

### **Task 5. Oxygenates**

The objective of this task is to obtain a better understanding of the factors that affects catalyst selectivity toward oxygenates for iron-based Fischer-Tropsch catalysts.

No scheduled activity to report.

### **Task 6. Literature Review of Prior Fischer-Tropsch Synthesis with Co Catalysts**

The objective of this task is to prepare a critical review of prior work on cobalt Fischer-Tropsch catalysts.

No scheduled activity to report.

### **Task 7. Co Catalyst Preparation**

The objective of this task is to prepare a limited number of cobalt-based Fischer-Tropsch catalysts that can be used to obtain baseline data on cobalt-based Fischer-Tropsch synthesis.

No scheduled activity to report.

### **Task 8. Cobalt Catalyst Testing for Activity and Kinetic Rate Correlations**

The objective of this task is to conduct initial screening of the cobalt catalysts prepared in Task 7 to select three baseline catalysts that will then be used to generate a data base on the performance of cobalt-based Fischer-Tropsch catalysts in slurry reactors.

#### **A. Effect of Water on the Catalytic Properties of Co/SiO<sub>2</sub> Fischer-Tropsch Catalyst**

##### **Introduction**

Water is one of the products of the Fischer-Tropsch synthesis and will always be present in smaller or larger amounts during synthesis, depending on the conversion, reactor system and catalyst. The effect of water on iron Fischer-Tropsch catalysts has widely been investigated and it is well know that water may reoxidize iron catalyst during synthesis. The effect of water on cobalt catalysts is less well understood. In previous study, we have investigated the effect of water on the catalytic properties of a Pt promoted Co/Al<sub>2</sub>O<sub>3</sub> catalyst during Fischer-Tropsch synthesis in a CSTR by (1) varying the conversion through changes of the space velocity and (2)

by including additional water into the feed gas and found that at higher space velocity ( $> 2$  SL/gcat./h), the catalyst was exposed to low water partial pressures and exhibited stable activity. The runs with lower space velocities 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  $P_{\text{H}_2\text{O}}/P_{\text{CO}} \sim 1$  in the feed resulted in a permanent deactivation of the catalyst. In this study, we will report the results of the effect of water on the catalytic properties of Co/SiO<sub>2</sub> Fischer-Tropsch catalyst. The procedures used were similar with those used for the Co/Al<sub>2</sub>O<sub>3</sub> catalyst.

## Experimental

The catalyst used was 21.9 wt% Co/SiO<sub>2</sub>, prepared by two time incipient wetness impregnation of SiO<sub>2</sub> support (PQ Co. CS-2133) with cobalt nitrate solution. The sample was dried at 60 °C for 24 hours. No calcination procedure was utilized.

The catalyst activation was conducted first *ex-situ* and then *in-situ*, according to the following procedure. The catalyst (about 15 g) was placed in a fixed bed reactor and pure hydrogen was introduced at a flow rate of 60 NLh<sup>-1</sup> (298 K, 0.1 MPa); the reactor temperature was increased from room temperature to 373 K at a rate of 120 Kh<sup>-1</sup>, then increased to 623 K at a rate of 60 Kh<sup>-1</sup> and kept 623 K 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*. The hydrogen was introduced to the reactor at atmospheric pressure with a flow rate of 30 NLh<sup>-1</sup> (298 K, 0.1 MPa). The reactor temperature was increased to 553 K at a rate 120 K h<sup>-1</sup> and maintained at this activation condition for 24 h.

After the activation period, the reactor temperature was decreased to 393 K and synthesis gas mixture (46.67% H<sub>2</sub>/23.33% CO/30% Ar) was introduced to increase the reactor pressure to 20 atm. The reactor temperature was then increased to 483 K at a rate of 10 Kh<sup>-1</sup>. During the entire run the reactor temperature was 483 K, the pressure was 20 atm, and the stirring speed was

maintained at 750 rpm. The ratio of reactants H<sub>2</sub> to CO was 2.0. The conversion of carbon monoxide and hydrogen and the formation of products were measured during a period of 24 h at each condition.

A series of measurements were conducted so that the pressure of CO and H<sub>2</sub> in the feed remained constant and was 70% of total pressure, with the remainder argon. 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. For these runs, the added water is then expressed as the fraction of argon that it has replaced. 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 indicated which is being used.

## **Results and discussion**

### 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, we run this catalyst at a space velocity of 8 SL/gcat./h and found that the catalyst 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, the run at 8 SL/gcat./h with a deactivation rate of 0.26% per day was used as a reference. After each period at some other space velocity, the space velocity was again adjusted to 8 SL/gcat./h to compare the conversion changes. The results are shown in Figure 1, 2 and Table 1. At higher space velocities (8, 5 SL/gcat./h), the CO conversion increased linearly with increasing space time. Continuing to decrease space velocity, the curve slightly bent down (Figure 2). Space velocity was also found to have a significant effect on the catalyst deactivation. At higher space velocities (SV= 5 and 3 SL/gcat./h), the catalyst did not show an apparent deactivation. When the space velocity was decreased to 2 SL/gcat./h, the catalyst started to deactivate, the average deactivation was 0.70% per day, two times higher than the reference deactivation rate. However,

when the space velocity was decreased to 1 SL/gcat./h, the catalyst showed a higher stability, after running for 2 weeks at 1 SL/gcat./h, the catalyst did not show an apparent deactivation. This result is completely different with the performance of Pt promoted Co/Al<sub>2</sub>O<sub>3</sub> catalyst, which displayed higher deactivation rate at the lower space velocity. It may be due to the effect of support.

The water partial pressure and the ratio of  $P_{H_2O}$  to  $P_{H_2}$  displayed similar trends with CO conversion as expected (Table 1). With decreasing space velocity, methane selectivity slightly decreased and CO<sub>2</sub> selectivity slightly increased (Figure 3).

#### Effect of water addition on the catalytic properties

To determine the effect of water on Fischer-Tropsch, different amount 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 H<sub>2</sub> and CO were kept constant during all periods by use of an inert gas (argon). When water was added it replaces some argon. After every run with added water, the reaction conditions were changed back to the same 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 4 and Table 2. In all the range of 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 addition of water increased the CO conversion. In order to determine the effect of water addition time on the catalyst activity, the smaller or larger amount of water (5 or 25 vol.%) was continuously added into the feed for 96 h, respectively. It was found that the long time addition of smaller amount of water did not show significant effect on the CO conversion and the catalyst deactivation rate. For the addition of the larger amount of water (25%), CO conversion was increased in the first day, but the long time addition resulted in a severe and irreversible deactivation of the catalyst. The deactivation rate was 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. The reason

may be that the cobalt atoms have partially been reoxidized under the long time exposure to the higher water partial pressure.

The effects of water partial pressure in the reactor on the catalytic properties are shown in Figure 5, 6 and 7. The CO conversion first increased, then kept almost constant with increasing  $P_{H_2O}/P_{H_2}$ . Methane selectivity decreased and CO<sub>2</sub> selectivity and olefin ratios slightly increased with increasing water partial pressure.

The effect of water on the silica supported cobalt catalyst displayed very different performance with the alumina supported cobalt catalyst. In our previous studies for Pt-Co/Al<sub>2</sub>O<sub>3</sub> 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 catalyst. However, in this study, water has a positive effect on the CO conversion for the Co/SiO<sub>2</sub> catalyst. The cobalt metal crystallite size may explain the different effects of water on these two catalysts. The alumina supported catalyst has smaller cobalt crystallite size than the silica supported catalyst, thus it is more easily oxidized by higher partial pressure water to form cobalt oxide and deactivated quickly.

