Effect of Space Velocity on Alumina-supported Cobalt Catalyst Performance for Fischer-Tropsch Reaction

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Abstract— **Co/ɣ-Al$_2$O$_3$ catalyst was prepared by incipient wetness impregnation of the ɣ-Al$_2$O$_3$ support using an aqueous solution of cobalt nitrate. The catalyst was characterized by XRD, BET and TPR. It was evaluated in a fixed-bed reactor to determine the effect of space velocity on the CO conversion, CO conversion rate, CH$_4$ selectivity and C$_{5+}$ selectivity during Fischer-Tropsch reaction. CO conversion decreased while the CO conversion rate linearly increased with increasing the space velocity. The CH$_4$ selectivity was not significantly affected by the space velocity as it fluctuated between 5 and 6%.**

Index Terms—**Co/Al$_2$O$_3$ catalyst, Fischer-Tropsch, Space velocity.**

I. INTRODUCTION

FISCHER-TROPSCH (FT) synthesis is a chemical reaction that transforms a mixture of carbon monoxide and hydrogen (recognized as syngas) gas into a series of hydrocarbons [1]. The reaction proceeds in the presence of a catalyst which can be employed to facilitate the process. Transition metals such as cobalt (Co), iron (Fe) and ruthenium (Ru) are the most commonly used [2]. However, FT catalysts are still allied with complications such as undesirable methane selectivity, water gas shift activity that negatively affects the carbon efficiency for the process, formation of metal-support compounds causing the loss of useful metals in an inactive form for FT reaction, etc. Studies that aims at addressing these challenges are constantly carried out. The general approach is either to improve the catalyst design or/and optimize operating conditions such as reaction temperature, pressure, feed composition and flow rate, etc.

The main objective of this study was to evaluate the effect of space velocity on the CO conversion, CO conversion rate, CH$_4$ selectivity and C$_{5+}$ selectivity during FT synthesis using cobalt catalyst supported on gamma alumina.

II. EXPERIMENTAL DETAILS

A. Catalyst preparation

The support was prepared by mixing 25g of Al$_2$O$_3$ (gamma alumina from Sigma Aldrich) with 20g of distilled water and dried in air at 120 ^{o}C for 24 hours. The support was then calcined in air at 500 ^{o}C for 10 hours.

The catalyst was prepared by wetness impregnation of the support using an aqueous solution of cobalt nitrate (CoN$_2$O$_6$.6H$_2$O). The impregnating solution was added to the Al$_2$O$_3$ to give a cobalt metal loading of ca. 15% by mass. This step was followed by sample drying and calcination in air at 120 ^{o}C and 500 ^{o}C (for 10 hours) respectively to decompose and transform the cobalt nitrate to cobalt oxide [3].

B. Catalyst characterization

The catalyst was characterized by X-Ray diffraction (XRD) analysis to determine the structure of the catalyst, Brunaure Emmett and Teller (BET) analysis to determine the surface area, pore volume and average pore size for both the catalyst and the blank calcined support. Temperature programmed reduction (TPR) was also used in order to study the reduction behavior of the catalyst in presence of H$_2$. The XRD analysis was performed using a Rigaku Ultima IV X-ray powder diffractometer which used PDXL analysis software to process the data. The radiation source was Cu-Kα (λ = 1.54 Å), the current and voltage were set at 30 mA and 40 KV respectively. The step width was 2θ = 0.01^o. BET analysis was performed by N$_2$ sorption at 77 K using a Micromeritics Tristar 3000 apparatus. TPR analysis was conducted on Micromeritics Autochem II apparatus.

C. Catalyst testing

The catalyst was evaluated for FT reaction in a fixed bed reactor. 0.5g of the catalyst was loaded in the reactor and activated by reduction with either 5%H$_2$ in Ar to convert cobalt oxide to metallic cobalt since this is the active form for FT. The flow rate of the reducing gas mixture

was set to 30 ml/min at atmospheric pressure. The temperature was elevated from room temperature to either 350 ^{o}C at a rate of 10 ^{o}C per minute and kept there for 17 hours.

The FT reaction was performed with syngas as a feed containing 10%N_2, 30%CO and 60%H_2. The outlet gas products were analyzed using a Dani master gas chromatograph (GC) equipped with Thermal conductivity detector (TCD) and flame ionization detector (FID). The following space velocities were selected for the study: 2, 14 and 20 ml/gCat/min.

