

ENHANCEMENT OF FTS ACTIVITY AND SELECTIVITY BY INTRODUCING CO DURING CATALYST REDUCTION

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Abstract

The effect of carbon monoxide (CO) on the Reduction of a calcined Ru-promoted Co/Al₂O₃ catalyst was investigated by introducing CO during the reduction procedure. The catalysts are characterized by different methods including: X-ray diffraction, hydrogen chemisorption, and temperature-programmed reduction. The effect of added CO (up to 7 %vol.) during reduction on the dispersion of the cobalt, activity and selectivity of FTS and reducibility of cobalt oxide species were investigated. The CO enhances the reducibility of the CoO to Co⁰ and small cobalt oxide particles with higher interaction with the support. The optimised addition of CO during the reduction increased selectivity and rate of C₅⁺, %42 and %48 respectively. Also it decreased CH₄ selectivity %29. So CO addition enhances the selectivity of Fischer-Tropsch synthesis towards the higher molecular weight hydrocarbons.

Keywords: Fischer-Tropsch, Cobalt, carbon monoxide, reducibility, Activity, C₅⁺ Selectivity, C₅⁺ Rate

Introduction

Due to their high activities^[6], high selectivities to linear hydrocarbon, and low activities for the water gas shift reaction^[4,7] supported cobalt (Co) catalysts are considered to be the most important catalysts for the Fischer-Tropsch synthesis (FTS) based on natural gas conversion. Cobalt surface atoms show high activity and C₅⁺ selectivity in Fischer-Tropsch synthesis Which currently provides the most economic path for the synthesis of liquid fuel from natural gas.

Catalyst productivity and selectivity to C₅⁺ hydrocarbons are critical design criteria in the choice of Fischer-Tropsch synthesis catalyst and reactors. It is proven that supported Ru catalysts are excellent FTS catalysts with high activity and chain growth probability. Indeed supported Ru catalysts for FTS produce C₅⁺ hydrocarbons with a selectivity of over 90% at temperature as low as 373K. The application of ruthenium catalyst in FTS is restricted due to its high price. Therefore, usually a small amount of ruthenium is used as a promoter of the supported cobalt catalyst. Iglesia^[2] reported that addition of Ru to a cobalt catalyst tripled the activity of the catalyst and increased the C₅⁺ selectivity from 84% to 91%^[2].

Tsubaki et al.^[5] investigated the effect of promotion of Co/SiO₂ catalyst with small amounts of Ru, Pt, and Pd. They found that the Ru promoted catalyst had the highest CO hydrogenation rates. Ru enhanced the reducibility of the cobalt catalyst and enriched on the surface of cobalt particles^[5].

In the present work, a ruthenium promoted cobalt catalyst (Ru, Co/Al₂O₃) has been formulated. All catalyst was extensively characterized by different methods including x-ray diffraction, hydrogen chemisorptions and temperature-programmed reduction. Due to importance of producing C₅⁺ and decreasing CH₄ rate in FTS reaction, some experiments were organized. It's found that adding of CO on the reduction affects on the rate and selectivity of C₅⁺ and rate of CH₄ in FTS reaction.

All the catalysts were evaluated in term of their Fisher-Tropsch activity and different product selectivity. CO enhances the reducibility of the CoO to Co⁰ and small cobalt oxide particles with higher interaction with support. The optimised addition of CO during the reduction increased the C₅⁺ rate and selectivity and decrease CH₄ rate and selectivity.

Experiment

Catalyst preparation

Catalyst was prepared with 15 wt% cobalt on alumina as the support. The alumina was calcined at 500°C for 10 h prior to its impregnation with cobalt nitrate solution. Ru promoter was added by incipient wetness impregnation of aqueous solutions of ruthenium (III) nitrosyl nitrate. After the impregnation, all catalysts were dried at 120°C and calcined at 450°C for 3 h with a heating rate of 1°C/min. The cobalt and promoter loadings were verified by an inductively coupled plasma (ICP) AES system.

Reduction

Standard reduction of the catalyst for determining the optimum temperature of reduction was performed employing H₂ flow (100% H₂, 60 ml/min) in a micro reactor using a temperature ramp from ambient to 325, 350, 365, 375 and 400 at 10°C/min and holding at these temp so that the time of reduction for each run became equal. The amount of catalyst used was 1gr.

Also to obtain the optimum time of reduction some experiments were performed in the same manner. In these experiments the catalyst reduction time at optimum temperature, varied 7, 14, 21, 28 and 32 hr.