Table 1

Effect of Space Velocity on CO Conversion and Water Partial Pressure<sup>a</sup> for CO/SiO

1/Space Velocity (h gcat/SL)	CO Conversion (%)	Water Partial Pressure (atm) <sup>b</sup>	$P_{H_2O} / P_{H_2}$ <sup>b</sup>
0.125	22.1	0.801	0.091
0.200	31.58	1.448	0.194
0.333	45.03	2.598	0.414
0.500	26.86	3.474	0.657
1.000	77.67	4.991	1.589

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

b. Based on reactor exit partial pressure.

Table 2

Effect of Water Addition on CO Conversion<sup>a</sup> for CO/SiO<sub>2</sub>

Water Amt. Added (volume %)	CO Conversion (%)	Water Partial Pressure (atm) <sup>b</sup>	$P_{H_2O} / P_{H_2}$ <sup>b</sup>
0	22.5	0.967	0.020
5	28.12	2.269	0.290
8	29.25	3.024	0.389
12	28.1	3.964	0.510
15	28.9	4.815	0.627
20	28.6	5.776	0.743
25	27.4	6.639	0.835

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

b. Based on reactor exit partial pressure.

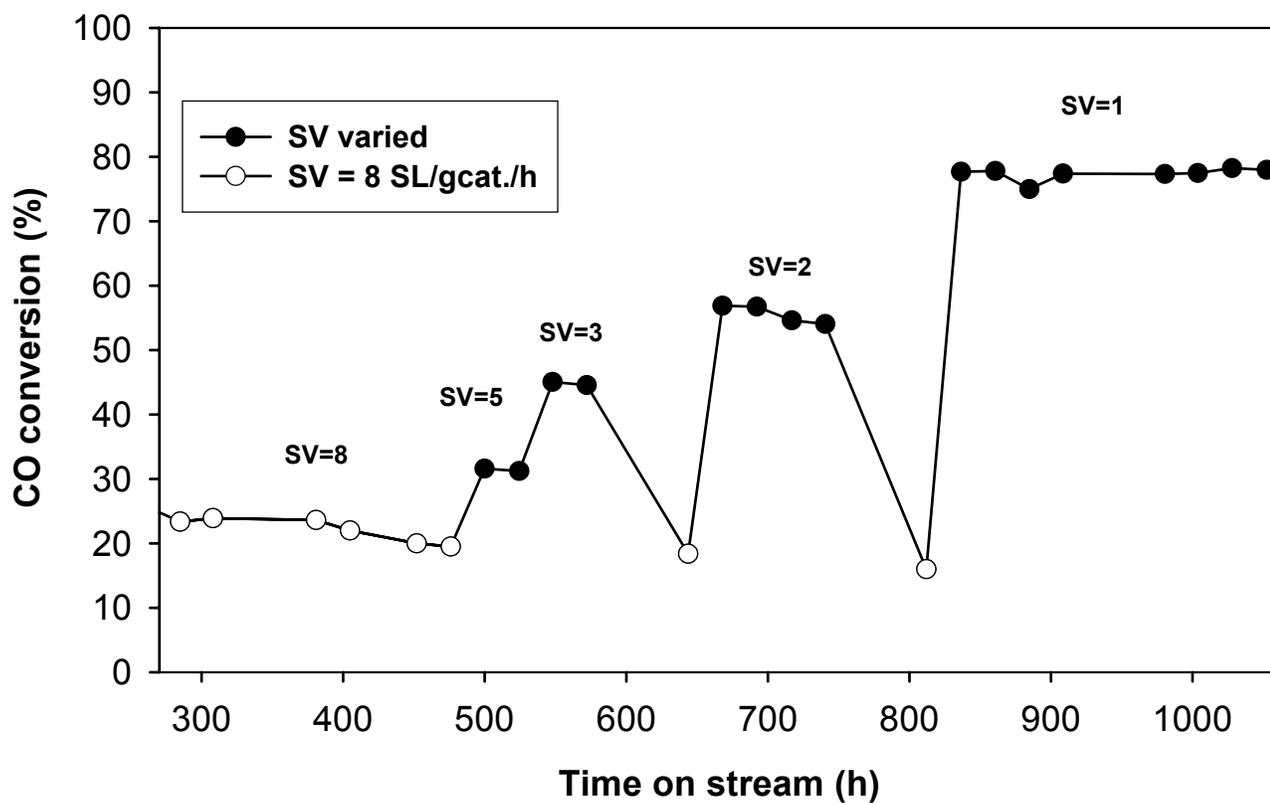


Figure 1. CO conversion as a function of time on stream and space velocity for a Co/SiO<sub>2</sub> catalyst [T = 483 K, P = 20 atm, H<sub>2</sub>/CO = 2.0].

