

Task 9. Cobalt Catalyst Life Testing

The objective of this task is to obtain life data on baseline cobalt Fischer-Tropsch catalysts.

A. Deactivation Study of Co-Re-Al₂O₃ Catalysts

It becomes more likely that, for the short term, the feed gas for a commercial Fischer-Tropsch synthesis operation will be based on natural gas instead of coal; therefore, cobalt catalysts may be preferred. Due to the high cost of cobalt catalysts, a stable catalyst is required to ensure extended runs. Thus, the cobalt catalyst must either be amenable to frequent regenerations over a long catalyst life or it must have a stable catalytic activity over a long (year or longer) period of time. A fundamental understanding of the deactivation mechanisms of cobalt catalysts is thus required to develop understanding that leads to the preparation of more stable catalysts and also to select the operating conditions to extend catalyst lifetime.

Supported cobalt catalysts deactivate during extended periods of time and commonly accepted reasons include: oxidation, carbon deposition, sintering, and sulfur poisoning. Sulfur poisoning can be avoided by deep desulfurization of the feed gas (at the expense of increases in the cost of synthesis gas). Carbon deposition may be minimized by careful control of the temperature protocol. The deactivation caused by sintering and oxidation will therefore be the major concerns. Investigations of the mechanism become very important.

Thermodynamically, bulk oxidation of cobalt to cobalt oxide by water is not favored under the reaction conditions (220°C, 275 psig, H₂:CO=2:1, 50-70% CO conversion). However, there are numerous literature citations to support the view that oxidation of supported catalysts occurs under the reaction conditions. A common belief is that the smaller the cobalt crystal size, the easier the oxidation. Thus, there may be a “magic” dispersion limit where, if the cobalt dispersion is higher than the “magic” number, oxidation takes place very rapidly, resulting in

rapid catalyst deactivation. Another hypothesis is that although bulk oxidation is unlikely, surface oxidation of the cobalt could occur during Fischer-Tropsch synthesis and this would also cause rapid catalytic activity decline.

The objective of the current study is to define the deactivation rate of the Co-Re-Al₂O₃ catalysts at different space velocities, to study the deactivation mechanism, to learn whether the deactivation is caused by sintering of the cobalt crystals, the oxidation of cobalt to cobalt oxide or the formation of cobalt aluminate.

Experimental

Catalysts. Three catalysts with a cobalt loading of 15 wt.% and rhenium loading of 0.2, 0.5 and 1.0 wt.%, respectively, were utilized.

Activation. The catalysts were reduced using 30 % H₂/70% He (V/V) in a fixed bed reactor at a space velocity of 10,000 GHSV at 350°C. The temperature was ramped to 350°C at 1°C per minute and held at 350°C for 4 hours. This was accomplished by overpressuring the reduction tube that contains the reduced catalyst and then opening the appropriate valves to force the entire catalyst volume into the autoclave containing the startup solvent. The reduction reactor was weighed prior to and after catalyst transfer to ensure that a quantitative transfer of the catalyst had been accomplished. The catalyst was then treated in hydrogen flow in the slurry phase reactor at 280°C for 4 hours.

Reaction Conditions. About 20 grams (actual catalyst weight for each run was accurately known) of catalyst was transferred into a 1L stirred autoclave which had been charged with 300g of C₃₀ oil (decene trimer obtained from Ethyl Corp.). Following catalyst reduction at 280°C in situ, the temperature was lowered to 150°C and synthesis gas was fed into the reactor. After the pressure reached 275 psig, the temperature was slowly increased to 220°C during 4 hours. A feed gas with H₂:CO ratio of 2:1 was used.

Results and Discussion

The activity and rate of loss of activity data are shown in figures 1 through 3. The activity measurements for the first two runs (using the two lower Re loaded catalysts) were started at 2.0 SL/g. cat./hr. Considering the scatter of the initial data for the run with the catalyst containing 0.5 wt.% Re (figure 2), the initial conversions for the 0.2 and 0.5 wt.% Re catalysts were essentially the same (70-75% CO conversion). These two catalysts exhibited a rapid and similar deactivation rate of the range 12-14% CO conversion/week. The catalyst containing 1.0 wt.% Re was started up at a higher flow rate so that the initial CO conversion was lower (37% compared to 70-75%) and the activity decline rate was lower (4.35 %CO conversion/week). Extrapolating the linear relation of the space velocity versus conversion data, described later, for these three catalysts, the initial conversion of CO with the 1% Re catalyst at a GHSV of 2.0 SL/g. cat/hr, as was used with the 0.2 and 0.5 wt.% Re catalysts, indicate an initial conversion of 95%. Considering the uncertainty associated with this extrapolation, a tentative conclusion is that the three catalysts with different Re content would have had a similar initial conversion for identical reaction conditions.. However, additional runs are required to better define this, and these will be done during the next quarter.

To establish a deactivation rate to cover a wide range of conversion levels will be a challenge. First, consider the data for the 0.2% Re catalyst. During the initial portion of the run at a space velocity of 2.0 SL/g. cat./hr, the rate of decline is high at 14.1% CO/week during about the first 200 hours of synthesis time. Returning to the same space velocity at about 700 hours of operation yielded a rate of decline that was much lower (figure 1); the rate of decline after returning to this same space velocity at about 1700 hours of synthesis is only 1.64% CO conversion/week. Compare the rate of decline of 4.61 %CO conversion/week when operating at 5 SL/g. cat./hr (during about 200-700 hours) with a conversion range of about 12-25% CO to the

rate at 2.0 SL/g. cat./hr of 1.64 %CO conversion/week at about 1700 to 2300 hours with a range of about 27-33% CO conversion. If the rate of decline was determined only by the conversion level, the rate at 2.0 L/g. cat./hr (1.64) should have been greater than the one at 5.0 L/g. cat./hr (4.61), and this was not the case. It therefore appears that time on stream may be as important, or even more important, than the conversion level. This has been observed with our Co-SiO₂ catalyst and has been reported by Sasol workers [1]. The Sasol workers, operating for a long period of time at the same operating conditions, have shown a rapid rate of decline in conversion during the initial synthesis period that is followed by a much longer period with a much smaller rate of decline (figure 4). The data for the 1% Re catalyst also appear to be consistent with this concept. These data are summarized in Table 1.

After more than 1800 hours of synthesis, regeneration (rejuvenation) was attempted with the catalyst containing 1% Re. The first rejuvenation was at reaction temperature with a H₂ flow rate of 7.5 SL/g. cat./hr and resulted in regaining 49% of the initial activity (figure 5) but this was followed by a rapid decline in CO conversion. The second rejuvenation was conducted at reaction temperature and pressure but at double the total flow (15 SL/g. cat./hr; H₂:Ar = 1:1) and for 4 hours. The second rejuvenation returned the CO conversion to 66% of the initial activity. However, during less than two days of operation, the CO conversion declined to about 40% of the initial activity. Following this rapid decline, there was a slower, but still high, rate of decline of about 17 %CO conversion/week.

Similar studies are continuing.

References

1. P. J. van Berge and R. C. Everson, Natural Gas Conversion. IV, (M. dePontes, et al., eds) Studies in Surface Science and Catalysis, **107**, 207 (1997).

Table 1

Deactivation Rate, % CO conversion/week

Promoter Level, wt. %	Rate	%CO conversion range	Rate	%CO conversion range
0.2	4.61	12-25	14.1	55-75
0.5	---	---	12.3	18-70
4.35	4.35	11-38	---	---

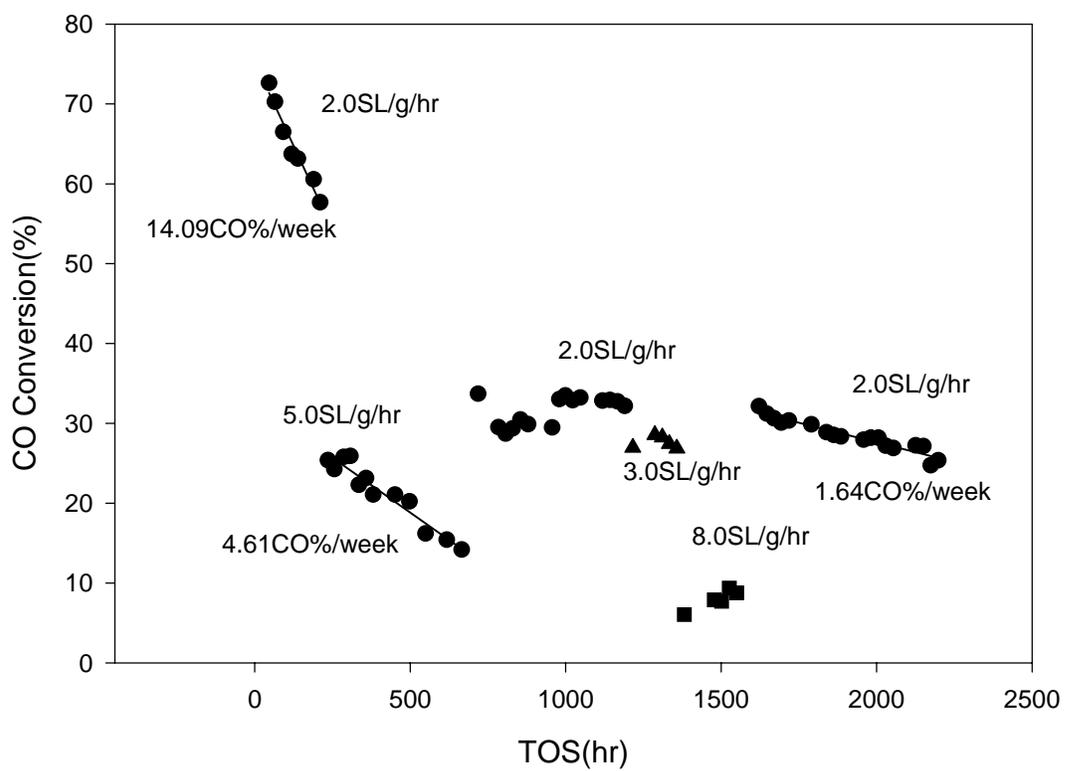


Fig 1 CO Conversion as a function of time on stream on 15%Co-0.2%Re/Al₂O₃

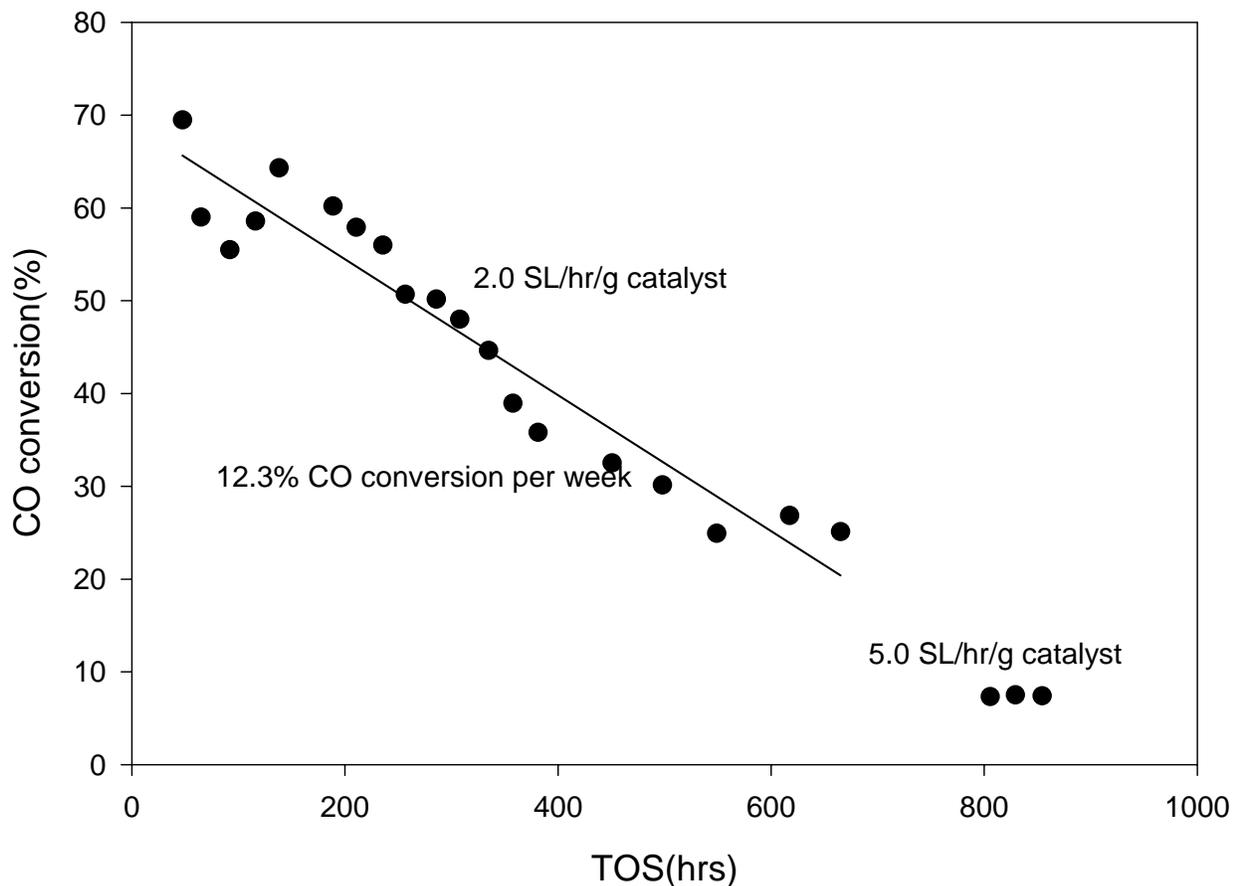


Fig 2 CO conversion as a function of time on stream for 15%Co-0.5%Re/ Al_2O_3 catalyst, regenerate at 220°C , just stop the CO flow for 24hrs(too long) has no recovery, regenerate at 280°C , activity goes up close to the initial activity, but the product was mainly methane

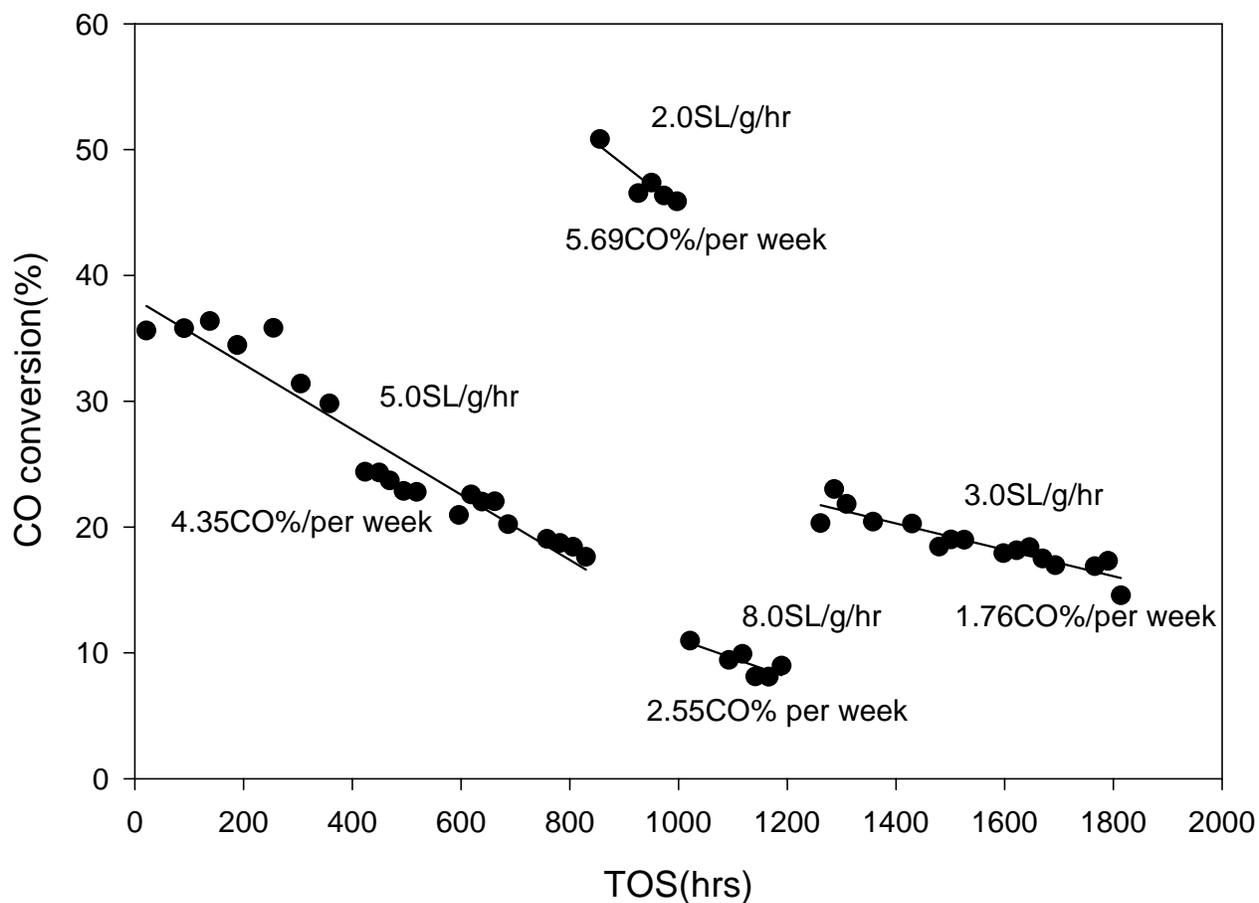
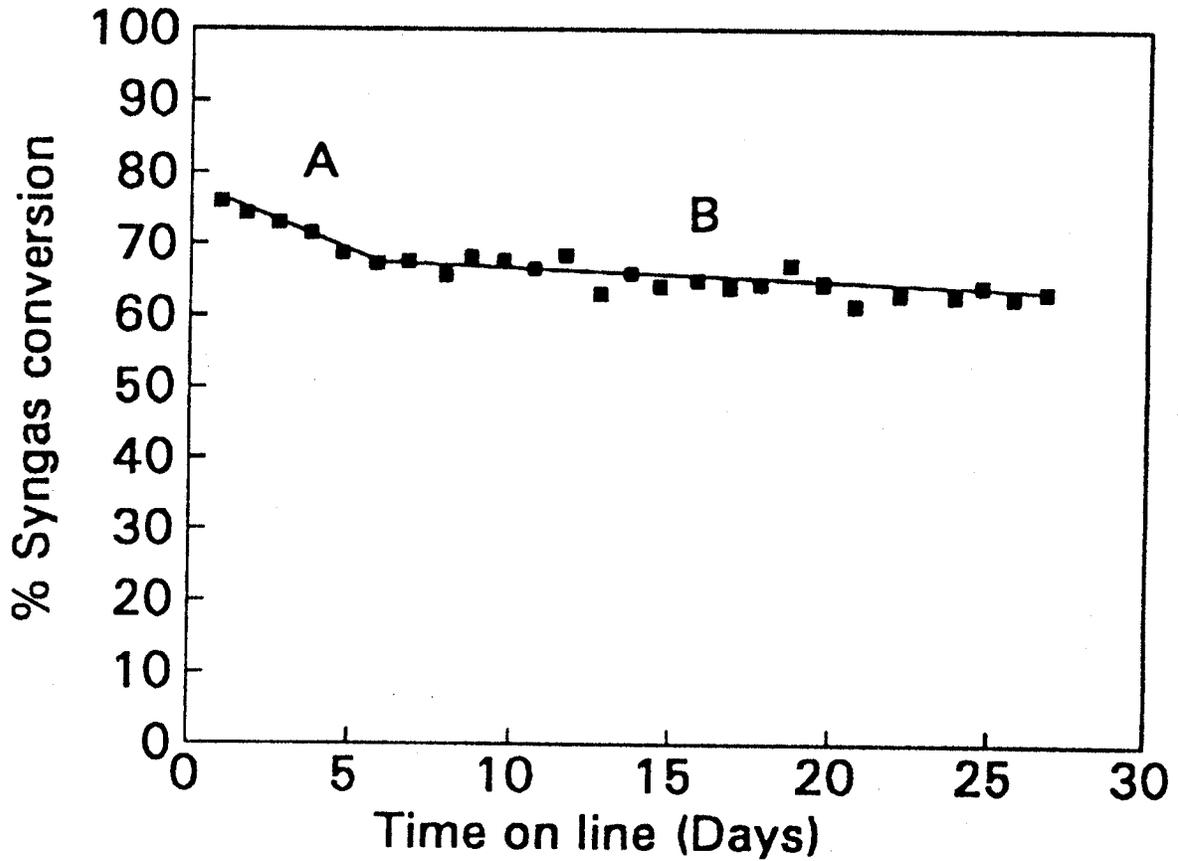


Fig 3 CO conversion as a function of time on stream for 15%Co-1%Re/Al₂O₃ catalyst

FIGURE 4. STABILITY RUN ON THE COBALT CATALYST



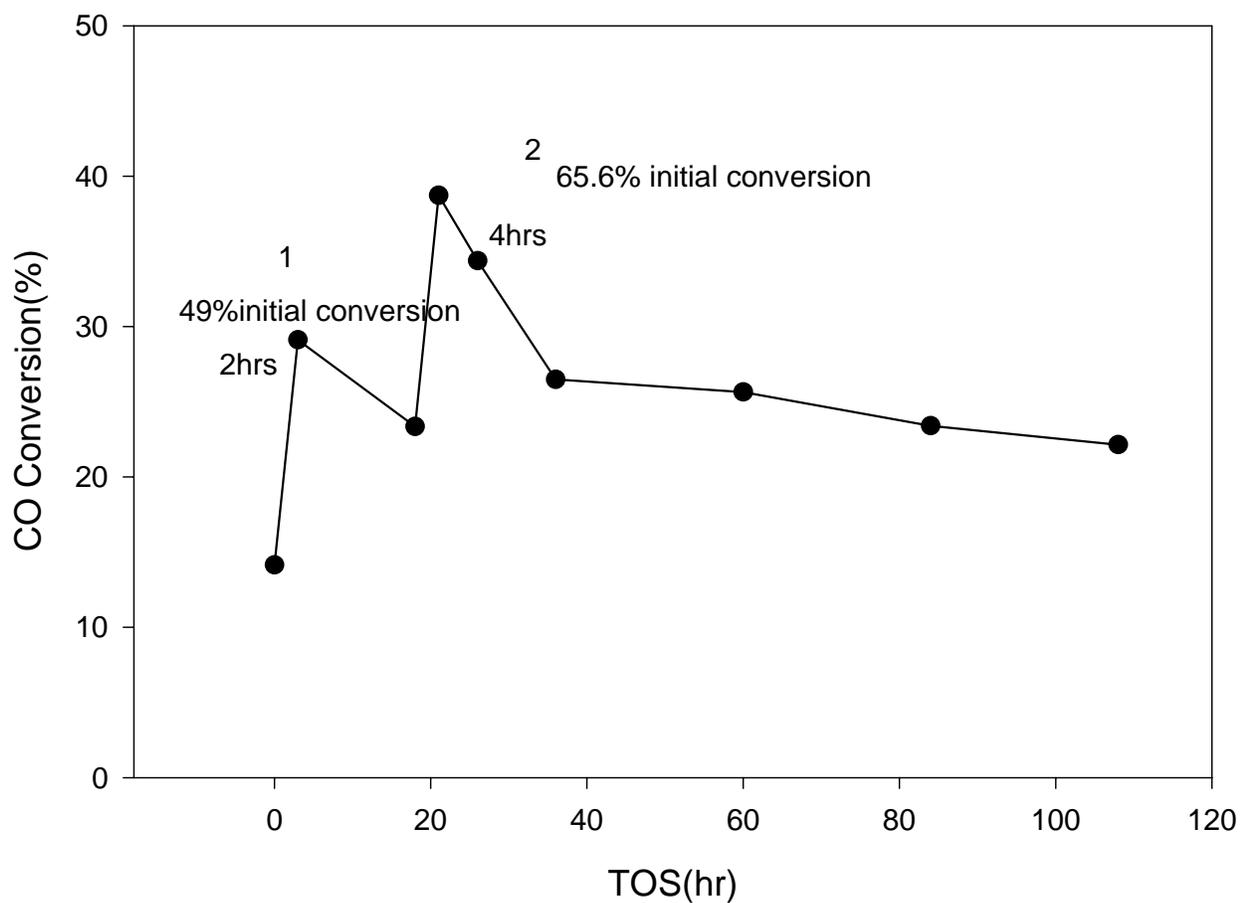


Fig 5 Rejuvenation of catalyst 15%Co-1%Re/Al₂O
 1: rejuvenate by H₂(7.5SL/hr/g), 2: rejuvenate by H₂ and Ar mixture(H₂:Ar)=1:1, 15SL/g/hr)

B. Effect of Water on the Fischer-Tropsch Catalytic Properties of Ruthenium Promoted Co/TiO₂ Catalyst

Introduction

Fischer-Tropsch synthesis produces hydrocarbons and water. The amount of water produced depends on the synthesis gas conversion, reactor system and catalyst used. The effect of water on the iron Fischer-Tropsch catalysts has widely been investigated. It is well known that water may reoxidize iron during synthesis [1]. Less information is available for the effect of water on the cobalt catalysts. Hilmen et al. [2] recently studied the effect of water on Co/Al₂O₃ and CoRe/Al₂O₃ catalysts by adding water to the synthesis gas feed and by model studies exposing the catalysts to various H₂O/H₂ ratios. It was found that the catalysts deactivated when water was added during Fischer-Tropsch synthesis and the catalysts oxidized in H₂O/H₂ mixtures with a ratio much lower than expected for oxidation of bulk cobalt. For silica supported cobalt catalysts, the addition of water to synthesis gas feed has been shown to decrease the CO conversion [3]. Schulz et al [4] found no deactivation of a CO/Ru/ZrO₂/Aerosil and Co/MgO/ThO₂/Aerosil catalysts when water was added to the feed. Schulz et al. [5] has even reported increased activity. Kim et al. [6, 7] also reported increased activity for Re promoted, non-promoted Co/TiO₂ and unsupported cobalt catalysts as a result of addition of water during the Fischer-Tropsch synthesis. It has been explained that water possibly destroys the strong metal-support interaction (SMSI) effect in titania supported catalysts. In this study, the effect of water addition on the Fischer-Tropsch catalytic properties of a ruthenium promoted Co/TiO₂ catalyst was investigated. The incipient wetness technique was applied to prepare the catalyst and catalytic properties were evaluated in a continuous stirred tank reactor (CSTR) by using varying space velocities.

Experimental

The catalyst used was Ru(0.2 wt%)/Co(10wt%)/TiO₂ prepared in our laboratory, and was found to have good Fischer-Tropsch activity and stability. The catalyst activation was conducted first *ex-situ* and then *in-situ*, according to the following procedure. The catalyst (about 15 g) was put in a fixed bed reactor and pure hydrogen was introduced at a flow rate of 60 NLh⁻¹ (298 K, 0.1 MPa); the reactor temperature was increased from room temperature to 373 K at a rate of 120 Kh⁻¹, then increased to 573 K at a rate of 60 Kh⁻¹ and kept 573 K for 16 h. The catalyst was transferred under the protection of helium to the CSTR where it was mixed with 300 g of melted poly-wax (P.W. 3000). The catalyst was then reduced *in-situ* in the CSTR; the hydrogen was introduced to reactor at atmospheric pressure with a flow rate of 30 NLh⁻¹ (298 K, 0.1 MPa). The reactor temperature was increased to 553 K at a rate 120 K h⁻¹ and maintained at this activation condition for 24 h.

After the activation period, the reactor temperature was decreased to 483 K and synthesis gas (2H₂/CO) was introduced to increase the reactor pressure to 2.35 MPa. The reactor temperature was then increased to 503 K at a rate of 10 Kh⁻¹. During the entire run the reactor temperature was 503 K, the pressure was 2.35 MPa, and the stirring speed was maintained at 750 rpm.

The space velocity of the synthesis gas varied from 1 to 8 NL g⁻¹cat.h⁻¹. Argon was added to the feed gas and the composition was set to 2H₂/1CO/0.5Ar. In order to investigate the effect of water on the catalytic properties of the catalyst, argon was substituted by same amount of water at different space velocity. The conversion of carbon monoxide and hydrogen and the formation of products were measured after a period of 24 h at each condition.