For determining the effect of CO on the performance of catalyst reduction was performed with introducing a mixture of H₂ flow and different percent of CO, 0, 1, 3, 4, 5 and 7% (total flow, 60 ml/min) in same micro-reactor using a temperature ramp from ambient to optimum temperature of reduction and proper time. After each run all catalyst were evaluated in term of their Fischer-Tropsch activity and product selectivity.

Characterization

X-ray diffraction

XRD was performed to determine the bulk crystalline phases of the catalyst samples following different reduction condition and passivation. XRD patterns of samples were collected using a Philips PW1840 X-ray diffractometer with monochromatized Cu/K_α radiation.

Temperature programmed reduction

Temperature programmed reduction (TPR) profiles of the calcined catalysts were recorded using a Micromeritics TPD-TPR 290 system, equipped with a thermal conductivity detector. The catalyst samples were first purged in a flow of argon at 573 K, to remove traces of water, and then cooled to 313 K. The TPR of 50 mg of each sample was performed using 5.1% hydrogen in

argon gas mixture with a flow rate of 40 cm³/min. The samples were heated from 313 to 1173 K with a heating rate of 10 K/min.

Hydrogen chemisorption and oxidation

The amount of chemisorbed hydrogen was measured using the Micromeritics TPD-TPR 290 system. 0.25g of the calcined catalyst was reduced under hydrogen flow at 673 K for 12 h and then cooled to 373 K under hydrogen flow. The flow of hydrogen was switched to argon at the same temperature, which lasted about 30 minutes in order to remove the weakly adsorbed hydrogen. Afterwards the temperature programmed desorption (TPD) of the samples was obtained by increasing the temperature of the samples, with a ramp rate of 10 K/min, up to 673 K under the argon flow. The TPD spectrum was used to determine the cobalt dispersion and its surface average crystallite size. After the TPD of hydrogen, the sample was reoxidized at 673 K by pulses of 10% oxygen in helium to determine the extent of reduction. It is assumed that Co⁰ is oxidized to Co₃O₄.

Fischer-Tropsch synthesis tests

The catalysts were evaluated in terms of their Fischer-Tropsch synthesis (FTS) activity and selectivity in a tubular fixed-bed micro-reactor. Typically, 1gr of the catalyst was charged into a 1/4" tube, as the reactor. For first step the optimum temperature and time of catalyst reduction based on C₅⁺ rate, were obtained. Then the catalysts were reduced at various reduction gas phase compositions. The FTS tests were carried out at 220°C, 1 atm, and a H₂/CO ratio of 2. The effluents of the reactor were analyzed for CO, CO₂, and C₁-C₂₀ hydrocarbons, using an on-line Varian 3800 gas chromatograph. CO conversion and different product selectivity were calculated based on the GC analyses. Anderson-Schultz-Flory (A-S-F) distribution line was plotted for C₅⁺ products to determine the chain growth probability, α.

Results and discussion

Effect of reduction temperature and reduction time

The catalysts were reduced at different temperature and time of reduction. The FTS tests were carried out at 220°C, 1 atm. The effluents of the reactor were analysed for CO, CO₂, and C₁-C₂₀ hydrocarbons, using an on-line Varian 3800 gas chromatograph. The catalysts were evaluated in terms of their Fischer-Tropsch synthesis (FTS) activity and selectivity of C₅⁺. The results are shown in fig. 1 and 2.