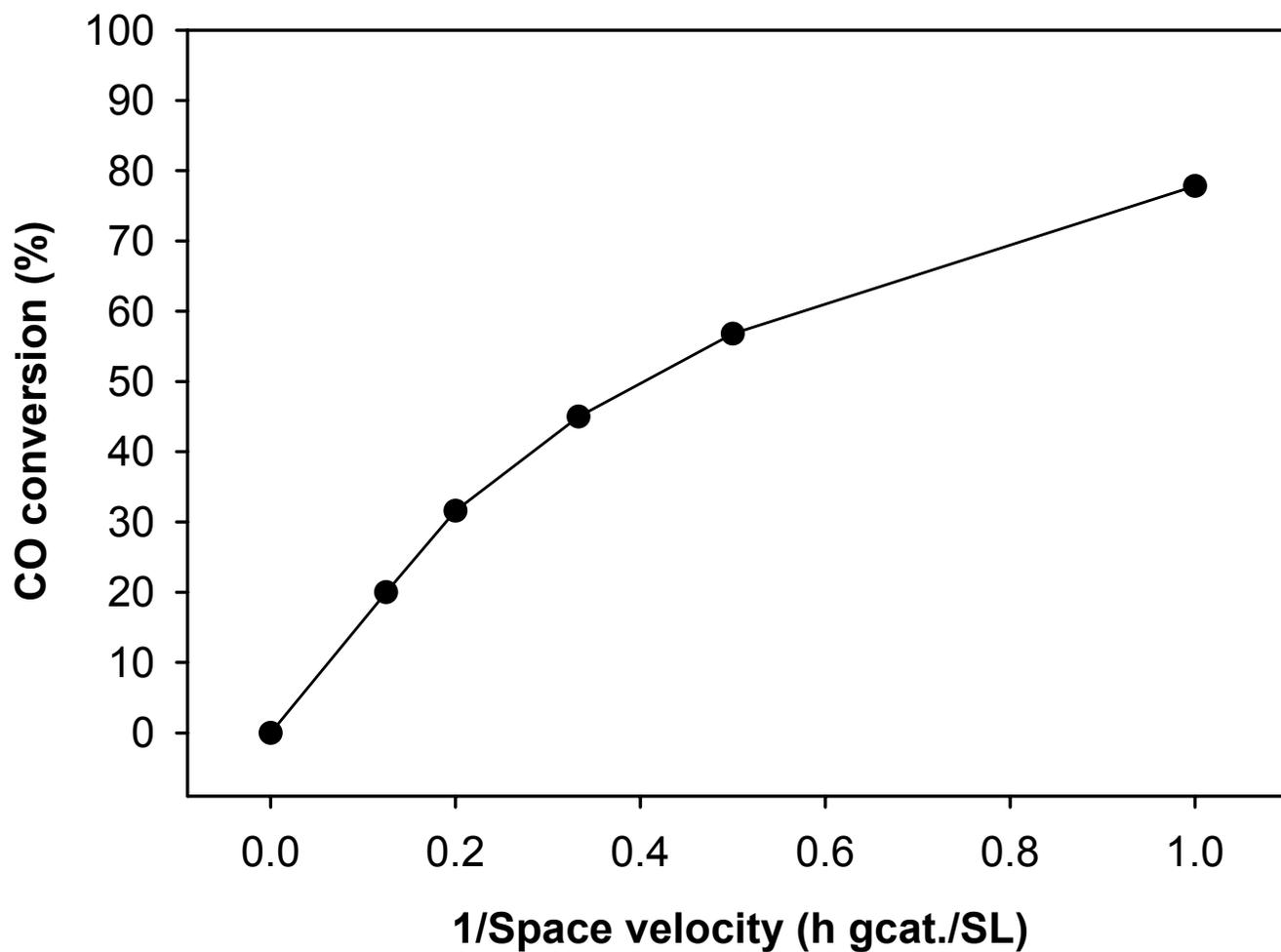


Figure 2. CO conversion as a function of space time for a Co/SiO<sub>2</sub> catalyst [T = 483 K, P = 20 atm, H<sup>2</sup>/CO = 2.0].

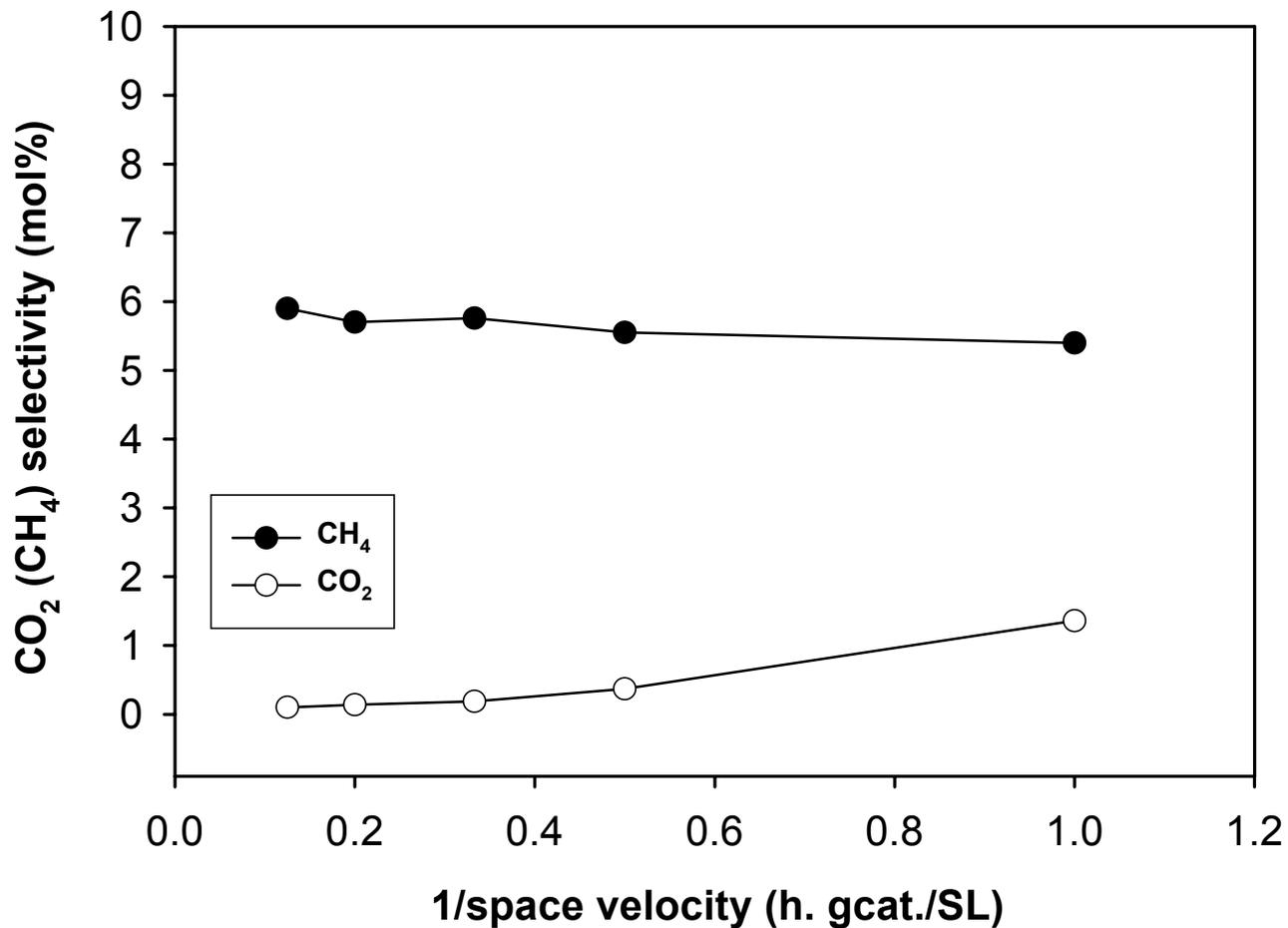


Figure 3. CO<sub>2</sub> and CH<sub>4</sub> selectivity as a function of space time for the Co/SiO<sub>2</sub> catalyst [T = 483 K, P = 20 atm, H<sub>2</sub>/CO = 2.0].

