

Task 3. Catalyst Characterization

The objective of this task is to obtain characterization data of the prepared catalysts using routine and selected techniques.

A Zeton-Altamira AMI-200 chemisorption instrument and a Micromeritics Tristar physisorption instrument have been installed for catalyst characterization.

Task 4. Wax/Catalyst Separation

The objective of this task is to develop techniques for the separation of catalysts from FT reactor slurries.

The filtration problems need to be addressed from two viewpoints: the ability to operate the CSTRs and the ability to filter at the pilot or commercial plant scale.

To date we have been able to filter the products from the operation of CSTRs when we operate with cobalt catalysts. In these operations we utilize 10 wt.% catalyst (total catalyst, not cobalt) and have operated for nearly 4,000 hours on occasion. Only on very rare occasions have we encountered problems with filtration. Thus, in 95+% of the runs, the pressure generated when we open the internal filter to remove reactor wax is less than 40 psig and the wax (up to 75 grams) can be removed in less than three hours, and usually in a shorter time period. Thus, from the viewpoint of operating a CSTR with alumina or silica supported cobalt catalysts, we have been able to remove wax and operate the CSTR for extended run periods. We have less experience with a titania supported catalysts but during about 10 runs we have been able to remove the reactor wax. In general, these cobalt catalysts are what we define as intermediate alpha (0.75-0.90) catalysts. Thus, while the wax is highly hydrogenated it does not have the very high molecular weight of a high alpha catalyst (alpha greater than 0.90).

We continue to have problems removing reactor wax from the CSTR when using the unsupported high-alpha iron catalysts. When we operate with a 0.5- or 2.0 micron Mott sintered metal filter, we find that the reactor wax that is withdrawn has a low iron content (30 ppm or less). Thus, the filter functions to retain the precipitated iron catalyst with particles in the 1 to 3 micron size range in the reactor. However, with time the ability to remove wax decreases.

The following data demonstrate the difficulty in quantifying the filtration ability during a run with a high-alpha precipitated iron catalyst. The particular catalyst used for run BAO-029 produced a soft wax that is representative of an intermediate alpha catalyst (alpha approaching 0.90). The filtration rate was obtained from the amount of reactor wax withdrawn and the time that the internal, submerged filter was open to the collection vessel. The removal line is fitted with a pressure gauge that permits us to reduce the pressure in the collection vessel by an amount that is known and is below that of the reactor in order to provide a driving force for the removal of wax. At present, we do not have the ability to adjust the pressure in the collector to maintain a constant head pressure to provide a constant driving force. Thus, as gas passes through the filter along with the reactor wax, the pressure in the collector increases and this results in a decrease in the driving force together with a decrease in the filtration rate.

Early in the run, the amount of wax removed was low, presumably because the small amount of startup solvent and the rate of production of wax did not keep the filter submerged in the liquid during the entire time that the filter was open to the collector (Figure 1). Thus, for about 50 hours of operation the filtration rate was increasing to attain a value of about 6,000 g/hr-ft² (100 g/min-ft²), a much higher value than reported in the last quarterly report (0.1 g/min-ft² or lower). During about 100 hours, the filtration rate remained at about 6,000 g/hr-ft², then appeared to gradually decline to about 1,000 g/hr-ft² (16 g/min-ft²) and then remain essentially

constant during 200 hours of operation. The run was terminated because of scheduled laboratory shut-down, and not due to filtration problems.

Attempts have been made to operate the reactor by calculating, based upon the experimental values of other samples collected and the gas flows, the amount of reactor wax that should be withdrawn and then withdrawing that amount of wax. This has had variable success. The cumulative grams of hydrocarbon products produced during the nearly 400 hour run are shown in Figure 2 together with the cumulative calculated grams of wax produced and the cumulative grams of wax withdrawn. According to the data shown in Figure 2 we should have accumulated about 754 grams of reactor wax but when we opened the reactor the amount was only about 500 grams. This amounts to less than 4% error in the mass balance during the entire run. Since some sample is lost due to flashing during the collection of the products from each of the three traps for each collection period, the mass balance is considered to be excellent.

The filtration rate shown in Figure 1 is not a reliable estimate of the actual filtration rate and is therefore impacted upon the sample removal technique. There was concern that too much wax was accumulating in the reactor so that at 216 hours, a large amount of wax was withdrawn during a 7-hour period. The average filtration rate during this 7-hour period was greater than 5,000 g/hr-ft² (shown as □ in Figure 1), near the maximum rate obtained earlier in the run. Thus, the low rate shown before and after 216 hours must be due to the sampling technique and this must be defined so that a more quantitative filtration rate can be obtained.

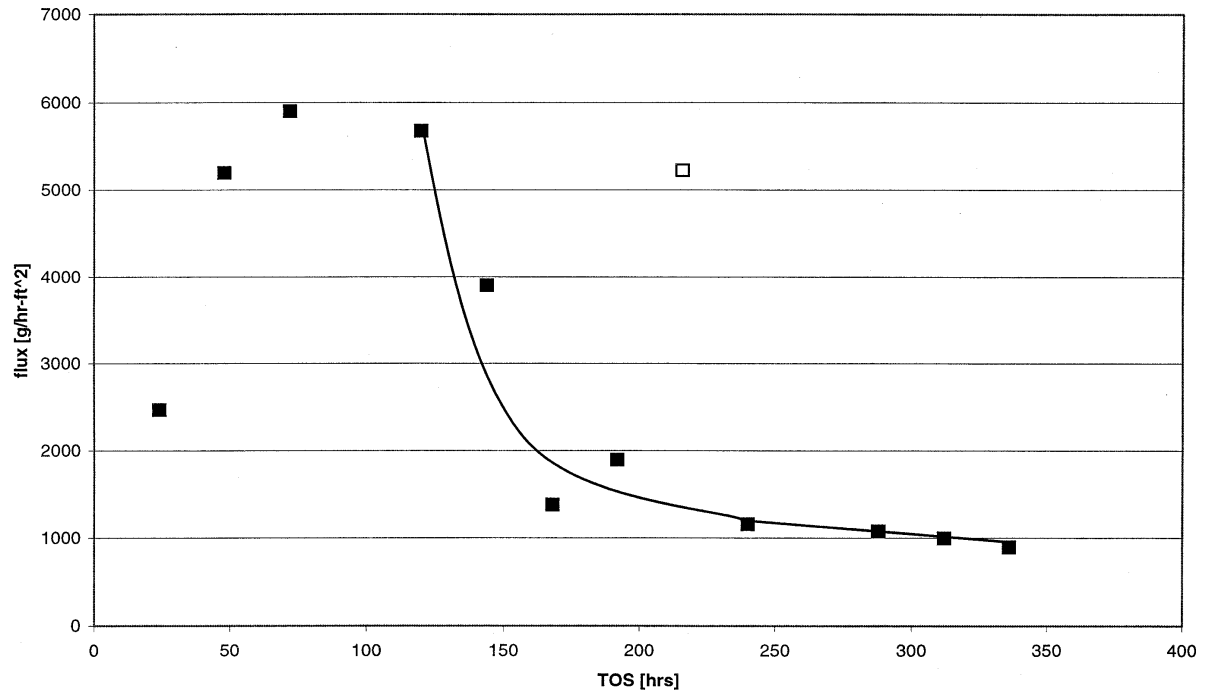


Figure 1. Filtrate rate as a function of time-on-stream.

