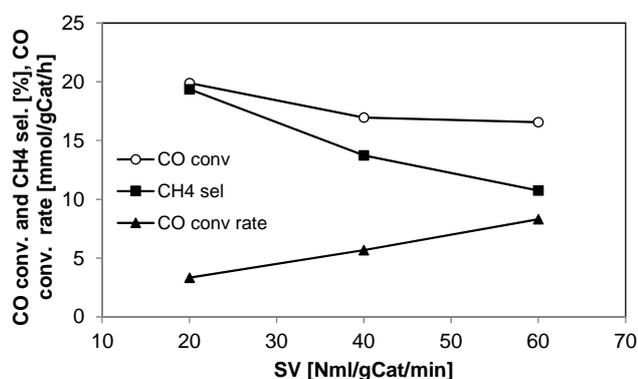


Fig. 2 CO conversion, CH₄ selectivity and CO conversion rate as function of space velocity

The effect of feed space velocity on C₂-C₄ and C₅₊ selectivities is reported in fig. 3. The data show that C₂-C₄ selectivity decreased while C₅₊ selectivity increased with an increase in space velocity. C₂-C₄ selectivities of ca. 13.2, 11.4 and 8.3%, and C₅₊ selectivities of ca. 67.1, 74.8 and 80.9 were respectively measured at 20, 40 and 60 Nml/gCat/min.

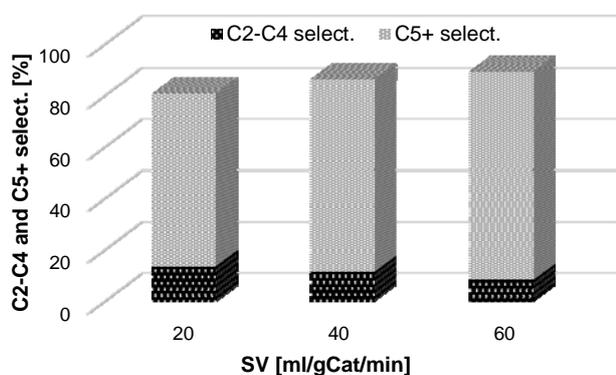


Fig. 3 Effect of space velocity on C₂-C₄ and C₅₊ selectivity
The effect of space velocity on olefin to paraffin ratios as function of carbon number is shown in fig. 4. All the data

show a significant increase in olefin to paraffin ratio when the space velocity was increased from 20 to 40 Nml/gCat/min and no significant change was observed when the space velocity was further increased to 60 Nml/gCat/min.

The overall olefin to paraffin ratio and alpha values as function of feed gas space velocity are summarized in table 1.

TABLE I
EFFECT OF SPACE VELOCITY ON LIGHT OLEFINS TO PARAFFINS RATIO AND CHAIN GROWTH PROBABILITY

SV [ml/gCat/min]	O/P ratio ^a	Alpha ^b
20	0.18	0.50
40	0.35	0.52
60	0.34	0.54

^a and ^b: based on C₃ to C₇ hydrocarbons in gas product after cooling at room temperature and depressurized to atmospheric pressure.

Olefin to paraffin ratios of 0.18, 0.35 and 0.34 were measured at 20, 40 and 60 Nml/gCat/min respectively. A significant change was observed when the space velocity was increased from 20 to 40 Nml/gCat/min with no significant effect when the space velocity was further increased. The alpha value was found to increase from 0.50 at 20 Nml/gCat/min to 0.52 at 40 Nml/gCat/min and to 0.54 at 60 Nml/min.

The results can possibly be explained as follows:

- i) At low space velocity, the residence time for the reactants is long and leads to high levels of CO conversion;
- ii) The partial pressure of reactants, for example CO, is related to the fractional CO conversion by the following expression:

$$P_{CO} = P_{COin} \times (1 - X_{CO}) \quad (1)$$

Where P_{COin} is the partial pressure of CO as it enters the reactor and X_{CO} the fractional CO conversion. At high space velocities, because the conversion (X_{CO}) is low, the partial pressure of CO (P_{CO}) and that for H₂ will be relatively higher and can explain the high CO conversion rate measured at high space velocity.