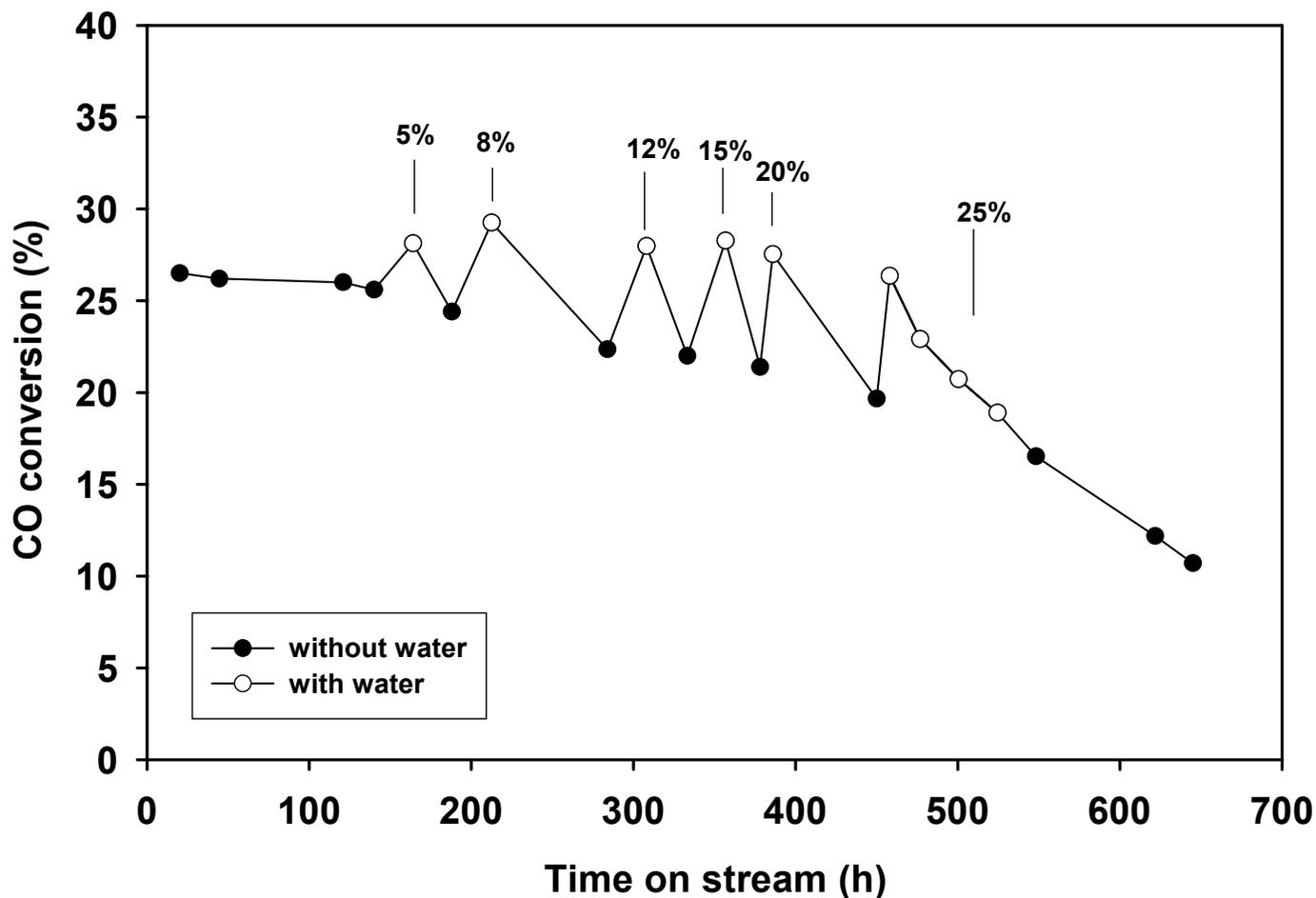


Figure 4. Effect of water on CO conversion for Co/SiO<sub>2</sub> catalyst (T=483K, P=20 atm, P<sub>H<sub>2</sub></sub>+P<sub>CO</sub>=14 atm, H<sub>2</sub>/CO=2.0, S.V.=8 SL/gcat.h; % is volume % of total feed).

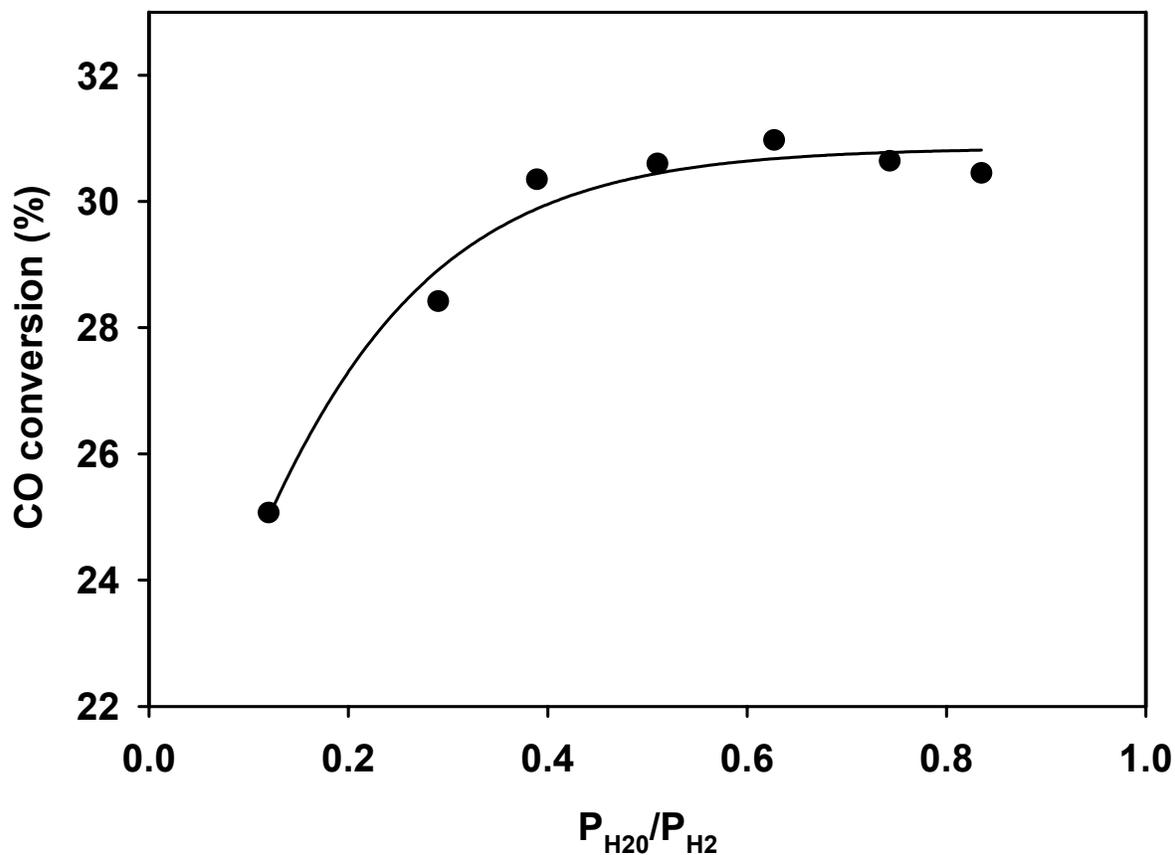


Figure 5. CO conversion as a function of  $P_{H_2O}/P_{H_2}$  for Co/SiO<sub>2</sub> catalyst (T = 483K, P = 20 atm,  $P_{H_2} + P_{CO} = 14$  atm, H<sub>2</sub>/CO=2.0 S.V.=8 SL/gcat.h; partial pressure is based on reactor exit).