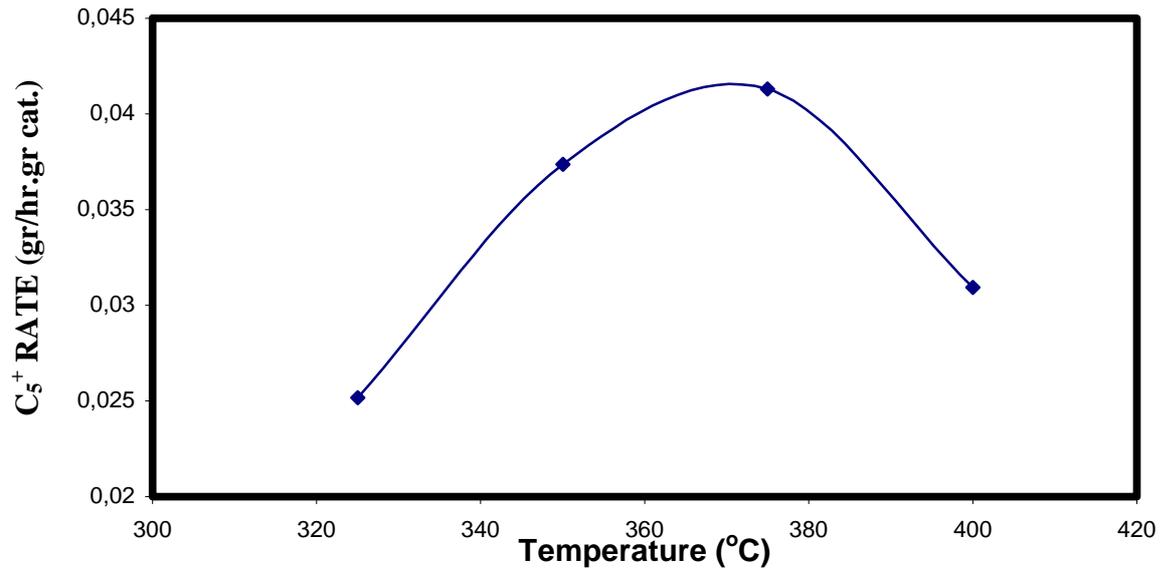


Fig. 1. C₅⁺ rate for Co catalysts reduced at different temperature

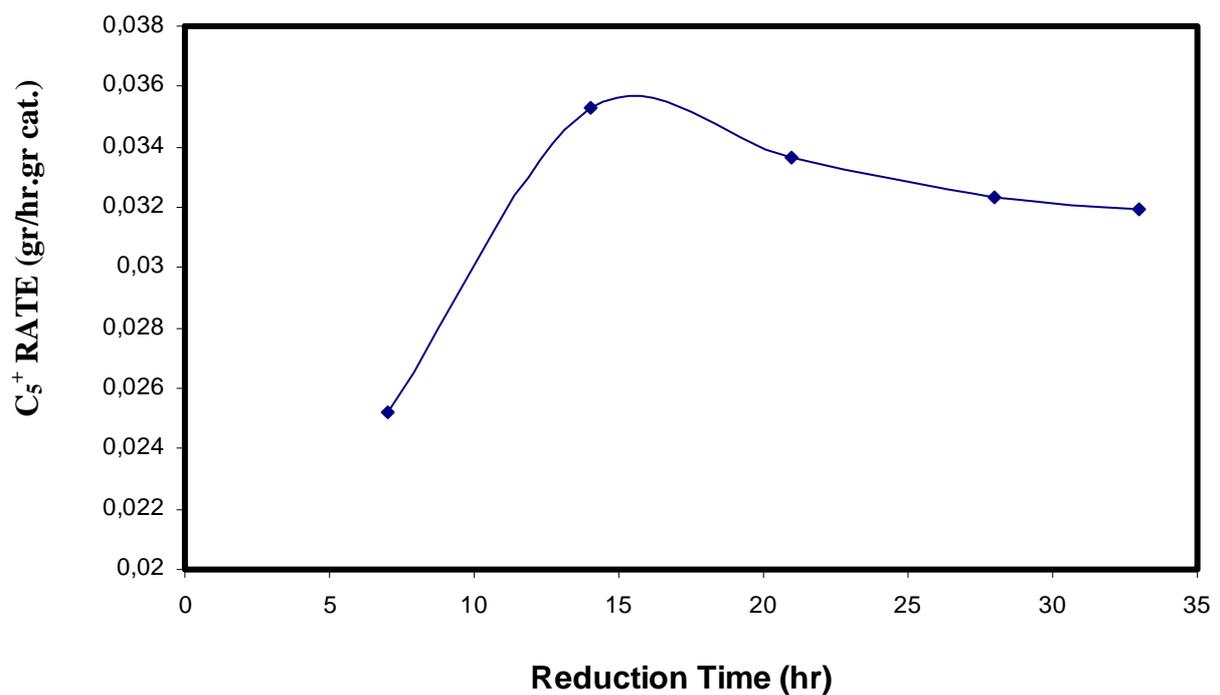


Fig. 2. C₅⁺ rate for Co catalysts reduced at various time

As it shown in these figures the optimum reduction temperature for our catalyst is 365°C and optimum time of the reduction as it shown in fig. 2 is 14hr.