Results and Discussion

Four runs have been done for the effect of water on the catalytic properties of the RuCo/TiO₂ Fischer-Tropsch catalyst using different space velocity procedures. The results for synthesis gas conversion are exhibited in Figures 1 and 2. For the first run, we started run with a space velocity of 2 NLg⁻¹cat.h⁻¹, then gradually increased the space velocity to 5, 7 and 8 NLg⁻¹cat.h⁻¹, respectively, to obtain the activity and selectivity data at different space velocities. After running at 8 NLg⁻¹cat.h⁻¹, the catalyst was treated with pure CO for 24 hours. It was found that CO treatment resulted in a decreased Fischer-Tropsch activity. The catalyst was regenerated by pure H₂ and the space velocity was then changed back to 1 NLg⁻¹cat.h⁻¹. The synthesis gas conversion was found to be almost the same as that obtained at space velocity of 2 NLg⁻¹cat.h⁻¹ before CO treatment. This indicates that the activity of the catalyst was not be recovered by the H₂ regeneration at 230°C. For the second run, we started the run with a low space velocity and obtained almost 100% CO conversion. However, when we changed space velocity to 2 NLg⁻¹cat.h⁻¹, the synthesis gas conversion decreased to about 50%, indicating that the reaction at high conversion level resulted in a deactivation of the catalyst. The results for the third run are strange, synthesis gas conversion decreased with decreasing space velocity, indicating that the catalyst deactivated very quickly. This appears to be due to a problem in the catalyst reduction procedure for that particular run. For the fourth run (Figure 2), we started the run with a space velocity of 7 NLg⁻¹cat.h⁻¹, then decreased the space velocity to 4, 2 and 1 NLg⁻¹cat.h⁻¹, respectively. The results were very similar to those obtained for first run except the data at space velocity of 1 NLg⁻¹cat.h⁻¹, which is much high than that of first and lower than second run.

During the fourth run, the water deactivation tests were made at synthesis gas space velocity of 2 NLg⁻¹cat.h⁻¹ by changing water flow back to same argon flow after feeding water for an extended period. The synthesis gas conversion was found to remain the same as that

obtained before the water addition. This indicated that the water addition did not cause a permanent deactivation of the catalyst.

From Figure 2, we can find that at low conversion levels (high space velocities; greater than $4 \text{ NLg}^{-1}\text{cat.h}^{-1}$), the addition of water to the feed did not have a significant effect on synthesis gas conversion. However, at high conversion levels (low space velocities), the addition of water resulted in a decrease in synthesis gas conversion. The higher the conversion, the more severe the water effect is. This indicates that the Fischer-Tropsch reaction rate is dependent on the partial pressure of water for the ruthenium promoted Co/TiO_2 catalyst and a $P_{\text{H}_2\text{O}}$ term existed in the kinetic equation. The Fischer-Tropsch synthesis kinetics of cobalt catalysts have been investigated by some researchers. However, for all the kinetic equations $P_{\text{H}_2\text{O}}$ term has not been included. A kinetic investigation for cobalt catalyst is being done in our laboratory.

The effect of water on the hydrocarbon production rate of catalyst is shown in Figure 3. The hydrocarbon rate increased with increasing space velocity for no water and adding water reaction systems. At high space velocities, the addition of water did not influence hydrocarbon rate. At low space velocities, the addition of water resulted in a decrease in the hydrocarbon rate.

Figure 4 shows methane selectivity vs space velocity. For no water addition, the methane selectivity increased slightly with increasing space velocity. Methane selectivity did change with the addition of water.

Figure 5 shows CO_2 selectivity as a function of reciprocal flow rate. CO_2 selectivity increased almost linearly with decreasing space velocity (increasing conversion) with and

without water addition. The addition of water increased the CO₂ formation about two times that of no water addition. This indicates that water also increased the water gas shift reaction.

References

2. M.E. Dry, Catal. Lett. 7 (1990) 204.
3. A.M. Hilmen, D. Schanke, K.F. Hanssen, A. Holmen, Appl. Catal. 186 (1999) 169.
4. J.K. Minderhoud, M.F.M. Post, S.T. Sie, Eur. Appl. Patent No. 83201557.2 (1988), to Shell Int. Res.
5. H. Schulz, M. Claeys, S. Harms, Stud. Surf. Sci. Catal. 107 (1997) 193.
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7. J.C. Kim, U.S. patent no. 5227407 (1993), to Exxon Res. Eng. Co.
8. J.C. Kim, Eur Appl. Patent no. 89304092.3 (1994), to Exxon Res. Eng. Co.

Fig. 1. Effect of water on the synthesis gas conversion of RuCo/TiO₂ F-T catalyst

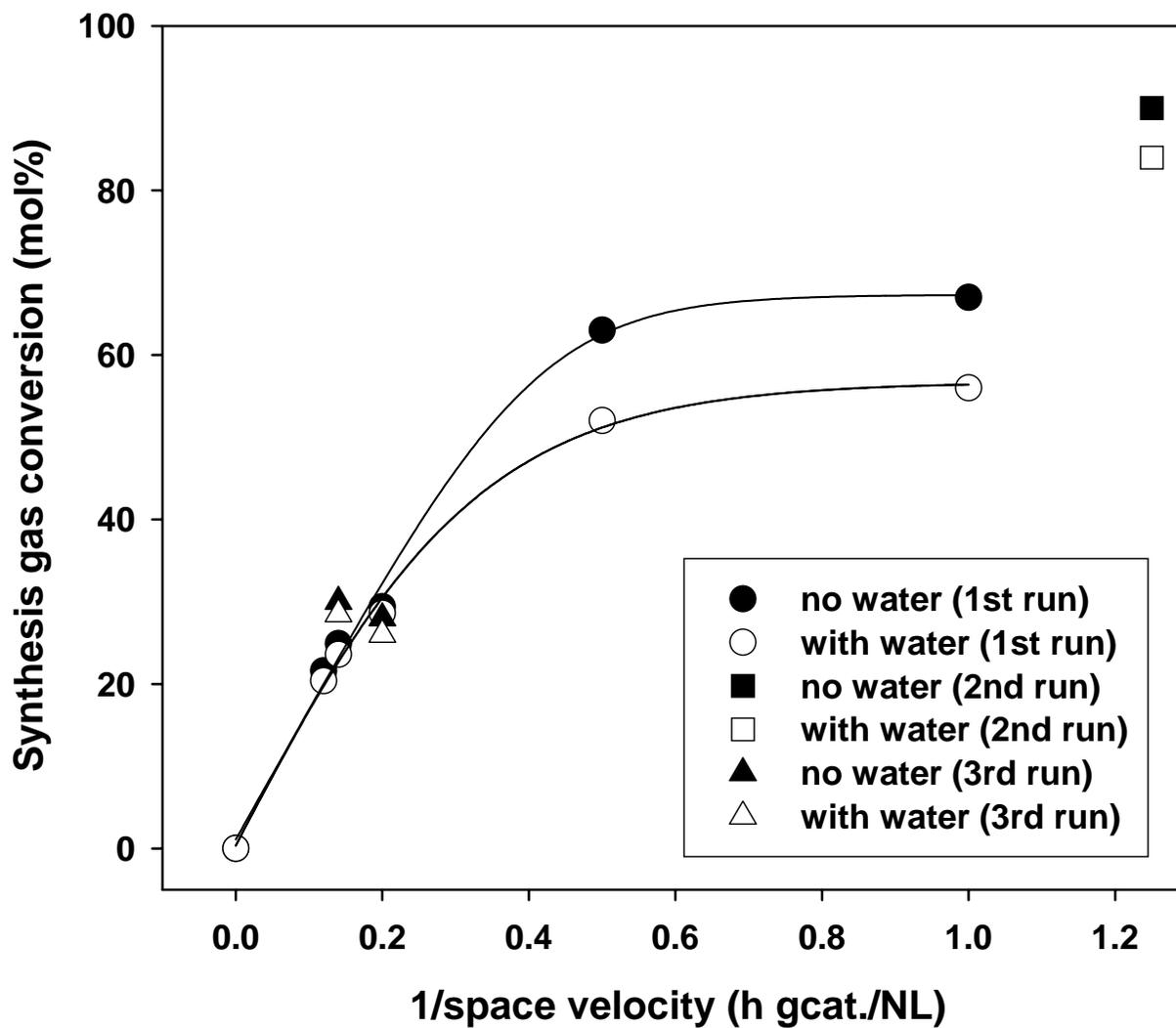


Fig. 2. Effect of water on synthesis gas conversion (fourth run)

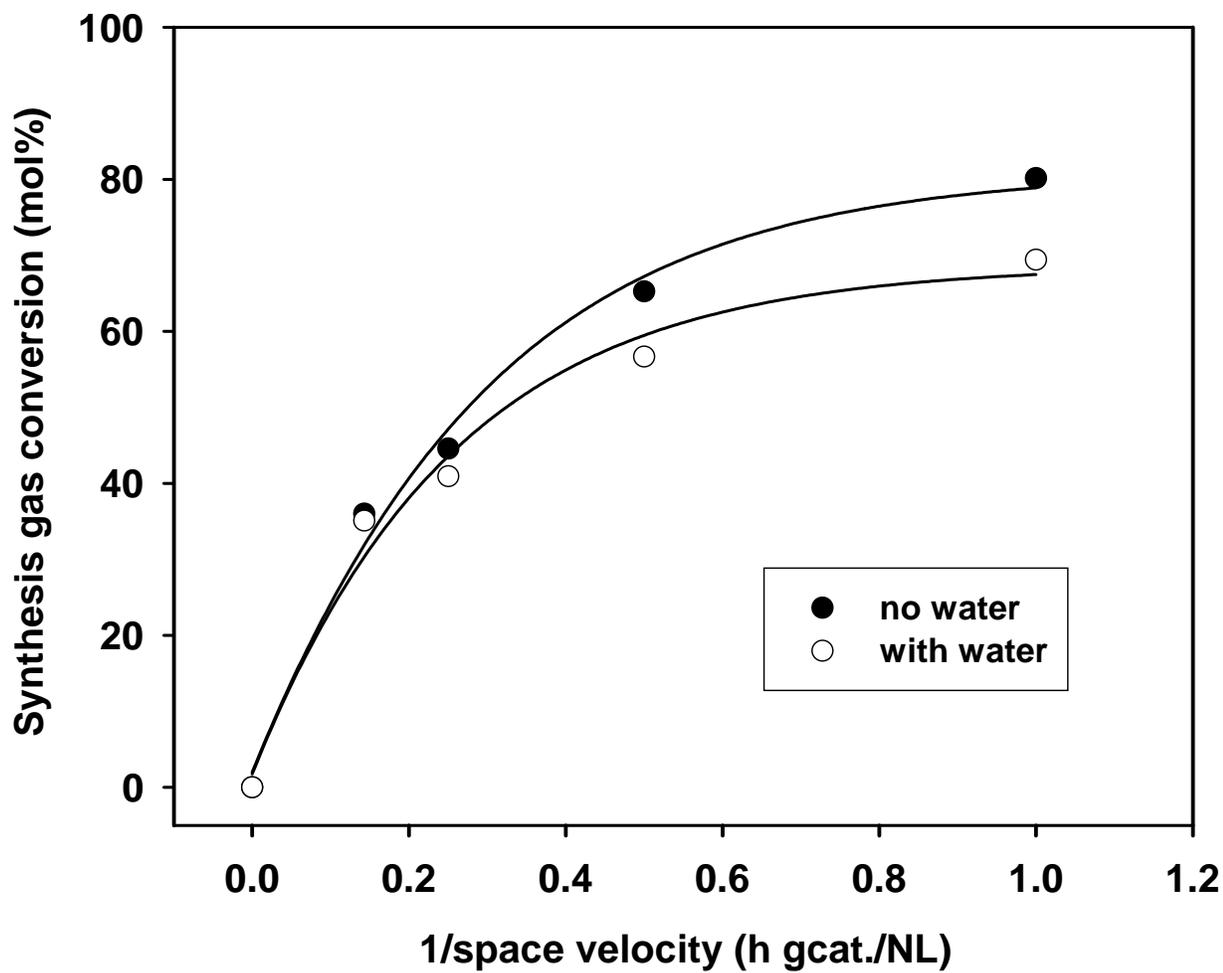


Fig. 3. Effect of water on hydrocarbon production rate

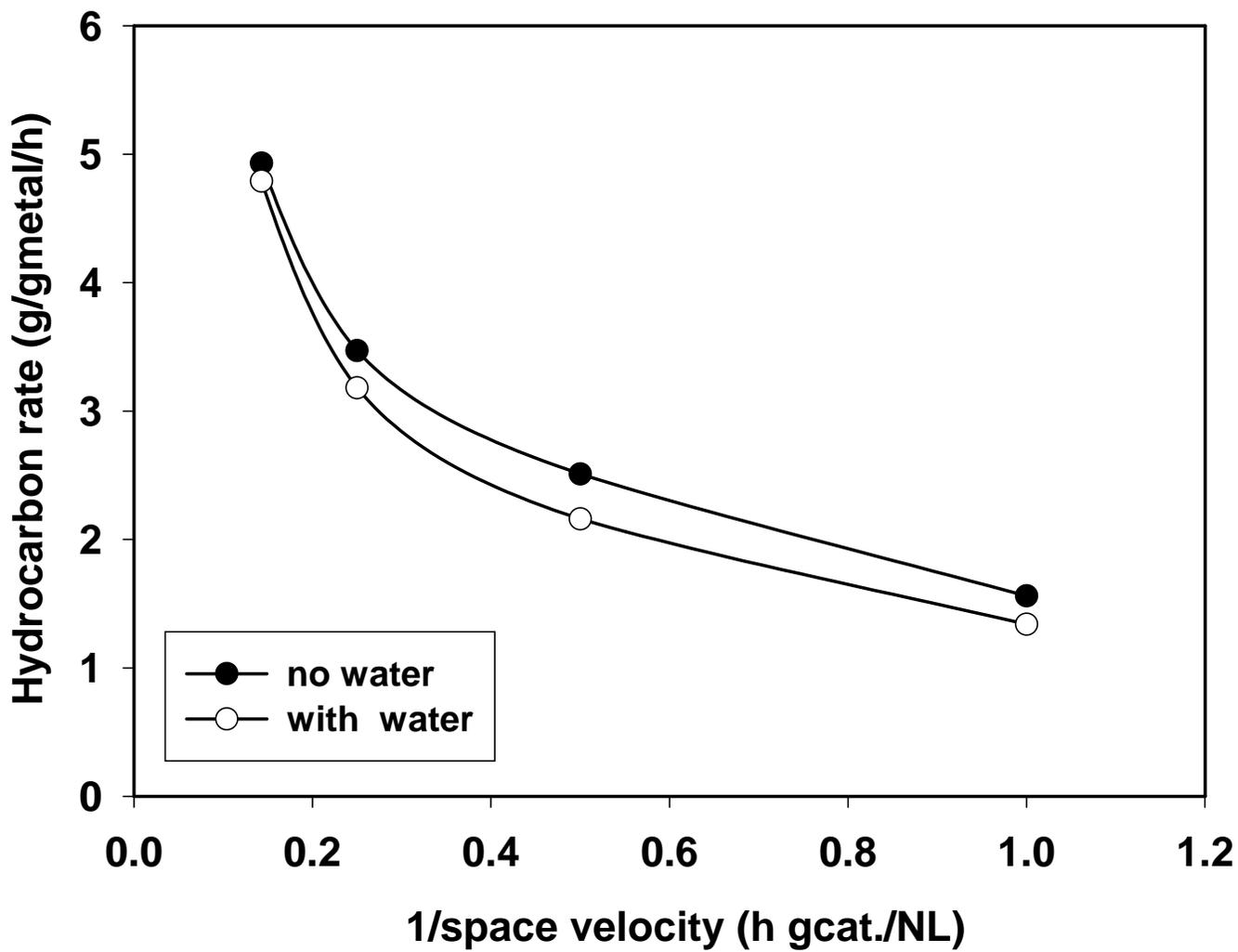


Fig. 4. Effect of water on methane selectivity

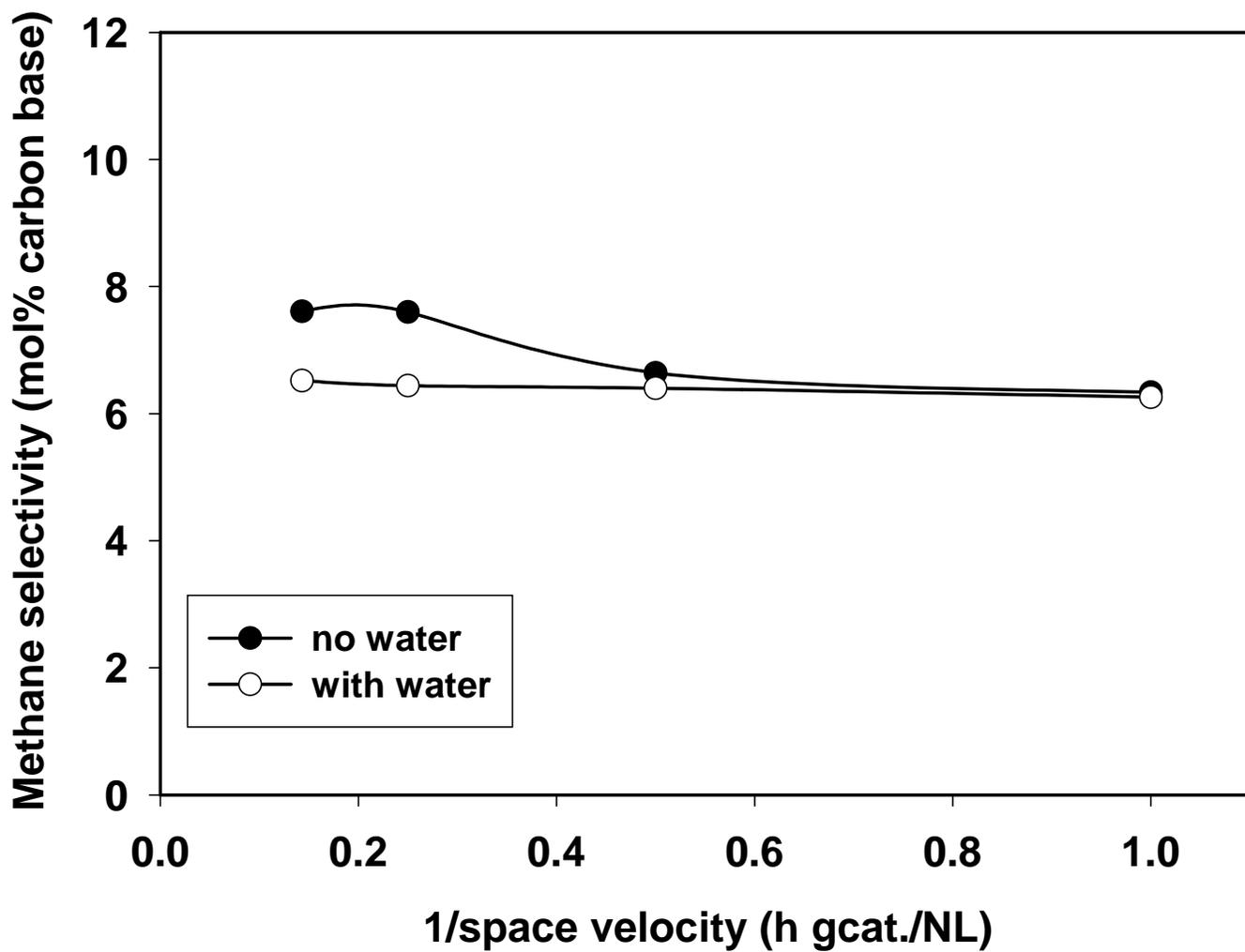
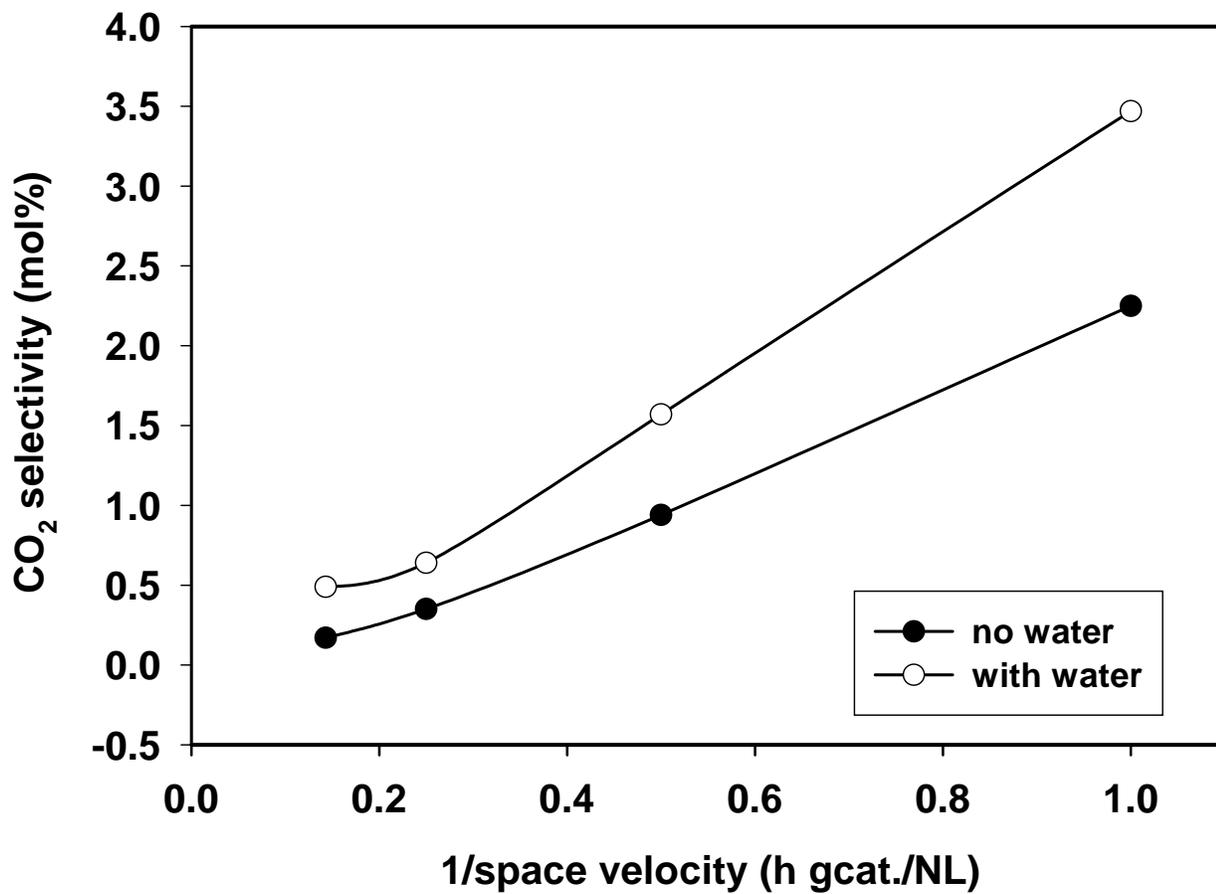


Fig. 5. Effect of water on CO₂ selectivity



C. Deactivation Rates for Co Catalysts

Introduction

In comparison with low cost Fe FTS catalysts, cobalt catalysts may work at relatively low reaction temperatures and pressures with higher yields of linear paraffins in the C₅₊ range and do not convert water by water gas shift reaction. The cobalt catalysts are believed to deactivate less than the Fe-based catalyst. The major drawback of cobalt catalyst is its high cost. Therefore, the present studies focused on improving the deactivation rates of these catalysts.

Experimental

Preparation of Cobalt Catalysts

The Co/Al₂O₃ catalyst was prepared by incipient wetness impregnation of Al₂O₃ (Condea Vista B alumina, BET surface area 200 m²/g, pore volume 0.4 cm³/g) with cobalt nitrate solution. The preparation procedure includes three step impregnations of cobalt salt and then followed by impregnation of promoter. Finally, calcined the sample at 400°C in the flow Air and Helium.

Pretreatment of the catalysts

The catalysts were pretreated first ex-situ and then in-situ, according to the following procedure. The catalysts were reduced ex-situ using 30% H₂ and 70% He (V/V) in a fixed bed reactor at a space velocity of 10,000 GHSV at 350°C. The temperature was ramped to 350°C at 1°C/min and held at 350°C for 10 hours. This reduced catalysts were transferred to CSTR in inert atmosphere. This was accomplished by overpressuring the fixed bed reactor that contain the reduced catalyst and then opening the appropriate valves to force the entire catalyst volume into the CSTR containing startup solvent. The reduction reactor was weighed prior to and after catalyst transfer to ensure that a quantitative transfer of catalyst had been accomplished. The catalyst was then reduced in-situ in the CSTR; the hydrogen was introduced to reactor at

atmospheric pressure with the flow rate of 30 SL/hr. The reactor temperature was increased to 230°C at the ramp rate 1°C for 12 hours.

Reaction conditions

Approximately 20 g of catalyst was transfer into a 1 liter stirred autoclave which had been charged with 300 g of C₃₀ oil(decene trimer obtained from Ethyl Corp.). The catalyst was reduced at 230°C in-situ in atmospheric pressure for 10 hours in the flow of hydrogen. After reduction, the reactor temperature was lowered to 180°C and synthesis gas was introduced into the reactor. Then the reactor was pressurized to 275 psig and temperature was slowly increased to 220°C during 3 hours. The feed gas used in the reaction was H₂ : CO ratio of 2:1.

Results and Discussion

Unpromoted 15%Co/Al₂O₃ catalysts

The activity and rate of loss of activity of the unpromoted Co/Al₂O₃ catalyst are shown in Fig. 1. The initial CO conversion, at space velocity 5 SL/hr/g catalyst, is 18%. The deactivation rate of unpromoted Co/Al₂O₃ catalyst is low (1.56% CO conversion/week) compared to Re or Ru promoted catalysts.

FT-Kinetic Studies of 15%Co/Al₂O₃ Catalysts

Typically, the activity of the fresh catalyst decreases with time on stream and then levels off in 5-7 days. After this period, the deactivation is slow and linear. The kinetic study was performed during the steady state. Two sets of kinetic studies were carried out with constant CO partial pressure (table 1) and constant H₂ partial pressure (table 2). Four H₂/CO ratios and five space velocities has been used to determine the rates. Argon gas used as the makeup gas to adjust the space velocity. The CO conversion with different space time at different H₂/CO ratio presented in Fig. 2 and Fig. 3. However, the additional calculations are required to determine the reaction rate and that will be done during the next quarter.

To determine the Activation Energy, we have carried out FT runs at four temperatures. The Arrhenius plots are presented in Fig. 4 and Fig. 5. The activation energy, calculated from CO conversion and H₂ conversion from Figs. 4 and 5, respectively, is approximately 17 Kcal/mole in both cases.

Pressure Effect over 0.2%Re-15%Co/Al₂O₃ catalyst

The effect pressure on CO conversion of the 0.2%-Re-15%Co/Al₂O₃ and space velocity 2 SL/hr/ g catalyst is shown in Fig. 6. The CO conversion increases with increasing pressure. The CO conversion increased significantly from 100 psig to 300 psig. The effect of pressure on methane selectivity and CO₂ selectivity is shown in Fig. 7. The methane selectivity decreases slightly with increase in pressure but the CO₂ selectivity remain almost same with increases in pressure.

Activity of 0.5%Ru-15%Co/Al₂O₃ and 0.5%Ru-20%Co/ZrO₂-SiO₂ Catalysts

The objective of this task is to find the stable Co-based Fischer-Tropsch catalysts. In this study, our aim was to determine the effect of support to the deactivation rate of the catalyst in comparison with the unpromoted Co/Al₂O₃ catalyst. The activities of 0.5%Ru-15%Co/Al₂O₃ and 0.5%Ru-20%Co/ZrO₂-SiO₂ Catalysts are shown in Fig. 8 and Fig. 9, respectively. Initial CO conversion of 0.5%Ru-15%Co/Al₂O₃ catalyst is two times greater than the initial activity of unpromoted 15%Co/Al₂O₃ catalyst at a space velocity of 5 SL/hr/g. However, the rate of deactivation is greater for the promoted Ru catalyst. While for the unpromoted catalyst, the CO conversion dropped by 18% of the initial activity after 85 h, and remained stable after that, the CO conversion dropped by 42% of the initial value after 1000 h for the Ru promoted catalyst. The activity of Ru-promoted ZrO₂-SiO₂ catalyst also showed a higher activity than the unpromoted catalyst. However, the deactivation rate is lower (3.53% CO conversion/week) than

for the Ru-promoted Al_2O_3 catalyst (4.2% CO conversion/week) at space velocity of 5 SL/hr/g. Similar studies are continuing .