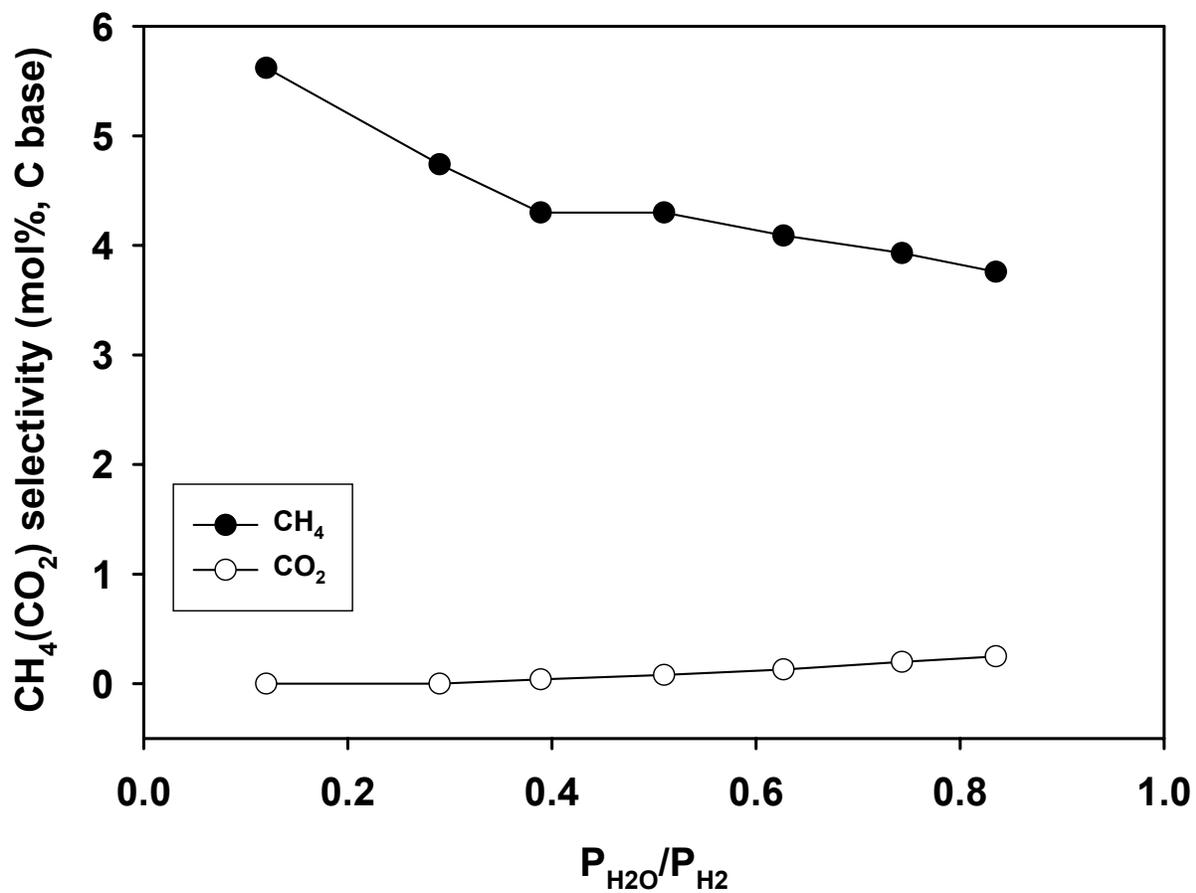


Figure 6. CH<sub>4</sub>(CO<sub>2</sub>) selectivity as a function of P<sub>H<sub>2</sub>O</sub>/P<sub>H<sub>2</sub></sub> for the Co/SiO<sub>2</sub> catalyst.

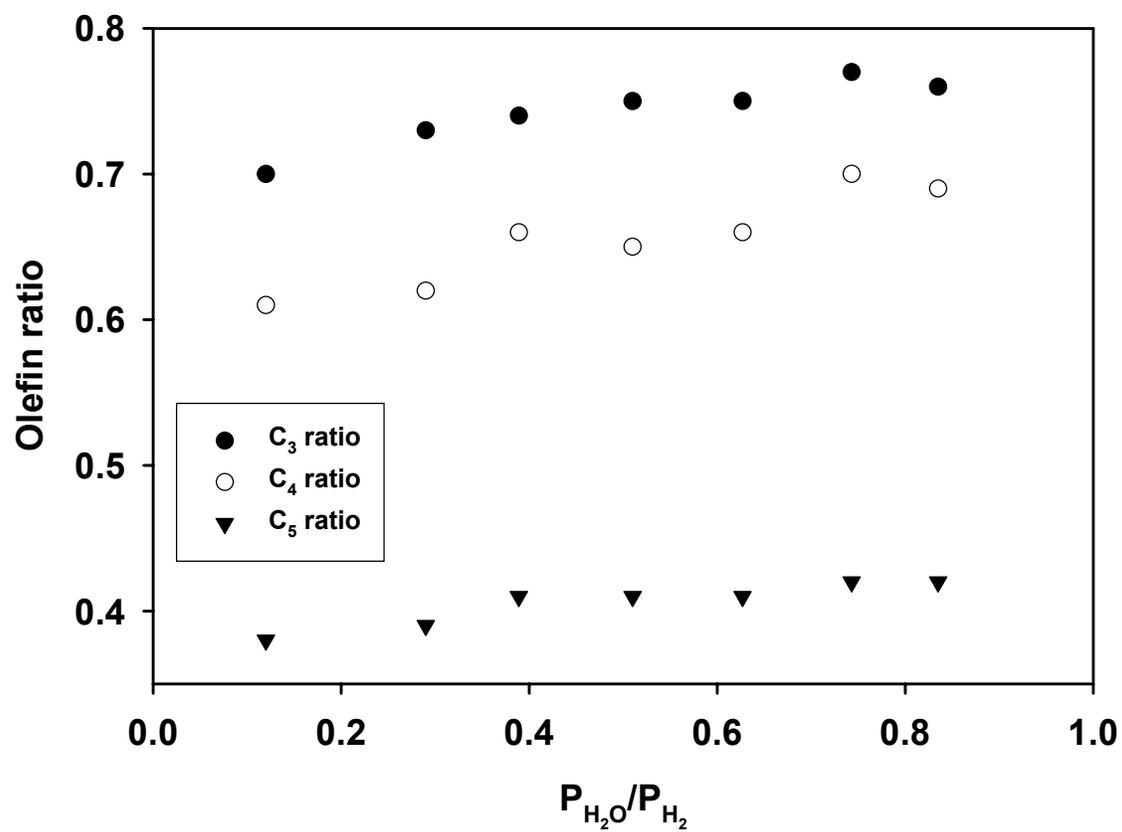


Figure 7. Olefin ratio as a function of  $P_{H_2O}/P_{H_2}$  for the Co/SiO<sub>2</sub> catalyst.

## **Task 9. Cobalt Catalyst Life Testing**

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

### **A. Cobalt Catalyst Life Testing and Deactivation**

#### ***Preparation of Cobalt Catalysts***

The 15%Co/Al<sub>2</sub>O<sub>3</sub> and 1.0%Re-15%Co/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by incipient wetness impregnation of Al<sub>2</sub>O<sub>3</sub> (Condea Vista B alumina, BET surface area 200 m<sup>2</sup>/g, pore volume 0.4 cm<sup>3</sup>/g) with cobalt nitrate solution. The preparation procedure includes three step impregnations of cobalt salt and then followed by impregnation of promoter. 25%Co/Al<sub>2</sub>O<sub>3</sub> and 0.5%Pt-15%Co/Al<sub>2</sub>O<sub>3</sub> 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% H<sub>2</sub> 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/Al<sub>2</sub>O<sub>3</sub> catalyst***

The activity and deactivation rate of unpromoted 25%Co/Al<sub>2</sub>O<sub>3</sub> 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/Al<sub>2</sub>O<sub>3</sub> 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 H<sub>2</sub> 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/Al<sub>2</sub>O<sub>3</sub> catalyst***

The activity and rate of loss of activity of Pt promoted 0.5%Pt-25%Co/Al<sub>2</sub>O<sub>3</sub> 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/Al<sub>2</sub>O<sub>3</sub> catalysts but the deactivation rate is more in case of Pt promoted catalyst as compared to unpromoted 25%Co/Al<sub>2</sub>O<sub>3</sub> catalysts. The initial activity of 0.5%Pt-25%Co/Al<sub>2</sub>O<sub>3</sub> 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 H<sub>2</sub> and Ar. After regeneration the CO conversion did not increase at all.