Effect of CO on catalyst reduction

Catalyst sample were reduced at 365°C and various reduction gas compositions for 14 hr, to know the effect of introducing CO on catalyst reduction. The catalysts were evaluated in same manner mentioned before. The results shown in figure 3 and 4.

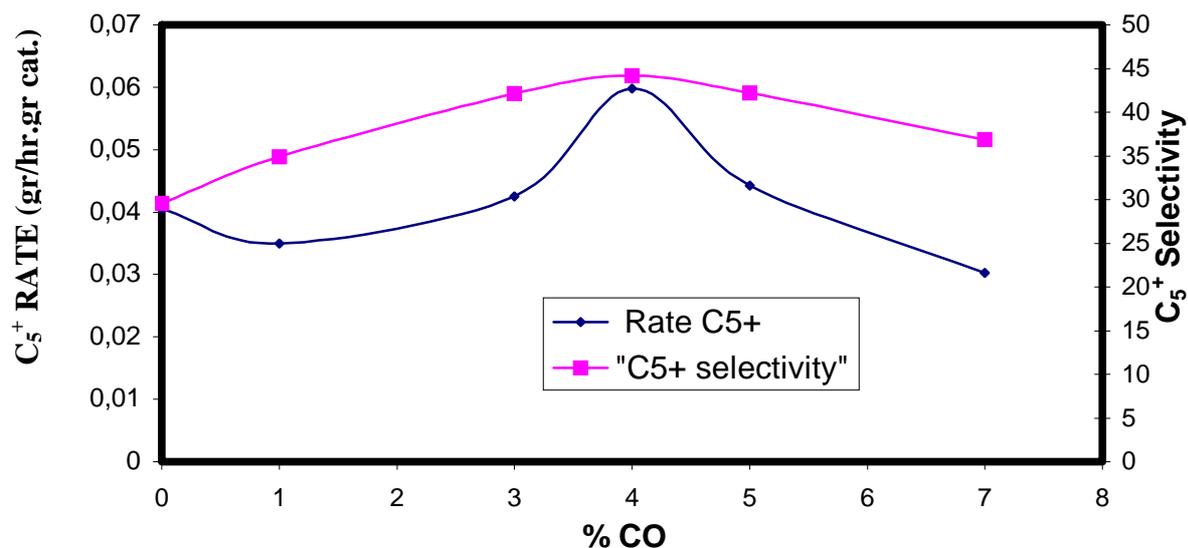


Fig. 3. C_5^+ selectivity and rate for Co catalysts reduced at various reduction gas compositions

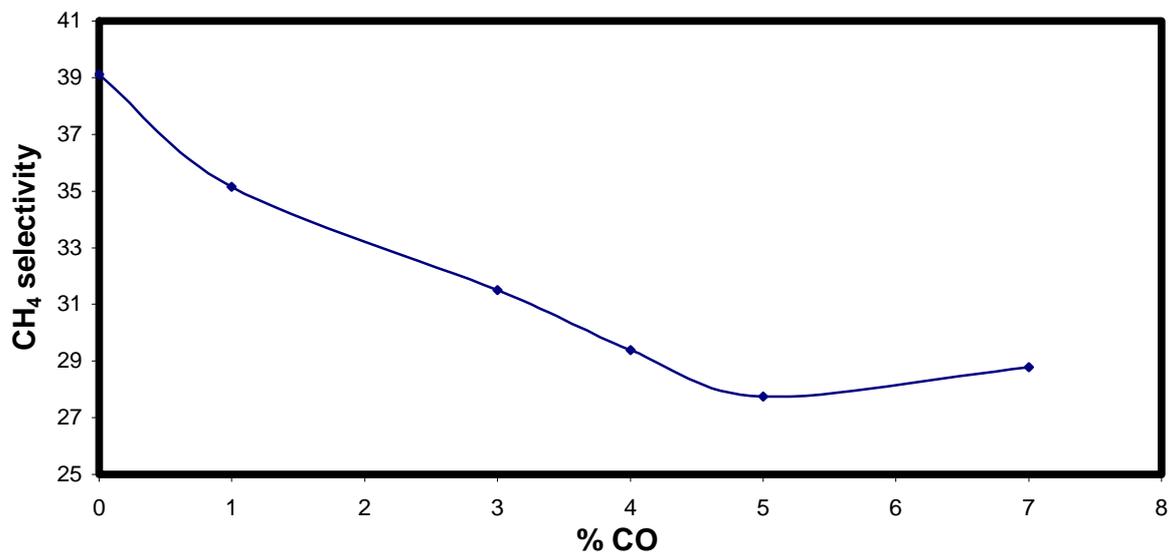


Fig. 4. CH_4 selectivity for Co catalysts reduced at various reduction gas compositions

As it shown in these figures, optimised addition of CO during the reduction increased the C_5^+ rate and selectivity and decrease CH_4 selectivity.

