

Reduction Behaviour for Co/Al₂O₃ Fischer-Tropsch Catalyst in Presence of H₂ or CO

Phathutshedzo R. Khangale, Reinout Meijboom, Kalala Jalama

Abstract—The main objective of this study was to investigate the effect of reducing Co/Al₂O₃ Fischer-Tropsch (FT) catalyst using H₂ or CO gas on catalyst properties. The catalyst was prepared by direct impregnation of the Al₂O₃ support with Co(NO₃)₂·6H₂O solution and calcined in air at 500 °C for 10 hours to decompose and transform the cobalt nitrate to cobalt oxide. XRF, XRD and BET analyses were used to characterize the catalyst. The study on catalyst reducibility was performed using Temperature programmed reduction (TPR) of 300 mg calcined Co/Al₂O₃ catalyst using H₂ and CO containing gas mixture respectively. The extent of catalyst reduction with CO and H₂ was calculated as a proportion of Co₃O₄ that was reduced to Co⁰ during the reduction process in presence of H₂ or CO. The extent of catalyst reduction was found to be 31.6 and 90.9% when catalyst was reduced with H₂ and CO respectively. It was concluded that more Co species were reduced when reduction was conducted in the presence of CO than in the presence of H₂.

Index Terms—Co/Al₂O₃ catalyst, CO, H₂, reduction

I. INTRODUCTION

FISCHER-TROPSCH is a process where hydrocarbons are produced from a mixture of CO and H₂ over a catalyst. Fe and Co are the catalysts used for industrial application. After preparation, cobalt catalyst are obtained in a form that is not active for FT reaction. An activation process where the cobalt species in the catalyst are reduced to metallic cobalt, the active form for the FT reaction, is usually required. This is usually done by using H₂ as a reducing gas. This activation process has received lot of research attention over the years as good catalyst reducibility is required for the process. Reports aiming at improving Co catalysts reducibility include promotion with noble metals [1-9], promotion with Au [10, 11], reduction with CO containing H₂ gas, etc. In this study, the effect of reducing Co/Al₂O₃ catalyst with H₂ or CO on the catalyst properties will be investigated.

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II. EXPERIMENTAL

A. Catalyst preparation

20g of Al₂O₃ (Sigma Aldrich) was mixed with 15.6g of distilled water and dried in air at 120°C for 16 hours and then calcined in air at 500°C for 10 hours to make the catalyst support.

The catalyst was prepared by incipient wetness impregnation of the Al₂O₃ support with a Co(NO₃)₂·6H₂O solution followed by drying in air at 120 °C for 16 h and calcination in air at 500 °C for 10 hours. The impregnating solution was added to the Al₂O₃ to give a cobalt metal loading of ca. 10% by mass.

B. Catalyst characterization

X-ray diffraction (XRD) analysis was conducted on a Philips PW 3040/60 X-ray diffraction apparatus with a CuK_α (λ = 1.54) radiation. Samples were scanned with a 0.02° step size and a scan speed of 0.04 s/step. The average size of Co₃O₄ particle was calculated according to the Scherrer equation:

$$d = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where:

d is the average crystallite diameter;

λ is the wavelength of X-ray, and;

β is the full width at half maximum in radian.

X-ray fluorescence (XRF) analysis was performed on a MAGIX PRO XRF spectrometer to determine the Co loading in the catalyst sample obtained after calcination.

Brunauer, Emmett and Teller (BET) analysis was performed on a Micromeritics ASAP 2000 apparatus to determine the surface area and pore size of the synthesized catalyst.