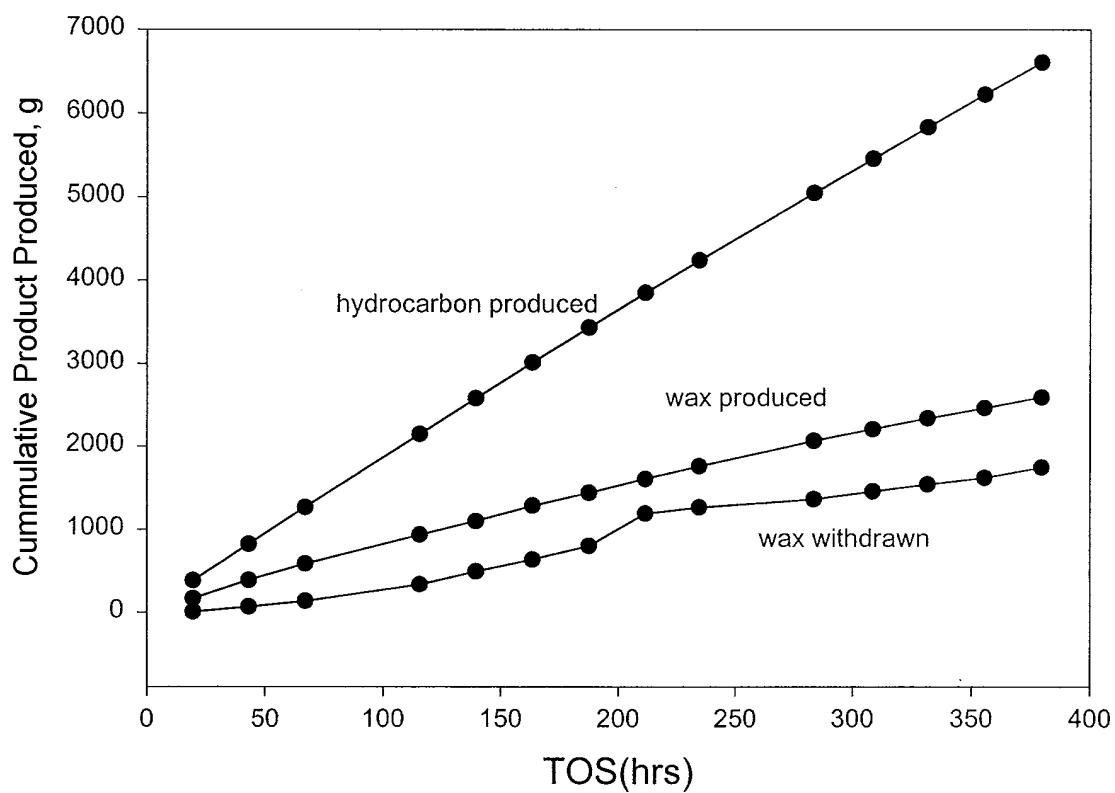


Figure 2. Cumulative hydrocarbon and wax produced and wax withdrawn as a function of time-on-stream.

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.

The new GC-AED instrument has arrived which will allow oxygenates to be analyzed in a carbon matrix.

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.

Additional summaries of the literature are completed as the manuscripts become available.

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.

Twenty-one cobalt catalysts have been prepared to study the effects of preparation method, pretreatment condition, support material, particle size and cobalt loading.

Particle size effect

ZYQ 015 to ZYQ 020 were prepared to study this effect. Instead of the incipient wetness impregnation technique, an impregnation solution (cobalt nitrate solution) with a volume of 2.5 times the volume of the calculated pore volume of the support was slowly added to the support. The support material was spherical form Shell 980F silica. It was broken down to different particle sizes of 500 μm , 250 μm , 150 μm and 50 μm , respectively. The surface area of Shell 980F silica is about 260 m^2/g and the pore volume is about 1.5 mL/g . The cobalt loading of all the catalysts was 15wt.% and 100 grams of each catalyst was prepared. In order to study the effect of

number of times of impregnations, one and two impregnations were used to prepare ZYQ 015 and ZYQ 016 on Shell 980F silica (500 μ m). ZYQ 018, ZYQ 019 and ZYQ 020 were prepared using two impregnations; the particle sizes of the support materials were 50 μ m, 150 μ m, 250 μ m, respectively. The support was dropped into a flask that contained cobalt nitrate solution that was 2.5 times the volume of calculated pore volume of the support; the flask was connected to a rotary evaporator. The catalysts were dried for four hours under 5mmHg of vacuum at 75°C, then calcined in flowing air at 400°C for three hours, the temperature increasing at a rate of 5°C/min.

Support effect

ZYQ 021-ZYQ 024 catalysts were prepared to study the support effect. Shell 980 G silica (100-200mesh, surface area 110m²/g, pore volume 0.8ml/g), Condea Vista B alumina (100-200mesh, surface area 243m²/g, pore volume 0.47g/ml), Davisil 952 silica (100-200mesh, surface area 309m²/g, pore volume 1.61ml/g) and Degussa Titania (P25,100-200mesh, surface area 45m²/g, pore volume 0.25ml/g) were used as the support materials. Incipient wetness impregnation method was applied (cobalt nitrate as precursor) three times for each catalyst, the final cobalt loading was 15%. The catalysts were then dried in a rotary evaporator and calcined in flowing air at 400°C for three hours for each catalyst, the temperature increasing at a rate of 5°C/min.

Calcination interval effect

ZYQ 025 was prepared with the calcination procedure being applied between the three incipient wetness impregnations; the support used was Davisil 952 silica (60-80mesh) and the total cobalt loading was 15%. The final calcination was also used.

Calcination protocol effect

A 2kg batch of 15%Co/SiO₂ catalyst was used to study the effect of the calcination protocol. The support was Davisil 644 silica (100-200mesh, surface area 300m²/g, pore volume 1.15ml/g). The catalyst was calcined under different conditions: YQZ001 was calcined in a furnace at 400°C for four hours while YQZ 026 was calcined in flowing air at 400°C for three hours, the temperature increasing at a rate of 5°C/min.

Preparation method effect

ZYQ 027 and ZYQ023 catalysts were prepared using the same support (Davisil 952 silica, 60-80 mesh, surface area 309m²/g, pore volume 1.61ml/g) and with the same cobalt loading (15%). However, different preparation methods were applied: ZYQ 027 was prepared using two incipient wetness impregnations while ZYQ 023 was prepared using the same method described in the study of the effect of particle size.

Catalyst loading effect

Catalysts with 5%, 10%, 15%, 20% and 25% cobalt loading on Davisil 952 silica support (60-80mesh, surface area 309m²/g, pore volume 1.61ml/g) were prepared using an incipient wetness impregnation. The catalysts were dried in a rotary evaporator and calcined in a furnace at 400°C for four hours.

Effect of calcination step

Catalysts ZYQ 033, ZYQ 034 and ZYQ 035 were prepared under the same condition as ZYQ 001, ZYQ 031 and ZYQ 032 except the previous ones were not calcined.

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. Comparison of Fischer-Tropsch synthesis in conventional fixed bed, CSTR and supercritical reactors on unpromoted cobalt catalyst

Introduction

Fischer-Tropsch synthesis has been studied in different reactor systems. Plug flow reactor, continuous stirring tank reactor and fluidized bed reactor have been used. Gas, liquid and supercritical reaction media were used in different reactor systems and under different operating conditions. Fischer-Tropsch synthesis reaction performed in the supercritical phase offers the opportunity to improve the heat transfer property and the ability to extract the heavy wax product from catalyst pores, and therefore extends catalyst lifetime. However, the introduction of the supercritical solvent into the reactor system would increase the operation cost not only because of the consumption of the solvent but also because of the much higher operating pressure. The continuously stirring tank reactor, on the other hand, is another alternative to the rapid catalyst deactivation in plug flow reactor. The heat transfer property is even better than the supercritical media; the disadvantage is that diffusion is slower in the slurry phase than plug flow reactor and therefore the overall reaction rate would be lower. The study conducted on supercritical Fischer-Tropsch synthesis using an unpromoted Co/SiO₂ catalyst prepared in this lab indicated that the lower rate of catalyst deactivation did occur; however, the selectivity of methane decreased by the application of the supercritical solvent. The same catalyst was studied in the continuously stirring tank reactor to compare the activity, selectivity, deactivation rate etc.