Characterization

X-ray diffraction

XRD pattern for representative catalyst samples reduced at various reduction gas phase compositions are shown in Fig. 5.

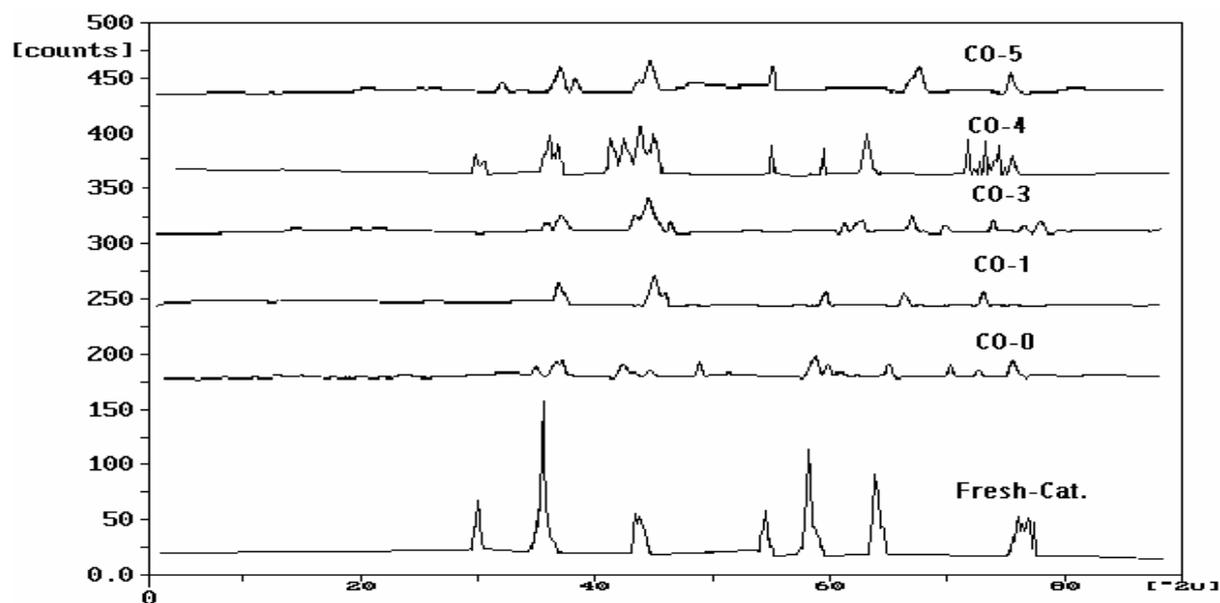


Fig. 5. XRD pattern for catalyst samples reduced at various reduction gas compositions

After comparing the XRD peaks with reference pattern for γ - Al_2O_3 , CoO, Co_3O_4 (spinel), and CoAl_2O_4 (spinel) for all the samples, only peaks of CoO at 37° , 46° and 61° as well as those for γ - Al_2O_3 were evident. The peaks at 66.5° correspond to γ -alumina. Peaks at 49° are attributed to the cobalt aluminate (Jongsomjit, 2002, Bechara, 2001). As it shown this peak is disappeared in CO added in regeneration catalysts process. The cobalt aluminate peak is only distinguishable for the catalyst reduced with H_2 only. The peak in 46° is more intensive due to introducing of %3-5 of CO on reduction. It may be the result of high activity and selectivity of catalyst to C_5^+ hydrocarbons.

Temperature programmed reduction

TPR was performed to determine the reduction behavior and reducibility of the catalysts. TPR profiles of the catalyst samples for various pretreatment conditions are shown in fig. 6. As shown in this figure, the temperature of reduction for first peak is become lower for optimize addition of CO on reduction.