III.   RESULTS AND DISCUSSION

A. Catalyst characterization

XRD analysis was performed on the blank calcined ɣ-Al_2O_3 support and the calcined fresh catalyst to determine the structure of the catalyst and the results are presented in fig. 1 below.
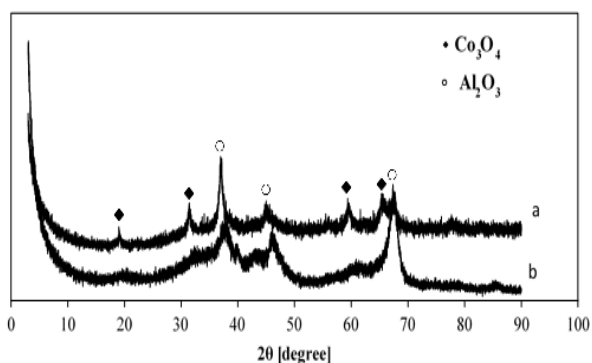

Fig. 1 XRD data for a) Co/Al_2O_3 catalyst and b) blank Al_2O_3 support

Three major diffraction peaks which were due to gamma Al_2O_3 were observed at diffraction angles 2θ equal to 39.9^o, 45.9^o and 67.7^o.Diffraction peaks corresponding to Co_3O_4 particles were detected at 20.5^o, 37.0^o, 59.2^o and 67.1^o. These are additional peaks which are not observed on the XRD patterns for the blank Al_2O_3 support. The particle size of Co_3O_4 as determined by using the Williamson-Hall method was found to be 50nm.

Table 1 below shows the summary of the BET analysis for fresh Co/Al_2O_3 catalyst as compared to the blank calcined ɣ-Al_2O_3 support.

TABLE I
SUMMARY OF BET ANALYSIS DATA

	Calcined blank Al_2O_3 support	Calcined 15%Co/Al_2O_3 catalyst
BET surface area [m^2/g]	123.6	110.0
Pore Volume [cm^3/g]	0.229	0.193
Pore size [nm]	56.2	62.0

The BET surface area (110 m^2/g) and the total pore volume (0.193 cm^3/g) for the calcined Co/ɣ-Al_2O_3 catalyst were found to be lower compared to the blank ɣ-Al_2O_3 support which had BET surface area and pore volumes of 123.6m^2/g and 0.229cm^3/g respectively. Nevertheless, the average pore size of the calcined ɣ-Al_2O_3-supported catalyst was found to be slightly bigger than that of the blank calcined ɣ-Al_2O_3 support. The surface area reduction after addition of cobalt metal is possibly due to some degree of pore obstruction by the cobalt deposited in the ɣ-Al_2O_3 support.

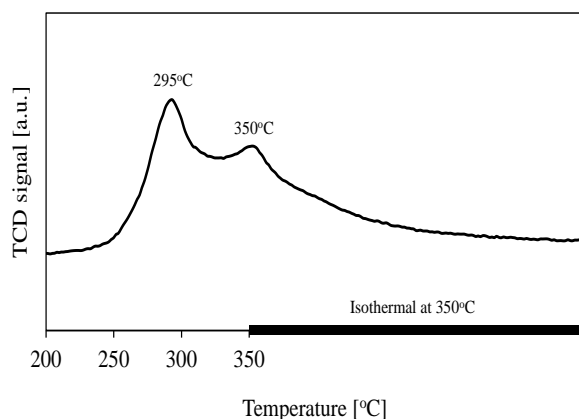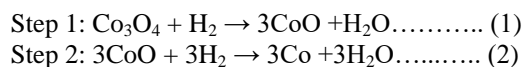TPR data for Co/ɣ-Al_2O_3 are reported in fig. 2.

Fig. 2 TPR profile for Co/Al_2O_3 catalyst in presence of H_2 (analysis gas: 10%H_2 in Ar, heating rate: 10°C/min to 350°C, then isothermal at 350°C, sample amount: ca. 0.04g)

Two reduction peaks were observed. The first reduction peak started around 230°C and reached its maximum at ca. 295 ^{o}C. The second peak started to appear around 310 ^{o}C and reached its maximum at 350 ^{o}C.