#### ***1.0%Re-15%Co/Al<sub>2</sub>O<sub>3</sub> catalyst***

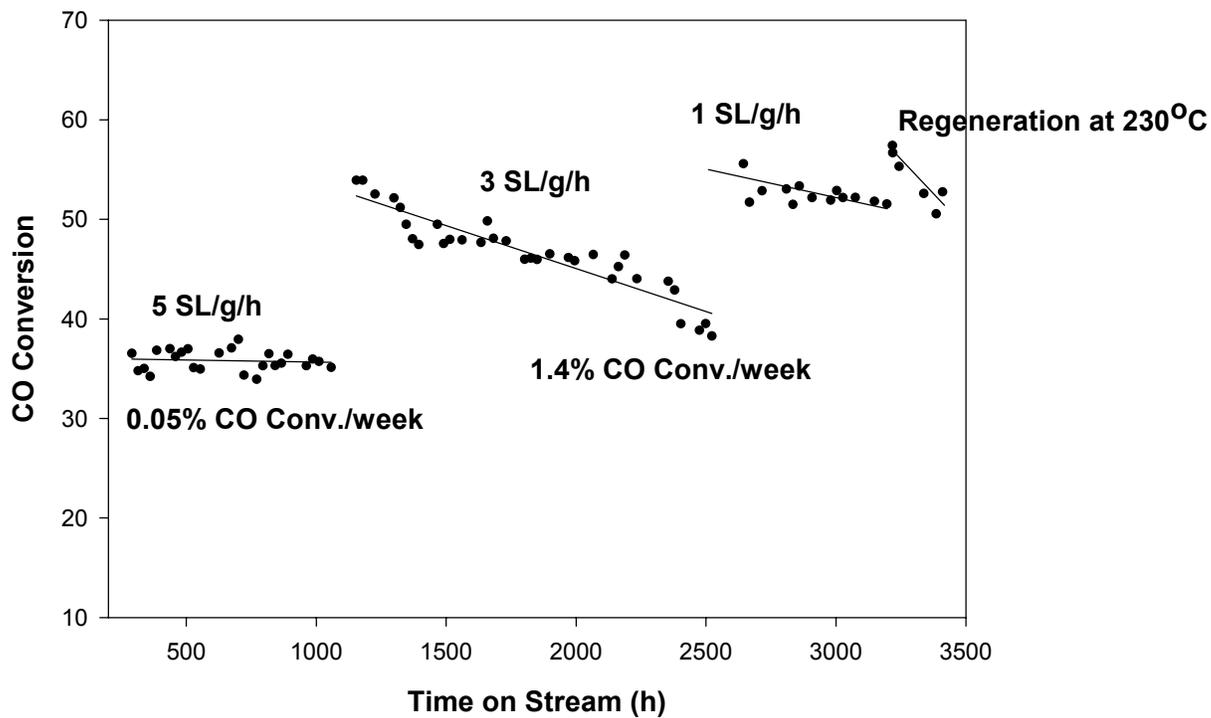
This catalyst run was performed to know the effect of start up solvent. It was found that polywax 3000 is the better start up solvent than the C-30 oil. The partial pressure of C-30 oil is much higher than the polywax 3000, apparently the C-30 oil evaporated more when the space velocity is relatively 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/Al<sub>2</sub>O<sub>3</sub> 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 H<sub>2</sub> and Ar. The CO conversion increases slightly after regeneration but the deactivation rate is more as compared to unregenerated catalysts.

#### ***Effect of Rreduction temperature of unpromoted 15%Co/Al<sub>2</sub>O<sub>3</sub> catalyst***

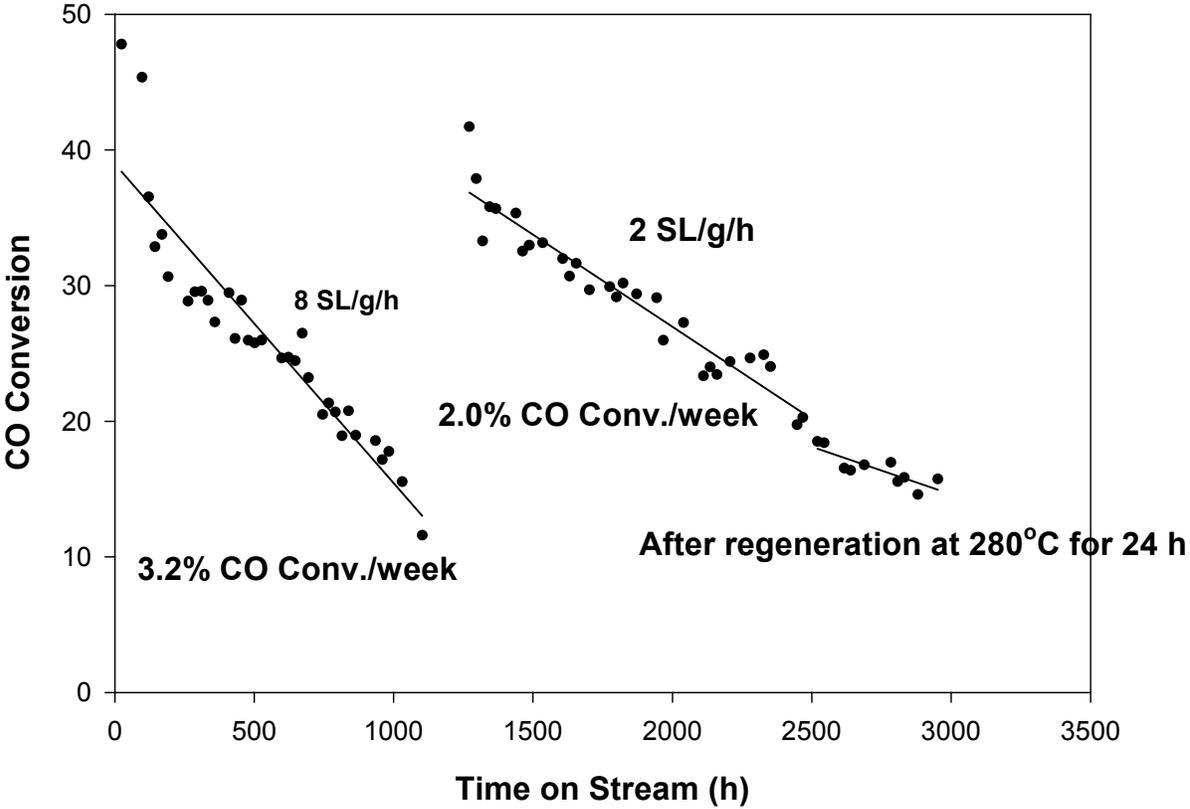
15%Co/Al<sub>2</sub>O<sub>3</sub> catalyst was reduced at 350°C and 500°C, respectively to study the effect of reduction temperature. The results are shown in Figs. 4 and 6. It seems that the increase in reduction temperature increases the CO conversion from 16% to 26%. The results of the degree of reduction 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/Al<sub>2</sub>O<sub>3</sub> 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.