Experimental

A 2kg batch Co/SiO₂ catalyst was prepared using an incipient wetness impregnation technique. The support material is Davisil silica 644 (surface area 300m²/g; pore volume: 1.15cm³/g) and the cobalt loading is 15%. The CSTR reactor was loaded with 17.7g of the catalyst. The initial conditions for the reaction were 350psig, 220°C, with the trap temperatures at 200, 130 and 0°C. The feed gas was initially set to 16.03 slph with a percentage composition of 10.73 H₂, 5.03 CO for a H₂:CO ratio of 2.02 and 6.04 WHSV. 300 Grams of startup oil PW3000 was used. The catalyst was pretreated in a fixed bed reactor under hydrogen at 350°C for 15hrs and then added to the startup oil without exposure to the atmosphere.

Results and discussion

Figure 1 shows the change of CO conversion with time on stream in the CSTR at a space velocity of 1.0 sl/g/hr. It shows that, except for the rapid decline of CO conversion in the first 24 hrs of time on stream, the catalyst deactivated at a fairly stable rate of 1.6% CO conversion per day. Figure 2 is the CO conversion curve for the fixed bed and supercritical Fischer-Tropsch synthesis over the same catalyst at the same syngas partial pressure, same temperature and under the same space velocity. The deactivation rate for the fixed-bed operation before using the supercritical solvent is about 9.9%CO conversion per day which is much faster than in the CSTR. The addition of the supercritical solvent into the reactor, on the other hand, decreases the deactivation rate of the catalyst significantly, as one can see from Figure 2. The methane selectivity vs time on stream curves of the CSTR and fixed bed reactors are described in Figures 3 and 4. Similar methane selectivity was obtained at the same level of CO conversion for the fixed-bed reactor and the CSTR. Nevertheless, the methane selectivity for the supercritical

Fischer-Tropsch synthesis is much lower than in both conventional fixed-bed and CSTR. The same trend can be observed for the CO₂ selectivity under these three conditions (Figures 5 and 6).

At the same space velocity, the hydrocarbon productivity rate of the catalyst in the conventional fixed-bed reactor, CSTR and supercritical Fischer-Tropsch synthesis are 0.50, 0.59 and 0.85 (under the most favorable condition), respectively. Therefore, the supercritical Fischer-Tropsch synthesis is still a promising alternative route compared to the conventional fixed-bed synthesis. However, the CSTR is also proved to have a lower catalyst deactivation rate. The choice between CSTR and supercritical reactor depends on the comparison between productivity and the investment and operation cost.

The activity and selectivity of the catalyst were tested in a CSTR at different space velocities, and the CO conversion vs 1/GHSV curve was plotted in Figure 7. It is concluded that the CO conversion changes linearly with the reciprocal of space velocity at the conversion range being studied.

Figure 8 shows the hydrocarbon productivity rate vs the reciprocal of space velocity. One can draw the conclusion that the productivity does not change over the space velocity range being studied. It again supports the idea that at low CO conversion range, Fischer-Tropsch synthesis rate on unpromoted cobalt catalyst in a CSTR is independent of CO concentration, provided the H₂/CO ratio remains constant.

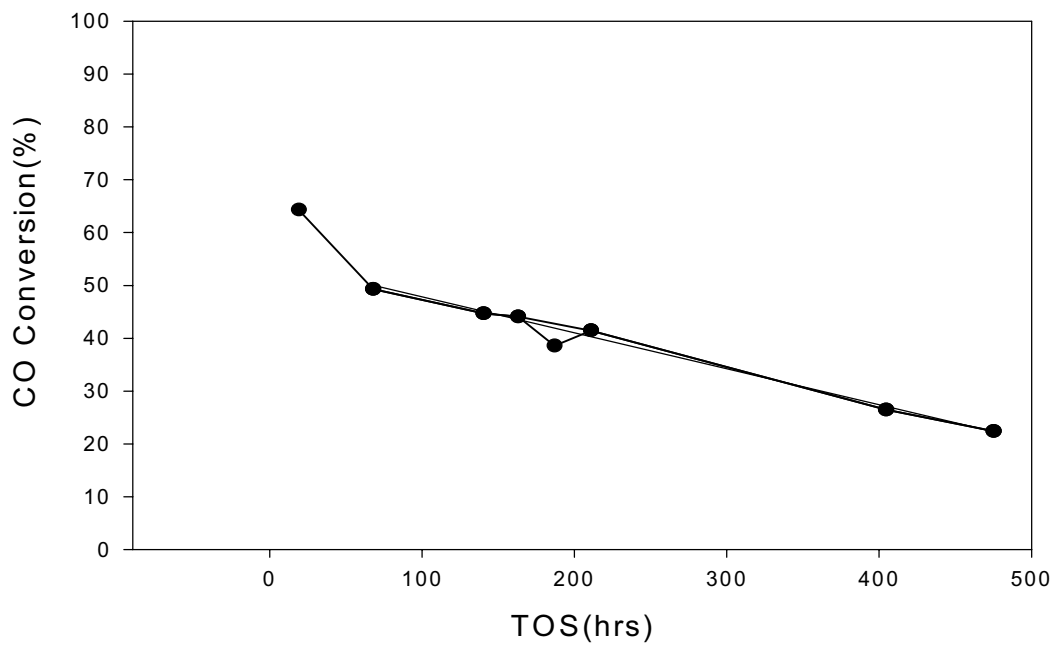


Figure 1. CO conversion vs time on stream in CSTR
(T = 220°C, GHSV = 1.0 SL/hr/g catalyst, P = 295 psig).