Reduction of Co_3O_4 by H_2 proceeds in two steps:

Step 1: $Co_3O_4 + H_2 \rightarrow 3CoO + H_2O$……….. (1)
Step 2: $3CoO + 3H_2 \rightarrow 3Co + 3H_2O$…....…. (2)

Two reduction peaks observed in fig.2 can be attributed to these two reduction steps with CoO as intermediate [4]. The second reduction peak was extended for a longer period and this could be due to reduction of Co species which may strong interaction with the support and are difficult to reduce.

B. Catalyst testing

The CO conversion, CH4 selectivity and CO conversion rate as a function of space velocity are plotted in fig. 3.
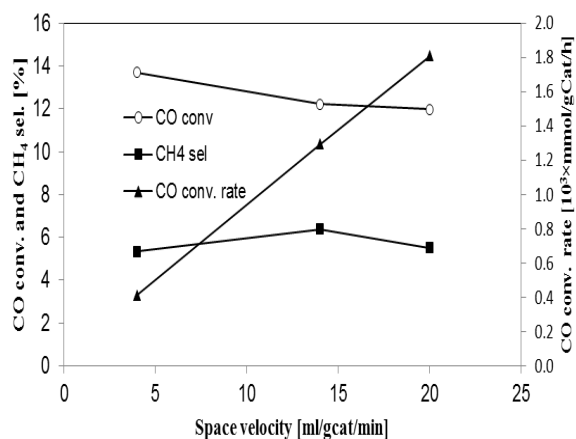
Fig. 3: Effect of space velocity on the CO conversion, CH_4 selectivity and CO conversion rate.

Fig. 4: C_{5+} selectivity as a function of space velocity Increasing the space velocity from 4 to 14 and 20 ml/gcat/min led to comparable C_{5+} product selectivities of 94.6, 93.6 and 94.5% respectively.

The CO conversion was found to possess inversely proportional trend with respect to the space velocity. Increasing the space velocity from 4ml/gCat/min to 14ml/gcat/min resulted in CO conversion decreasing from 13.7% to 12.2%. Further increase of the space velocity from to 20 ml/gcat/min decreased the CO conversion to ca. 12%. This trend was indeed predictable since increasing the space velocity leads to shorter residence time of the reactants in the reactor. The CH_4 selectivity did not show any dependency on the space velocity at least the range considered in this study. It was observed to fluctuate between 5% and 6%. However, the rate of CO conversion was found to linearly increase with the space velocity. As the latter was increased from a lower value of 4ml/gcat/min to 14ml/gcat/min and 20ml/gcat/min, the CO conversion rate increased from 0.414×10^3 to 1.293×10^3 and 1.810×10^3 mmol/gcat/h respectively. A similar behavior was also observed by Liu *et al*. [5] who measured an increase in specific of a Co/SiC catalyst from 0.46 to 0.55 and 0,77 gHC/ gCat/h upon increasing the gas hourly space velocity (GHSV) from 1900 to 2600 and 3800 h^{-1} respectively. This can be explained by a higher rate of removal of liquid hydrocarbons formed on the catalyst at higher space velocities [5].

The effect of space velocity on the selectivity towards the formation of C_{5+} hydrocarbon products is presented in fig. 4 and like for methane, the selectivity to C_{5+} hydrocarbons was not significantly influenced by the feed space velocity.
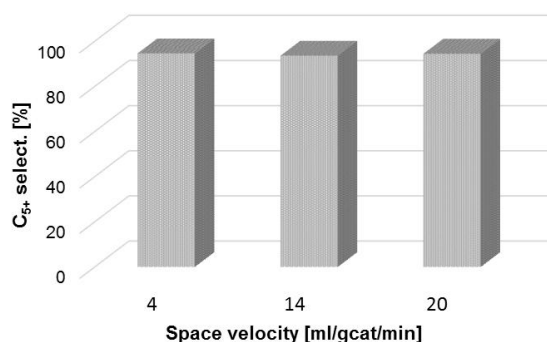
IV. CONCLUSION

The effect of space velocity on CO conversion, CO conversion rate, CH_4 selectivity and C_{5+} selectivity was studied. CO conversion was found to decrease with increasing the space velocity. The CO conversion rate was found to increase with space velocity and this was probably due to mass transfer improvement as a result of improved removal liquid hydrocarbons from the catalyst at higher space velocities. The methane and C_{5+} hydrocarbons selectivities were not practically affected by the change in space velocity.

References:

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