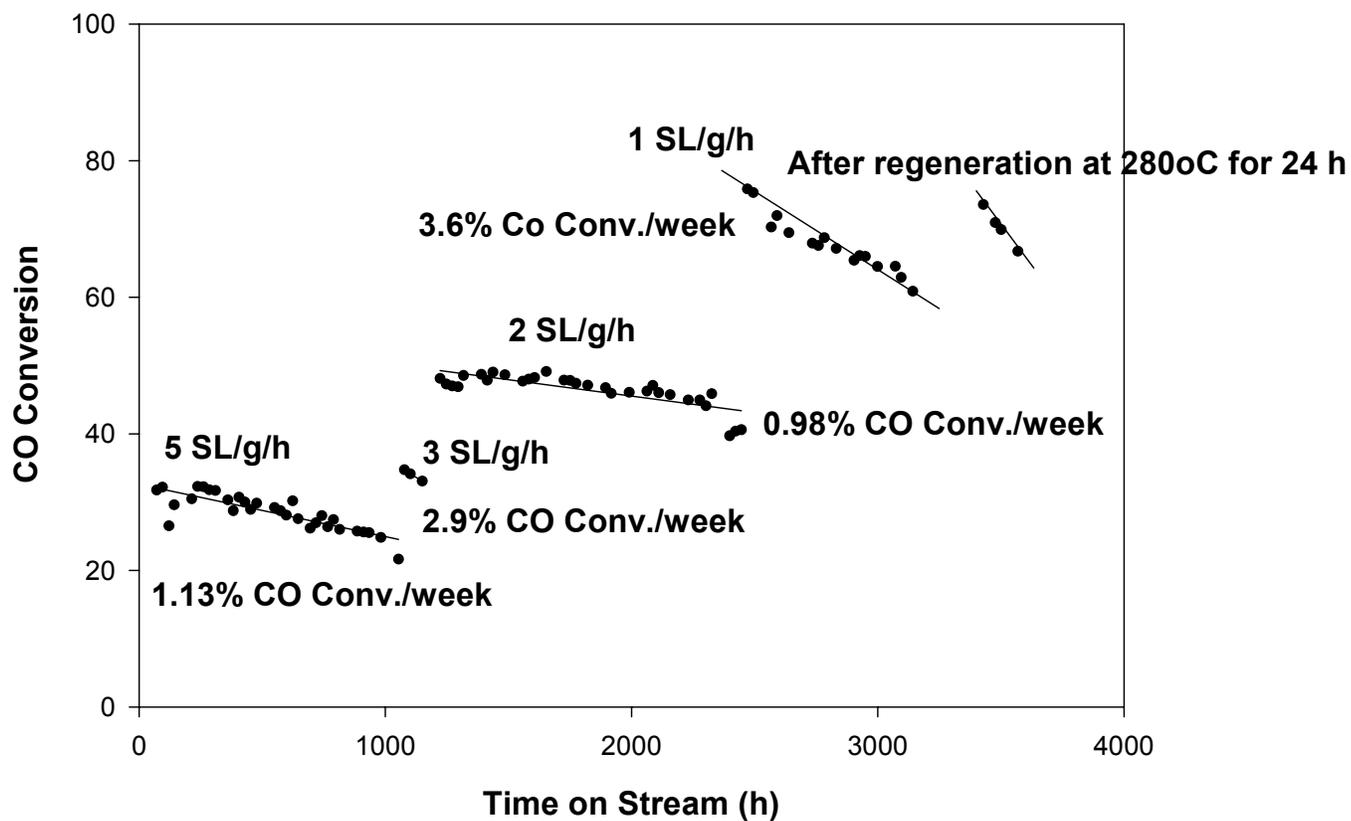
**Fig. 1 : Activity of 25%Co/Al<sub>2</sub>O<sub>3</sub> catalyst at 220°C and 275 psig (Reduced at 350°C)**



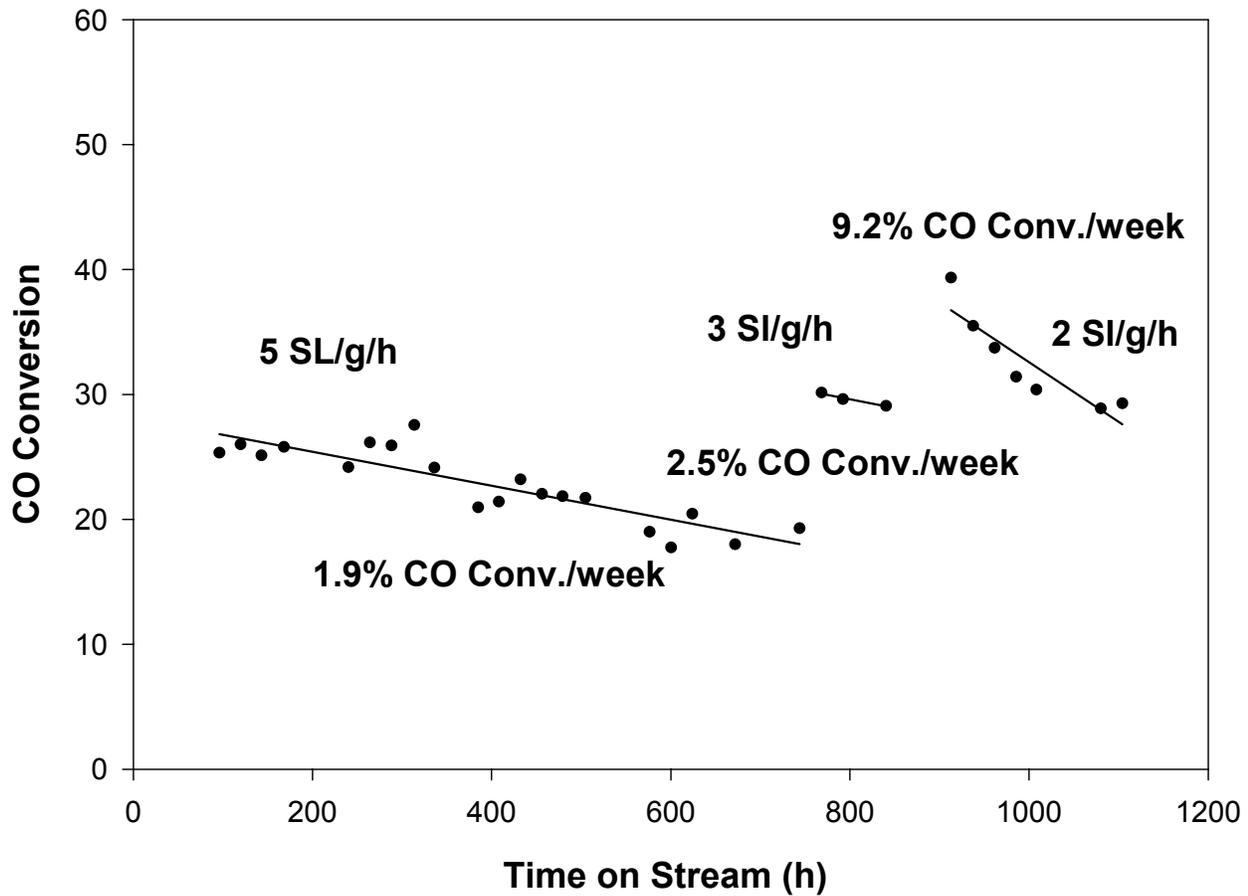
**Fig. 2 : Activity of 0.5%Pt-25%Co/Al<sub>2</sub>O<sub>3</sub> catalyst at 220°C and 275 psig**