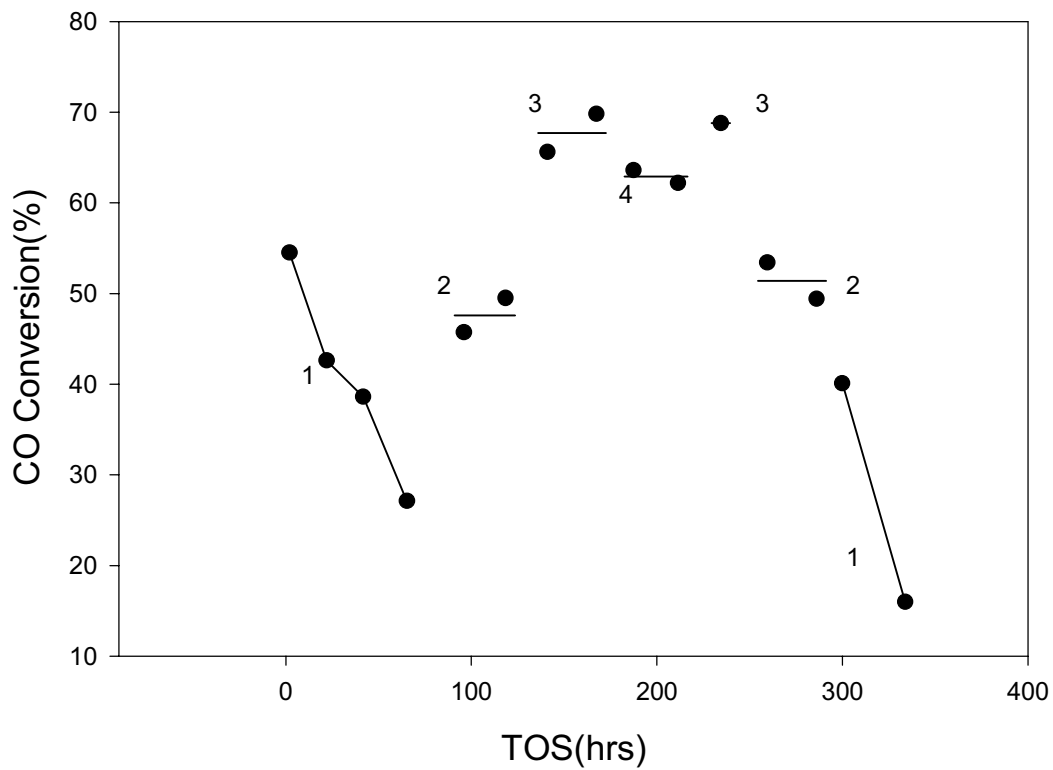


Figure 2. CO Conversion vs. time on stream ($T=220^{\circ}\text{C}$, $P_{\text{total}}=8.0\text{ MPa}$, $P_{\text{syngas}}=2.0\text{ MPa}$, $\text{H}_2:\text{CO}=2:1$, (1) $P_{\text{He}}=6.0\text{ MPa}$, $P_{\text{C5+C6}}=0$; (2) $P_{\text{He}}=4.0\text{ MPa}$, $P_{\text{C5+C6}}=2.0\text{ MPa}$; (3) $P_{\text{He}}=2.5\text{ MPa}$, $P_{\text{C5+C6}}=3.5\text{ MPa}$; (4) $P_{\text{He}}=0$, $P_{\text{C5+C6}}=6.0\text{ MPa}$).

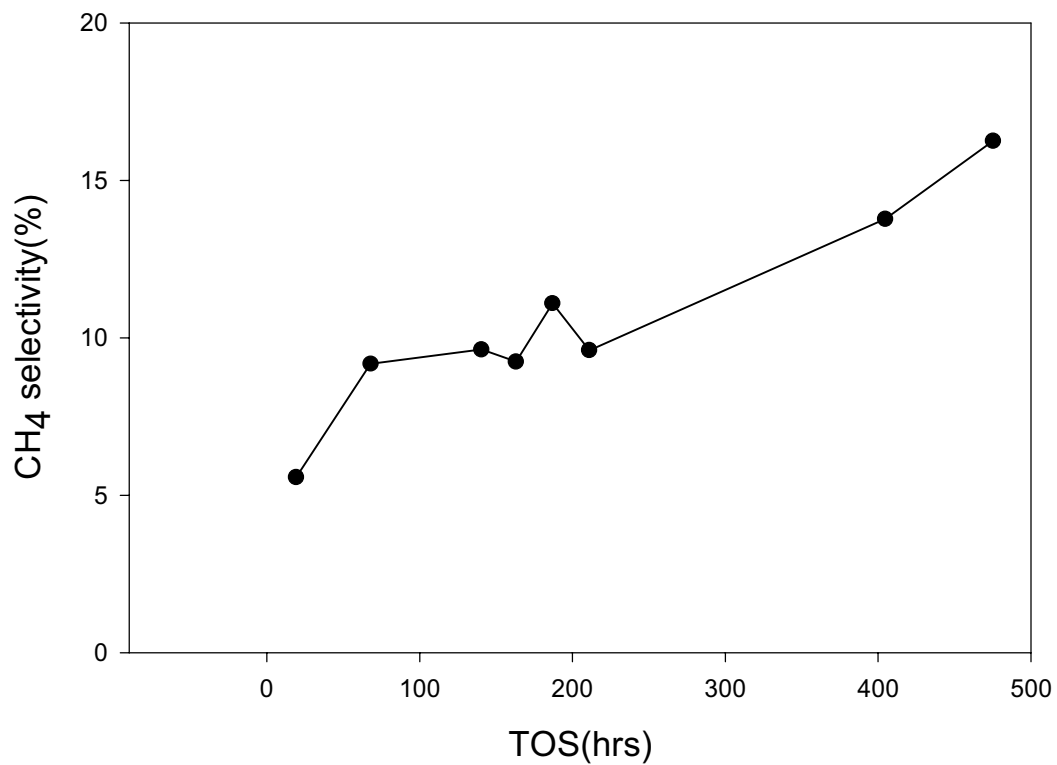


Figure 3. CH₄ selectivity vs time on stream in CSTR
(T = 220°C, P = 295 psig, GHSV = 1.0 SL/hr/g-catalyst).

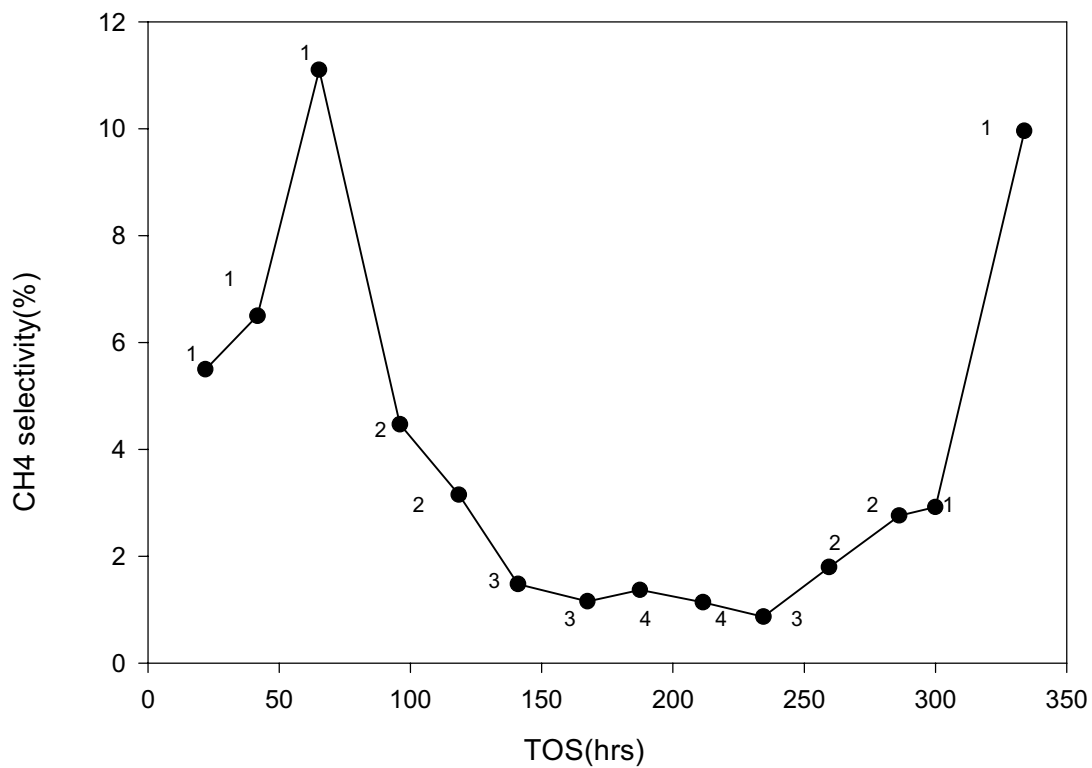


Figure 4. CH₄ selectivity vs time on stream in fixed bed and supercritical reactors ($T=220^{\circ}\text{C}$, $P_{\text{total}}=8.0\text{ MPa}$, $P_{\text{syngas}}=2.0\text{ MPa}$, $\text{H}_2:\text{CO}=2:1$). (1) $P_{\text{He}}=6.0$, $P_{\text{C}_5+\text{C}_6}=0$; (2) $P_{\text{He}}=4.0$, $P_{\text{C}_5+\text{C}_6}=2.0$; (3) $P_{\text{He}}=2.5$, $P_{\text{C}_5+\text{C}_6}=3.5$; (4) $P_{\text{He}}=0$, $P_{\text{C}_5+\text{C}_6}=6.0$).

