

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

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Abstract— Co/ γ -Al₂O₃ catalyst was prepared by incipient wetness impregnation of the γ -Al₂O₃ 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, CH₄ selectivity and C₅₊ selectivity during Fischer-Tropsch reaction. CO conversion decreased while the CO conversion rate linearly increased with increasing the space velocity. The CH₄ selectivity was not significantly affected by the space velocity as it fluctuated between 5 and 6%.

Index Terms—Co/Al₂O₃ 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.

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The main objective of this study was to evaluate the effect of space velocity on the CO conversion, CO conversion rate, CH₄ selectivity and C₅₊ 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 Al₂O₃ (gamma alumina from Sigma Aldrich) with 20g of distilled water and dried in air at 120 °C for 24 hours. The support was then calcined in air at 500 °C for 10 hours.

The catalyst was prepared by wetness impregnation of the support using an aqueous solution of cobalt nitrate (CoN₂O₆·6H₂O). The impregnating solution was added to the Al₂O₃ to give a cobalt metal loading of ca. 15% by mass. This step was followed by sample drying and calcination in air at 120 °C and 500 °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, Brunauer 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 H₂. 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-K α ($\lambda = 1.54 \text{ \AA}$), the current and voltage were set at 30 mA and 40 KV respectively. The step width was $2\theta = 0.01^\circ$. BET analysis was performed by N₂ 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%H₂ 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 °C at a rate of 10 °C per minute and kept there for 17 hours.

The FT reaction was performed with syngas as a feed containing 10%N₂, 30%CO and 60%H₂. 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 γ -Al₂O₃ support and the calcined fresh catalyst to determine the structure of the catalyst and the results are presented in fig. 1 below.

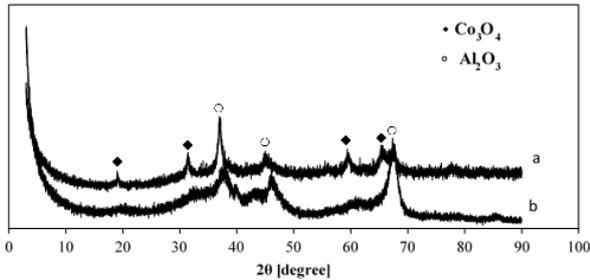


Fig. 1 XRD data for a) Co/Al₂O₃ catalyst and b) blank Al₂O₃ support

Three major diffraction peaks which were due to gamma Al₂O₃ were observed at diffraction angles 2θ equal to 39.9°, 45.9° and 67.7°. Diffraction peaks corresponding to Co₃O₄ particles were detected at 20.5°, 37.0°, 59.2° and 67.1°. These are additional peaks which are not observed on the XRD patterns for the blank Al₂O₃ support. The particle size of Co₃O₄ 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/Al₂O₃ catalyst as compared to the blank calcined γ -Al₂O₃ support.

TABLE I
SUMMARY OF BET ANALYSIS DATA

	Calcined blank Al ₂ O ₃ support	Calcined 15%Co/Al ₂ O 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 m²/g) and the total pore volume (0.193 cm³/g) for the calcined Co/ γ -Al₂O₃ catalyst were found to be lower compared to the blank γ -Al₂O₃ support which had BET surface area and pore volumes of 123.6m²/g and 0.229cm³/g respectively. Nevertheless, the average pore size of the calcined γ -Al₂O₃-supported catalyst was found to be slightly bigger than that of the blank calcined γ -Al₂O₃ 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 γ -Al₂O₃ support.

TPR data for Co/ γ -Al₂O₃ are reported in fig. 2.

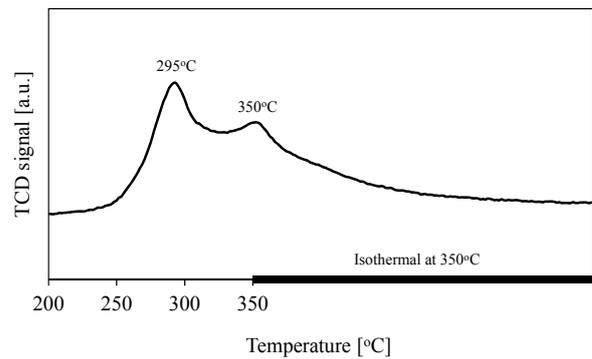
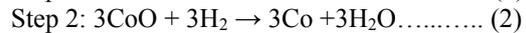
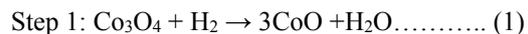


Fig. 2 TPR profile for Co/Al₂O₃ catalyst in presence of H₂ (analysis gas: 10%H₂ in Ar, heating rate: 10°C/min to 350°C, then isothermal at 350°C, sample amount: ca. 0.04g)

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

Reduction of Co₃O₄ by H₂ proceeds in two steps:



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.

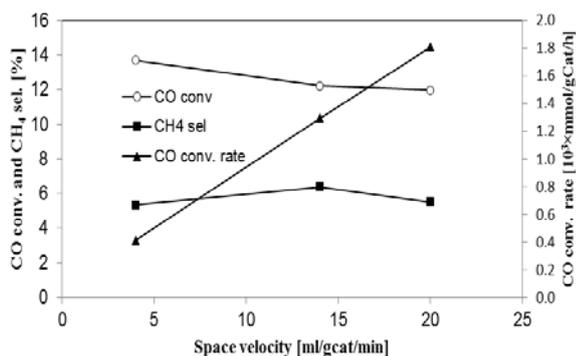


Fig. 3: Effect of space velocity on the CO conversion, CH₄ selectivity and CO conversion rate.

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 14 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 CH₄ 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 C₅₊ hydrocarbon products is presented in fig. 4 and like for methane, the selectivity to C₅₊ hydrocarbons was not significantly influenced by the feed space velocity.

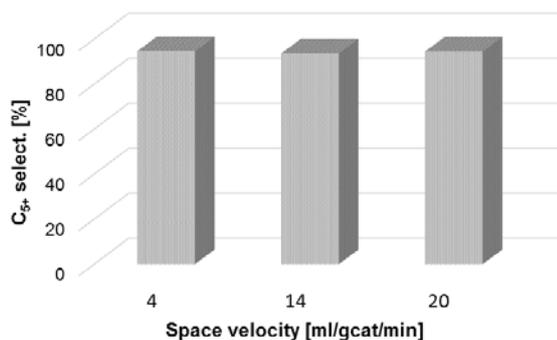


Fig. 4: C₅₊ selectivity as a function of space velocity. Increasing the space velocity from 4 to 14 and 20 ml/gcat/min led to comparable C₅₊ product selectivities of 94.6, 93.6 and 94.5% respectively.

IV. CONCLUSION

The effect of space velocity on CO conversion, CO conversion rate, CH₄ selectivity and C₅₊ 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 C₅₊ hydrocarbons selectivities were not practically affected by the change in space velocity.

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