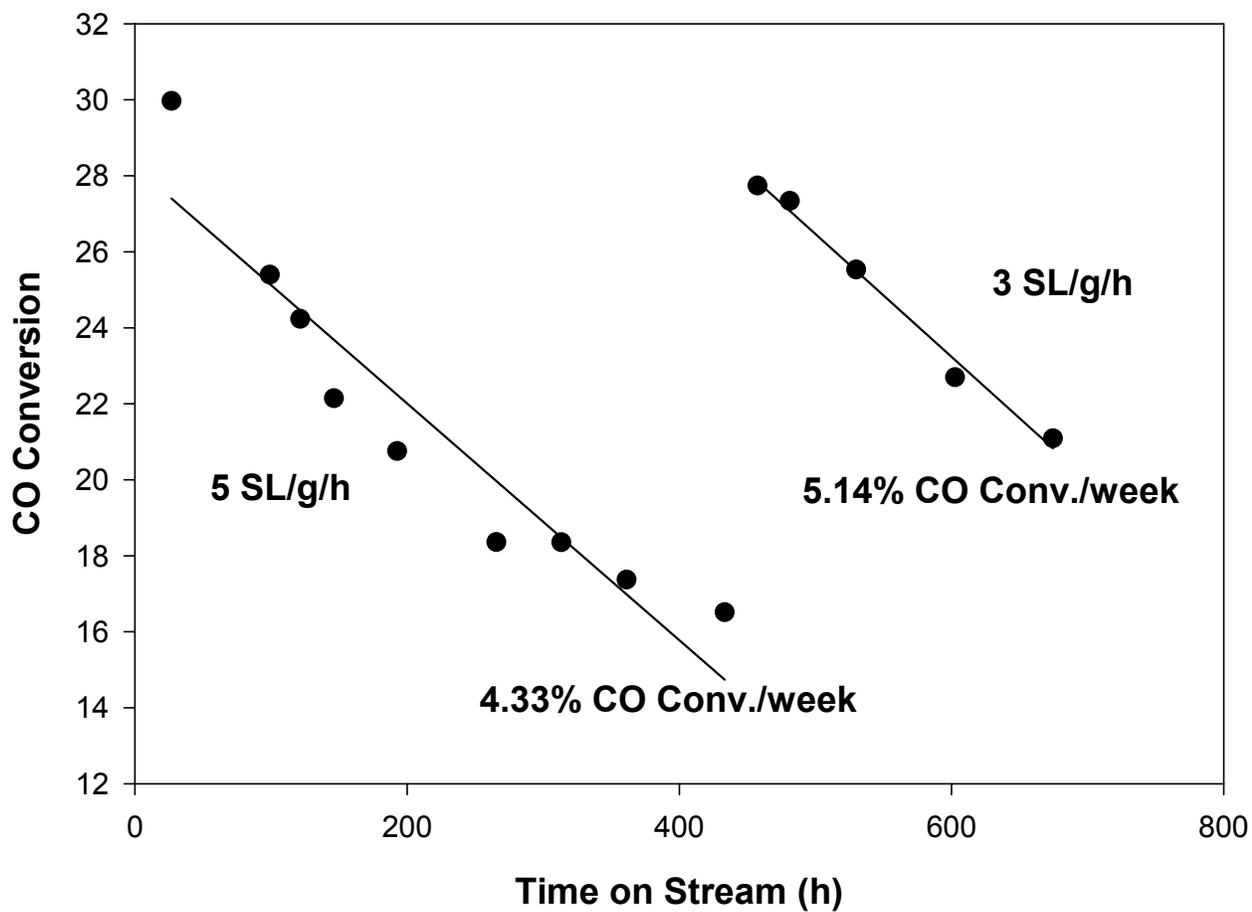
**Fig. 3 : Activity of 1.0%Re-15%Co/Al<sub>2</sub>O<sub>3</sub> catalyst at 220°C and 275 psig**



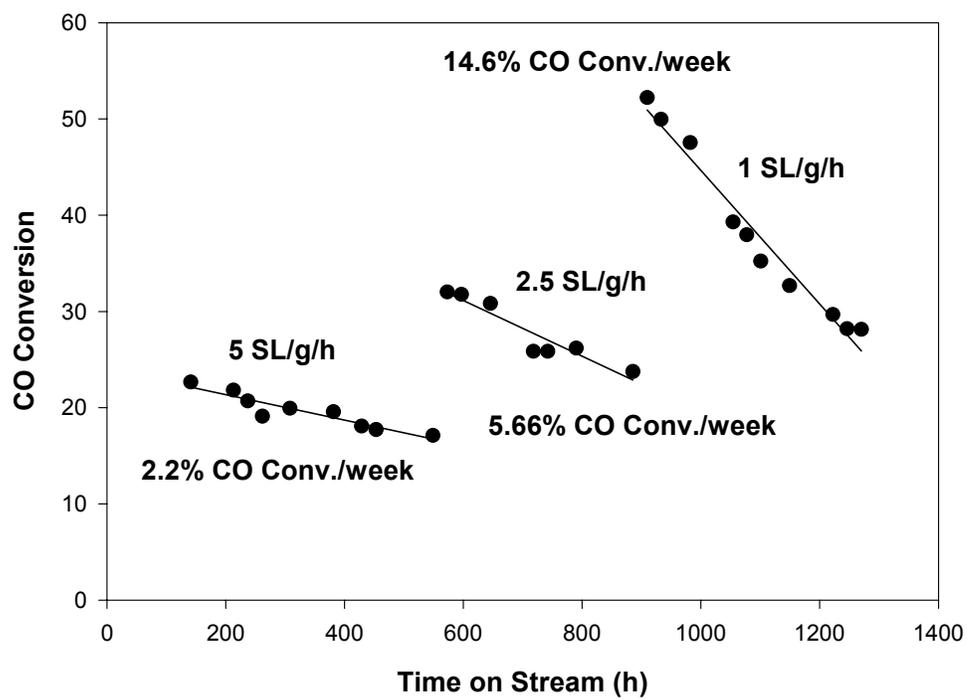
**Fig. 4 : Activity of 15%Co/Al<sub>2</sub>O<sub>3</sub> catalyst reduced at 500°C  
(Temp. 220°C and Pressure 275 psig)**



**Fig. 5 : Activity of 25%Co/Al<sub>2</sub>O<sub>3</sub> catalyst reduced at 450°C  
(Reaction Temp. = 220°C, Press. = 275 psig)**



**Fig. 6 : Activity of 15%Co/Al<sub>2</sub>O<sub>3</sub> catalyst at 220°C and 275 psig(Reduced at 350°C)**



**Task 10. Cobalt Catalyst Mechanism Study**

The objective of this task is to determine the impact of secondary reactions on the relationship of cobalt Fischer-Tropsch catalysts under conditions appropriate to slurry bubble column reactors.

**Task 11. University of California, Berkeley (Subcontract)**

The objective of this task is the characterization of the structure and function of active sites involved in the synthesis of high molecular weight hydrocarbons from CO and H<sub>2</sub> on multi-component catalysts based on Fe as the active component.