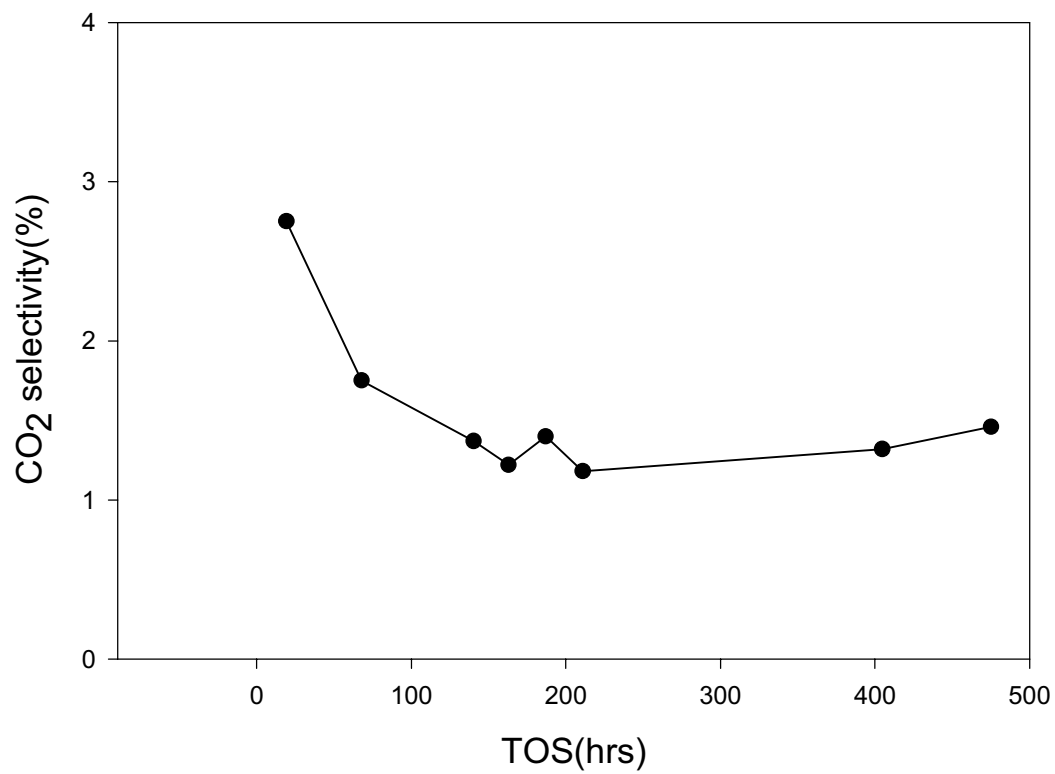


Figure 5. CO₂ selectivity vs time on stream in CSTR (T=220°C, GHSV=1.0 SL/hr/g catalyst, P=295 psig).

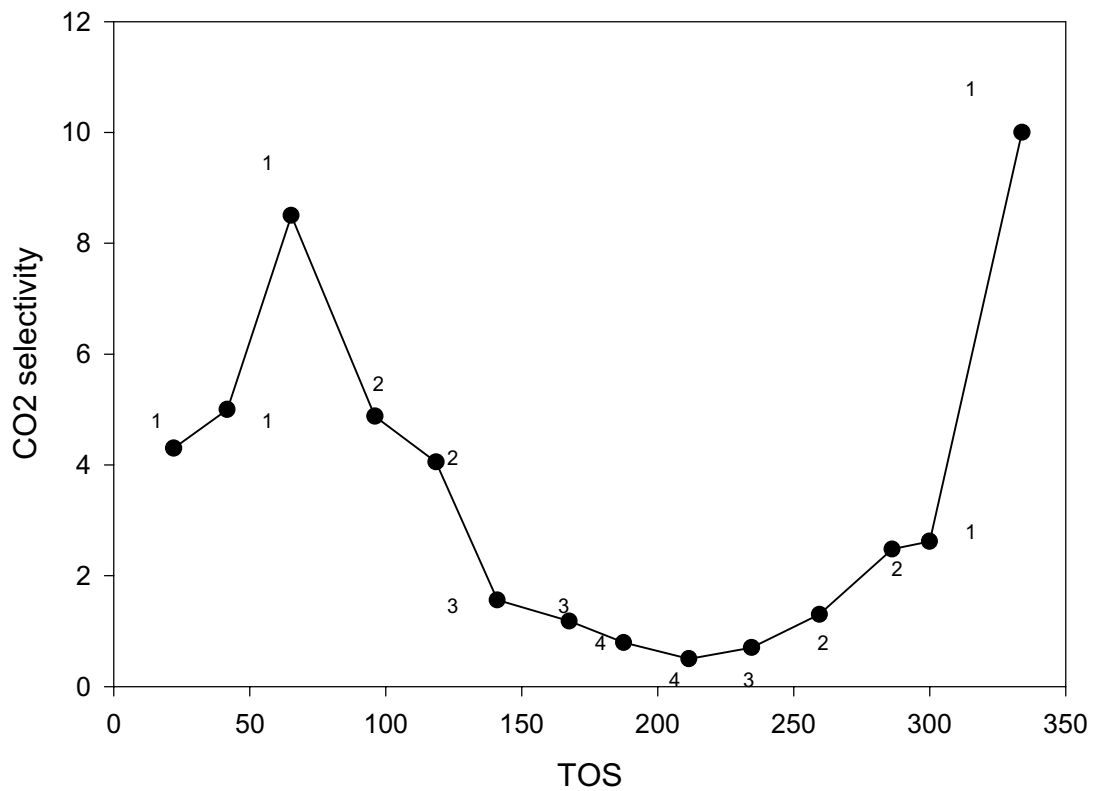


Figure 6. CO₂ selectivity vs time on stream in fixed bed and supercritical reactors (T=220oC, Ptotal=8.0 MPa, P_{syngas}=2.0 MPa, H₂:CO=2:1. (1) P_{He}=6.0, P_{C5+C6}=0; (2) P_{He}=4.0, P_{C5+C6}=2.0; (3) P_{He}=2.5, P_{C5+C6}=3.5; (4) P_{He}=0, P_{C5+C6}=6.0).

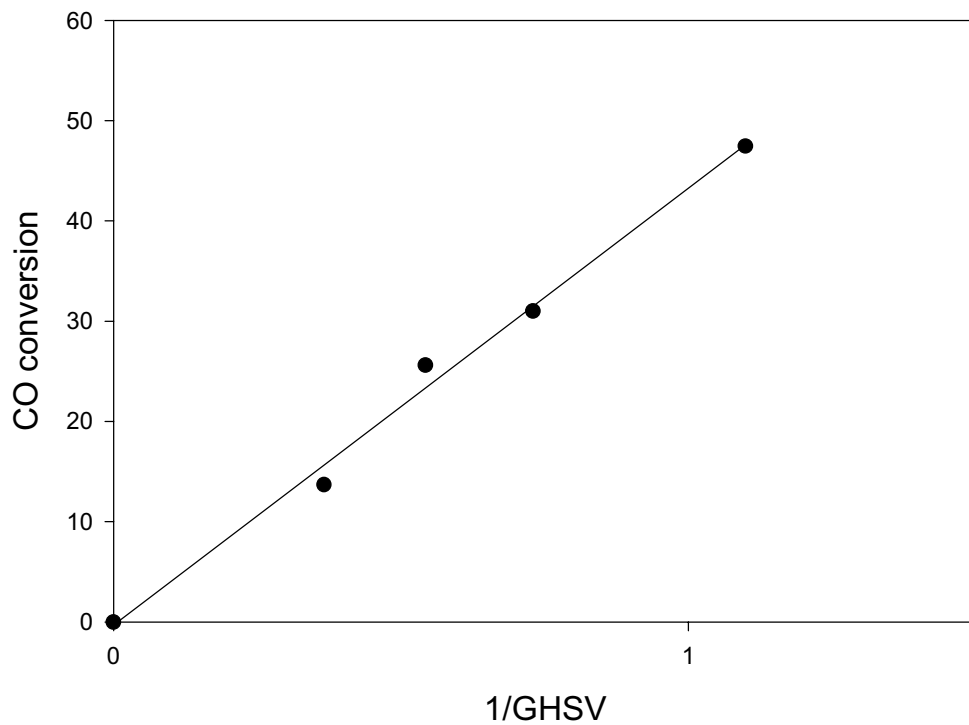


Figure 7. CO conversion vs 1/GHSV at 100hrs time on stream in CSTR (T=220°C, P=295 psig).