Activity of 0.5%Pt-15%Co/ Al_2O_3 Catalyst

The activity tests performed in CST and Fixed-bed reactor are presented in Fig. 10 and Fig.11, respectively. The initial activity of Pt-catalyst is about the same as the Ru-promoted catalyst at space velocity 5 SL/hr/g. The CO conversion in the fixed-bed reactor at 210°C is ~30.0% after 500 hrs time on stream (Fig. 11).

Table 1 : Inlet gas composition for the kinetic studies (constant CO partial pressure)

H ₂ /CO ratio	1.0	1.5	2.0	2.4
CO%	25	25	25	25
H ₂ %	25	37.5	50	60
Ar%	50	37.5	25	15

Table 2 : Inlet gas composition for the Kinetic studies (constant H₂ partial pressure)

H ₂ /CO ratio	1.0	1.5	2.0	2.4
CO%	25	16.7	12.5	10.4
H ₂ %	25	25	25	25
Ar%	50	58.3	62.5	64.6

**Fig. 1 : Time on Stream vs CO conversion over
Co/Al₂O₃ at 220°C and 275 psig**

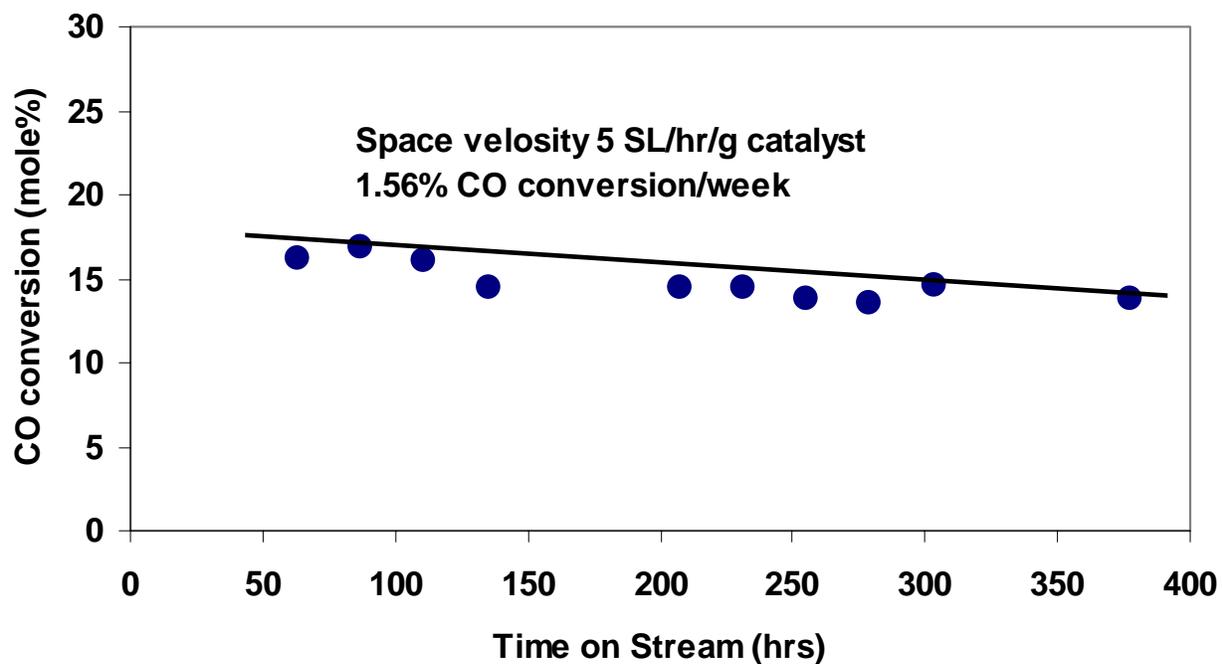


Fig. 2 : Kinetic of 15%Co/Al₂O₃ at 220°C and 275 psig pressure
(constant CO partial press.)

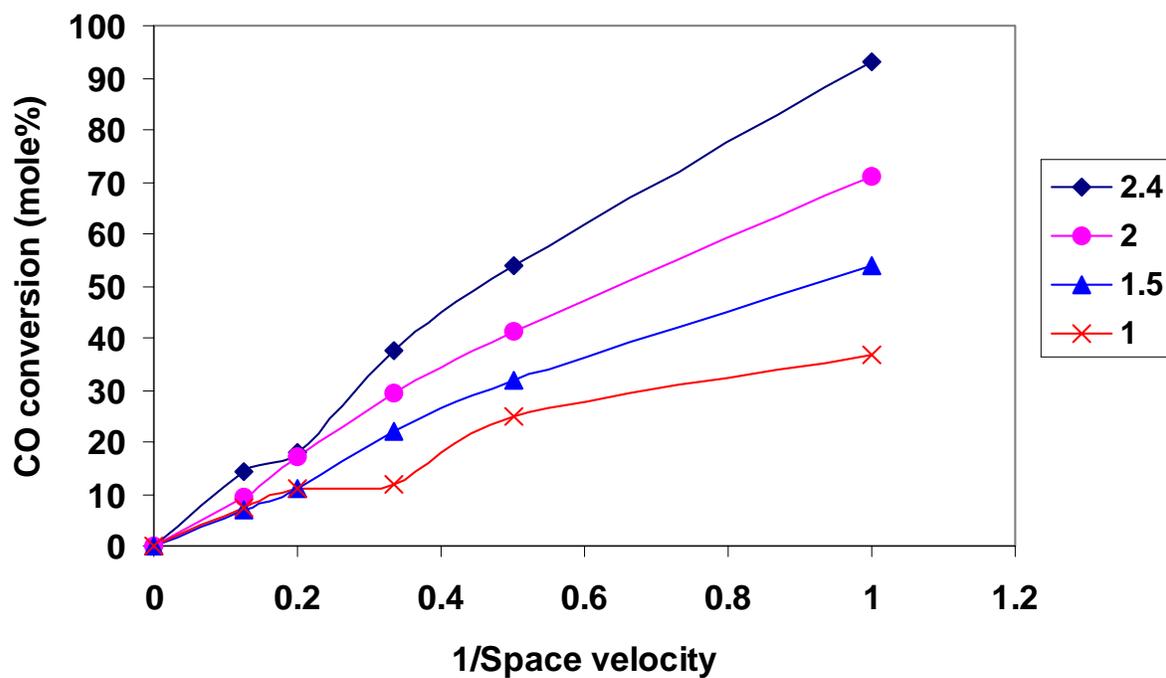


Fig. 3 : Kinetic of CO/Al₂O₃ catalyst at 220°C and 275 psig pressure (contant H₂ partial Press.)

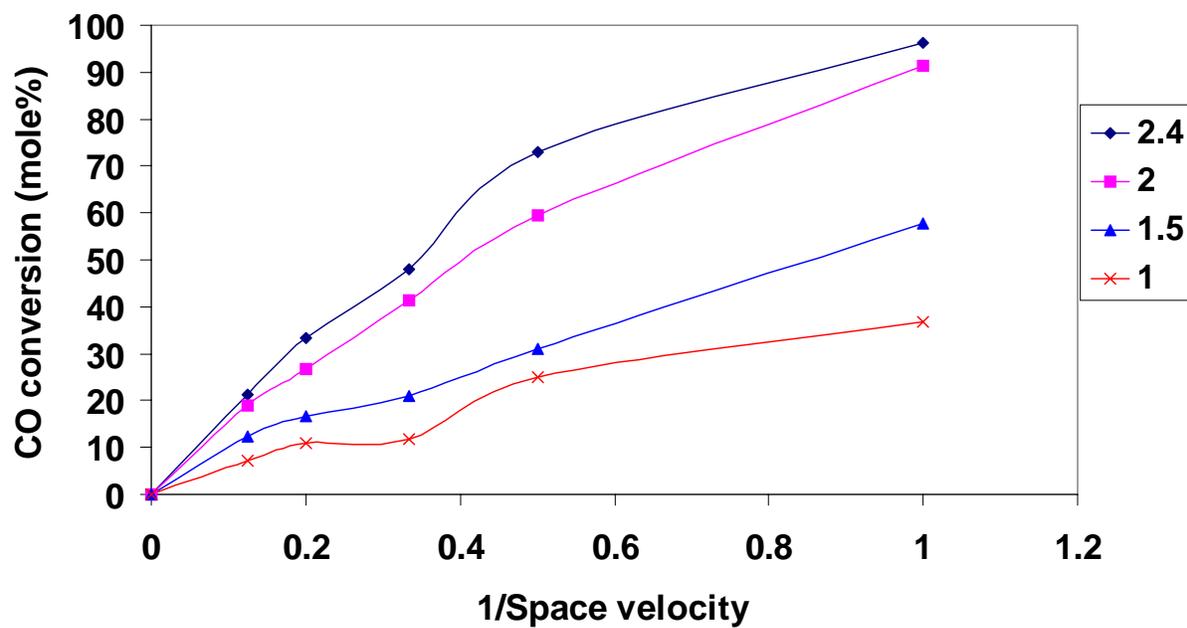


Fig. 4 : Arrhenius plot for Activation energy

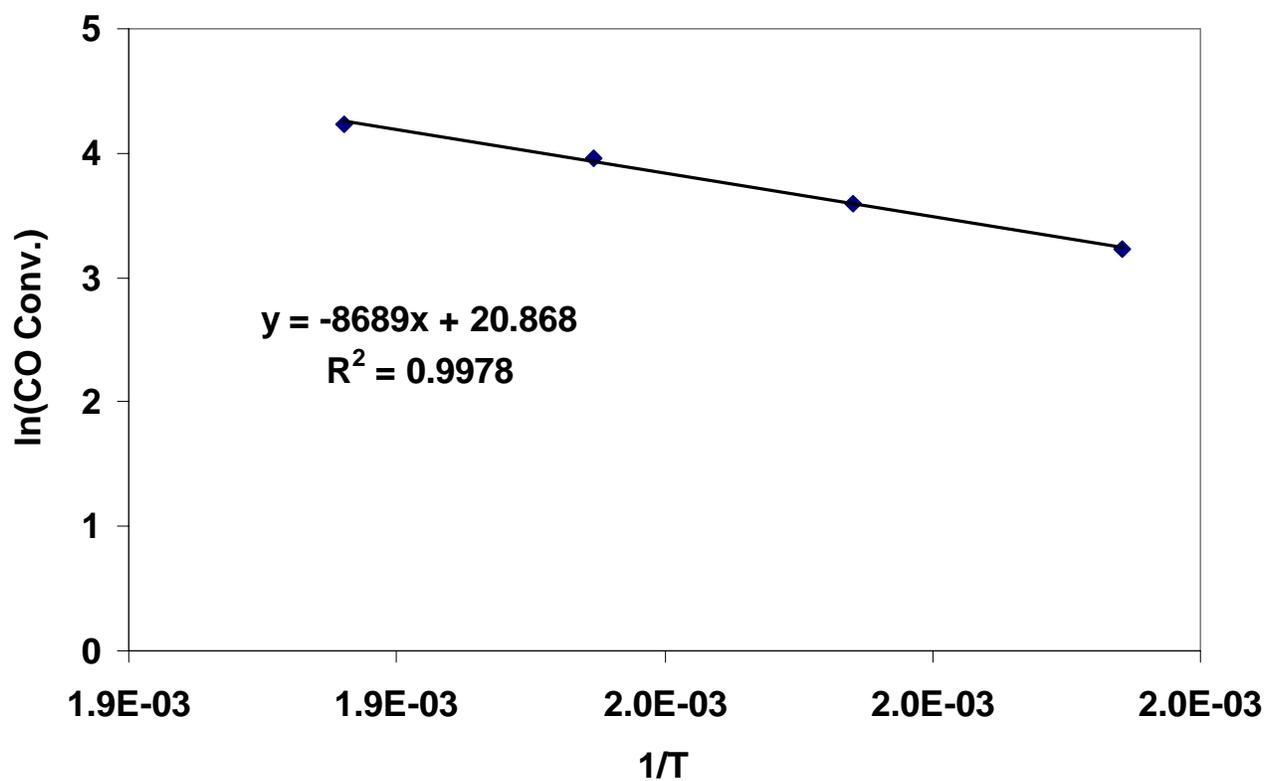


Fig. 5 : Arhenius plot for Activation energy

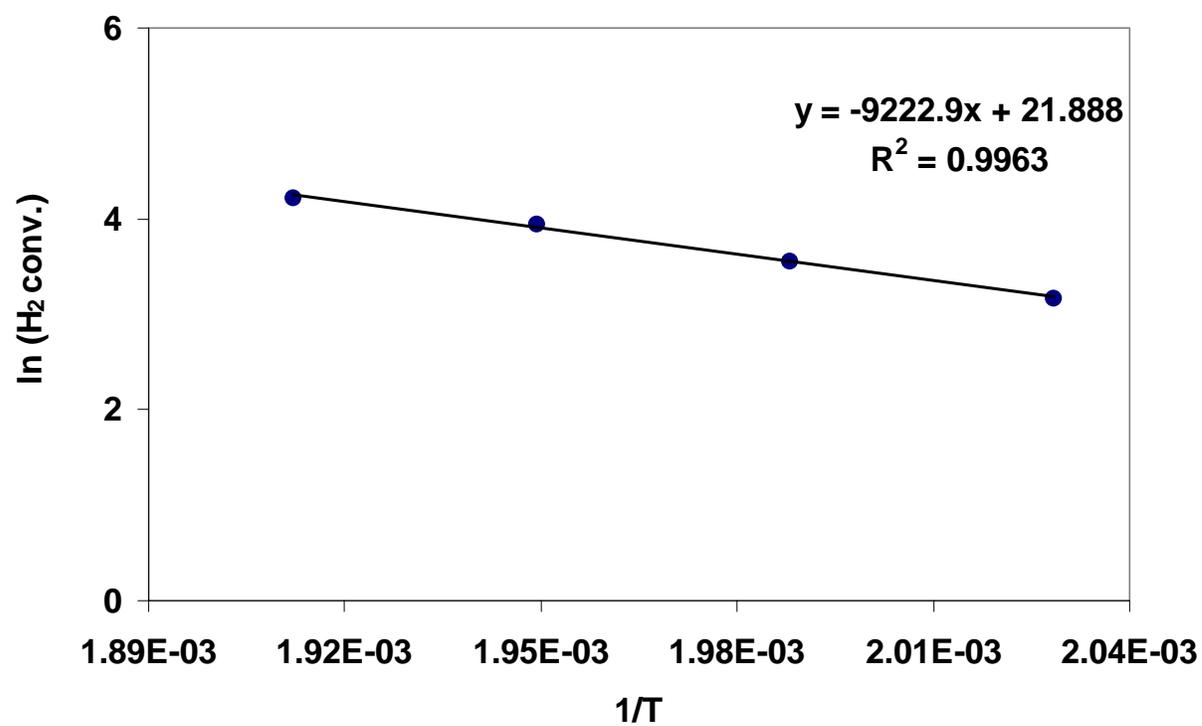


Fig. 6 : Pressure effect on CO conversion over 0.2%Re-15%Co/Al₂O₃ at 230°C

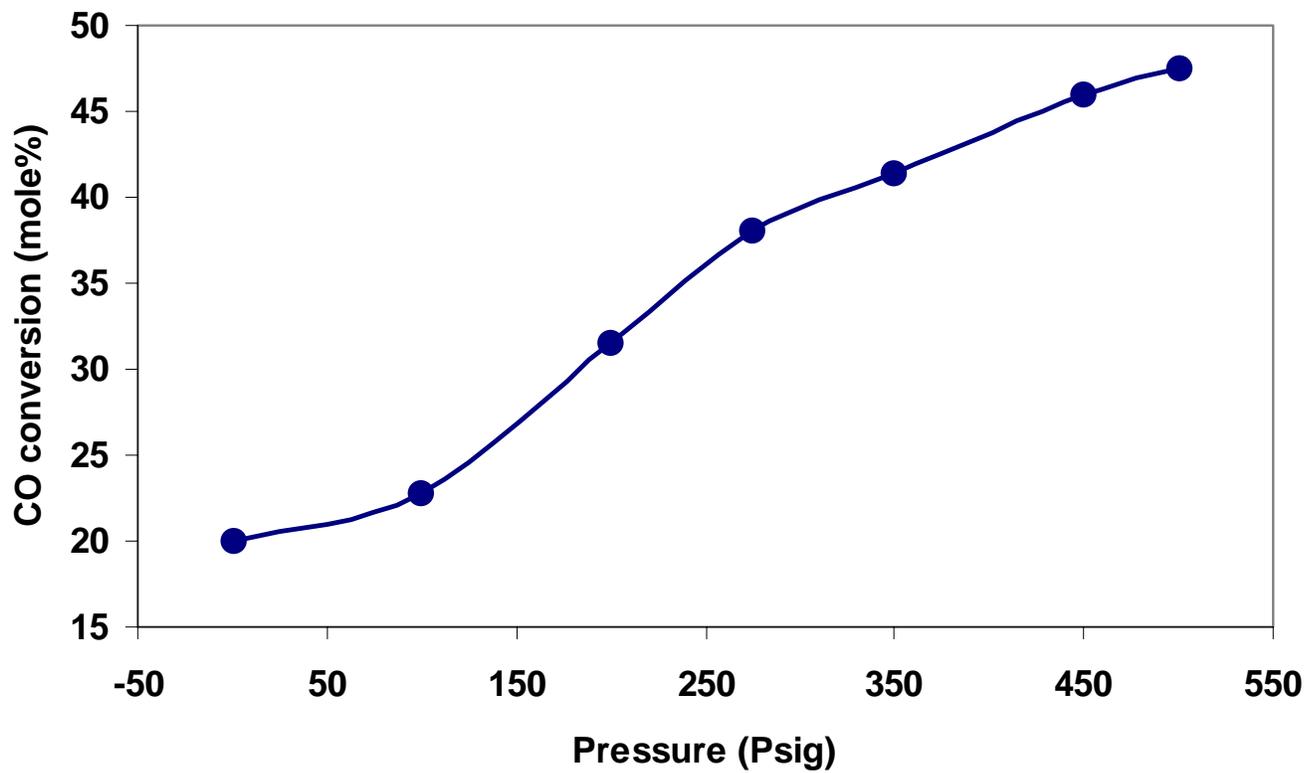


Fig. 7 : Effect of Pressure on CH₄ and CO₂ Selectivity

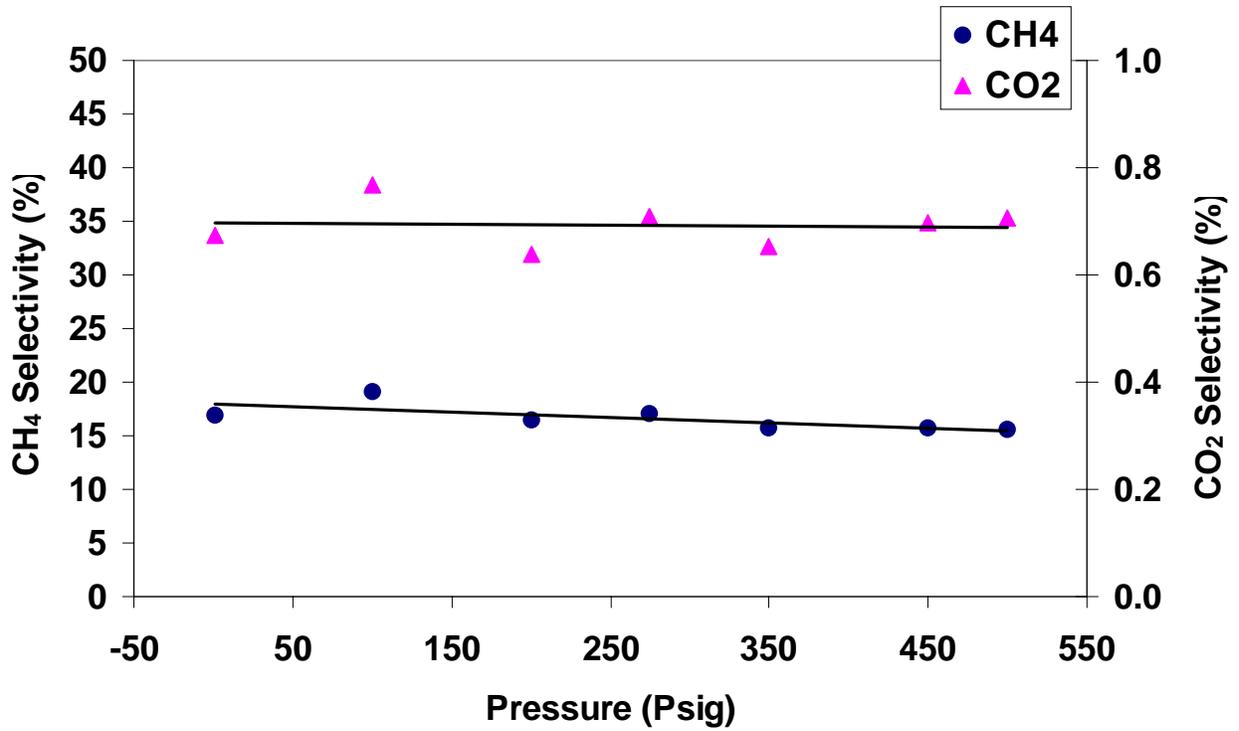


Fig. 8 : Time on stream vs CO conversion on 0.5%Ru-15%Co/Al₂O₃ at 220°C and 275 psig

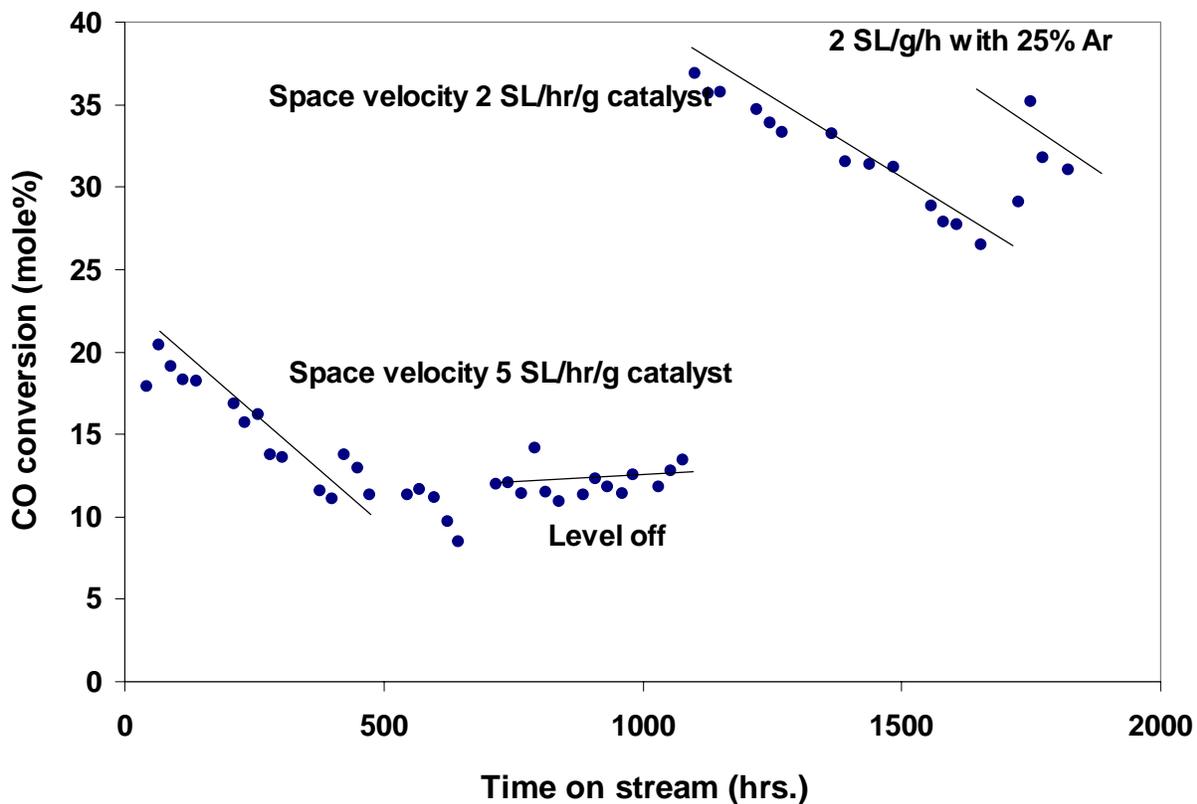


Fig. 9 : Time on stream vs CO conversion over 0.5%Ru-20%Co/ZrO₂-SiO₂ at 220°C and 275 psig

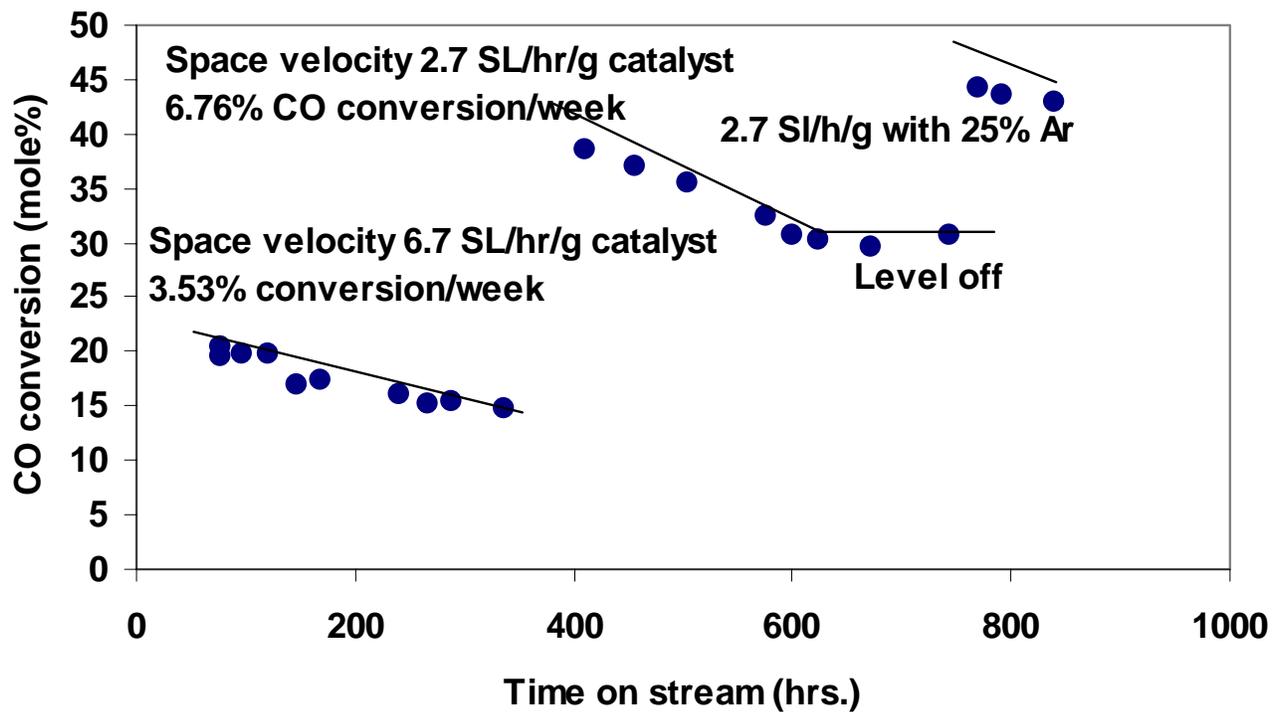


Fig. 10 : Time on stream vs CO conversion on 0.5%Pt-15%Co/Al₂O₃ at 220°C and 275 psig