Temperature programmed reduction (TPR) analysis was performed on a machine that was customized in our laboratory. The analysis was done to compare the reduction behaviour of Co catalyst in the presence of H₂ and CO respectively. The first analysis was done using a gas mixture containing 5% H₂ in Ar and the second was done using a gas mixture containing 5% CO in He. 300 mg of calcined catalyst sample were first loaded in a U-shaped stainless steel tube reactor and degassed in a flow of nitrogen (30 ml/min) at 150 °C for 60 min and cooled to room temperature. The catalyst sample was thereafter exposed to

a continuous flow of reducing gas (5% H₂ in Ar or 5% CO in He) and the reactor temperature was increased to 350 °C at a rate of 10 °C/min and maintained at this temperature for the rest of the experiment. The analysis temperature was limited to 350 °C to protect the equipment from excessive carbon deposition when CO was used. The flow-rate of the reducing gas was maintained at 20 ml/min for all the analyses and a thermal conductivity detector (TCD) was placed at the reactor outlet to measure the H₂ or CO uptake. The data were processed using Clarity software.

III. RESULTS AND DISCUSSION

A. XRD and XRF analyses

XRD analyses were performed on the catalyst to compare the structure of the calcined Al₂O₃ support and the Al₂O₃-supported cobalt catalyst. The data are reported in fig. 1.

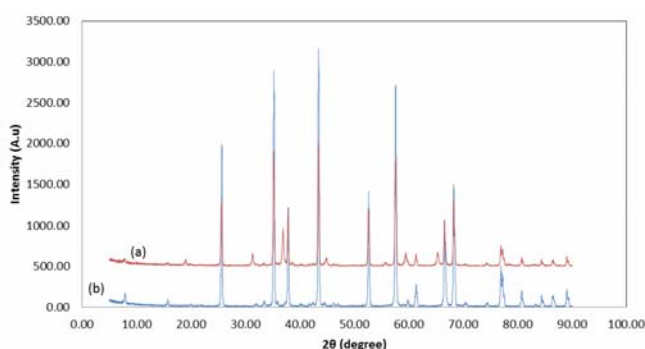


Fig. 1. XRD patterns for (a) calcined Al₂O₃-supported cobalt catalyst and (b) calcined blank Al₂O₃ support

Diffraction peaks corresponding to Co₃O₄ particles in the catalyst were observed at diffraction angles 2θ equal to 36.9°, 55.9° and 65.3°. These are additional peaks which are not observed on the XRD patterns for the blank Al₂O₃ support. The most intensive peak for Co₃O₄ was identified at a diffraction angle (2θ) of 36.9° and was used to determine Co₃O₄ particle size using the Scherrer equation. The XRD particle size (d_{XRD}) obtained from XRD pattern indicates the average particle size [13]. The calculated average Co₃O₄ particle size was found to be ca. 5.5 nm. The XRD analysis data also revealed that the catalyst contained ca. 9.6 wt.% Co₃O₄. These data were compared to the catalyst composition determined by XRF analysis and the results are summarized in table 1. The Co contents determined by the two techniques were similar and were within an experimental error, acceptable as they were close to the target value of 10%.

TABLE I: COMPARISON BETWEEN TARGET COBALT CONTENT IN THE CATALYST AND THE ACTUAL CONTENT AS DETERMINED BY XRD AND XRF

Co content by XRF (%)	Co Content by XRD (%)	Target Co content (%)
9.86	9.6	10

B. BET analysis

The BET surface area, total pore volume and average pore diameter for the blank Al₂O₃ support and the Al₂O₃-supported catalyst samples are reported in table 2.

TABLE II: BET RESULTS FOR THE BLANK AL₂O₃ SUPPORT AND THE CO/AL₂O₃ CATALYST

	Al ₂ O ₃	Co/Al ₂ O ₃
BET Surface Area (m ² /g)	0.45	1.85
Total Pore Volume (m ³ /g)	0.0014	0.0107
Average Pore Diameter (nm)	12.4	23.1

The BET surface area for the calcined Co/Al₂O₃ catalyst is greater (ca. 1.85 m²/g) than that of the blank Al₂O₃ support which has a surface area of ca. 0.45 m²/g. On the other hand, the total pore volume and the average pore diameter for blank calcined Al₂O₃ support are smaller ca. (0.0014m³/g and 12.4 nm respectively) than those of the calcined Co/Al₂O₃ catalyst (0.0107m³/g and 23.1 nm respectively). It appears that cobalt addition to the support resulted in the stabilization on small cobalt species in the support and contributed to the increase in BET surface area. The increase in pore volume and size upon adding Co to the catalyst could be explained by a possibility of some pores collapsing during catalyst treatment after Co species addition.