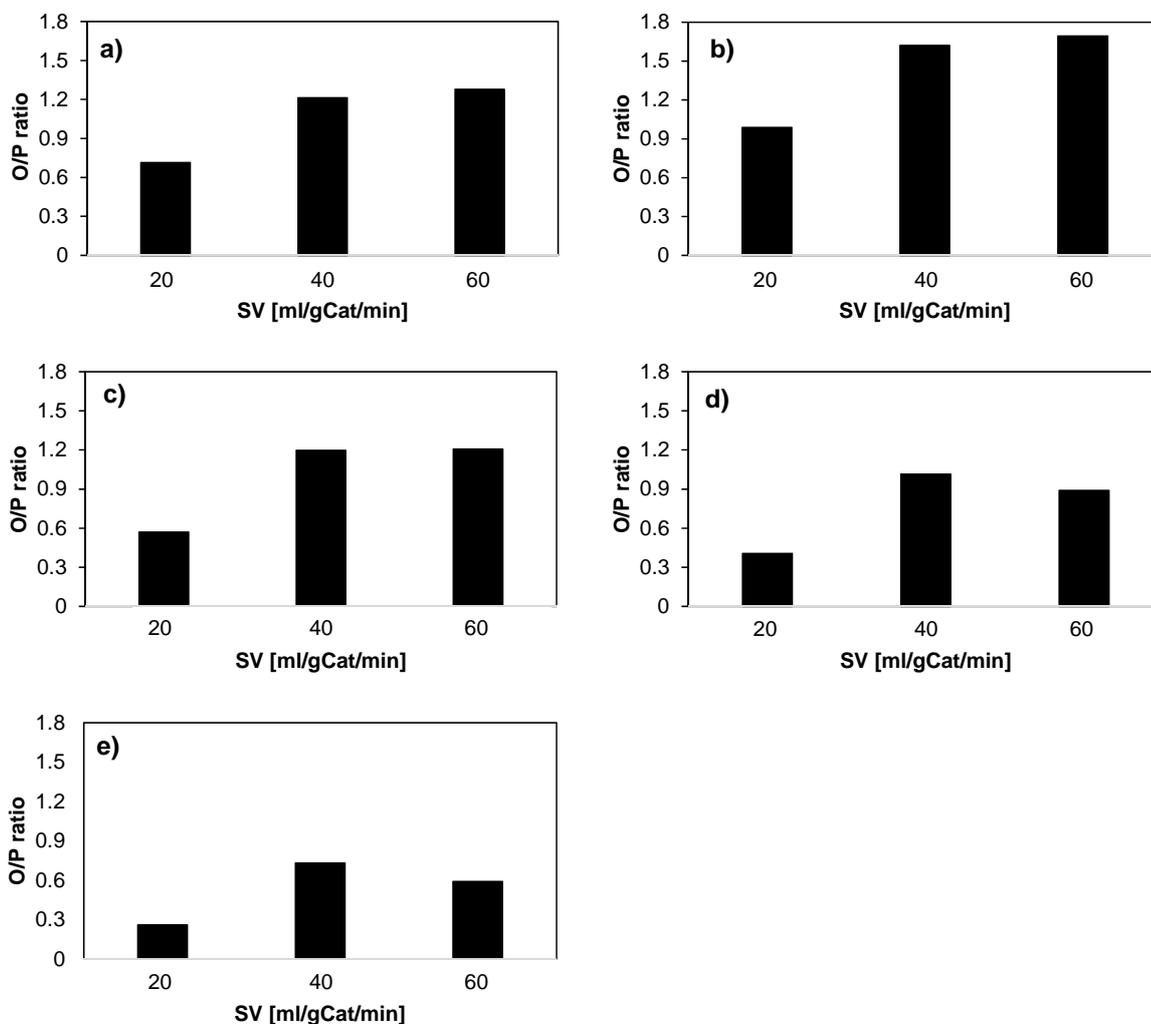


Fig. 4 Effect of space velocity on olefin to paraffin ratios as function of carbon number: a) C₃; b) C₄; c) C₅, d) C₆ and e) C₇

iii) The proportion of products present in the reactor during FT reaction is also function of CO conversion. Because of low selectivity to oxygenates and limited water-gas-shift activity for cobalt-based FT catalysts, for every mole of CO converted to hydrocarbons, there will be approximately one mole of water formed. The water increases with the hydrocarbon products formed. From equation (1) we can approximate the partial pressure of water formed during FT reaction over a cobalt catalyst as:

$$P_{H_2O} = P_{CO_{in}} \cdot X_{CO} \quad (2)$$

As the space velocity is increased, the CO conversion X_{CO} decreases, therefore the partial pressure of water and the proportion of hydrocarbon products also decrease in the reactor. This could result in better mass transfer that can also explain higher CO conversion rates measured at high space velocities. This could also lead to a change in

composition of the liquid present in the pores of the catalyst and explain the changes in product selectivity observed upon increasing the space velocity.

I. CONCLUSION

The CO consumption rate, olefin to paraffin ratio, C₅₊ selectivity and the chain growth probability (α) were found to increase with an increase in space velocity. The results were explained in terms of reactants partial pressures and mass transfer in the catalyst as function of CO conversion that in turn depends on space velocity.

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