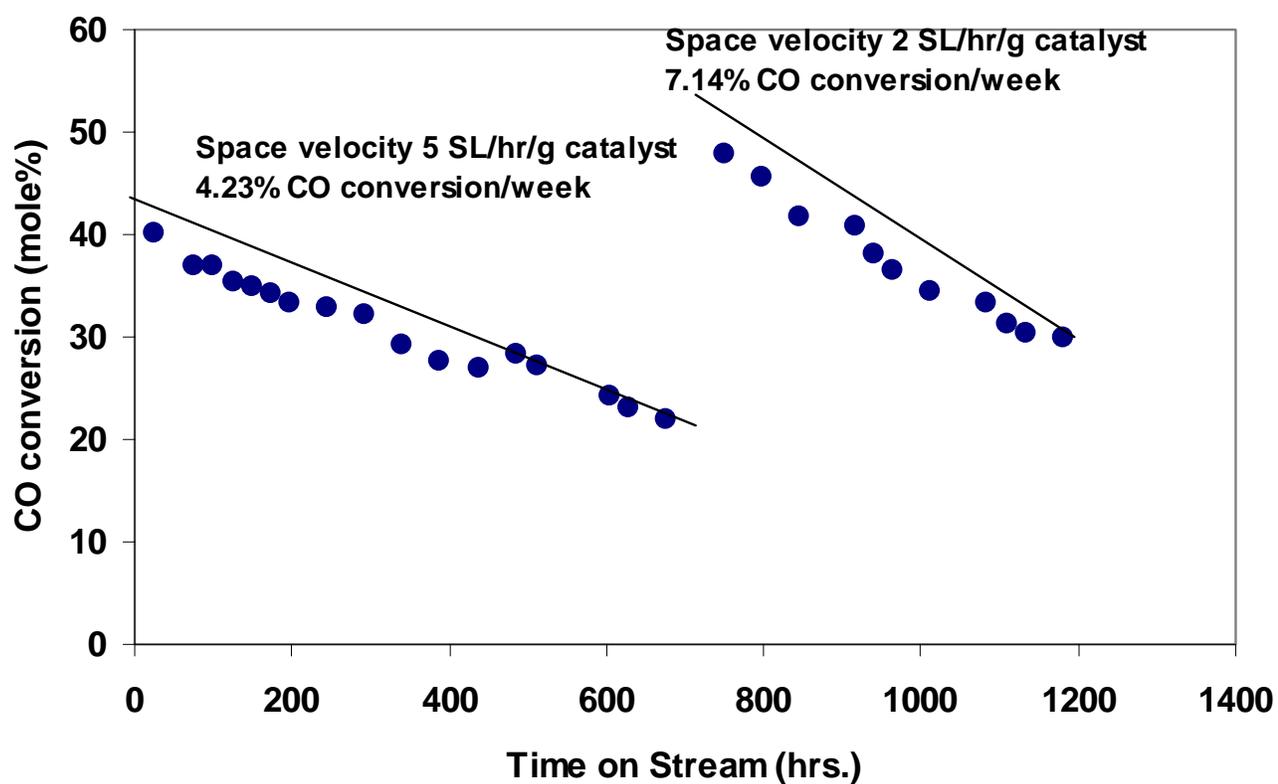
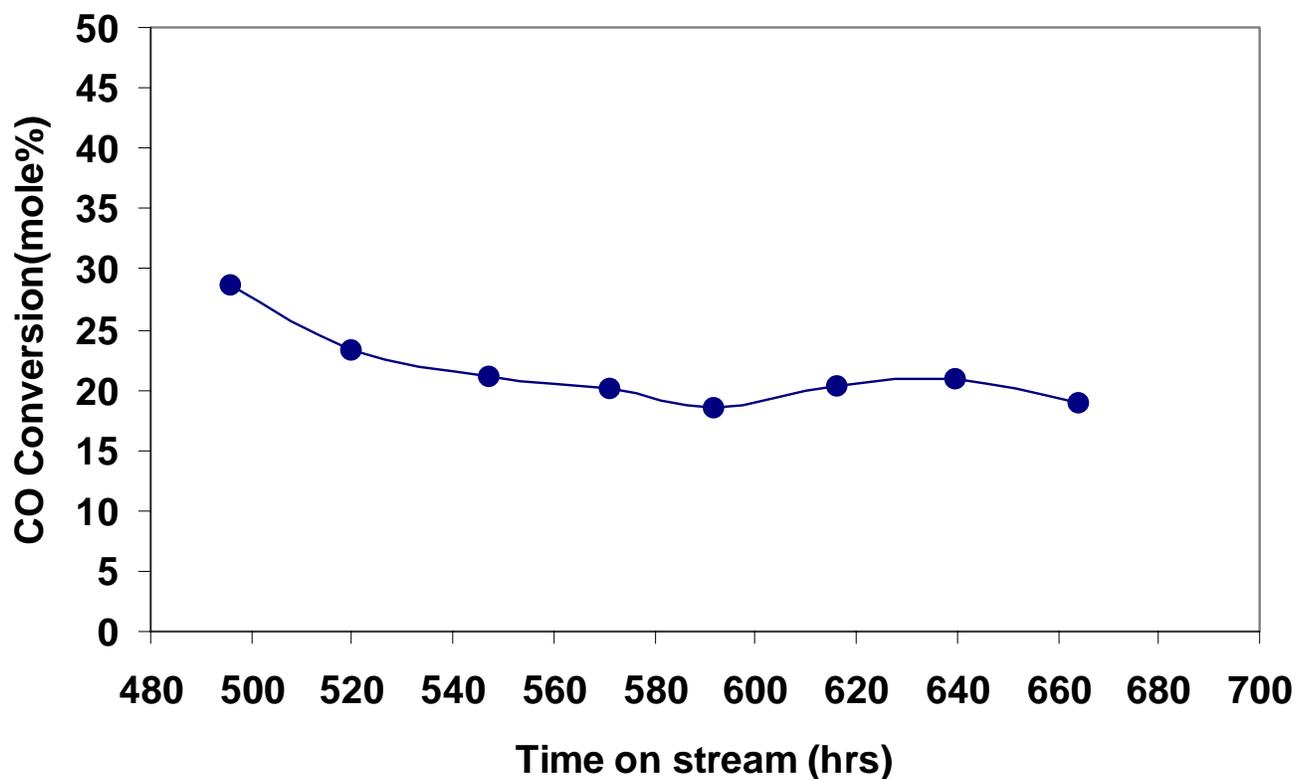


Fig. 11 : Time on stream vs CO conversion over 0.5%Pt-15%Co/Al₂O₃ at 210°C, 350 psig, H₂:CO = 2:1, GHSV = 5 SL/hr/g catalysts in Fixed-bed



D. Fischer-Tropsch Synthesis: Deactivation of Noble Metal Promoted Co/Al₂O₃ Catalysts

Abstract

Fresh and used unpromoted and noble metal promoted 15%Co/Al₂O₃ catalysts were analyzed by XANES and EXAFS to provide insight into catalyst deactivation. XANES analysis of the catalysts gave evidence of oxidation of a fraction of the cobalt clusters by water produced during the reaction. Comparison of XANES derivative spectra to those of reference materials, as well as linear combination fitting with the reference data, suggest that some form of cobalt aluminate species was formed. Because bulk oxidation of cobalt by water is not permitted thermodynamically under normal Fischer Tropsch synthesis conditions, it is concluded that the smaller clusters interacting with the support deviate from bulk-like cobalt metal behavior and these may undergo oxidation in the presence of water. However, in addition to the evidence for reoxidation, EXAFS indicated that significant cobalt cluster growth took place during the initial deactivation period. Promotion with Ru or Pt allowed for the reduction of cobalt species interacting with the support, yielding a greater number of active sites and, therefore, a higher initial catalyst activity on a per gram catalyst basis. However, these additional smaller cobalt clusters that were reduced in the presence of the noble metal promoter, deviated more from bulk-like cobalt, and were therefore, more unstable and susceptible to both sintering and reoxidation processes. The latter process was likely in part due to the higher water partial pressures produced from the enhanced activity. The rate of deactivation was therefore faster for these promoted catalysts.

Keywords: alumina, cobalt, Fischer-Tropsch synthesis, metal-support interaction, XANES, promoters

INTRODUCTION

Decreasing the deactivation rates of Co/Al₂O₃ catalysts for Fischer Tropsch synthesis (FTS) has been one of the important challenges facing the commercial development of these catalysts for the conversion of coal and natural gas to liquid fuels as alternative resources to crude oil. In comparison with low cost iron catalysts, cobalt FTS catalysts produce less water by the water-gas shift reaction. Furthermore, cobalt catalysts are believed to deactivate less rapidly and yield a higher fraction of linear alkanes than their iron counterparts. However, a major drawback of cobalt is its high cost, making catalyst replacement undesirable. Therefore, studies in the literature have focused on decreasing the deactivation rates of these catalysts [1-5]. Cobalt alumina catalysts for FTS have received renewed interest with the development of slurry phase and slurry bubble column reactors (SBCR). A recent article [6] indicated that slurry phase reactor processes employing a highly stable and active cobalt alumina catalyst will likely be employed commercially in the near future, and pilot plants are already in operation.

The aim of the present study is to employ a number of characterization techniques to investigate the causes of cobalt alumina catalyst deactivation. For example, potential causes include sintering of the cobalt, sintering and segregation of the noble metal promoter, and oxidation of the cobalt surface and/or small cobalt clusters. In this investigation, the nature of the deactivation of unpromoted, 0.5% Ru promoted, and 0.5% Pt promoted 15%Co/Al₂O₃ catalysts was studied using a combination of techniques including XANES, EXAFS, and XRD. These methods were particularly amenable to the characterization of used catalysts, because while the paraffinic hydrocarbon products from FTS must be extracted in the case of adsorption studies to characterize used catalysts, a procedure which may alter the state of the cobalt clusters, XAS allows for direct characterization of the used catalysts suspended in the solid wax matrix. These results are compared with reaction testing results obtained from continuously stirred tank reactors

(CSTRs). From the characterization results, it was concluded that important structural changes occurred during reaction which contributed to the initial catalyst deactivation.

EXPERIMENTAL

Catalyst Preparation

Condea Vista Catalox (high purity γ -alumina, 100-200 mesh, 200 m²/g) was used as the support for the cobalt FTS catalysts. To obtain a cobalt loading of 15%, a three-step incipient wetness impregnation method was used with drying at 353 K in a rotary evaporator following each impregnation. Catalysts with different loadings of ruthenium or platinum promoter were prepared by impregnation (see Table 1) using a ruthenium nitrosyl nitrate solution or tetraamineplatinum (II) nitrate, respectively. After promoter addition, the catalysts were dried in a rotary evaporator at 353K again and calcined only one time at 673K for 4hrs.

BET Measurements

BET measurements for the catalysts were conducted to determine the loss of surface area with loading of the metal. These measurements were conducted using a Micromeritics Tri-Star system. Prior to the measurement, samples were slowly ramped to 433K and evacuated for 4hrs to approximately 50mTorr. Results of physisorption measurements are shown in Table 1.

Hydrogen Chemisorption with Pulse Reoxidation

Hydrogen chemisorption measurements were performed using a Zeton Altamira AMI-200 unit, which incorporates a thermal conductivity detector (TCD). The sample weight was always 0.220 g. The catalyst was activated at 623K for 10hrs using a flow of pure hydrogen and then cooled under flowing hydrogen to 373K. The sample was held at 373 K under flowing argon to prevent physisorption of weakly bound species prior to increasing the temperature slowly to 623K. At that temperature, the catalyst was held under flowing argon to desorb the remaining

chemisorbed hydrogen so that the TCD signal returned to the baseline. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibrated hydrogen pulses. Prior to experiments, the sample loop was calibrated with pulses of nitrogen in helium flow and compared against a calibration line produced from gas tight syringe injections of nitrogen under helium flow.

After TPD of hydrogen, the sample was reoxidized at 623K by injecting pulses of pure oxygen in helium referenced to helium gas. After oxidation of the cobalt metal clusters, the number of moles of oxygen consumed was determined, and the percentage reduction calculated assuming that the Co^0 reoxidized to Co_3O_4 . While the uncorrected dispersions are based on the assumption of complete reduction, the corrected dispersions reported in Table 2 include the percentage of reduced cobalt as follows:

$$\%D_{\text{uncorr}} = (\% \text{Co}^0 \text{ atoms on surface} \times 100\%) / (\text{total \#Co atoms})$$

$$\%D_{\text{actual}} = (\# \text{ of Co}^0 \text{ atoms on surface} \times 100\%) / (\text{total \# Co}^0 \text{ atoms})$$

$$\%D_{\text{actual}} = (\# \text{ of Co}^0 \text{ atoms on surface} \times 100\%) / [(\text{total \# Co atoms})(\text{fraction reduced})]$$

Temperature Programmed Reduction

Temperature programmed reduction (TPR) profiles of fresh catalyst samples were obtained using a Zeton Altamira AMI-200 unit. Calcined fresh samples were first heated to 623 K and purged in flowing argon to remove traces of water. TPR was performed using 30 cc/min 10% H_2/Ar mixture referenced to argon. The ramp was 5K/min from 303K to 623K, and the sample was held at 623K for 30 min.

X-ray Diffraction

X-ray diffraction (XRD) measurements were conducted at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), Upton, NY, using beamline X10b. The experimental apparatus consisted of a six circle Huber diffractometer, ion chambers,

and Bicron scintillation detectors. The scanning step was 0.020° and each point was scanned for approximately 13.8 s.

EXAFS/XANES

XAS measurements on reference samples, calcined catalysts, reduced/passivated fresh catalysts, and used catalysts were conducted at NSLS at BNL, using this time beamline X-18b equipped with a Si (111) channel cut monochromator. The crystal was detuned to prevent glitches from the interference of harmonics. The X-ray ring at the NSLS has a flux of 1×10^{10} photons per second at 100 mA and 2.5 GeV, and the energy range capability was 5.8-40 keV. XAFS data were recorded near the *K* edge of cobalt. The XAFS spectra were recorded at liquid nitrogen temperatures in a cell to minimize the contribution from the dynamic Debye Waller factor. Several scans were taken and the average obtained by adding the scans. The pre-edge background was subtracted by using power series curves and then the post-edge background was removed using appropriate splines. The spectra were normalized by dividing by the height of the absorption edge. XANES spectra were compared after normalization, and these were fitted using WinXAS 97 [7]. References used for XANES measurements included a Co foil, Co_3O_4 , CoO, and CoAl_2O_4 . For EXAFS, χ -data were obtained by truncating the normalized spectra 50 eV after the edge jump and background subtracting with appropriate splines based on the Nyquist criteria, to avoid damaging the data. The χ -results in energy space were converted to *k* space and weighted with either k^0 or k^3 weighting for examination of the changes in degree of coordination for the different *Z* scatterers. To obtain qualitative information on the Co-O and Co-Co coordination, the k^0 and k^3 weighted spectra were transformed from *k* space to *r* space to obtain the radial distribution functions. Furthermore, to obtain quantitative information of the degree of cobalt-cobalt coordination for the used catalysts, the first Co-Co coordination shell was isolated and the

inverse Fourier Transform was conducted. Fitting of the spectra in k space was carried out using FEFFIT [8]. The k -range used was from 3 to 17 \AA^{-1} . Theoretical EXAFS were generated using FEFF [8] for model cobalt metal crystal parameters generated by Atoms [9]. In order to use coordination number N_1 as a fitting parameter, S_0^2 was first obtained from analysis of the Co foil assuming a fixed coordination number N_1 of 12 for the first shell. The other fitting parameters utilized by FEFFIT included the overall E_0 shift e_0 applied to each path, $delr$ to account for lattice expansion, and σ^2 , which is based on a correlated Debye model used to approximate the mean square disorder in the path length of each path.

Reaction Testing

Catalyst activation was conducted first ex-situ at 623K for 10 h in a fixed bed reactor and then re-reduced in-situ in a CSTR operating at 750 rpm. Approximately 15 g of catalyst (weight accurately determined) was used in each test. The H_2 :CO ratio used for all catalysts was 2. The total pressure of syngas used was 1.8 MPa and the reaction temperature was 493K.

RESULTS AND DISCUSSION

Figure 1 shows TPR of the unpromoted Co/ Al_2O_3 catalyst in comparison with TPR spectra for Ru promoted catalysts with increasing loadings of ruthenium, and the 0.5% Pt promoted catalyst. Note that during TPR, the temperature was not ramped high enough to observe the reduction of the small fraction of cobalt aluminate species, which has been demonstrated above 1073 K with up to 30% loading of cobalt [10]. The low temperature peak (500-650K) is typically assigned to reduction of Co_3O_4 to CoO, though a fraction of the peak likely includes the reduction of the larger, bulklike CoO species to Co^0 . This is based on our previous TPR study [11], which showed that increasing the cobalt loading caused a new peak appear in the TPR on the high temperature side of this low temperature peak, which increased

with loading, resembling the second step of CoO to Co⁰ in the reduction of bulk Co₃O₄. Although the precise identity is not clear, the broad peak on the unpromoted catalyst (700 to 1000 K) is attributed to the reduction of cobalt species interacting with the support, and the different shoulders are likely due to varying degrees of interaction that depends on the size. In a previous study [3], XRD was scanned after reduction of the first peak in TPR. The observation was made that the 31.2° and 59.4° peaks for Co₃O₄ disappeared, while the 42.4° and 61.3° peaks for CoO appeared. Therefore, the broad high temperature peak in the TPR may be due to the reduction of small CoO clusters interacting with the support. From this perspective, the smallest species, with the highest degree of interaction with the support, would likely reduce to produce the 950K shoulder in the TPR. A somewhat different viewpoint [12] suggests that the broad peak is the result of the reduction of a surface overlayer of, for the most part, Co²⁺ species containing atoms of the support in their structure. The addition of Ru caused the peaks to shift markedly to lower temperatures, presumably due to spillover of hydrogen from the reduced promoter to reduce the cobalt oxide species, in agreement with an earlier study [13]. Of particular importance, peaks that are attributed to the cobalt species interacting with the support are reduced at lower temperatures with increasing Ru loading, or with addition of Pt. Results of hydrogen chemisorption by TPD (Table 2) indicate that the number of surface sites increases with addition of either Ru or Pt promoter. By performing pulse reoxidation, it is clear that the gain in the number of active sites is mainly due to an enhancement in the percentage reduction, and not to improvements in the actual dispersion (cluster size) [14]. However, addition of Ru or Pt causes a slight contraction in the average cluster size. This is reasonable, because the comparison was conducted on samples treated at the same reduction temperature of 623 K, and the addition of Ru or Pt causes a fraction of the smaller cobalt species interacting with the support to be reduced at this temperature, resulting in a slight decrease in the average cobalt metal cluster size.

XRD patterns for the calcined fresh unpromoted and Ru promoted catalysts are shown in Figure 2. The peaks at 46.1° and 66.5° correspond to the $\gamma\text{-Al}_2\text{O}_3$ support, while other peaks correspond to the different crystal planes of Co_3O_4 [10]. From line broadening analysis using the Winfit program for the peak at 36.8° corresponding to diffraction by the (311) planes, it was determined that the average Co_3O_4 cluster size after calcination was approximately 10.6 nm (unpromoted) and 10.3 nm (0.5% Ru promoted) corresponding to 7.95 nm and 7.73 nm when reduced to the metal, respectively. This agrees reasonably well in comparison to the results of hydrogen chemisorption/pulse reoxidation. XRD on the used catalysts was also performed and the resulting spectra were very complex. The benefit of using synchrotron radiation is that the intensity of X-rays decreases the signal to noise ratio considerably, allowing for the analysis of species which would otherwise be below detectable limits. Interestingly, the series of 16 complex peaks between 30° and 80° were identical for both the promoted and unpromoted used catalysts. Tentative assignments of peaks for cobalt metal were made at 2θ values of 43.9° , 51.1° , 91.4° , and 75° in the spectra, which correlate with the reported literature values of 44.2° , 51.5° , 92.2° , and 75.8° for a cubic cobalt structure. The presence of CoO was also suggested by the peaks located at 42.5° and 36.5° . Also, it appears that a small amount of Co_2C may also have been formed during the synthesis. Clearly, peaks are present at 42.5° , 41.3° , 56.6° , and 71.4° which correlate well with Co_2C . In addition, peaks for Co_2C may be present at 36.8° and 45.7° , but these are likely hidden in the broad peaks. Support peaks were also still observed at 46.1° and 66.5° in the used catalysts. The identification of the remaining peaks is not clear. However, the relative intensities and positions of the sharp peaks located at 29.6° and 35.8° values indicate some form of a spinel structure. Peaks were also observed at 39.3° , 40.0° , 52.4° , and 54.4° , but no assignment for these peaks could readily be ascertained.

XANES analysis was conducted for the reference compounds CoO, Co₃O₄, CoAl₂O₄, and the Co foil and for the calcined, freshly reduced/passivated, and used unpromoted, 0.5% Ru promoted, and 0.5% Pt promoted catalysts. The normalized and derivative spectra are displayed in Figures 3 and 4. The XANES of the *K*-edges of some cobalt compounds contain a pre-edge only a few electron volts below the edge, a feature useful for identifying various species. The pre-edge appears for tetrahedral cobalt environments but is forbidden for octahedral environments [15], and arises from the 1s to 3d absorption transition. The intensity is inversely dependent on the degree of inversion symmetry in the first coordination shell, as well as the extent of occupancy of the 3d shell. Atoms in tetrahedral sites often exhibit pre-edge peaks due to lack of symmetry [16], while the peak is very low for octahedral environments, due to the center of symmetry. Therefore, the intensities follow the order CoAl₂O₄ > Co₃O₄ > CoO, as the cobalt atoms in CoAl₂O₄ are in a tetrahedral environment, the cobalt atoms in the spinel structure of Co₃O₄ are in a mixed environment (one Co atom in a tetrahedral environment, while the other two are in octahedral), and the cobalt atoms in CoO are in an octahedral environment [15].

The XANES analysis of the calcined catalysts, in agreement with XRD, clearly display Co₃O₄ as the major species present on the support. After performing a linear combination (LC) fitting with WinXAS97 of the XANES spectra for the calcined catalysts using reference materials, the result revealed that only Co₃O₄ was present. For the derivative spectra, the calcined catalysts have a pre-edge feature that is similar to Co₃O₄, while the reduced/passivated catalysts have a smaller pre-edge feature similar to that of CoO. Also, for the reduced/passivated catalysts, the XANES spectra are very similar in shape to that of CoO. This is in agreement with the conclusion from TPR. After reduction at 623K, the cobalt species associated with the first peak in the TPR, assigned to reduction of Co₃O₄ and bulk-like CoO, is completely reduced, while the species in interaction with the support are only partially reduced. From pulse reoxidation

measurements, the extent of reduction is 20% and 30% greater for Ru and Pt promoted catalysts, respectively, than for the unpromoted sample. Based on the previous discussion on the nature of the broad peak in the TPR, it is reasonable that the XANES features of the reduced/passivated catalysts will most resemble the reference spectrum of CoO. As expected, after performing a linear combination (LC) fitting of the XANES with WinXAS 97, CoO was found to contribute 93.6%, 99.2%, and 48.2% to the XANES LC fitting for unpromoted, Ru promoted, and Pt promoted catalysts, respectively, as shown in Table 3.

For the used catalysts, the spectra appear to be very similar for both the promoted and unpromoted catalysts. It is clear that the resulting complex spectra for the used catalysts represent a combination of superimposed spectra of different species rather than the case of one dominating contribution. The presence of a large fraction of cobalt metal is clearly indicated, and since the edge energy of bulk metallic cobalt is 7709 eV, the pre-edge features from oxidized phases that are present are obscured. However, the XANES display features which suggest the presence of either Co_3O_4 or CoAl_2O_4 , and these are superimposed over the signal of the metal.

To further strengthen this conclusion, three separate fittings were performed on the data for the used catalysts, and the results are shown in Table 3 for the unpromoted, Ru, and Pt promoted catalysts. In fitting number 1, the XANES spectra were fitted with Co^0 , Co_3O_4 , and CoO, while CoAl_2O_4 was omitted. The resulting residual was calculated to be 2.00, 1.43, and 1.6 for the unpromoted, Ru-promoted, and Pt-promoted catalysts, respectively. In fitting number 2, the spectra were fitted with Co^0 , CoAl_2O_4 , and CoO, and Co_3O_4 was omitted from the fitting. In this case, the residuals for all three spectra were lower, indicating a better fit, with the values of 1.49, 1.29, and 1.54, respectively. In fitting number 3, both Co_3O_4 and CoAl_2O_4 were included in the fitting procedure, and the results for the unpromoted and Ru-promoted catalysts showed no further improvement, indicating that the CoAl_2O_4 was a better fit. The Pt-promoted catalyst

displayed some further improvement with both species present in the fitting; however, the cobalt aluminate percentage was higher than that of Co_3O_4 . Note that samples of the used catalysts were taken after reactor shutdown, where the catalyst was cooled in the solid wax under argon, and the reactors were not shut down at different times on-stream. Therefore, the catalysts exhibited different stages of deactivation. The primary aim of this work was to identify potential reoxidized species responsible for deactivation. Further studies are currently being carried out to obtain better quantitative information on the evolution of cobalt oxide/aluminate formation, as well as information on the sintering of the metal clusters as a function of time on-stream. For example, we are currently implementing a technique to sample catalyst directly from the reactor with time on-stream, suspending the catalyst in the solid wax under inert gas, a method ideal for XAS investigation.

Nevertheless, the results here suggest that H_2O produced from the FTS reaction may have oxidized a fraction of the small cobalt clusters, which do not exhibit the same properties as the bulk metal. Note that very large $P_{\text{H}_2\text{O}} / P_{\text{H}_2}$ ratios (>50) are needed to reoxidize bulk cobalt metal [17], and these ratios are not encountered under normal FTS conditions. It has been suggested [2] that the support interaction promotes the deviation of small clusters from bulk-like behavior. Therefore, the very small clusters may undergo reoxidation during FTS. It is clearly of interest to continue to investigate the effect of increasing the cluster size for Al_2O_3 supported cobalt catalysts to determine the impact of the cluster size on the deactivation rate of the catalyst.

EXAFS was also employed as a qualitative method to analyze the used catalysts, and determine if the catalysts displayed Co-O coordination matching that of either Co_3O_4 or CoAl_2O_4 . Also, it was of interest to determine if shifts in the position of the peak for Co-Co coordination occurred, indicating reoxidation. As shown in Figure 5, both the k^0 and k^3 weighted Fourier

transform magnitude spectra of the used catalysts strongly match the spectrum of the cobalt metal foil. Results of the fitting shown in Table 4 of the first Co-Co shell (k^3 weighted) indicate that the resulting degree of Co-Co coordination N_1 for all three used catalysts is very similar. Also, the low r-factor values (<0.02) suggest good fits with only the Co metal foil. However, there is detected a small contribution for Co-O, which appears in the k^0 -weighted spectra for the used catalysts, which suggests that reoxidation occurred for a small fraction of the cobalt.

To examine the change in the cobalt metal cluster size, EXAFS was conducted on the freshly reduced/passivated and the used catalysts. The k^3 -weighted Fourier Transform magnitudes are displayed in Figure 6 in reference to the Co foil, which displays a coordination of 12. Note that the XANES LC results suggest that the reduced/passivated catalysts may not be representative of the freshly reduced catalyst at the onset of reaction. However, our current investigation, where samples of catalyst are removed with time onstream, should provide more conclusive evidence on the extent of sintering by following the changes in the degree of Co-Co coordination with deactivation time. Interestingly, both reduced/passivated catalysts (promoted and unpromoted) displayed similar Fourier Transform magnitudes for Co-Co metal coordination, indicating a similar cluster size. After reaction testing, the degree of Co-Co coordination was slightly higher for the Ru and Pt promoted catalysts than the unpromoted. Based on the good fits obtained in Table 4 using only Co metal as a standard for the first Co-Co shell, the results strongly suggest sintering of the clusters occurred during the initial deactivation period. However, in light of the XANES spectra for the used catalysts, one cannot rule out the possibility that the smaller clusters reoxidized during reaction, leaving a higher intensity of Co-Co coordination in the k^3 weighted Fourier Transform for the used catalyst.

Reaction testing in the CSTR revealed that higher conversions and, therefore, increasing P_{H_2O} , resulted in a higher catalyst deactivation rate. In a previous investigation for a 0.5% Pt promoted 15%Co/Al₂O₃ catalyst, whereby water was added to the feed, $P_{H_2O} > 28\%$ of the total pressure resulted in drastic irreversible deactivation to the catalyst, while the catalyst recovered activity between 3% and 25% due to the reversible kinetic effect of water [5]. In the present investigation, the unpromoted and Ru promoted catalysts were run at the same space velocity on a per gram catalyst basis, but the number of active sites was higher for the Ru catalyst, resulting in higher initial activity. In agreement with our previous findings, more active catalysts displayed a higher rate of deactivation, as shown in Figure 7. For the unpromoted catalyst, the CO conversion declined by 18% of the initial activity after 85 h, and was stable after that. In contrast, the CO conversion decreased by 42% of the initial value after 1000 h for the Ru-promoted catalyst, and 43% after 620 h for the Pt-promoted catalyst (note lower space velocity). The influence of pressure and temperature on FTS has been well-documented. Studies on Co catalysts have shown that while increasing temperature results in a shift of products to lower carbon numbers, increasing total pressure shifts product selectivities to heavier products. The process conditions used in this work were T = 493K and 1.8 MPa. Note that while the space velocity was the same (33 SL CO/ hr g cat) for the unpromoted and Ru promoted catalyst, a lower space velocity (5 SL CO/g cat) was employed for the Pt promoted catalyst.