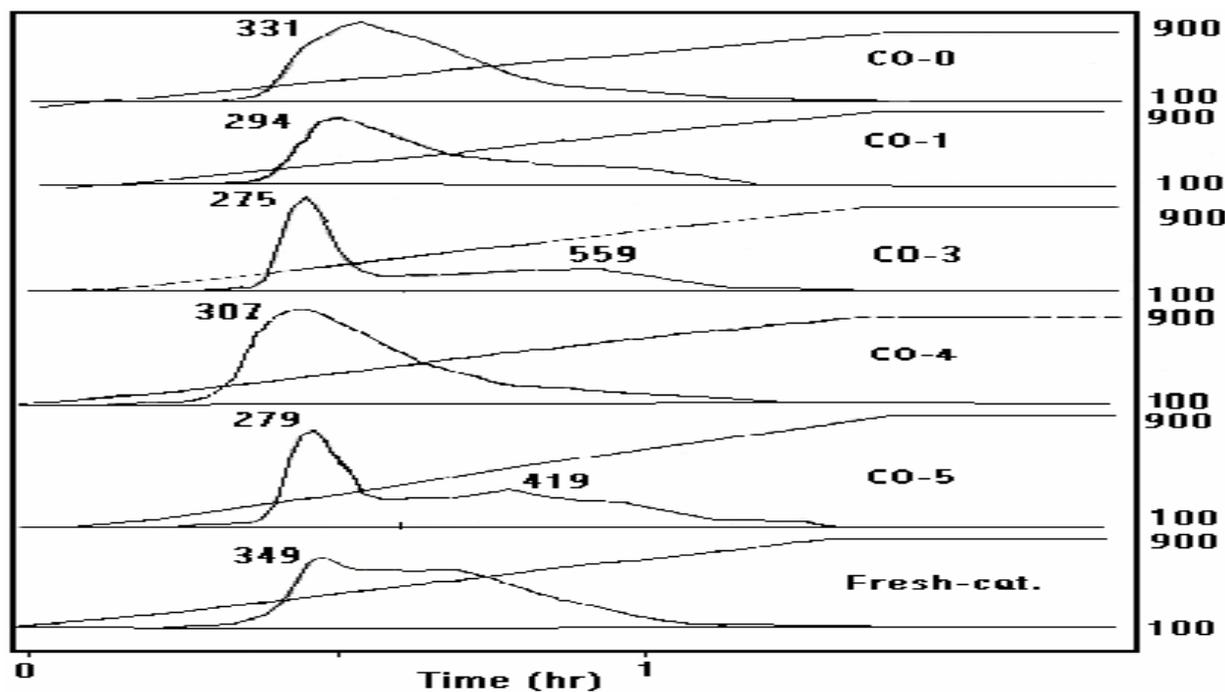


Fig. 6. TPR profiles of the catalyst samples for various pretreatment conditions

This matter shows that the diffusivity of hydrogen in reduction processing is become very easier and consequently the Co distribution is better than other ones. H_2 chemisorptions data that will be presented later confirmed this matter. Some Co sites are in optimum crystallinity size, so in reaction step diffusivity of heavier molecules is

better and chain growth probability is become larger. So FTS selectivity is toward the heavier hydrocarbon molecules as shown in figure 7.

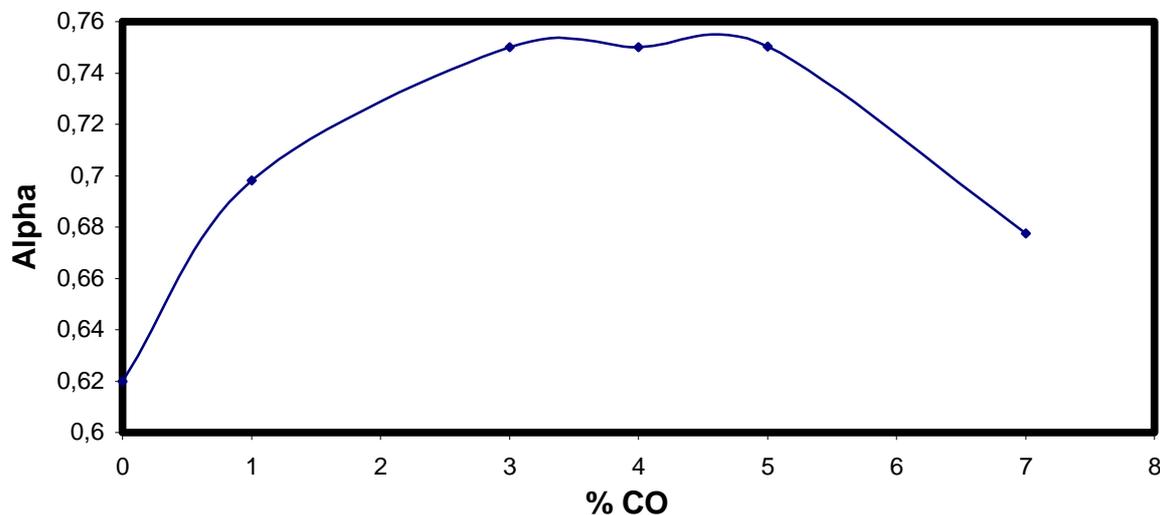


Fig. 7. Chain growth probability of the catalyst for various pretreatment conditions