C. TPR analysis

Fig. 2 shows the TPR profiles for the catalyst activated by H₂ (fig. 2a) and by CO (Fig. 2b).

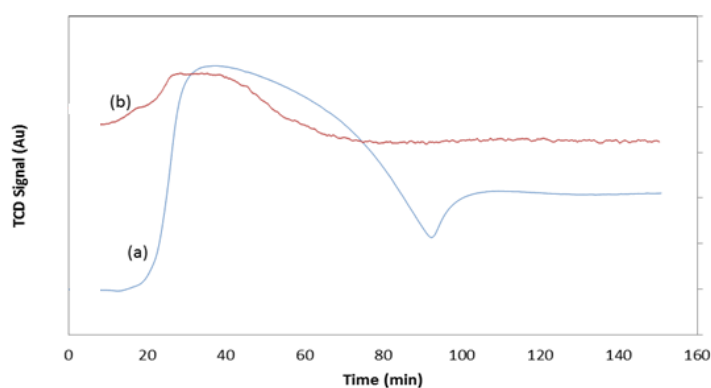
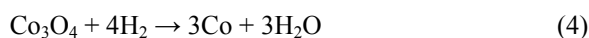


Fig. 2. TPR profile for Co₃O₄ catalyst in presence of a) H₂ and b) CO

It can be observed that when reduction was done with H₂, a reduction peak started after ca. 12 minutes, corresponding to a temperature of 220°C and reached a maximum value after ca. 38 minutes, at a temperature of 350°C. Thereafter, the TCD signal went down at a low rate and proceeded isothermally at 350°C, until new peak started to appear. This new peak reached maximum value after 105 minutes on stream still at temperature of 350°C and extended until the analysis was stopped after 150 minutes. The Co₃O₄ reduction to metallic cobalt proceeds in two steps as follows:



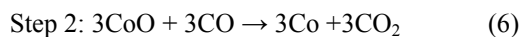
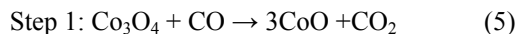
And the overall reaction is written as:



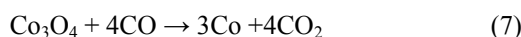
The first reduction peak observed was not symmetrical and suggests the two reduction steps for Co_3O_4 . The second reduction peak which started to appear after 91 minutes indicates the reduction of Co species which are strongly interacted with the support and are difficult to reduce. These species require more active H_2 in order to take place. It is possible that more H_2 was activated on the metallic Co particles after the reduction indicated by the first reduction peak and facilitated the reduction of the Co species in strong interaction with the support by a spill over mechanism.

The TPR data in presence of CO (fig. 2b) show the first reduction peak starting after 7 minutes, corresponding to a temperature of 170°C . This temperature was ca. 50°C lower than the corresponding temperature at which the first reduction peak started in presence of H_2 . A peak shoulder was observed after 18 min (at 280°C) and a maximum value was reached after 29 minutes at 350°C compared to the corresponding 38 minutes in the case of reduction with H_2 . This peak then started to decrease until it gets back to the base line after ca. 71 minutes 350°C . No other significant peaks were observed until the end of the TPR analysis after 150 minutes.