In a previous investigation of unpromoted and Re promoted Co/Al₂O₃ catalysts, Schanke et al. [2] showed by gravimetric analysis and XPS that reoxidation occurs when water is introduced after reduction of the catalyst. The extent of reoxidation was found to be dependent on the partial pressure of water and the composition of the feed mixture. Even at atmospheric pressure and a low water partial pressure of 2 kPa, without hydrogen in the feed, complete surface

reoxidation was found to occur after short exposure times, while only slight indications of reoxidation were seen under hydrogen. However, at high pressure conditions of 2 MPa, which is comparable to the pressure in a FTS reactor, reoxidation occurred to a greater extent. In their investigation, the Re promoted catalyst was found to be more susceptible to reoxidation than the unpromoted catalyst. The authors noted that bulk cobalt metal will not reoxidize in H₂O/H₂ mixtures, as predicted by thermodynamic calculations. However, the influence of the support on metal and metal oxide clusters causes deviations from bulk behavior. Re, Pt, and Ru allow the reduction of smaller clusters which will not be reduced on the unpromoted catalyst [11]. It is suggested that these smaller clusters may deviate more strongly from bulk-like behavior and will be more susceptible to reoxidation. Therefore, the faster deactivation rate observed for the Ru and Pt promoted catalysts in this work can be likely attributed to two factors. First, the increased activity, due to more active sites, will yield a higher water partial pressure in the reactor. Also, with a higher fraction of smaller clusters after reduction, the promoted catalyst is more susceptible to reoxidation. Secondly, smaller metal clusters, with a greater fraction of surface atoms, are more unstable than the larger clusters, and therefore more susceptible to sintering processes.

A recent study [3] reported on the effect of water partial pressure on the reducibility of Co for a Ru-promoted cobalt catalyst. Increasing the water partial pressure was found to increase the temperature of the second peak of the TPR, which was assigned to the reduction of well dispersed cobalt species that strongly interact with the support. Furthermore, adding water decreased the overall degree of reduction. This latter result suggests that water promotes interactions between cobalt oxide species and the γ -Al₂O₃ support, so that some type of irreducible cobalt aluminate was formed. Therefore, in the case of catalyst deactivation, one cannot rule out the possibility of cobalt aluminate formation. Although the exact identity of the

cobalt aluminate-like structure cannot yet be determined, it is possible that the structure may be indicated in XRD as the unknown spinel assignment. It is conceivable that, once oxidized by water, the well dispersed clusters, for which there exists a strong interaction with the support, may diffuse as ions into the support in the presence of water produced from reaction, and form some type of irreducible tetrahedral cobalt aluminate species.

CONCLUSIONS

XANES analysis of used unpromoted and Ru or Pt promoted 15% Co/Al₂O₃ catalysts gave evidence of oxidation of a fraction of the catalyst by water produced during the reaction. Analysis of the XANES normalized and derivative spectra indicated that either Co₃O₄ or cobalt aluminate was formed. The two are not easily distinguished by either XRD or XANES but comparison of XANES spectra of used and calcined catalysts and linear combination fitting against reference spectra suggested cobalt aluminate formation. Because bulk oxidation of cobalt by water is not permitted by thermodynamics under FTS conditions, the results suggest that only the small clusters interacting with the support and deviating from bulk-like behavior reoxidize in the presence of water produced during the reaction.

However, EXAFS results strongly suggested that the deactivation was due in large part to sintering, as growth in the Fourier transform magnitudes for Co-Co metal coordination in the used catalysts was observed. Furthermore, both k^0 and k^3 weighted radial distribution functions strongly matched the spectra of the cobalt metal foil.

TPR and hydrogen chemisorption/pulse reoxidation results indicated that promoting the catalyst with Ru or Pt allowed for the reduction of a fraction of cobalt species in interaction with the support which were not reduced for the unpromoted catalyst. Therefore, the resulting smaller cobalt metal clusters deviated even more so from the bulk, making them susceptible to reoxidation and sintering processes. While the noble metal promoted catalyst displayed higher

initial activity due to the presence of a greater number of active sites from enhanced reducibility, the deactivation rates for these catalysts were higher than the unpromoted catalyst.

ACKNOWLEDGMENTS

This work was supported by U.S. DOE contract #DE-FC26-98FT40308 and the Commonwealth of Kentucky, and research carried out (in part) at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. DOE, Divisions of Materials Science and Chemical Sciences. Special thanks to Dr. Syed Khalid (Beamline X18b) for help with XAFS, Joel Young for XAFS cell construction, and Prof. Mark Dry for helpful discussions.

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Table 1			
BET Measurements			
<i>Catalyst Description</i>	<i>BET Surface Area (m²/g)*</i>	<i>Average Pore Radius (nm)</i>	<i>Pore Volume (cm³/g)</i>
Al ₂ O ₃	200 (211)	4.7	0.500
15%Co/Al ₂ O ₃	158	4.2	0.328
0.5%Pt-15%Co/Al ₂ O ₃	162	4.1	0.328
0.5%Ru-15%Co/Al ₂ O ₃	161	3.9	0.310
0.2%Ru-15%Co/Al ₂ O ₃	154	4.0	0.305
1.0%Ru-15%Co/Al ₂ O ₃	159	3.1	0.293
*Measured value in brackets for Al ₂ O ₃ support.			

Sample Description	$\mu\text{mol H}_2$ desorbed per g cat	Uncorr % <i>D</i>	Uncorr diam. (nm)	$\mu\text{mol O}_2$ pulsed per g catalyst	% Red	Actual % <i>D</i>	Actual diam. (nm)
15%Co/Al ₂ O ₃	66.9	5.3	19.6	509	30	17.5	5.9
0.5%Pt-15%Co/Al ₂ O ₃	140.6	9.3	11.0	1024	60	18.4	5.6
0.5%Ru-15%Co/Al ₂ O ₃	115.5	9.7	11.4	823	50	18.2	5.7

Table 3
XANES LC Fits

Fitting	Sample Name	Co ⁰	E ₀ shift (eV)	Co ₃ O ₄	E ₀ shift (eV)	CoO	E ₀ shift (eV)	CoAl ₂ O ₄	E ₀ shift (eV)	Res
-	15% Co/Al ₂ O ₃ calcined	ND	ND	100	1.11+/- 0.002	ND	ND	ND	ND	-
-	15% Co/Al ₂ O ₃ reduced/passivated	6.4	-0.672 +/-0.072	ND	ND	93.6	1.189 +/-0.003	ND	ND	2.19
fitting #1	15% Co/Al ₂ O ₃ used	36.8	0.045 +/-0.007	24.5	0.174 +/-0.093	38.7	-0.095 +/-0.054	not included	not included	2.00
fitting #2	15% Co/Al ₂ O ₃ used	38.3	-0.105 +/-0.070	not included	not included	31.9	-0.086 +/-0.058	29.8	0.813 +/-0.055	1.49
fitting #3	15% Co/Al ₂ O ₃ used	38.3	-0.105 +/-0.070	ND	ND	31.9	-0.086 +/-0.058	29.8	0.813 +/-0.055	1.49
-	0.5% Ru-15% Co/Al ₂ O ₃ cal	ND	ND	100	1.03+/- 0.002	ND	ND	ND	ND	-
-	0.5% Ru-15% Co/Al ₂ O ₃ reduced/passivated	0.8	-0.385 +/-0.001	ND	ND	99.2	1.031 +/-0.003	ND	ND	2.60
fitting #1	0.5% Ru-15% Co/Al ₂ O ₃ used	52.1	-0.235 +/-0.087	12.2	0.577 +/-0.298	35.7	-0.128 +/-0.093	not included	not included	1.43
fitting #2	0.5% Ru-15% Co/Al ₂ O ₃ used	53.2	-0.315 +/-0.083	not included	not included	33.2	-0.094 +/-0.011	13.5	1.32 +/-0.189	1.29
fitting #3	0.5% Ru-15% Co/Al ₂ O ₃ used	53.2	-0.315 +/-0.083	ND	ND	33.2	-0.094 +/-0.011	13.5	1.32 +/-0.189	1.29
-	0.5% Pt-15% Co/Al ₂ O ₃ reduced/passivated	32.3	-0.287 +/-0.052	19.5	0.876 +/-0.067	48.2	1.375 +/-0.026	ND	ND	1.81
fitting #1	0.5% Pt-15% Co/Al ₂ O ₃ used	67.2	-0.153 +/-0.007	11.1	1.035 +/-0.034	21.7	-1.45 +/-0.015	not included	not included	1.60
fitting #2	0.5% Pt-15% Co/Al ₂ O ₃ used	69.3	-0.189 +/-0.007	not included	not included	19.9	-1.38 +/-0.016	10.9	1.65 +/-0.026	1.54
fitting #3	0.5% Pt-15% Co/Al ₂ O ₃ used	64.9	-0.238 +/-0.008	6.9	-0.251 +/-0.071	20.8	-1.873 +/-0.017	7.4	3.718 +/-0.043	1.49

Table 4

Best-fit values for average coordination number (N_1) for the first Co-Co shell, shift in E_0 , Debye-Waller factor (σ^2), lattice expansion ($deltar$), and fractional misfit (r). Relative uncertainties are also shown.

<i>Used Catalyst</i>	<i>n</i>	Δn	e_0	Δe_0	σ^2	$\Delta\sigma^2$	<i>deltar</i>	Δdeltar	<i>r-factor</i>
Unpromoted	5.69	0.2913	5.6315	0.5942	0.00422	0.00045	-0.0179	0.0039	0.0187
w/ 0.5%Ru	6.44	0.1568	7.6258	0.2852	0.00371	0.00021	-0.00838	0.0018	0.00441
w/ 0.5%Pt	6.29	0.1952	6.6122	0.3653	0.00382	0.00027	-0.0116	0.0023	0.0071

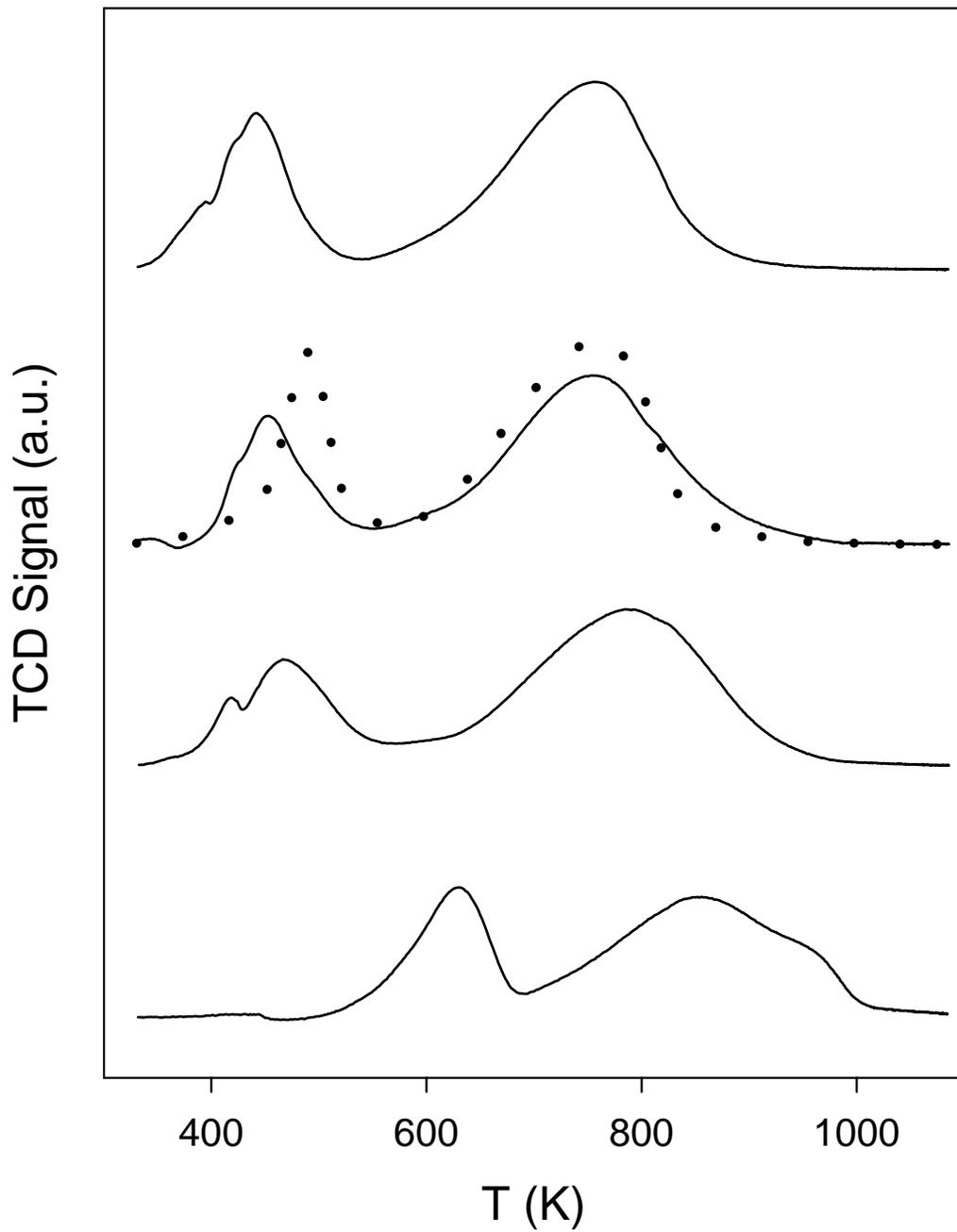


Figure 1: Comparative TPR spectra of unpromoted (bottom) 15% Co/Al₂O₃ catalyst with those promoted with (moving up, solid) 0.2%, 0.5%, and 1.0% Ru and 0.5%Pt (dotted).

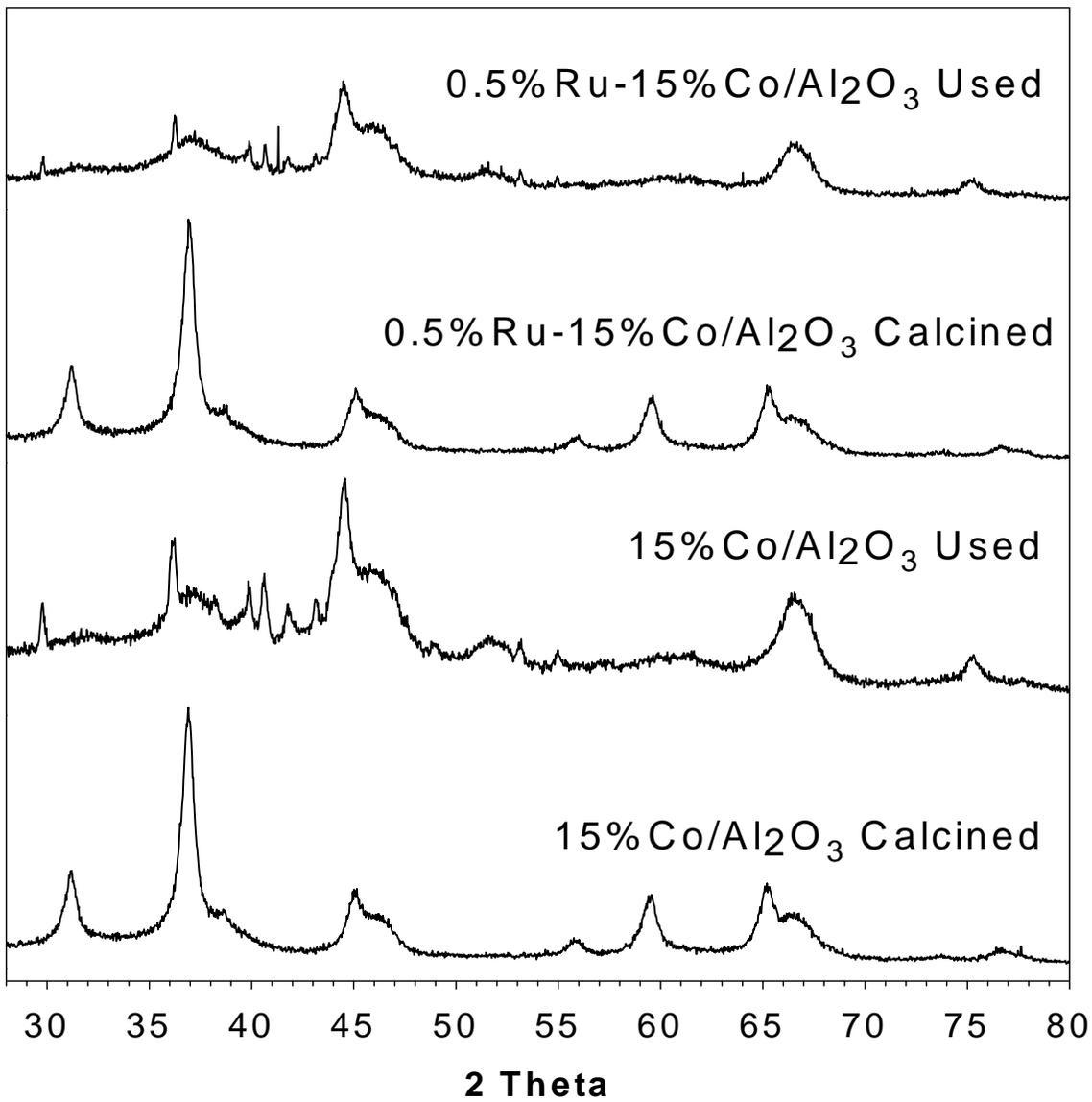


Figure 2: XRD patterns for calcined and spent Ru-promoted and unpromoted 15% loaded Co/Al₂O₃ catalysts.

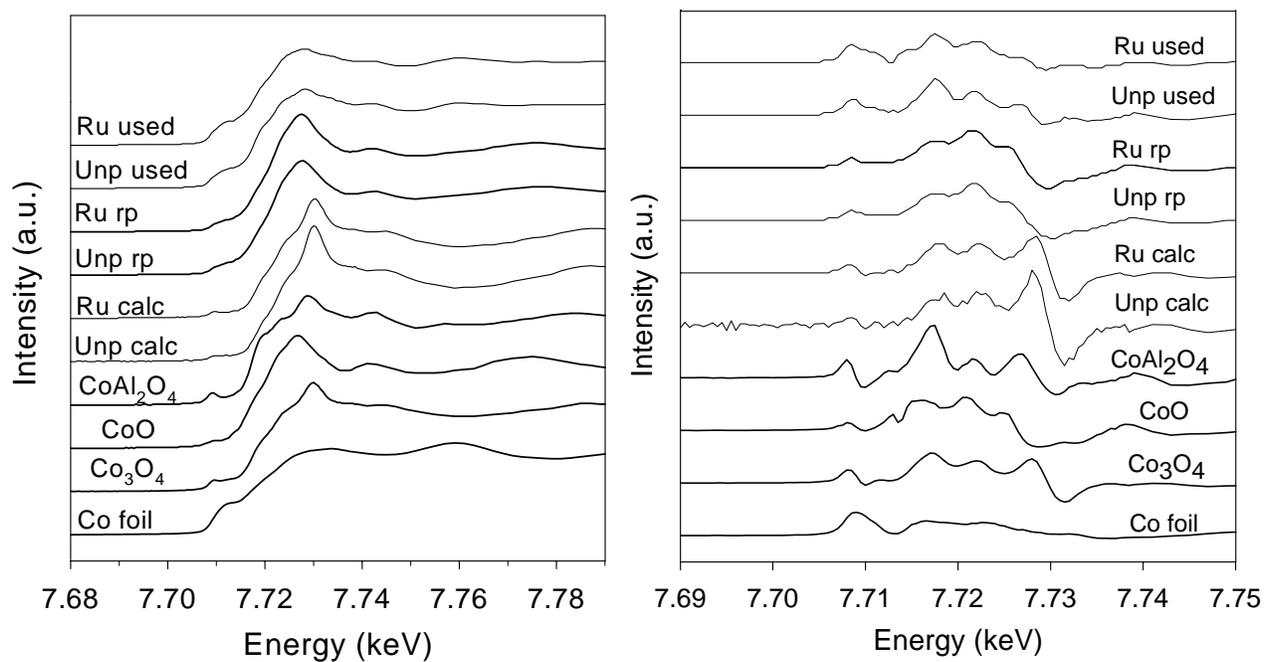


Figure 3: (left) Normalized XANES and (right) XANES derivative profiles for references, calcined, freshly reduced/passivated catalysts, and used catalysts for a comparison of Ru promoted and unpromoted FTS catalysts [rp, reduced/passivated; calc, calcined; unp, unpromoted].

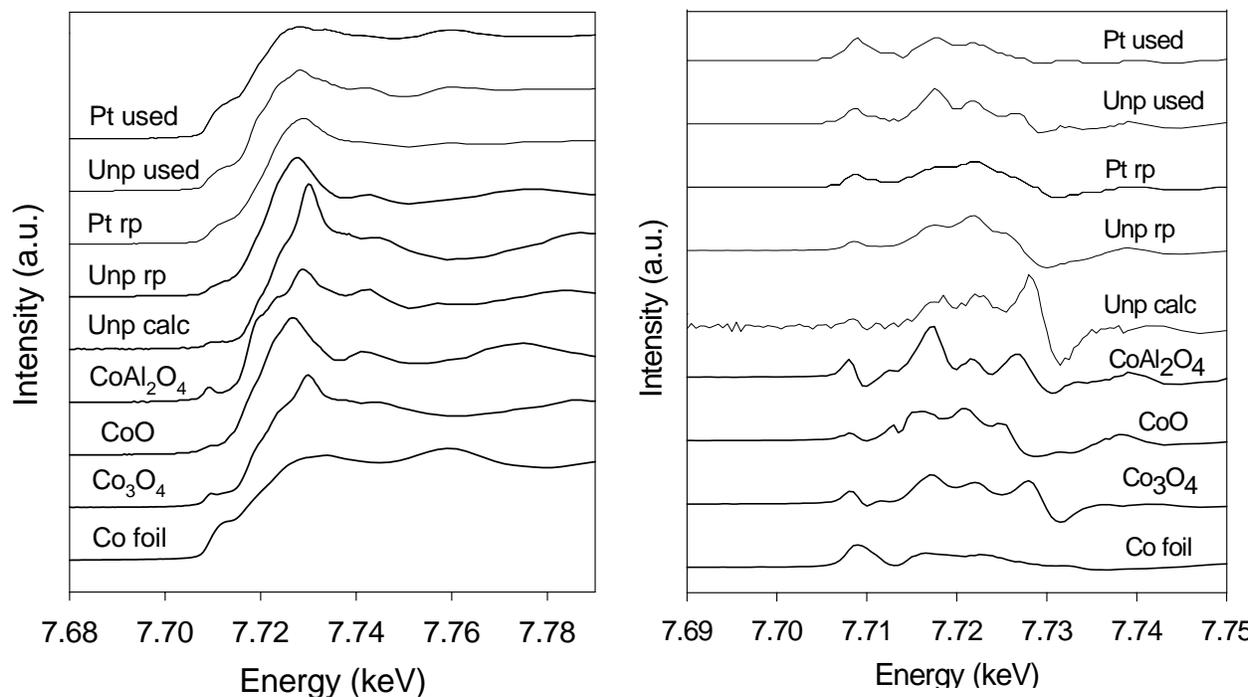


Figure 4: (left) Normalized XANES and (right) XANES derivative profiles for references, calcined, freshly reduced/passivated catalysts, and used catalysts for a comparison of Pt promoted and unpromoted FTS catalysts [rp, reduced/passivated; calc, calcined; unp, unpromoted].

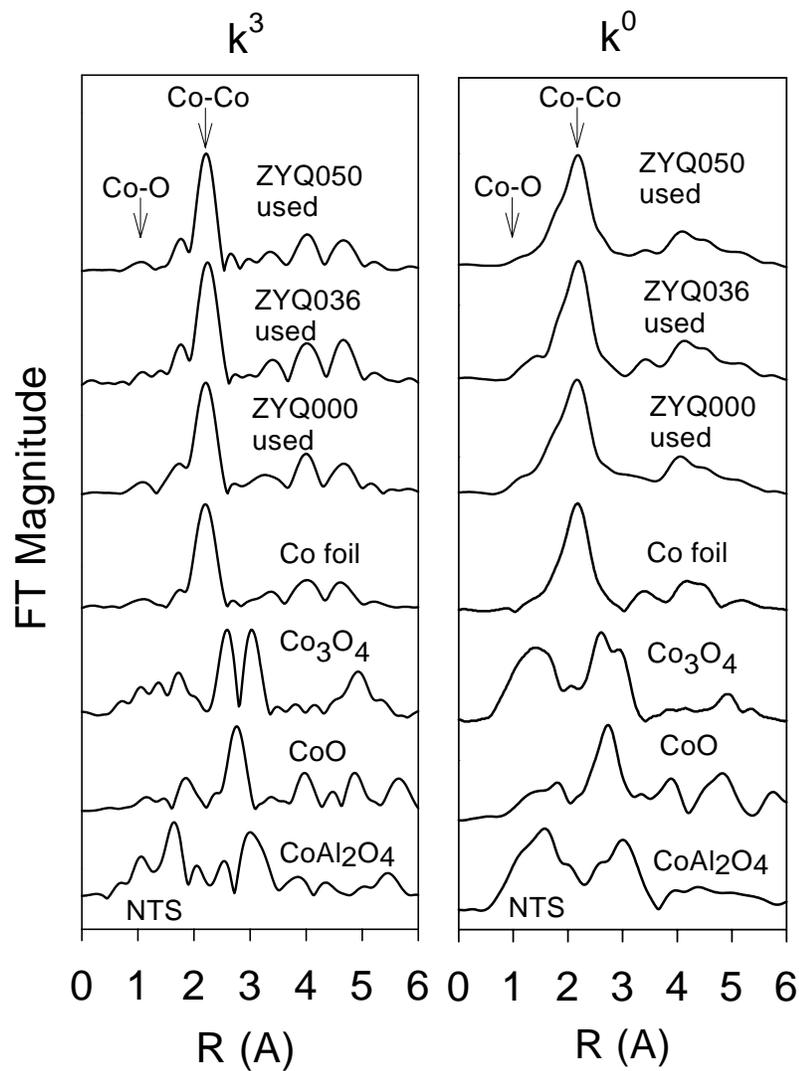


Figure 5. k^3 and k^0 -weighted Fourier transform magnitudes of Co K -edge EXAFS spectra of the used catalysts (unpromoted, ZYQ000; Pt promoted, ZYQ036; Ru promoted, ZYQ050) after Fischer-Tropsch synthesis in the CSTR reactor versus those of comparative standards, including Co metal foil, Co_3O_4 , CoO, and CoAl_2O_4 .

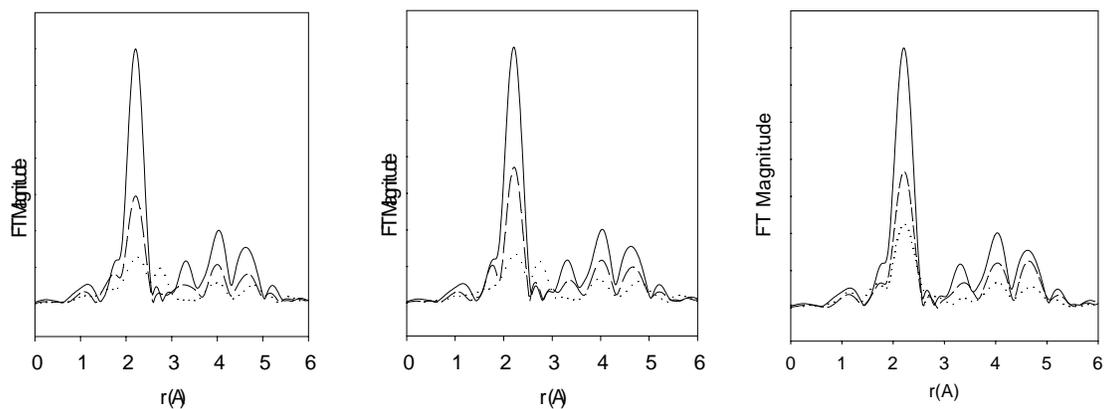


Figure 6. k^3 weighted Fourier transform magnitudes of Co foil (solid), reduced/passivated catalyst (dotted), and used (dashed) catalyst for (left) unpromoted, (center) 0.5% Ru promoted, and (right) 0.5% Pt promoted catalysts.