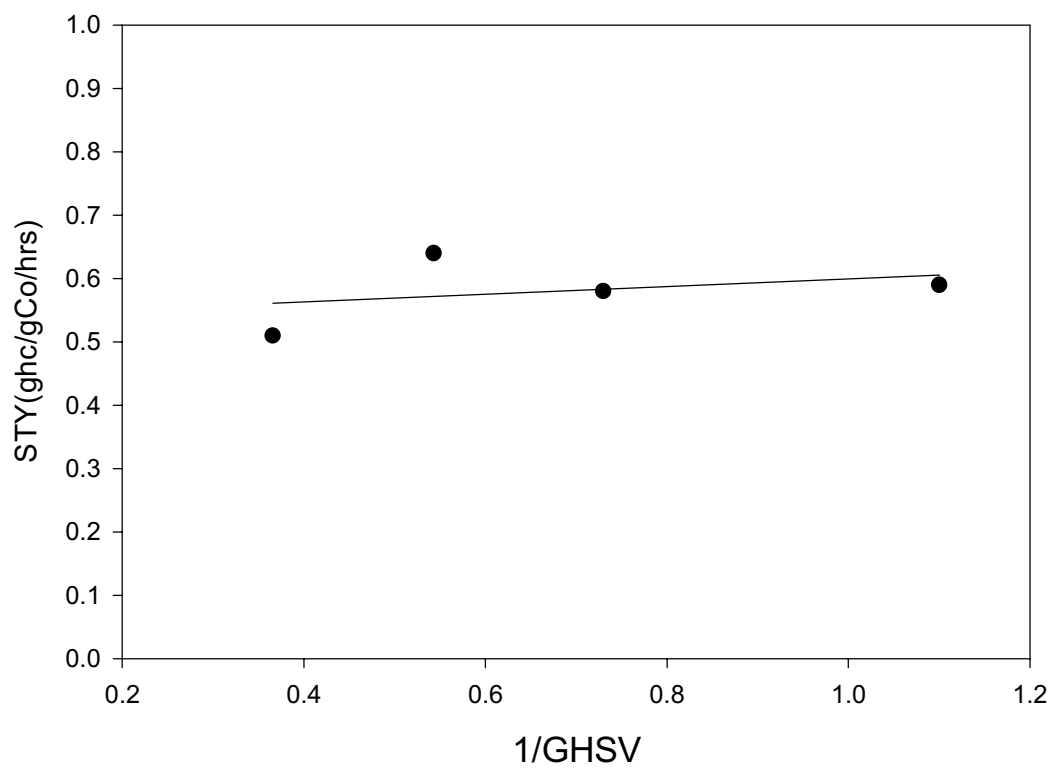


Figure 8. STY vs 1/GHSV in CSTR
(T = 220°C, P = 295 psig).

B. Fischer-Tropsch Synthesis. Effect of CO pretreatment on a ruthenium promoted Co/TiO₂

ABSTRACT

The effect of pretreatment, using hydrogen or carbon monoxide, on the activity and selectivity of a ruthenium promoted cobalt catalyst [Ru(0.20wt%)/Co(10wt%)/TiO₂] during Fischer-Tropsch (F-T) synthesis was studied in a continuous stirred tank reactor (CSTR). The hydrogen reduced catalyst exhibited a high initial synthesis gas conversion (72.5%) and reached steady state after 40 h on stream, after which the catalyst deactivated slightly with time on stream. The carbon monoxide reduced catalyst reached steady state quickly and showed a lower activity and a good stability. Methane selectivity on the carbon monoxide reduced catalyst was 15 –20 % (carbon base), much higher than that on the hydrogen reduced catalyst (5 – 10%). Carbon monoxide regeneration increased the activity on the hydrogen reduced catalyst; however, it did not have significant effect on the carbon monoxide reduced catalyst.

Introduction

Pretreatment conditions used for the supported cobalt Fischer-Tropsch (FT) catalysts often have significant effect on the catalyst activity, selectivity and lifetime (1-9). A number of researchers focused on the study of pretreatment of the catalyst with hydrogen, including the effects of calcination and hydrogen reduction temperatures. Calleja et al. (6) investigated the FT reaction over a Co/HZSM-5 catalyst, and found that the calcination and reduction temperatures did not have an effect on the catalyst activity. The results obtained by Rathousky et al. (8), however, revealed that the calcination and reduction temperatures have a significant effect on the catalytic properties of both Co/Al₂O₃ and Co/SiO₂ catalysts. The turnover frequency (TOF) for the F-T reaction decreased with increasing calcination temperature for both Co/Al₂O₃ and

Co/SiO₂. However, the total reaction rate increased for Co/Al₂O₃ while it decreased for Co/SiO₂ (7-9). Belambe et al. (10) studied the pretreatment effects on the activity of a Ru-promoted Co/Al₂O₃ catalyst for the FT reaction. The calcination temperature was found to have a pronounced effect on the overall activity of the catalyst, but not on the TOF. The reduction temperature had only a negligible effect on the overall activity and TOF. Also, there have been a few related studies on the effect of treatment with carbon monoxide or syngas for the supported cobalt catalysts. It has been reported that the supported cobalt catalyst pretreated with a gas containing carbon monoxide had increased activity and greater selectivity towards producing C₅+ hydrocarbons (11).

The present work was undertaken to investigate the effect of carbon monoxide pretreatment on the titania supported cobalt catalyst. The results obtained have been compared with these of catalyst pretreated with hydrogen. The catalyst chosen for the present study is Ru(0.20 wt%)Co(10 wt%)/TiO₂. Our previous study [12] have shown that this catalyst had good catalyst activity and selectivity for Fischer-Tropsch synthesis.

Experimental

Catalyst preparation

The titania supported cobalt catalyst was prepared by pore volume impregnation of Degussa P-25 TiO₂ (72% anatase, 45 m²/g, calcined at 673 K for 6 h before use) with a cobalt nitrate (Alfa) solution. The sample was dried at 393 K for 16 h and calcined at 573 K for 6 h. The ruthenium promoted catalysts was prepared by impregnating pretreated Co/TiO₂ with a solution containing ruthenium nitrosyl nitrate (Alfa). The sample was dried at 393 K for 16 h and calcined at 573 K for 6 h. The ruthenium and cobalt contents were 0.20 and 10 wt% respectively, corresponding to a atomic Ru/Co of 0.0117.

Reaction system and procedure

A 1-liter autoclave, operated as a continuous stirred tank reactor (CSTR), was used for the slurry FT reaction. Analysis of the gaseous, liquid, and solid (at room temperature) products was conducted both on and off line using a variety of gas chromatographs.