These data suggest that reducing the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst with CO improves the catalyst reducibility as the reduction shifts to lower temperatures as also reported by an earlier study [14] compared to the case where H_2 was used for reduction. Also the reduction peak at extended reduction times that was observed in H_2 -reduced catalyst completely disappeared from the TPR profile of the CO-reduced catalyst. At least two possibilities could explain this: i) CO was active enough to even reduce the Co species in strong interaction with the support or ii) reduction with CO prevented the formation of the difficult-to-reduce Co-support compounds. This could be due to the absence of water during Co catalyst reduction with CO [15]. This supports the advantage for using CO for $\text{Co}/\text{Al}_2\text{O}_3$ catalyst reduction with CO as compared to H_2 . The Co_3O_4 reduction with CO also proceeds in two steps as follows:



The overall reaction is



CO_2 is produced during the reduction process instead of water in the case of reduction with hydrogen. This has decreased the sensitivity of the TCD for the generation of the TPR profile in presence of CO. In fact during catalyst reduction a number of moles of CO are consumed and an equal number of moles of CO_2 are produced resulting in two peaks with opposite sign with He as a carrier gas. For this

reason, the TPR profile in fig. 2b is the difference between the CO consumption and CO_2 production peaks respectively. The resultant peak took the sign of the most sensitive signal between CO and CO_2 as a result of difference in thermal conductivity of the two gases with respect to He. The thermal conductivities of CO, CO_2 and their differences with respect to He are reported in Table 3.

TABLE III: THERMAL CONDUCTIVITY OF CO, CO_2 AND THEIR DIFFERENCES WITH RESPECT TO HE

Gas	Thermal conductivity at 25°C [$\text{W}/\text{m}^\circ\text{K}$]	Difference in thermal conductivity with respect to He [$\text{W}/\text{m}^\circ\text{K}$]
CO	0.024	-0.118
CO_2	0.0146	-0.127
He	0.142	-

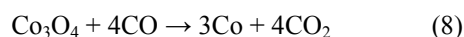
The data show that CO_2 has the highest difference in thermal conductivity with respect to He that was used a carrier gas and therefore implies that for the same amount of CO and CO_2 , CO_2 will have a bigger TCD signal than CO. The signal in fig. 2b is the difference between CO_2 and CO signals and this explains its lower magnitude compared to the TPR signal in presence of H_2 where the whole signal represents the H_2 uptake with no interference of the water as it was not detected because Ar was used as a carrier gas.

The extent of catalyst reduction was calculated as the proportion of Co_3O_4 that was completely reduced to Co^0 during the reduction process in presence of H_2 or CO. Table 4 below summaries the calculations for the extent of reduction for $\text{Co}/\text{Al}_2\text{O}_3$ catalysts.

TABLE IV: EXTENT OF CATALYST REDUCTION

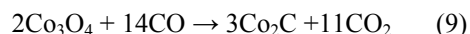
	Reduction with CO	Reduction with H_2
Mass of Catalyst (mg)	300	300
Amount of Co in the Catalyst (m.mol)	0.37	0.37
Required amount of H_2 for complete Co_3O_4 reduction to Co^0	Not applicable	0.49
Required amount of CO for complete Co_3O_4 reduction to Co^0	0.49	Not applicable
Consumed amount of H_2 during Reduction (m.mol)	Not applicable	0.16
Consumed amount of CO during Reduction (m.mol)	0.45	Not applicable
Extent of reduction (%)	90.9	31.6

The extent of catalyst reduction in presence of H_2 after 150 minutes was found to be ca. 31.6%. This value confirms that more Co species still existed in more dispersed form that was in strong interaction with the Al_2O_3 support and which requires extended reduction times. Reduction with CO was assumed to lead to Co^0 as follows:



The extent of reduction obtained was 90.9%.

There is also a possibility of cobalt carbide formation as follows:



The extent of reduction when assuming this reaction was 487.7% and does not make any sense. Also equation 9 shows that cobalt carbide formation is favoured at higher pressures of CO but in this study the lower partial pressure for CO of 0.1 bar can explain why the data do not suggest significant cobalt carbide formation during reduction in presence of CO.

IV. CONCLUSION

The effect of reducing gas (CO or H₂) on Co/Al₂O₃ Fischer-Tropsch catalysts activation was investigated. Based on the results obtained, it was concluded that more Co species were reduced when reduction was performed in the presence of CO than in the presence of H₂. In addition to that, the extent of reduction in the presence of CO was found to be ca. 90.9% while in the presence of H₂ was 31.6%.

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