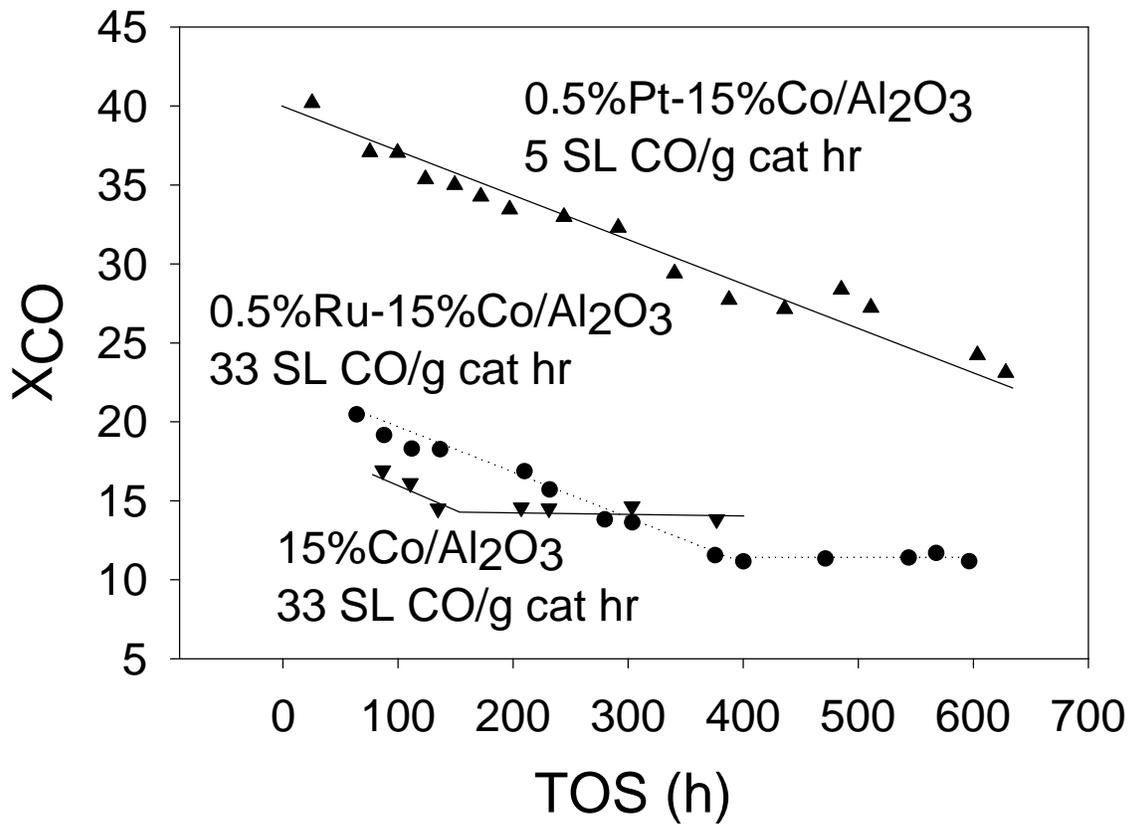


Figure 7. Deactivation of Ru and Pt promoted and unpromoted 15%Co/Al₂O₃ catalysts in during FTS in a CSTR (493K, 1.8 MPa).

E. Cobalt Catalyst Life Testing and Deactivation

Preparation of Cobalt Catalysts

The 15%Co/Al₂O₃ and 1.0%Re-15%Co/Al₂O₃ catalysts were prepared by incipient wetness impregnation of Al₂O₃ (Condea Vista B alumina, BET surface area 200 m²/g, pore volume 0.4 cm³/g) with cobalt nitrate solution. The preparation procedure includes three step impregnations of cobalt salt and then followed by impregnation of promoter. 25%Co/Al₂O₃ and 0.5%Pt-15%Co/Al₂O₃ were prepared by slurry impregnation method using Catalox-Sba-150 (Condea Vista) alumina support. The volume of impregnation solution was 2.5 times of the pore volume of the support. The catalysts were dried and calcined immediately at 400°C in the flow Air and Helium.

Pretreatment of the catalysts

The catalysts were pretreated first ex-situ and then in-situ, according to the following procedure. The catalysts were reduced ex-situ using 30% H₂ and 70% He (V/V) in a fixed bed reactor at a space velocity of 10,000 GHSV at 350°C. The temperature was ramped to 350°C at 1°C/min and held at 350°C for 10 hours. This reduced catalysts were transferred to CSTR in inert atmosphere. This was accomplished by over pressuring the fixed bed reactor that contain the reduced catalyst and then opening the appropriate valves to force the entire catalyst volume into the CSTR containing startup solvent. The reduction reactor was weighed prior to and after catalyst transfer to ensure that a quantitative transfer of catalyst had been accomplished. The catalyst was then reduced in-situ in the CSTR; the hydrogen was introduced to reactor at atmospheric pressure with the flow rate of 30 SL/hr. The reactor temperature was increased to 230°C at the ramp rate 1°C for 12 hours.

Reaction conditions

~20 g of catalyst was transferred into a 1 liter stirred autoclave which had been charged with 300 g of Polywax 3000. The catalyst was reduced at 230°C in-situ in atmospheric pressure for 10 hours in the flow of hydrogen. After reduction, the reactor temperature was lowered to 180°C and synthesis gas was introduced into the reactor. Then the reactor was pressurized to 275 psig and temperature was slowly increased to 220°C during 3 hours.

Results and discussion

Unpromoted 25%Co/Al₂O₃ catalyst

The activity and deactivation rate of unpromoted 25%Co/Al₂O₃ catalyst at 220°C and 275 psig pressure are shown in Fig. 1. The initial CO conversion at space velocity 5 SL/h/g catalyst is ~35% as compared to 18% CO conversion of unpromoted 15%Co/Al₂O₃ at same space velocity. This catalyst is very stable catalyst and the deactivation rate is ~0.05% CO conversion/week on 1200 hours time on stream at space velocity 5 SL/h/g catalyst. The deactivation rate increases with decrease in space velocity. The deactivation rate is ~1.4% CO conversion/week at space velocity 3 SL/h/g catalyst. After time on stream ~3200 h, the catalysts were regenerated at 230°C for 4 h in the flow of H₂ and Ar. The activity of the catalysts increases slightly after regeneration but rate activation rate very high as compared to nonregenerated catalysts at same space velocity.

Pt promoted 0.5%Pt-25%Co/Al₂O₃ catalyst

The activity and rate of loss of activity of Pt promoted 0.5%Pt-25%Co/Al₂O₃ catalyst at 220°C and 275 psig pressure are shown in Fig. 2. The initial activity of Pt promoted catalyst is higher than the unpromoted 25%Co/Al₂O₃ catalysts but the deactivation rate is more in case of Pt promoted catalyst as compared to unpromoted 25%Co/Al₂O₃ catalysts. The initial activity of 0.5%Pt-25%Co/Al₂O₃ catalyst is ~38% CO conversion at space velocity 8 SL/h/g catalyst. The deactivation rate at space velocity 8 SL/h/g catalyst is found to be ~3.2% CO conversion/week.

The catalyst was regenerated at 280°C for 24 h in flow of H₂ and Ar. After regeneration the CO conversion did not increase at all.

1.0%Re-15%Co/Al₂O₃ catalyst

This catalyst run was performed to know the effect of start up solvent. It was found that polywax 3000 is the better start up solvent than the C-30 oil. The partial pressure of C-30 oil is much higher than the polywax 3000, apparently the C-30 oil evaporated more when the space velocity is relatively high which caused the liquid level drop in the autoclave. Therefore the catalyst particles stuck on the wall of the reactor and did not make the contribution to the Fischer Tropsch reaction. The activity and deactivation rate of 1.0%Re-15%Co/Al₂O₃ catalyst are shown in Fig. 3. This catalyst is very stable when the polywax 3000 is used as start up solvent at the CO conversion level ~50% and space velocity 2 SL/h/g catalyst and the deactivation rate is ~0.98% CO conversion/week. The regeneration of catalyst was performed at 280°C for 24 h in the flow of H₂ and Ar. The CO conversion increases slightly after regeneration but the deactivation rate is more as compared to unregenerated catalysts.

Effect of Reduction temperature of unpromoted 15%Co/Al₂O₃ catalyst

15%Co/Al₂O₃ catalyst was reduced at 350°C and 500°C, respectively to study the effect of reduction temperature. The results are shown in Figs. 4 and 6. It seems that the increase in reduction temperature increases the CO conversion from 16% to 26%. The results of the degree of reduction and chemisorption indicated that 57% of cobalt oxide has been reduced to metallic cobalt at 500°C and only 30% was reduced at 350°C. The average particle size of cobalt changed from 5.9 nm to 6.2 nm. But the overall metal dispersion is almost same at 350°C and 500°C reduction. As the percentage reduction of cobalt oxide is more at 500°C reduction, the overall availability of surface cobalt sites increased therefore leads to higher activity. Similarly, 25%Co/Al₂O₃ catalyst was reduced at 350°C and 450°C, respectively and the activity was tested.

The activity and the deactivation rates are shown in Figs. 1 and 5. The deactivation rate for 500°C reduction is more (~4.33% CO conversion/week) than 350°C reduction (0.05% CO conversion/week). The smaller clusters are reduced high temperature and those smaller clusters could be oxidized easily during the Fischer Tropsch synthesis therefore caused deactivation.

Fig. 1 : Activity of 25%Co/Al₂O₃ catalyst at 220°C and 275 psig (Reduced at 350°C)

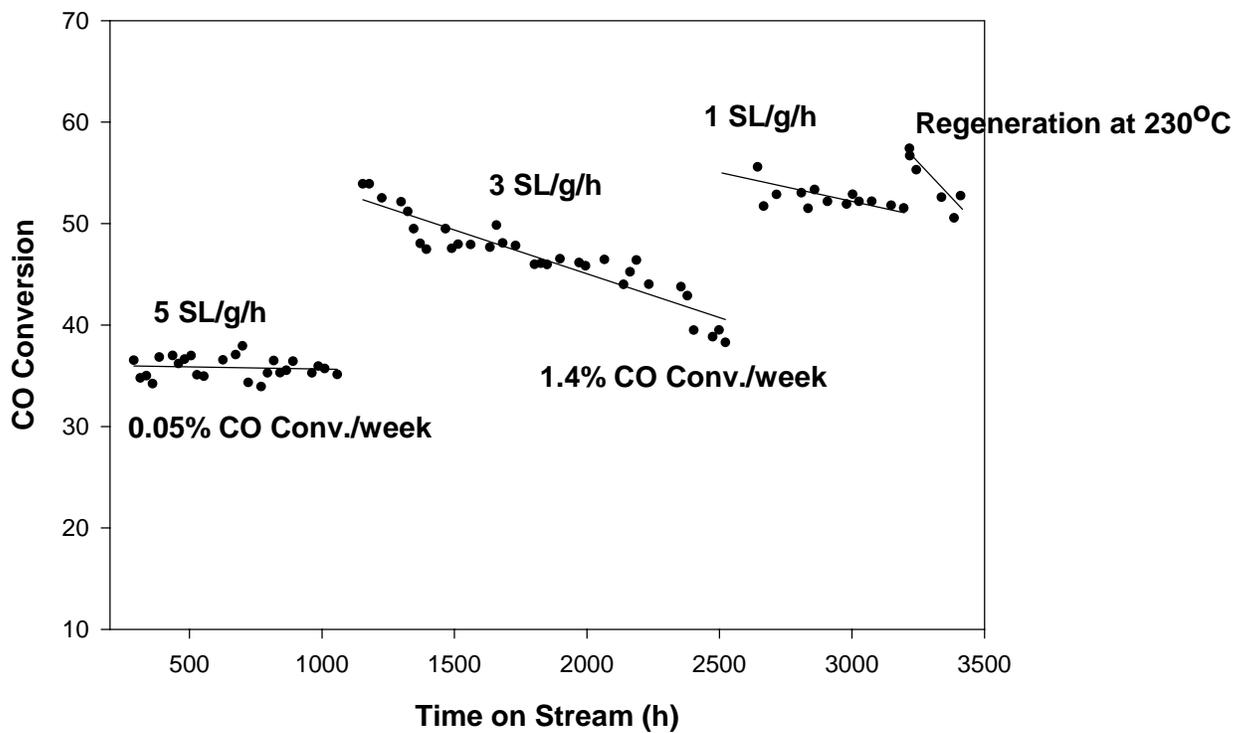


Fig. 2 : Activity of 0.5%Pt-25%Co/Al₂O₃ catalyst at 220^oC and 275 psig

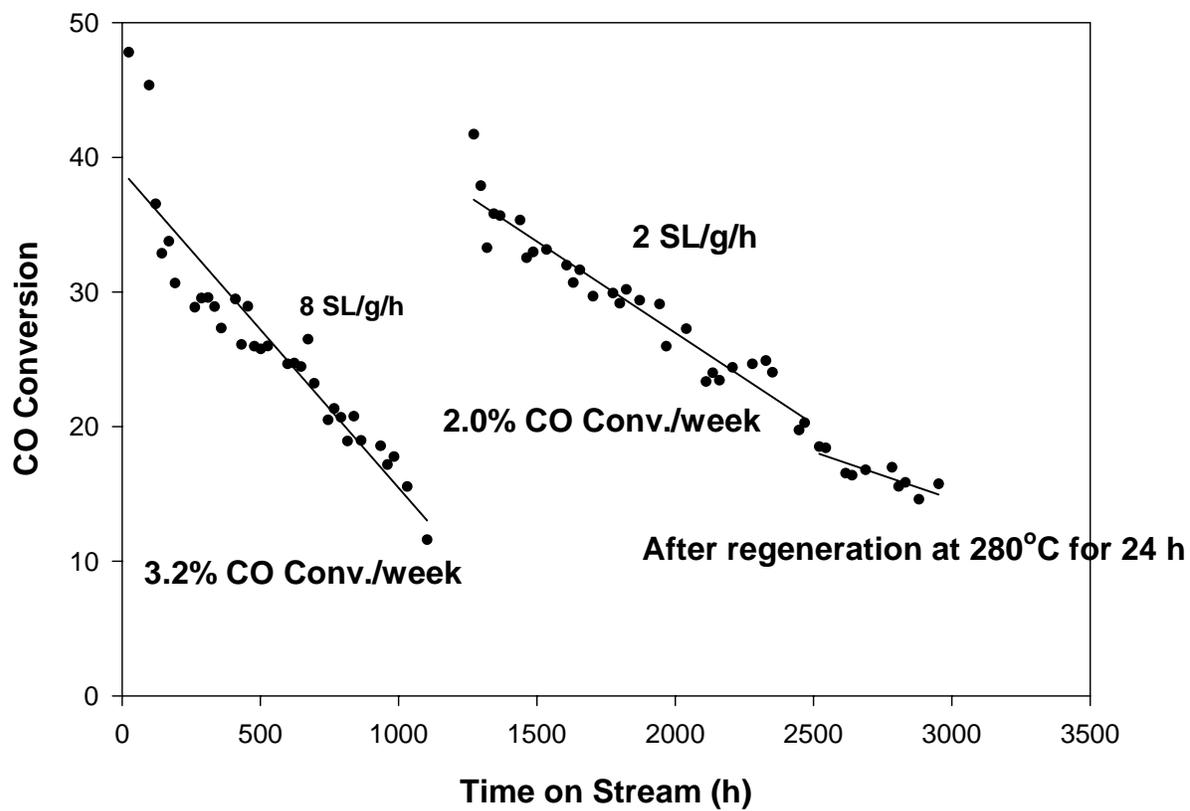
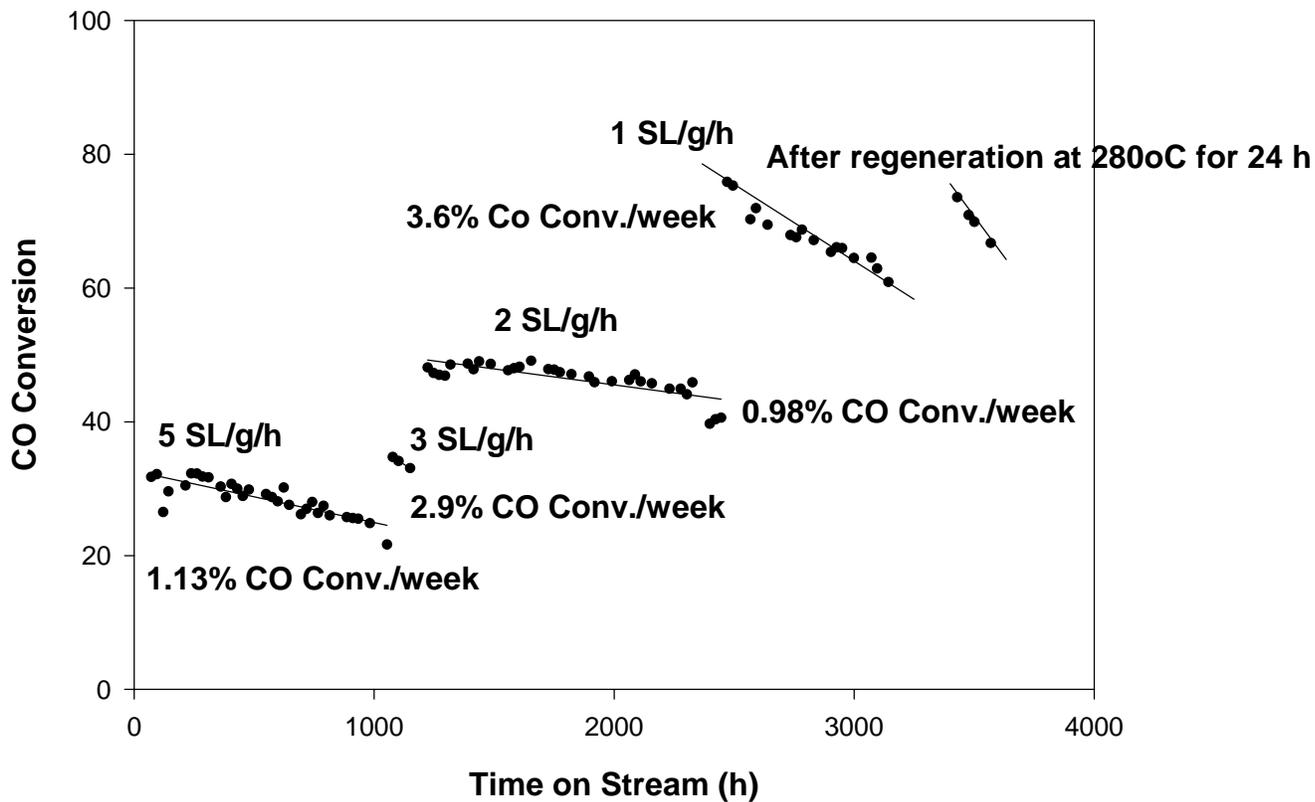
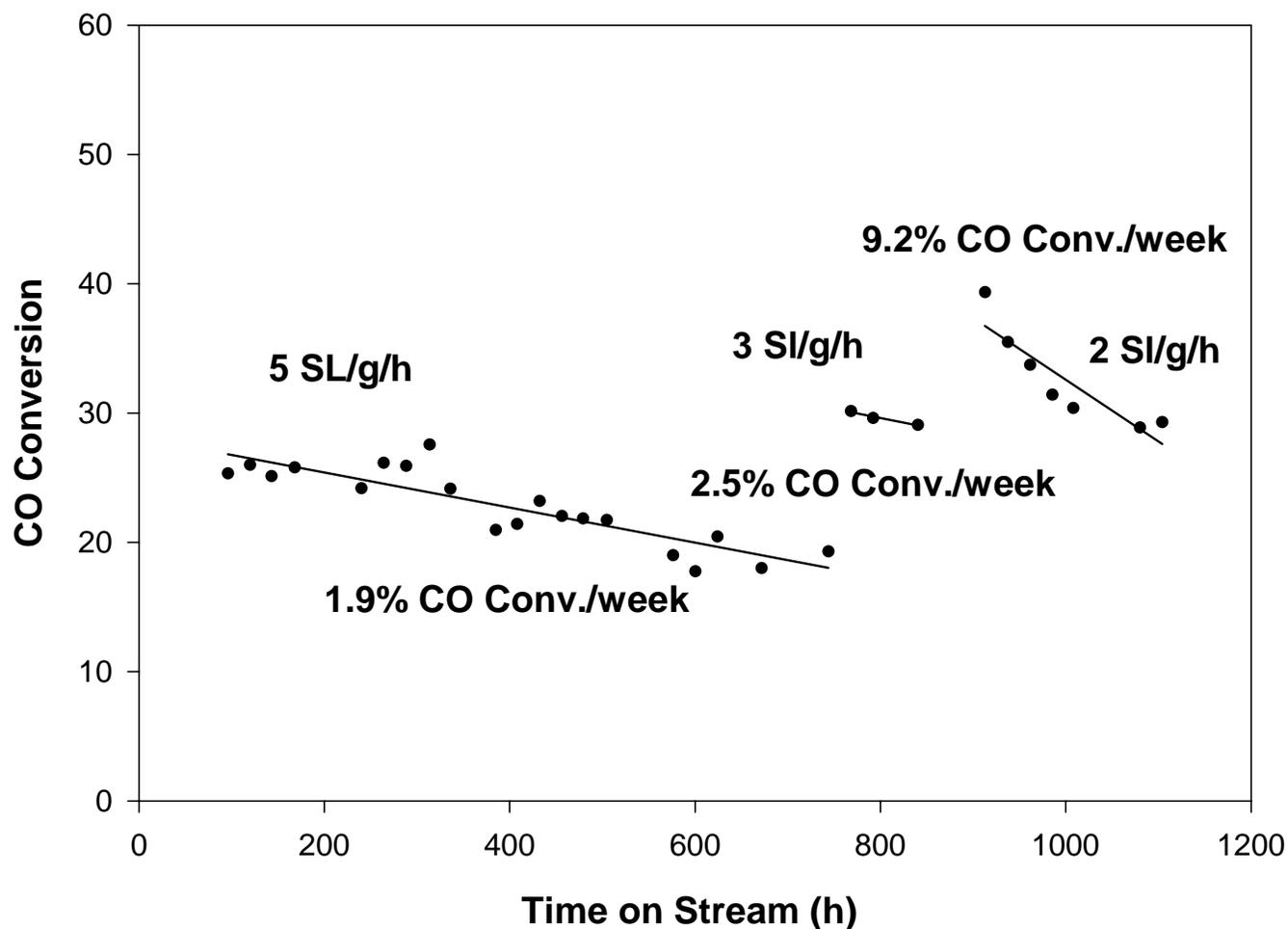


Fig. 3 : Activity of 1.0%Re-15%Co/Al₂O₃ catalyst at 220°C and 275 psig



**Fig. 4 : Activity of 15%Co/Al₂O₃ catalyst reduced at 500°C
(Temp. 220°C and Pressure 275 psig)**



**Fig. 5 : Activity of 25%Co/Al₂O₃ catalyst reduced at 450°C
(Reaction Temp. = 220°C, Press. = 275 psig)**

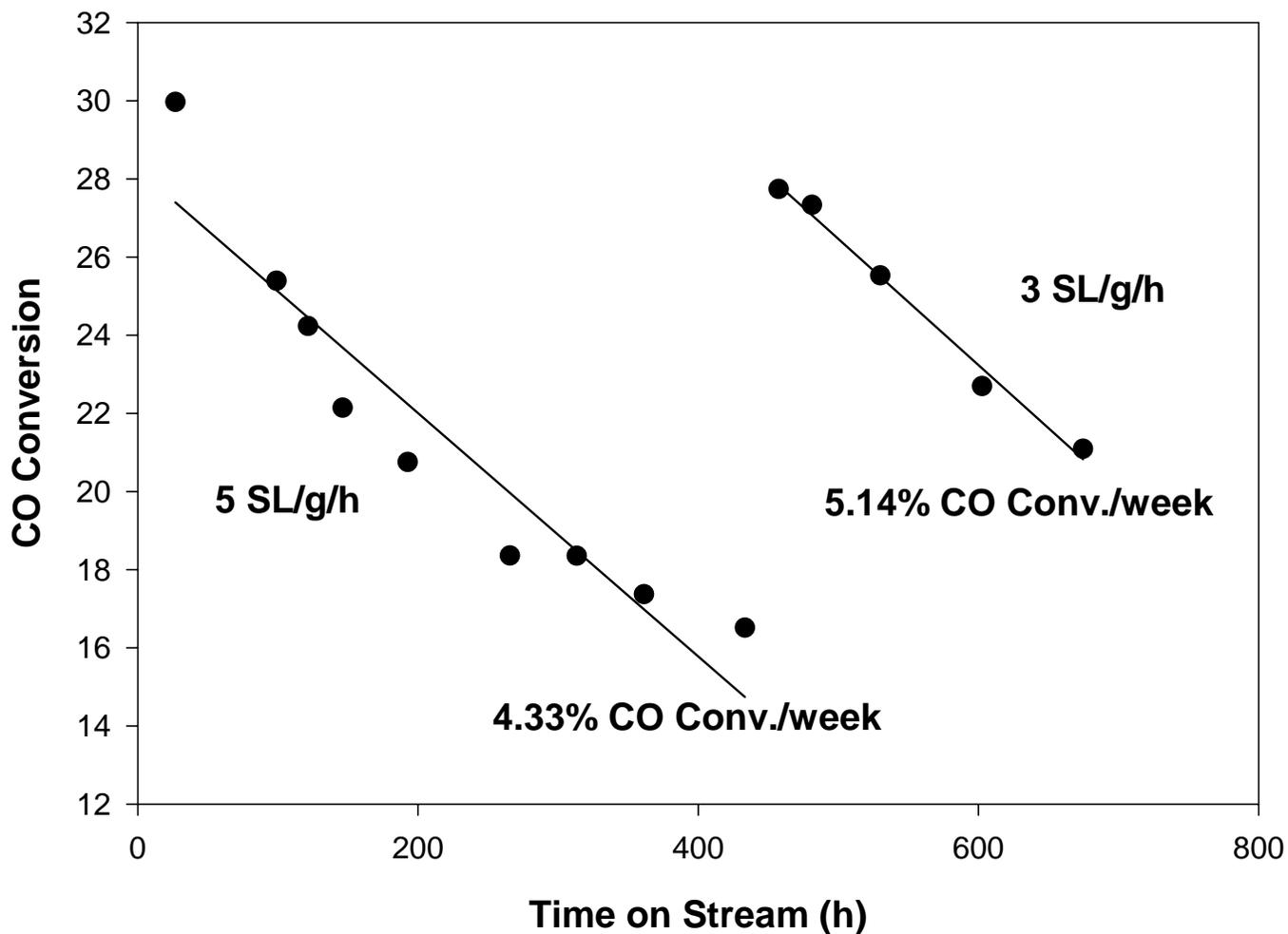
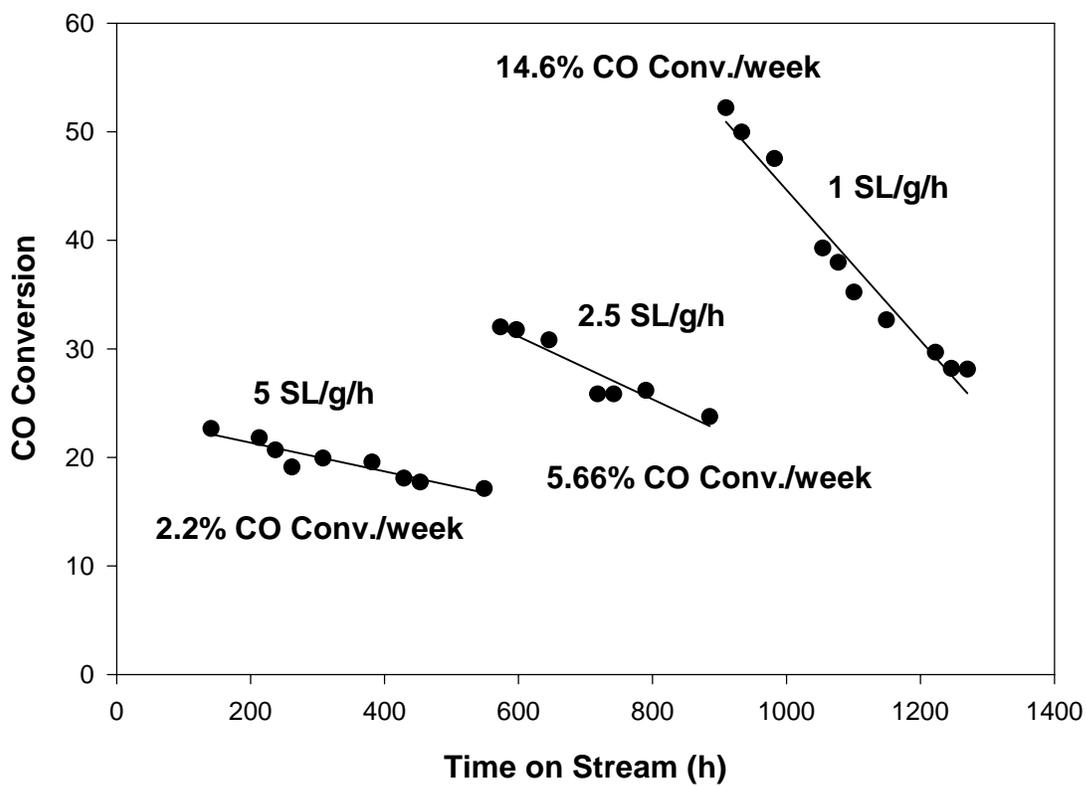


Fig. 6 : Activity of 15%Co/Al₂O₃ catalyst at 220°C and 275 psig(Reduced at 350°C)



F. Fischer-Tropsch Synthesis: Effect of water on the catalytic properties of a Co/SiO₂ catalyst

Abstract

The effect of water on the catalytic properties of a Co/SiO₂ catalyst (12.4 wt%) during Fischer-Tropsch (FT) synthesis was investigated in a continuously stirred tank reactor (CSTR) using two approaches: (1) changing the space velocity to change the CO conversion and therefore the water partial pressure and (2) by adding varying amounts of water into the feed gas. Even at a space velocity of 1 SL/gcat./h at a CO conversion of about 75%, the catalyst displayed very high stability. The addition of water in the range of 5 to 25% (vol.%) increased the CO conversion. Continuous addition of small amounts of water (5 vol.%) over a period of days caused an increase of CO conversion and did not have a significant effect on the catalyst deactivation; however, for larger amounts of water, continuous addition resulted in a severe catalyst deactivation.