As it shown in these figures CO enhances the reducibility of CoO to Co^0 and small cobalt oxide particles with higher interaction with support. The optimized addition of CO during the reduction increased

the C_5^+ rate and selectivity and decrease CH_4 selectivity.

H_2 chemisorptions was performed to determine the overall Co metal dispersion after different reduction conditions. The results are shown in fig. 8.

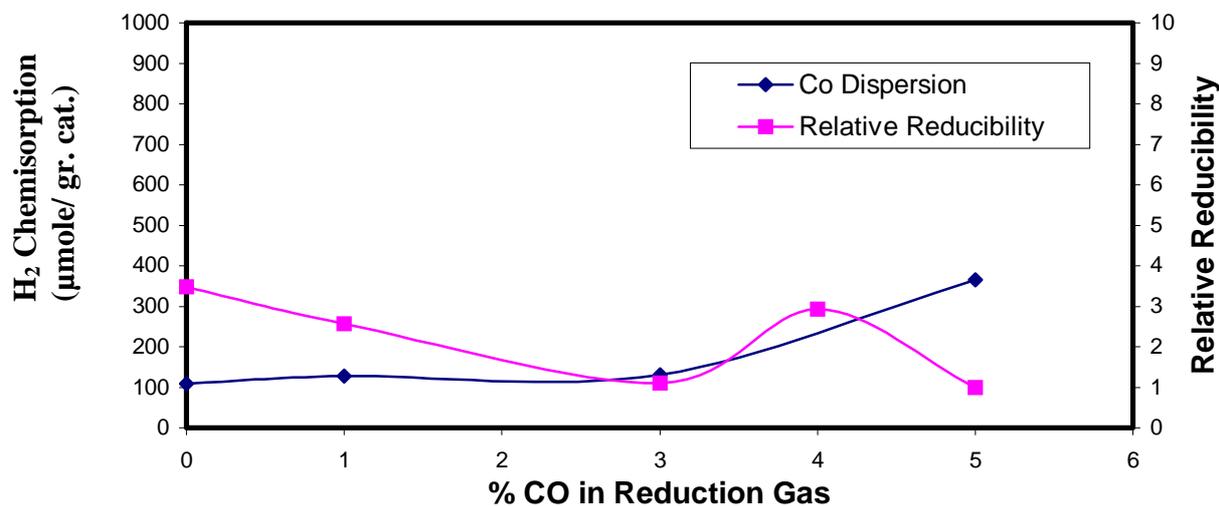


Fig. 8. H_2 chemisorptions of the catalyst for various pretreatment conditions

The Co metal dispersion increased with increasing CO concentration. As it shown in this figure, catalyst which reduced with %4 Co has maxi-

imum relative reducibility. These may be some reasons for maximum C_5^+ activity and selectivity of catalyst.

Conclusion

The optimised addition of CO during the reduction increased selectivity and rate of C_5^+ , %42 and %48 respectively. Also it decreased CH_4 selectivity %29. The CO enhances the reducibility of the CoO to Co^0 and small cobalt oxide particles with higher interaction with the support. So CO addition enhances the selectivity of Fischer-Tropsch synthesis towards the higher molecular weight hydrocarbons, and diffusivity limitation of reaction for producing heavier hydrocarbons became lower. Chain growth probability went through a maximum for 3-5 %vol. CO added dur-

ing H_2 reduction. Carbon deposition Was detected upon increasing the amount of added CO. the effect of CO addition may be due to one or more of possibly three reasons: (i) co may help to prevent the formation of Co species strongly interacting with the support, thereby facilitating its reduction, (ii) CO may decrease sintering of Co metal resulting an increase in Co dispersion, and (iii) CO may block Co "aluminate" formation by minimizing the impact of water vapour even at low partial pressure.

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