The catalyst was pretreated with pure hydrogen or with pure carbon monoxide at different temperatures. The hydrogen activation was first conducted *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 a helium blanket to the CSTR to mix with 300 g of melted P.W. 3000. The catalyst was then reduced *in-situ* in the CSTR; the hydrogen was introduced to the reactor at atmospheric pressure with a flow rate of 30 NLh⁻¹ (298 K, 0.1 MPa). The temperature was increased to 553 K at a rate 120 K h⁻¹ and maintained at this activation condition for 24 h.

The carbon monoxide activation was conducted *in-situ* in the CSTR according to the following procedure. Approximately 15 g of catalyst was mixed with 300 g of melted polyethylene P.W. 3000 in the CSTR. The reactor pressure was increased to 1.68 MPa with carbon monoxide at a flow rate 30 NLh⁻¹ (298 K, 0.1MPa). The reactor temperature was then increased to 523 K at a rate of 120 Kh⁻¹. These activation conditions were maintained for 24 h. In order to void any deposition of refractory carbon residues, a lower carbon monoxide pretreatment temperature (523 K) was chosen for this study.

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 K h⁻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 was 2 and 3 NL h⁻¹ gcat.⁻¹ and the feed H₂/CO ratio was kept a constant of 2. The conversion of carbon monoxide and hydrogen and the formation of products were measured during a period of 24 h at each condition. Test duration was 210 h on stream for the hydrogen reduced catalyst or 350 h on stream for the carbon monoxide reduced catalyst.

Results and discussion

Catalyst activity

The synthesis gas conversion is a rough measure of the overall Fischer-Tropsch activity of a supported cobalt catalyst. The synthesis gas conversions (mol%) for RuCo/TiO₂ catalysts reduced with hydrogen and with carbon monoxide as a function of time on stream are shown in Figure 1 to illustrate the effect of pretreatment gas on catalyst activity. The space velocity used were 2 and 3 NL/gcat./h. Firstly, a space velocity of 2 NL/gcat./h was used. The hydrogen reduced catalyst exhibited higher initial synthesis gas conversion (73.5%), and it reached the steady state at about 40 h on stream. After steady state, the catalyst deactivated slightly with time on stream. After 120 h on stream, the synthesis gas conversion had decreased to 66.7%. The deactivation rate was about 0.6% per day. When the space velocity was changed to 3 NL/gcat./h, the synthesis gas conversion decreased rapidly, reaching 45.0% at 140 h on stream.

The carbon monoxide reduced catalyst exhibited a very different catalytic performance compared with the hydrogen reduced catalyst. The synthesis gas conversion was lower and it reached the steady state value (32.0%) quickly. After 40 h on stream, the synthesis gas

conversion increased slightly and then remained almost constant (34.0 %) with time on stream during 250 h. When the space velocity was increased to 3 NL/gcat./h, the synthesis gas conversion decreased to 24.0%, lower than on the hydrogen reduced catalyst.

The rate of hydrocarbon production follows the same trend as the synthesis gas conversion, i.e., the hydrogen reduced catalyst exhibited higher hydrocarbon rate than the carbon monoxide reduced catalyst.

Catalyst selectivity

Methane selectivities for the catalysts reduced with hydrogen or with carbon monoxide (calculated as $100 \times (\text{moles of CO converted to CH}_4) / (\text{total moles of CO converted} - \text{moles of CO converted to CO}_2)$), as a function of time on stream are shown in Figure 2. Methane selectivity slightly changed between 15-20% with time on stream on the carbon monoxide reduced catalyst, and the values were higher than the hydrogen reduced catalyst (5-10%). The higher methane selectivity on the carbon monoxide reduced catalyst may be due to some cobalt carbide phase that was produced by the carbon monoxide reduction. However, the methane selectivity varied with synthesis gas conversion, and even a small change on synthesis gas conversion could influence methane selectivity. From Figure 3 it is seen that the same trend can be observed for the catalysts pretreated with hydrogen or with carbon monoxide; i.e. the methane selectivity decreased with increasing conversion for the two catalysts.

It therefore appears that a product is poisoning the methanation reaction relative to the FT reaction. Since water partial pressure increases with increasing CO conversion, it appears most likely that water selectively poisons the methane production. The most reasonable explanation is that there is a cobalt site that produces only methane, or low alpha FT products, that is poisoned

by water. It does not appear that less methane could be produced as the CO conversion increases in a single conventional pathway that follows Anderson-Schulz-Flory (ASF) kinetics.

C₅+ selectivity (expressed as a mass fraction of liquid and wax hydrocarbons in total hydrocarbons) exhibited a trend opposite to the methane selectivity. C₅+ selectivity on the hydrogen reduced catalyst was between 71.5 and 77.8%, higher than the carbon monoxide reduced catalyst (57.4 – 63.2%).

Comparing the two pretreatment methods, the hydrogen pretreatment resulted in a higher Fischer-Tropsch activity, a lower methane selectivity and a higher C₅+ selectivity.

CO regeneration effect

In order to investigate the effect of carbon monoxide treatment on the used catalysts, we switched off synthesis gas after 140 h on stream for the hydrogen reduced catalyst (after 280 h on stream for the carbon monoxide reduced catalyst) and only passed pure carbon monoxide in an attempt to regenerate the catalysts. The regeneration was carried out at reaction temperature (503 K) and a pressure of 1.68 MPa for 24 h. It was found that the carbon monoxide treatment (regeneration) led to an improved catalytic performance in a subsequent FT reaction for the hydrogen reduced catalyst. After regeneration, the synthesis gas conversion increased from 45.0 % to 58.0 % (at 3 NL/gcat./h) during the first 24 h and then gradually decreased to 52%. The methane selectivity firstly decreased from 9.8 to 5.6 % and then gradually increased. However, the carbon monoxide regeneration did not have a significant effect on the carbon monoxide reduced catalyst and the synthesis gas conversion remained essentially constant (at 3 NL/gcat./h). The methane selectivity was not influenced by the regeneration (Figures 1 and 2).

Conclusions

The pretreatment gas (reductant) was found to have a remarkable effect on the catalyst performance of a ruthenium promoted cobalt catalyst during Fischer-Tropsch synthesis. The hydrogen reduced catalyst exhibited a higher initial synthesis gas conversion (72.5%) and reached steady state after 40 h on stream. The catalyst deactivated slightly with time on stream. The carbon monoxide catalyst reached steady state quickly, exhibiting low activity and good stability. Methane selectivity for the carbon monoxide reduced catalyst was 15 –20 % (carbon basis), higher than that on the hydrogen reduced catalyst (5 – 10%). However, methane selectivity depends upon CO conversion and this can account for much of the differences in methane selectivity. Carbon monoxide regeneration increased the activity on the hydrogen reduced catalyst; however, it did not have a significant effect on the carbon monoxide reduced catalyst.