Keywords: silica, cobalt, Fischer-Tropsch synthesis, synthesis gas conversion, deactivation, water effect

Introduction

Supported cobalt catalysts are important for the Fischer-Tropsch (FT) synthesis of long chain hydrocarbons from synthesis gas. The effect of water on iron-based Fischer-Tropsch catalysts has been investigated widely and it is well known that water may reoxidize iron catalysts during synthesis [1]. The effect of water on cobalt catalysts is less well understood. In a previous study [2], we have investigated the effect of water on the catalytic properties of a Pt promoted Co/Al₂O₃ catalyst during Fischer-Tropsch synthesis in a continuous stirred tank reactor (CSTR) by (1) varying the conversion through changes of the space velocity and (2) by including additional water in the feed gas. At higher space velocities (> 2 SL/gcat./h), the catalyst was exposed to low water partial pressures and exhibited stable activity. The runs with lower space

velocities with the alumina supported catalyst resulted in higher water partial pressures and higher catalyst deactivation rates. The addition of small amounts of water slightly decreased CO conversion and the effect was reversible. Increasing the amount of added water to provide $P_{H_2O}/P_{CO} \sim 1$ in the feed resulted in permanent deactivation of the catalyst. Hilmen et al. [3,4] studied the effect of water on Co/Al₂O₃ and CoRe/Al₂O₃ catalysts by adding water to the synthesis gas feed and by model studies exposing the catalysts to H₂O/H₂. It was found that the catalysts deactivated when water was added during Fischer-Tropsch synthesis and the catalysts oxidized in H₂O/H₂ mixtures with a ratio much lower than expected for oxidation of bulk cobalt. On silica supported cobalt catalysts, the addition of water to the synthesis gas feed has been shown to slightly decrease the CO conversion [5]. Schulz et al. [6] investigated the effect of water addition on Co/Ru/ZrO₂/Aerosil and Co/MgO/ThO₂/Aerosil catalysts and found that CO conversion was not influenced significantly and, remarkably, the product selectivity was improved when water was added to the feed. Schulz et al. [7] even found increased activity. Kim et al. [8,9] also reported increased activity for a Re promoted and an unpromoted Co/TiO₂ catalysts and for an unsupported cobalt catalyst as a result of addition of water during the Fischer-Tropsch synthesis. In contrast, Li et al. [10] found that water decreased CO conversion of a Co/TiO₂ catalyst. An explanation that has been offered is that water possibly destroys the strong metal-support interaction (SMSI) effect for titania supported catalysts. In this study, the effect of water on the catalytic properties of Co/SiO₂ Fischer-Tropsch catalyst was investigated and, since the procedures used were similar with those used in our earlier studies with Pt promoted Co/Al₂O₃ and CoTiO₂ catalysts, the results allow a comparison of the support effect as it impacts the influence of water [2] on CO conversion and product selectivity.

Experimental

Catalyst preparation and characterization

A 12.4 wt% Co/SiO₂ catalyst was prepared by two incipient wetness impregnations of a SiO₂ support (PQ Co. CS-2133, BET surface area: 352 m²/g; pore volume: 2.36 cm³/g; average pore size: 12.9 nm) with cobalt nitrate solution. The sample was dried at 333 K for 3 hours, 353 K for 2 hours and 373 K for 5 hours under vacuum. Calcination was not utilized between impregnations.

The catalyst was characterized by BET, TPR, H₂ chemisorption and pulse reoxidation; the methods have been described earlier [11]. BET measurements were conducted for calcined and uncalcined catalysts using a Micromeritics Tri-Star system. Prior to the measurement, the sample was slowly ramped to 433 K and evacuated for 4 hrs to approximately 50 mTorr. Temperature programmed reduction (TPR) profiles of catalysts were recorded using a Zeton Altamira AMI-200 unit. The sample was first purged in flowing argon to remove traces of water. TPR was performed using a 10% H₂/Ar mixture referenced to argon at a flow rate of 30 cm³. The sample was then heated from 323 K to 1073 K using a heating ramp of 10 K/min. The hydrogen chemisorption and reducibility by reoxidation were measured using the Zeton Altamira AMI-200 unit, which incorporates a thermal conductivity detector (TCD). The sample weight was always 0.220 g. The catalyst was reduced using hydrogen at 623 K for 10 hours and cooled under flowing hydrogen to 373 K. The sample was held at 373 K under flowing argon to eliminate physisorbed and weakly bound species prior to increasing the temperature slowly to the reduction temperature. At that temperature, the catalyst was held under flowing argon to desorb the remaining chemisorbed hydrogen until the TCD signal returned to the baseline. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibration pulses of hydrogen in argon. Prior to experiments, the

sample loop was calibrated with pulses of nitrogen in a helium flow and compared against a calibration line produced from data generated using gas tight syringe injections of known amounts of nitrogen into a helium flow.

After TPD of hydrogen, the sample was reoxidized at the activation temperature by injecting pulses of pure oxygen in helium carrier referenced to helium gas. After oxidation of the cobalt metal clusters (when the entire oxygen pulse was observed by the TCD), the number of moles of oxygen consumed was determined, and the percentage reducibility was calculated assuming that Co^0 oxidized to Co_3O_4 .

Reactor system and procedure

An uncalcined catalyst was used for activity testing. The catalyst activation was conducted first *ex-situ* and then *in-situ*, according to the following procedure. The uncalcined catalyst (about 15 g; actual weight accurately known) was placed in a fixed bed reactor and pure hydrogen was introduced at a flow rate of 60 NLh^{-1} (298 K, 0.1 MPa); the reactor temperature was increased from room temperature to 373 K at a rate of 120 Kh^{-1} , then increased to 623 K at a rate of 60 Kh^{-1} and kept at 623 K in a hydrogen flow for 16 h. The catalyst was transferred under the protection of helium to the CSTR to mix with 300 g of melted poly-wax (P.W.) 3000. The catalyst was then reduced *in-situ*. Hydrogen was introduced to the reactor at atmospheric pressure with a flow rate of 30 NLh^{-1} (298 K, 0.1 MPa). The reactor temperature was increased to 553 K at a rate 120 K h^{-1} and maintained at this activation condition for 24 h.

The FTS reactor system has been described earlier [12]. Separate mass flow controllers were used to add hydrogen, carbon monoxide and inert gas at the desired rate to a mixing vessel that was preceded by a lead oxide-alumina containing vessel to remove iron carbonyls. The mixed gases entered the CSTR below the stirrer operated at 750 rpm. Products were continuously removed from the vapor and passed through two traps, one maintained at 373 K and the other at

273 K. The uncondensed vapor stream was reduced to atmospheric pressure through a pressure letdown valve. The gas flow was measured with a bubble-meter and composition quantified using an on-line GC. The accumulated reactor liquid products were removed every 24 hrs by passing through a 2 μm sintered meter filter located below the liquid level in the CSTR. The contents of the 273 K and 373 K traps were combined, the hydrocarbons and water fractions separated, and then each was analyzed by GC. The reactor wax sample was analyzed by a high-temperature GC to obtain a carbon number distribution for $\text{C}_{20}\text{-C}_{80}$ products.

After the activation period, the reactor temperature was decreased to 453 K and the synthesis gas mixture (46.67% H_2 /23.33% CO /30% Ar) was introduced to increase the reactor pressure to 20 atm (2.02 MPa). The reactor temperature was then increased to 483 K at a rate of 10 K h^{-1} . During the entire run, the reactor temperature was 483 K, the pressure was 20 atm (2.02 MPa), and the stirring speed was maintained at 750 rpm. The ratio of H_2 to CO was 2.0. The conversion of carbon monoxide and hydrogen and the formation of products were measured after a period of 24 h at each condition. Conversion was varied using a range of space velocities.

A series of measurements were conducted so that the pressure of carbon monoxide and hydrogen in the feed remained constant and was 70% of the total pressure, with the remainder being argon. A high precision, high pressure ISCO syringe pump was used to add water to the reactor. When water was added, a fraction of the argon was replaced by water. Thus, the sum of water added plus argon partial pressure was always 6 atm (0.606 MPa). The added water, along with the water produced by the reactor, was collected in two traps (a hot and a cold trap) and results were quantified and combined to ensure that the water balance was accurate. The added water is expressed in one of two ways; in the first the water added to the feed is expressed as the percentage of the total feed and in the second it is expressed as the partial pressure in the reactor. The text indicates which is being used.

Results and Discussion

Characterization

Figure 1 shows the TPR profiles for the uncalcined and calcined catalysts. Two peaks are apparent and these are attributed to the reduction of Co_3O_4 to CoO , which then reduces at higher temperatures to metallic Co^0 . The calcination shifted the position of the high temperature peak to a lower temperature, indicating a larger cluster size and therefore a decreased interaction of the cluster with the support [11,13]

Table 1 shows the hydrogen chemisorption data, where dispersion calculations are based on the assumption that the H:Co stoichiometric ratio is 1:1. Without taking into account the amount of oxidized Co remaining after reduction, estimates of dispersion are much lower than the true value, leading to considerable overestimates of the cluster size. For the calcined catalyst, twice the amount of Co was reduced in comparison to the uncalcined sample. After correcting for the percentage reduction, the two catalysts displayed large differences in dispersion and cluster size. The cluster size for the calcined catalyst was 38.2 nm, twice that of the uncalcined catalyst. This was consistent with the results of TPR.

Effect of Space Velocity/Conversion on Deactivation

The effects of space velocity on catalytic properties were investigated by changing the synthesis gas flow rate. Firstly, the catalyst was used at a space velocity of 8 SL/gcat/h, and the catalytic activity was quite stable at this space velocity. The catalyst deactivation rate, based on CO conversion, was only 1.8% per week (0.26% per day). Thus, a space velocity of 8 SL/gcat/h, with a deactivation rate of 0.26% per day, was used as a reference condition. After each period at some other space velocity, the space velocity was again adjusted to 8 SL/gcat/h to compare the conversion change. After several days at the reference flow, 5 vol.% water was added to the feed for 5 days. The water effect will be discussed in the next section. After the water addition was

terminated, the run was continued at a space velocity of 8 SL/gcat./h for a week to re-establish the earlier rate. The catalyst was then utilized with different space velocities (5, 3, 2 and 1 SL/gcat./h). The results are shown in Figures 2 and 3 and Table 2. At higher space velocities (8, 5 SL/gcat./h), the CO conversion increased linearly with increasing space time but deviated from linearity as the space velocity was decreased to lower values (Figure 3). At higher space velocities (SV= 5 and 3 SL/gcat/h), the catalyst did not show an apparent deactivation. Even when the space velocity was decreased to 1 SL/gcat/h, the catalyst showed stability; during a 2 week period at 1 SL/gcat/h, the catalyst did not show a measurable deactivation. This result is completely different from the performance of Pt promoted Co/Al₂O₃ catalyst, which displayed higher deactivation rate at the lower space velocity, and higher water partial pressure [2]. The cobalt metal crystallite size may explain the different effects for these two catalysts. It was found that the average cobalt crystallite size of the alumina supported catalyst was 5.6 nm [2], much smaller than the silica supported catalyst (13.2 nm). The cobalt metal with smaller crystallite size appears to be more easily oxidized by higher partial pressure water to form cobalt oxide and the catalyst deactivates more rapidly [11,13].

Figure 4 shows the effect of space velocity on methane and carbon dioxide selectivities. With decreasing space velocity, methane selectivity decreased slightly while CO₂ selectivity increased slightly.

Effect of Water Addition on the Catalytic Properties

To determine the effect of water on Fischer-Tropsch synthesis with the Co/SiO₂, different amounts of water (5.0 to 25 vol.%) were added into the feed gas at a total space velocity of 8 SL/gcat./h. The partial pressures of the inlet hydrogen and carbon monoxide were kept constant during all periods by use of an inert gas (argon). When water was added it replaced some or all of the argon. After every run with added water, the reaction conditions were changed back to the

standard conditions, but without added water, in order to compare the effect of different amounts of water on the FTS rate. The results are shown in Figure 5 and Table 3. In the range from 5 to 25 vol.% water added ($P_{H_2O}/P_{H_2} = 0.12$ to 0.8 , $P_{H_2O}/P_{CO} = 0.24$ to 1.6), the additional water increased the CO conversion. In order to determine the effect of water addition time on the catalyst activity, a smaller or a larger amount of water (5 or 25 vol.%, respectively) was added continuously into the feed for 96 h. It was found that the continuous addition of the smaller amount of water maintained the higher CO conversion in comparison to that without water addition, and did not show a significant effect on the catalyst deactivation rate (Figure 2). The deactivation rate with water addition was 0.36% per day, slightly higher than the value of 0.26%/day without water addition during the initial period (0 to 120 hrs). The deactivation rate, based on the values at the standard condition following the addition of water (150 to 475 hrs. on stream) is 0.37%/day (Figure 5). Thus, the deactivation during the intermittent water addition is about the same as obtained during the constant addition of 5 vol%/water (Figure 2). For the addition of the larger amount of water (25%), CO conversion increased the first day, but the continuous addition of this level of water resulted in rapid deactivation of the catalyst at a rate of 1.5 % per day. More importantly, the catalyst activity was not recovered to the expected value after the addition of water was terminated, indicating that the catalyst had deactivated permanently. It is likely that the cobalt was partially oxidized during the long time exposure to the higher water partial pressure. Furthermore, the activity declined about as rapidly following termination of the addition of 25% water as it did during water addition (Figure 5).

The effects of water partial pressure in the reactor on the catalytic properties are shown in Figures 6, 7, 8 and 9. The CO conversion first increased, then remained nearly constant as P_{H_2O}/P_{CO} was increased to ~ 1 at a constant space velocity (Figure 6). Methane selectivity

decreased while CO₂ selectivities increased slightly with increasing water partial pressure (Figure 7). The C₂⁼ fraction was not effected, and remained essentially zero over the entire P_{H_2O}/P_{CO} range; the C₃⁼ and C₄⁼ fractions increased slightly with increasing water partial pressures (figure 8).

The effect of water on the silica supported cobalt catalyst is in marked contrast to the alumina supported cobalt catalyst. In our previous studies for Pt-Co/Al₂O₃ catalyst, it was found that water decreased the CO conversion in the range of the water added (3 to 25 vol.%). Increasing the amount of added water to 28 vol.% resulted in a permanent deactivation of the alumina supported catalyst [2]. Water also exhibited a deactivating effect on CO conversion while it was added with the feed for a CoRu/TiO₂ catalyst. However, in this study, water had a positive effect on the CO conversion for the Co/SiO₂ catalyst. Iglesia et. al [14] as well as some early workers [7-9] also found similar results, with water having an accelerating effect on the Fischer-Tropsch reaction for a silica-supported cobalt catalyst. At current, we do not have a reasonable explanation for the support effect. A series of cobalt catalysts prepared with different pore size supports are being tested in our laboratory. There was a slight increase in the C₅+ yield as P_{H_2O}/P_{H_2} increased to about 0.4 and then remained constant (Figure 9).

The impact of water partial pressure on catalyst deactivation is puzzling. The conditions during the period at a space velocity of 1 SL/gcat./hr. (Figure 2) that produces nearly 80% CO conversion provides $P_{H_2O} = 4.99$ atm (0.502 MPa) and $P_{H_2O}/P_{H_2} = 1.6$; under these conditions the catalyst did not lose measurable catalytic activity during a period of about 260 hours. On the other hand, adding water (25%) when operating at a space velocity of 8 SL/gcat./hr. with a CO conversion in the 20-27% CO conversion range to give P_{H_2O}/P_{H_2} of 0.84 and P_{H_2O} of 6.6 atm

(0.667 MPa) caused a rapid loss in catalytic activity during a period approaching 100 hours on stream (Figure 5). These data indicate that it is not P_{H_2O}/P_{H_2} or P_{H_2O}/P_{CO} , that determines whether the catalyst will lose its catalytic activity. The water partial pressure was slightly higher (6.6 atm vs. 5.0 atm) when the catalyst underwent deactivation. Significantly, the catalytic activity continued to decline after the addition of 25% water had been terminated even though the P_{H_2O}/P_{H_2} ratio was now only about 0.08

One could devise a number of possible reasons for the different impact of water on the loss of catalytic activity. The situation is complex and requires much more study. However, it appears that the presence of a reasonably high P_{CO} is necessary if catalyst deactivation is to occur. This suggests that some complex that involves both P_{H_2O} and P_{CO} is involved in the loss of catalytic activity. The formation of a cobalt formate like species is a potential explanation although this is very speculative with the data available.

Another possibility is the formation of cobalt silicates. In a previous TPR study [15], it was shown that hydrothermal treatment of a reduced Co/SiO₂ catalyst with H₂O (and subsequent calcination) led to the formation of both nonreducible and reducible mixed species of Co that interact with the support silica. These species have been referred to as Co-silicates, although their precise identify is not clear. Higher H₂O pressures and extended exposure times led to greater fractions of the cobalt-silica species. Since it is not known what effect the calcination step has on their formation, direct correlation of the results of that study with the results of a catalyst under reaction conditions is speculative. This is supported by a comparison of the differences observed at a H₂O partialpressure of about 5 atm. between the high conversion condition (Figure 2) and the water co-feed experiments (Figure 5). In the latter case, the H₂ partial pressure is higher, and may

result in a greater fraction of reduced Co, which could be more susceptible to interactions with the support in the presence of water. Also, examination of the used catalyst by XANES may provide conclusive evidence in the future. XANES has already been employed to demonstrate the presence of cobalt aluminate species in used Co/Al₂O₃ catalyst samples taken from the reactor and stored in solidified wax [16].

Conclusions

The space velocity and water addition were found to have a significant effect on the properties of a silica supported cobalt catalyst during Fischer-Tropsch synthesis. The short time addition of water in the range of 5 to 25% (vol.%) was found to have a positive effect on the CO conversion. The long time addition of small amounts of water (5 vol.%) increased CO conversion and did not have a significant effect on the catalyst deactivation; however, for larger amounts of water, long time addition resulted in a severe catalyst deactivation.

Acknowledgment

This work was supported by U.S. DOE contract number DE-AC22-94PC94055 and the Commonwealth of Kentucky.

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Table 1							
H ₂ chemisorption and pulse reoxidation results for Co/SiO ₂ catalysts							
Catalyst	Calcination	μmol H ₂ per g	Uncorr %D	Uncorr. Diam (nm)	% Red	Corr. %D	Corr. Diam (nm)
12.4%Co/SiO ₂	None	25.6	3.04	33.9	39	7.79	13.2
12.4%Co/SiO ₂	623K in air	18.2	1.73	59.7	64	2.70	38.2

Table 2			
Effect of space velocity on CO conversion and water partial pressure ^a for Co/SiO ₂			
1/Space Velocity (h gcat/SL)	CO Conversion (%)	Water partial Pressure (atm) ^b	P_{H_2O}/P_{H_2} ^b
0.125	22.1	0.801	0.091
0.200	31.6	1.45	0.194
0.333	45.0	2.60	0.414
0.500	56.9	3.47	0.657
1.000	77.7	4.99	1.589

a. Reaction condition: 483 K, 20 atm, $P_{H_2} + P_{CO} = 14$ atm, H₂/CO=2.0.

b. Based on reactor partial pressure.

Table 3			
Effect of water addition on CO conversion ^a for Co/SiO ₂			
Water Amount Added (volume%)	CO Conversion(%)	Water Partial Pressure atm ^b (MPa)	P_{H_2O}/P_{H_2} ^b
0	22.5	0.967	0.120
5	28.1	2.27	0.290
8	29.2	3.02	0.389
12	28.1	3.96	0.510
15	28.9	4.82	0.627
20	28.6	5.78	0.743
25	27.4 ^c	6.64	0.835
<p>a. Reaction condition: 483 K, 20 atm (2.02 MPa), H₂/CO=2.0, $P_{H_2} + P_{CO} = 14$ atm (1.41 Mpa).</p> <p>b. Based on reactor partial pressure.</p> <p>c. Based on conversion after first day at this condition.</p>			

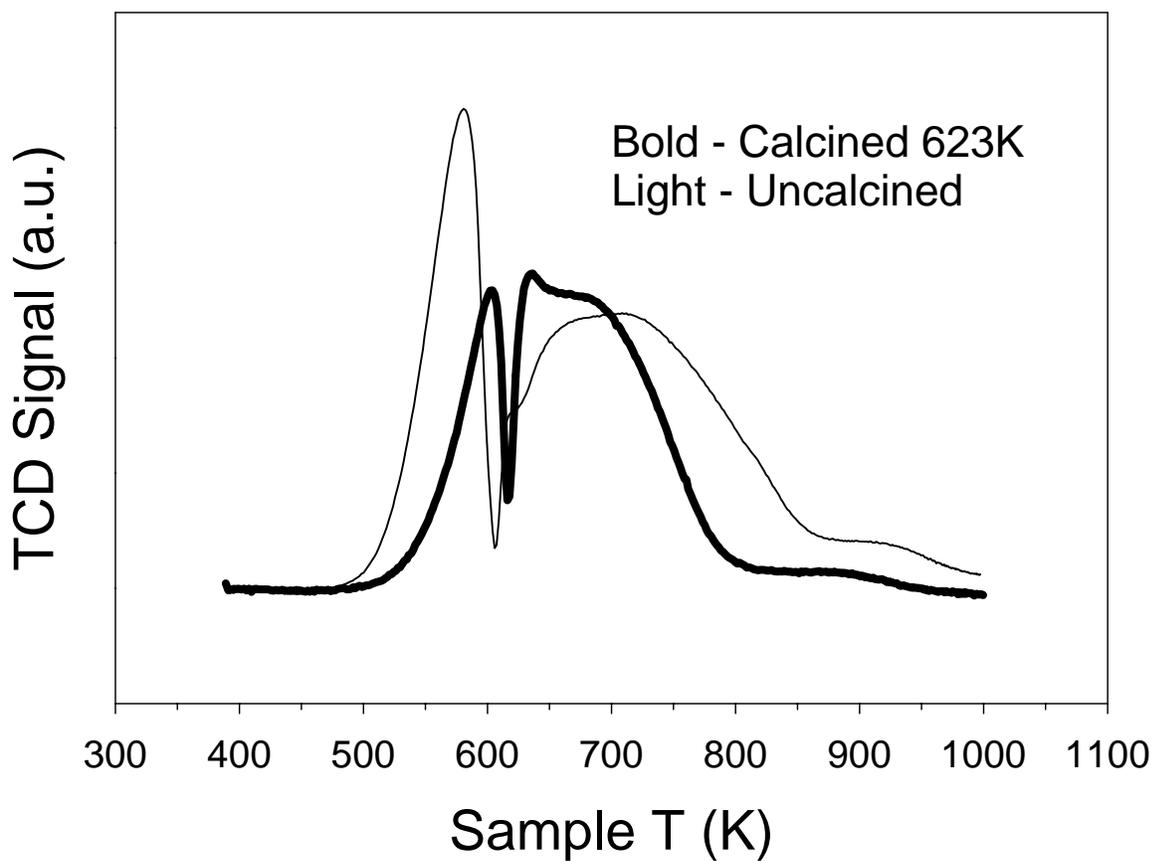


Figure 1. TPR profiles of uncalcined and calcined Co/SiO₂ catalysts.

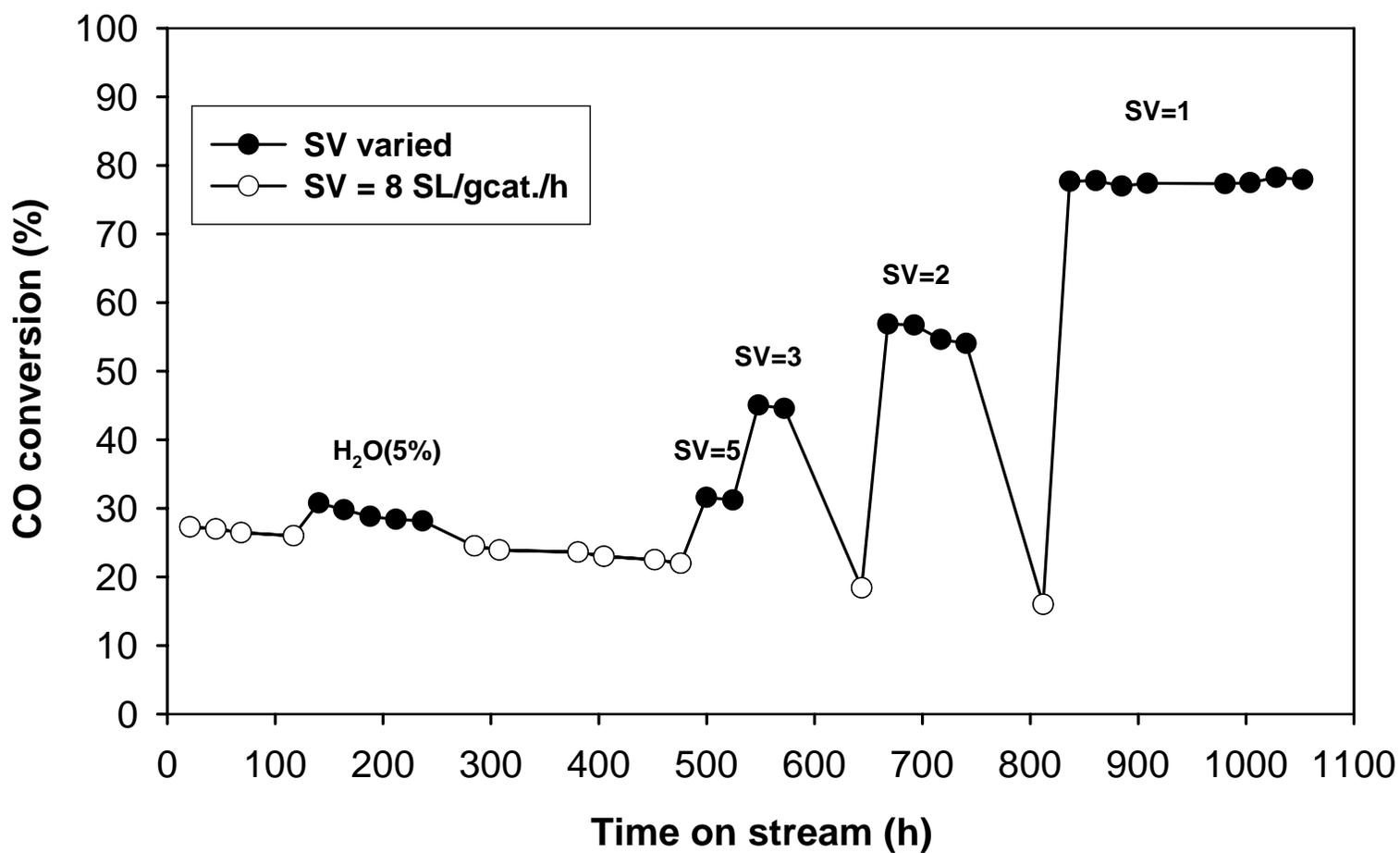


Figure 2. CO conversion as a function of time on stream and space velocity for a Co/SiO₂ catalyst (T = 483 K; P = 20 atm (2.02 MPa); H₂/CO = 2.0).