Acknowledgement

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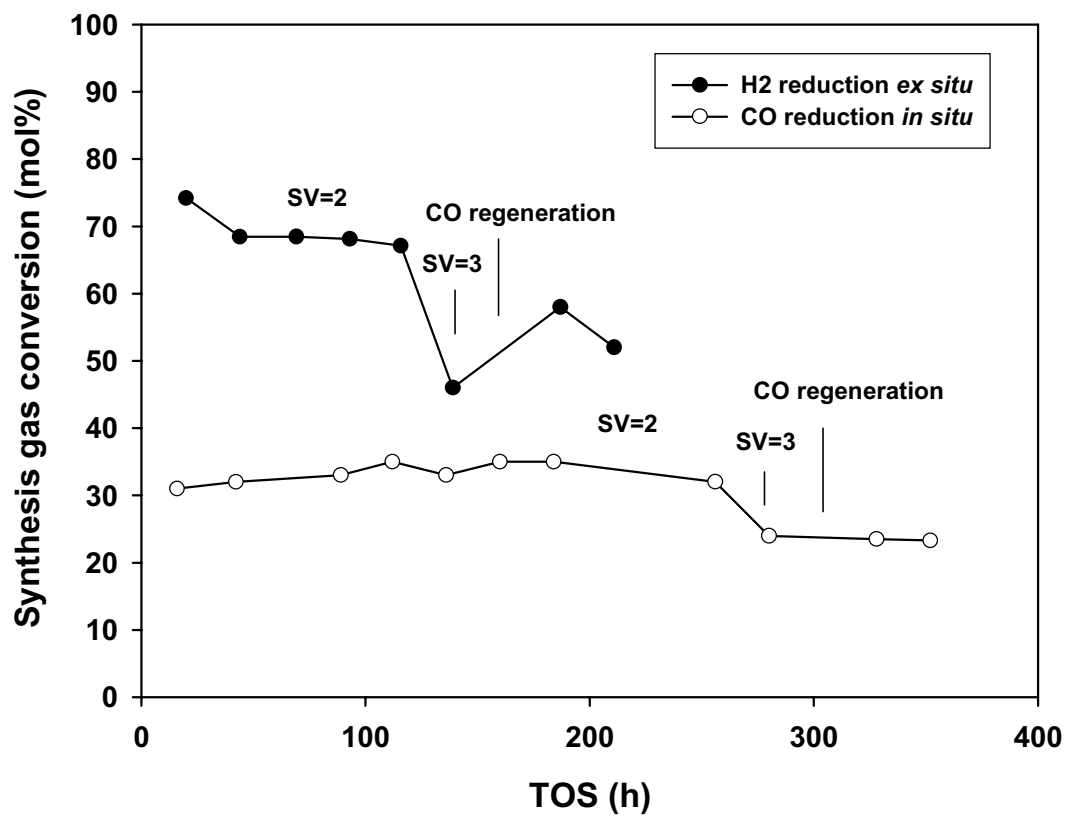


Figure 1. Effect of reduction gas on synthesis gas conversion of RuCo/TiO₂ catalyst

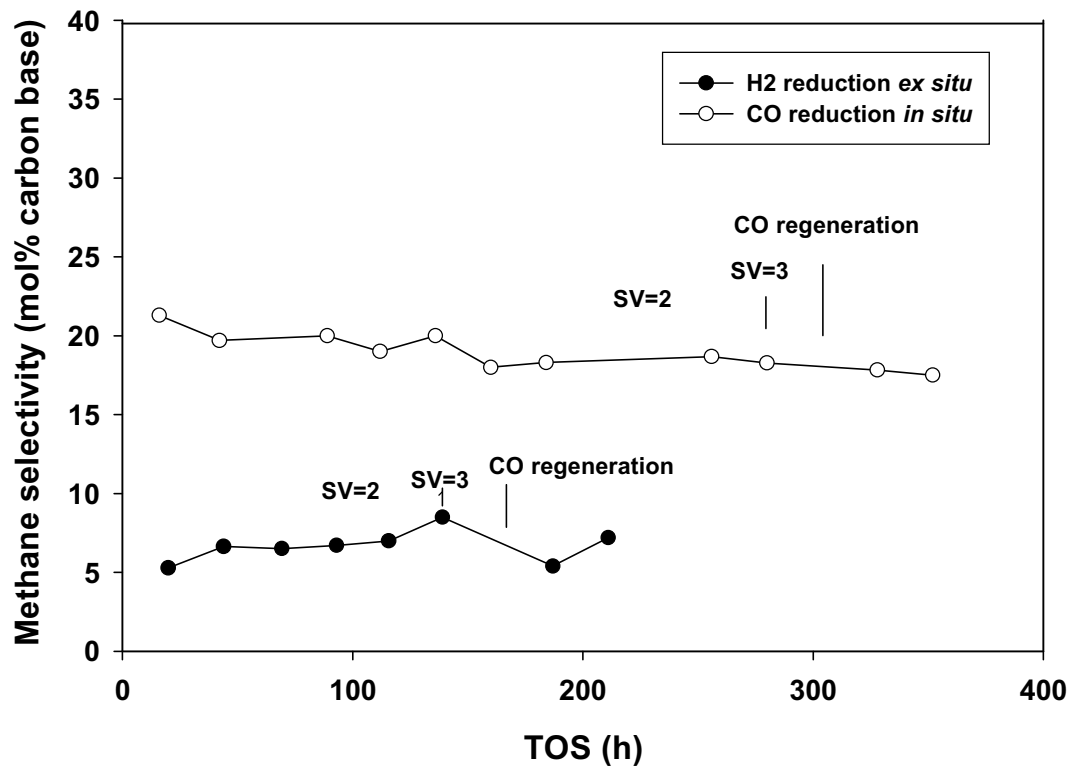


Figure 2. Effect of reduction gas on methane selectivity of RuCo/TiO₂ catalyst

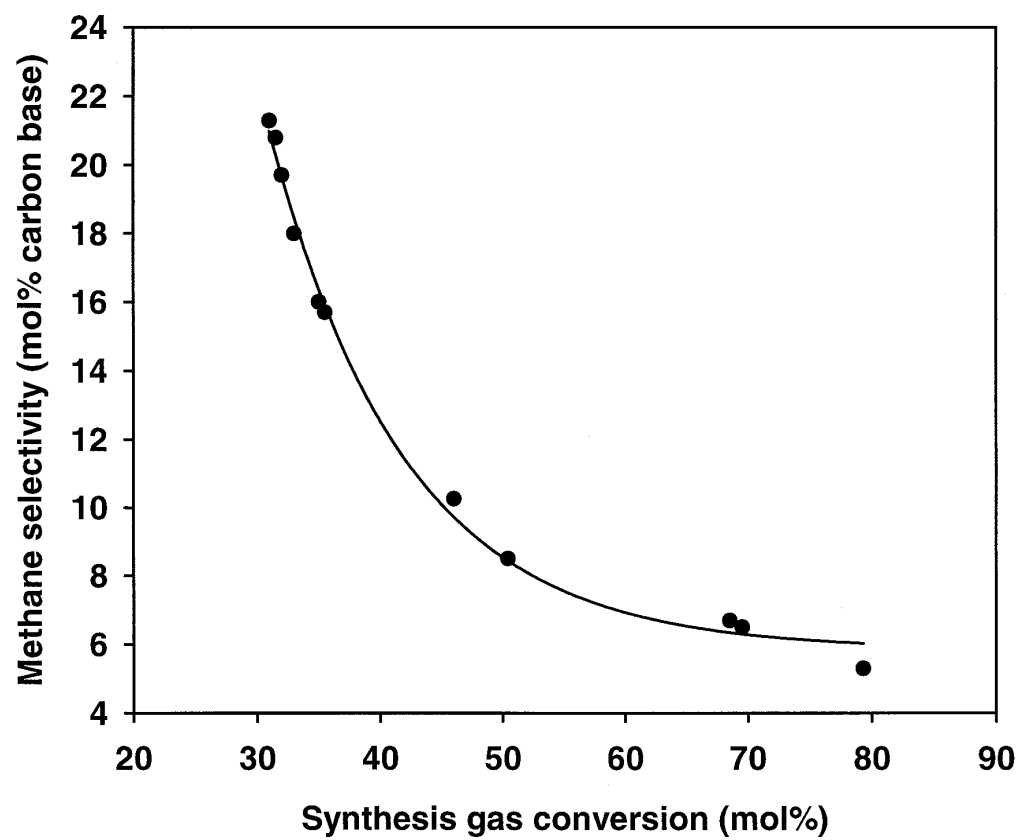


Figure 3. Methane selectivity vs. synthesis gas conversion.