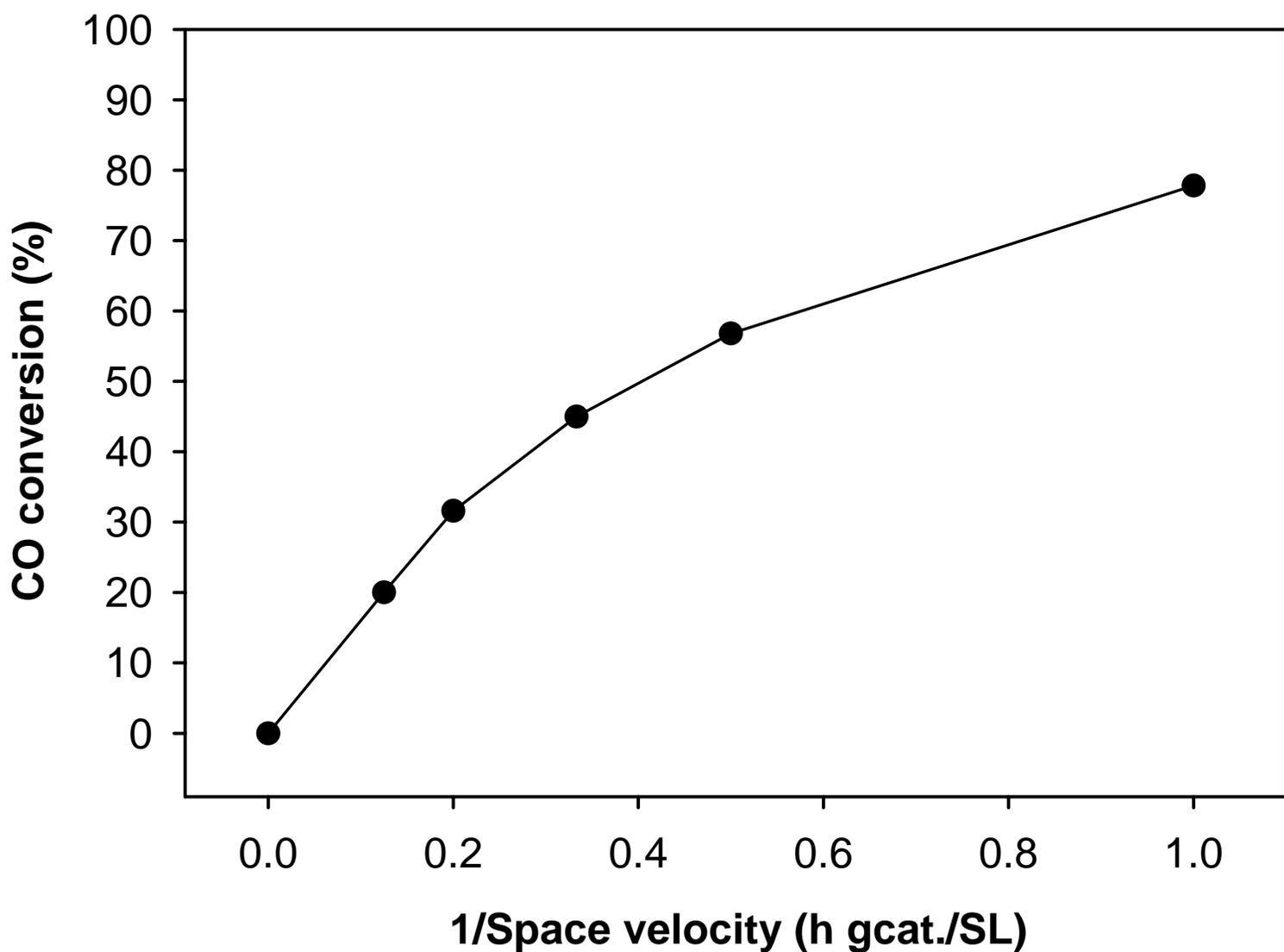


Figure 3. CO conversion as a function of space time for a Co/SiO₂ catalyst [T = 483 K, P = 20 atm (2.02 MPa), H₂/CO = 2.0].

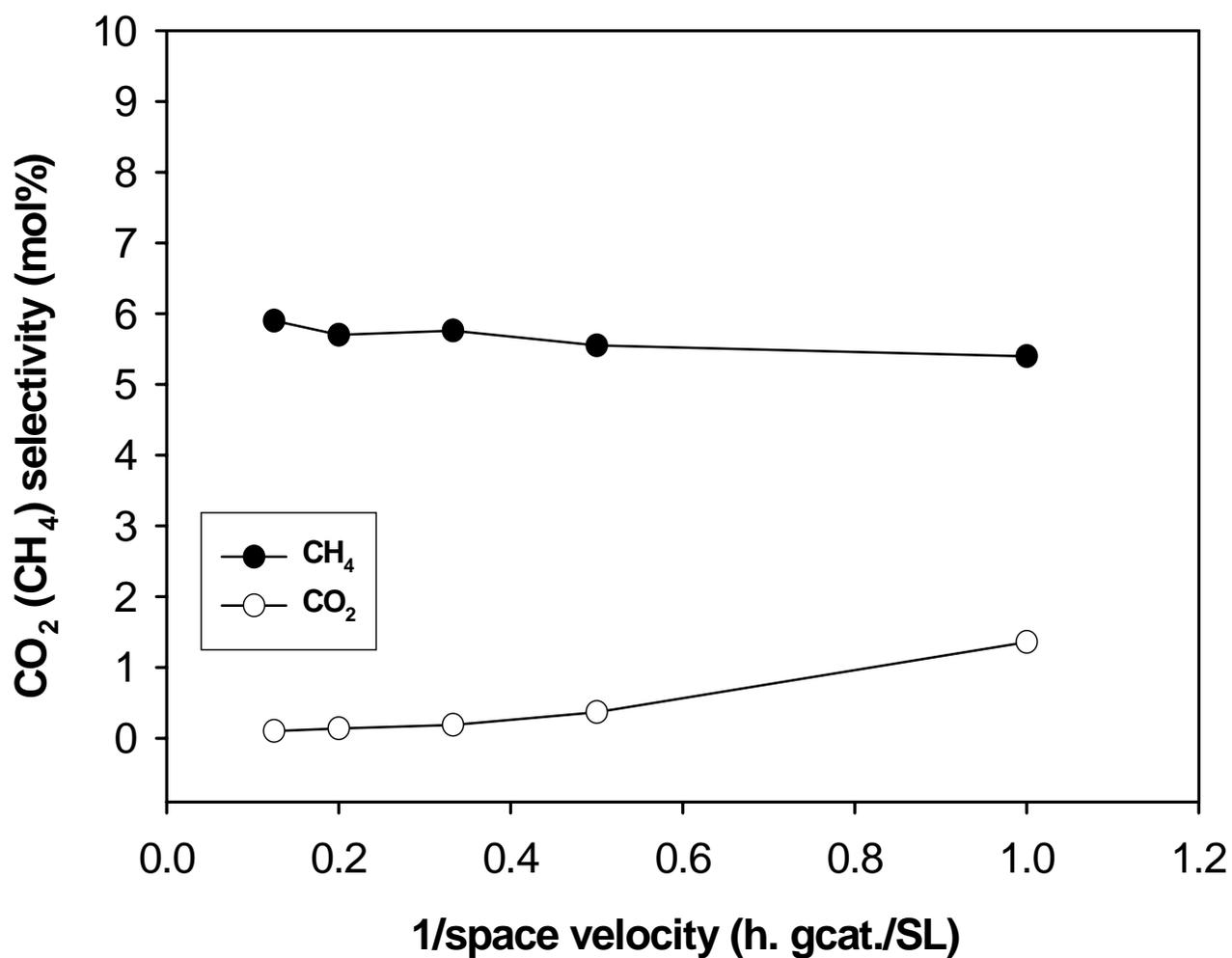


Figure 4. CO₂ and CH₄ selectivity as a function of space time for the Co/SiO₂ catalyst [T = 483 K, P = 20 atm (2.02 MPa), H₂/CO = 2.0].

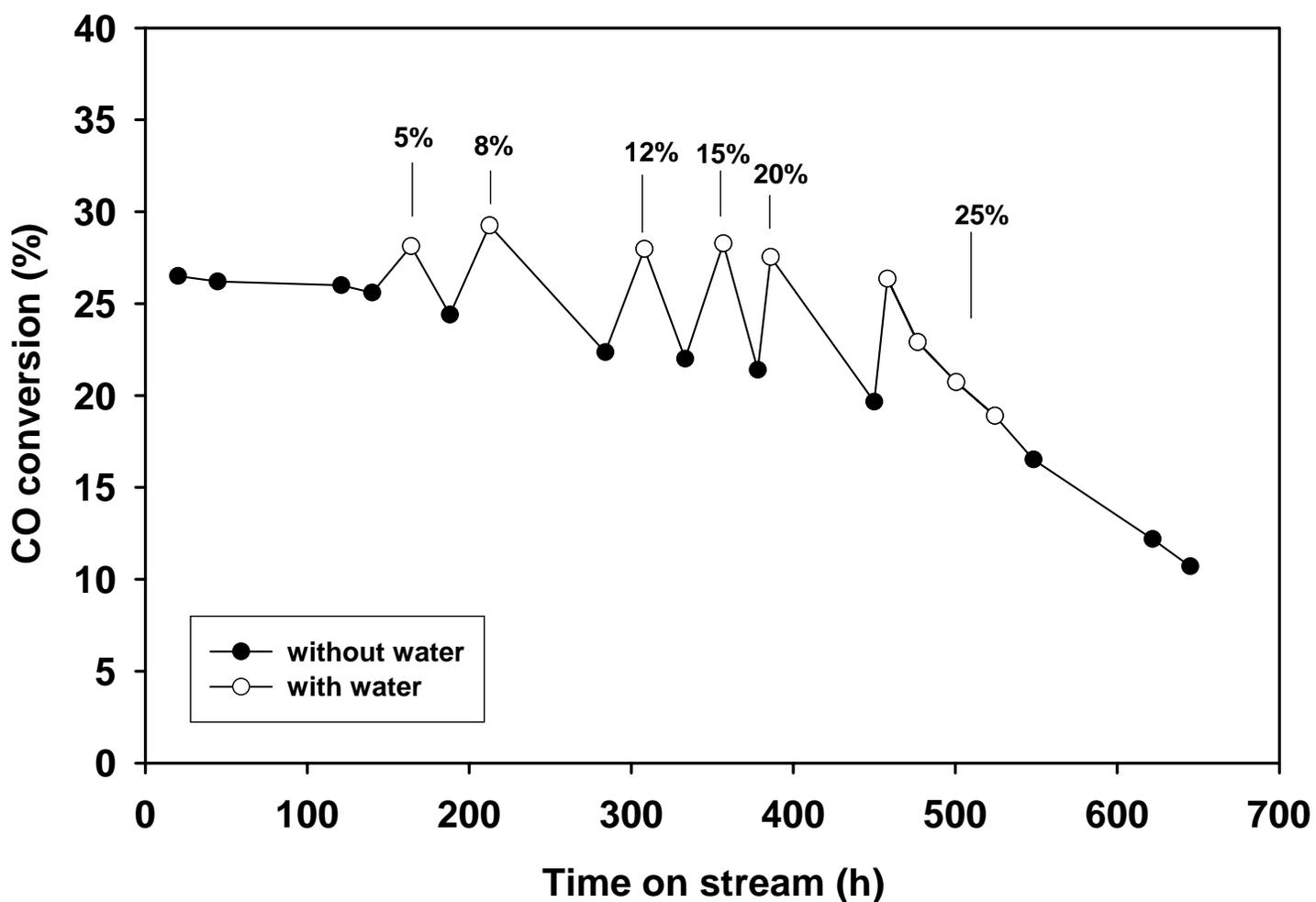


Figure 5. Effect of water on CO conversion for Co/SiO₂ catalyst (T=483K, P=20 atm (2.02 MPa), P_{H₂}+P_{CO}=14 atm (1.41 MPa), H₂/CO=2.0, S.V.=8 SL/gcat.h; % is volume % of total feed).

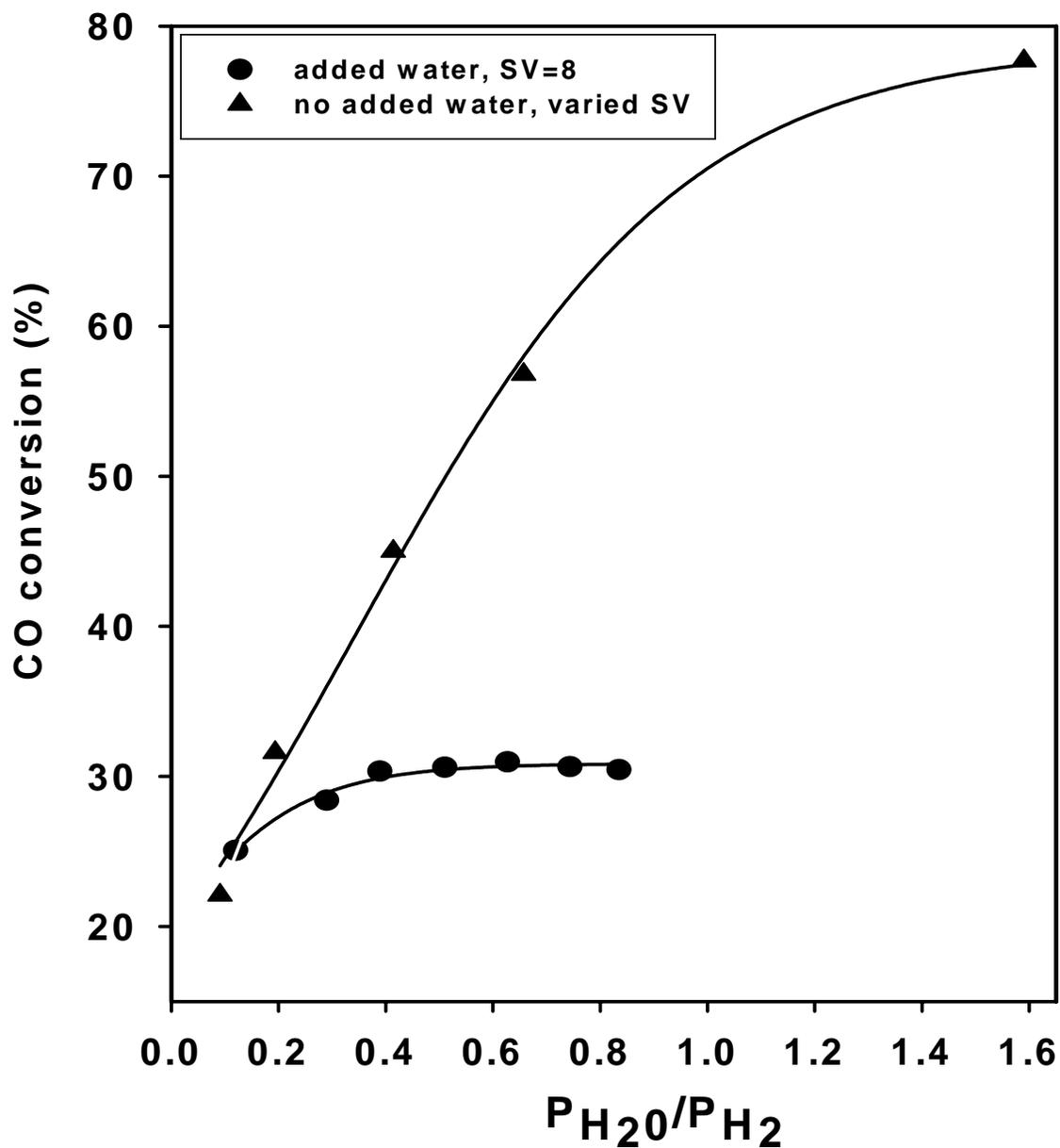


Figure 6. CO conversion as a function of P_{H_2O}/P_{H_2} for Co/SiO₂ catalyst (T = 483K, P = 20 atm (2.02 MPa), $P_{H_2} + P_{CO} = 14$ atm (1.41 MPa), $H_2/CO = 2.0$, partial pressure is based on reactor exit).

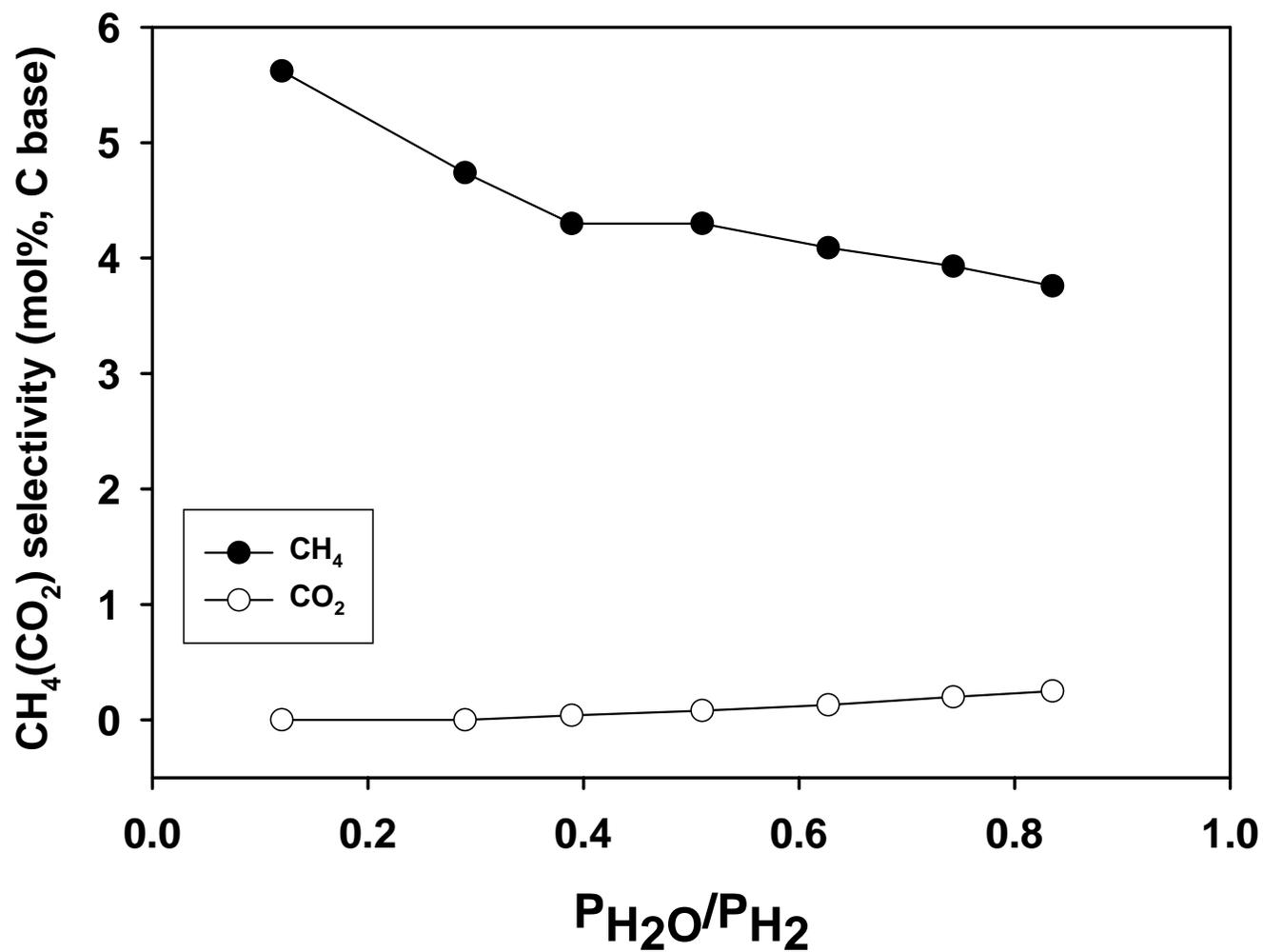


Figure 7. CH₄(CO₂) selectivity as a function of P_{H₂O}/P_{H₂} for the Co/SiO₂ catalyst

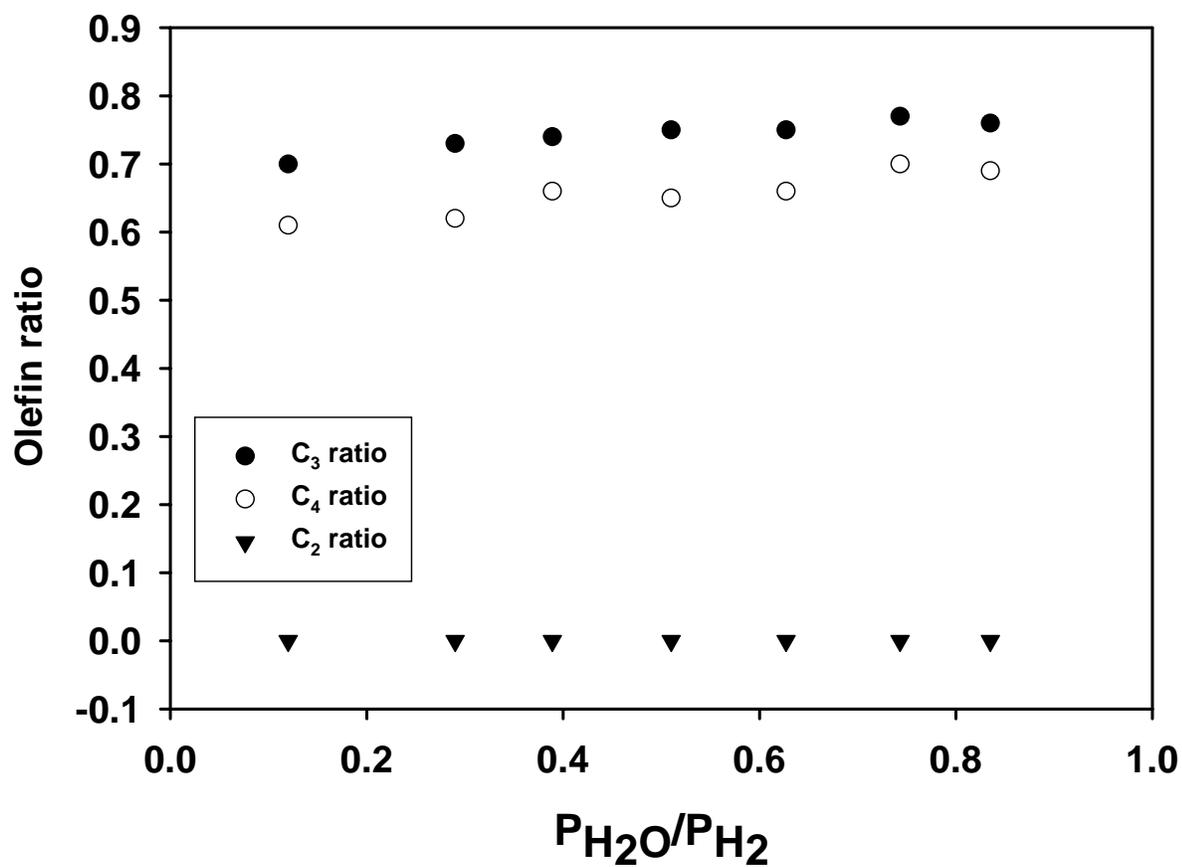


Figure 8. Olefin ratio as a function of P_{H_2O}/P_{H_2} for the Co/SiO₂ catalyst

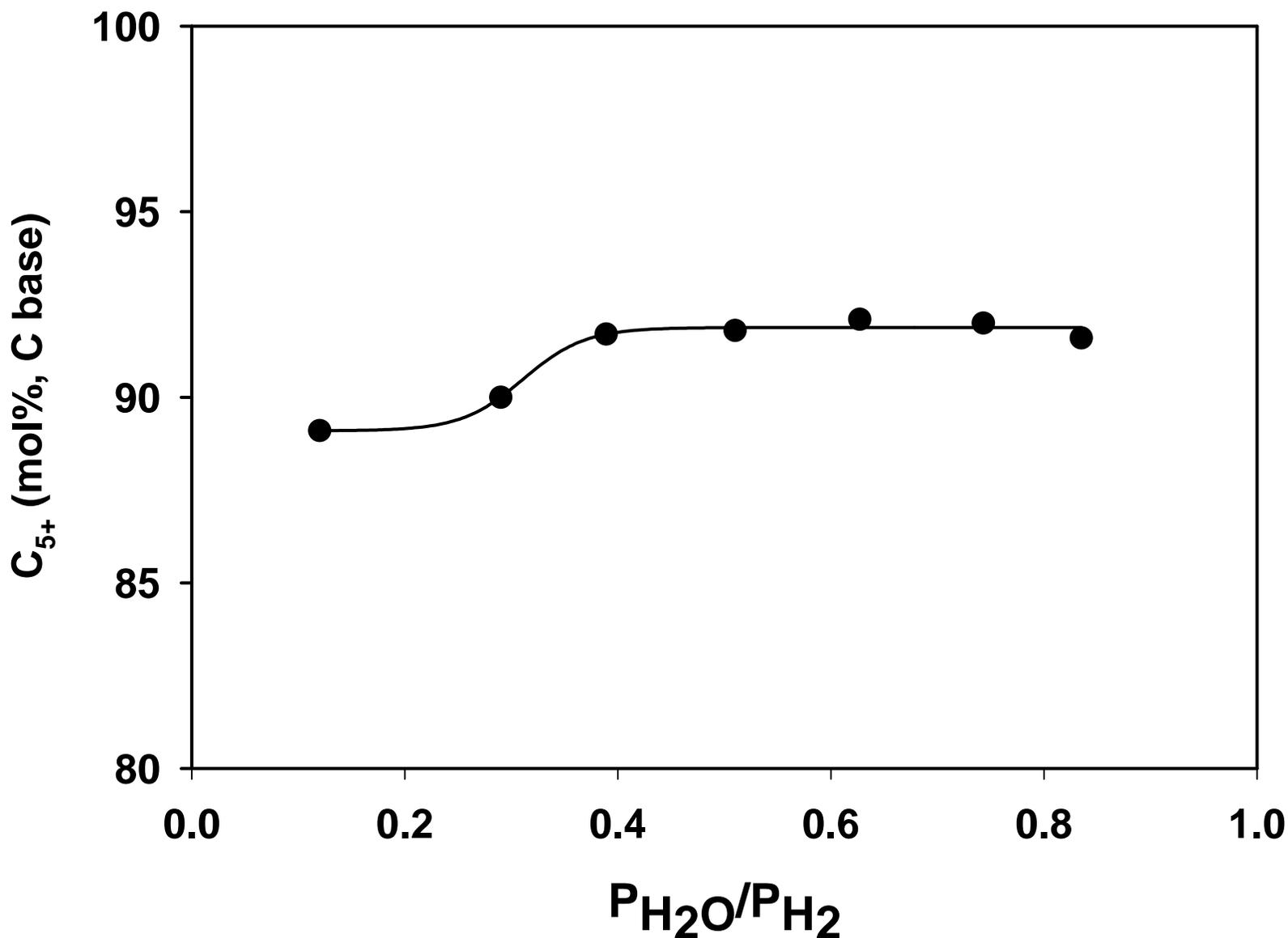


Figure 9. C₅₊ selectivity as a function of P_{H_2O}/P_{H_2} for the Co/SiO₂ catalyst [T=483 K, P=20 atm. H₂/CO=2, SV=8 SL/gcat./h]