

**VI.6. CO PRETREATMENT OF AN IRON BASED FISCHER-TROPSCH CATALYST
IN THE SLURRY PHASE: COMPARISON OF CSTR AND BUBBLE COLUMN
REACTORS (Liguang Xu, Robert L. Spicer, Shiqi Bao, Robert J. O'Brien
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VI.6.1. INTRODUCTION

The slurry phase Fischer-Tropsch Synthesis (FTS) was developed by Kölbel in the 1940's using a bubble column reactor with precipitated iron catalysts suspended in a high boiling oil (VI.6.1). Kölbel obtained CO conversions in excess of 90% with process conditions of 270°C, 12 atm and a synthesis gas flow of 2.6 Nm³/hr-kg(Fe). Conducting the FTS in the slurry phase has several advantages over conventional fixed bed reactors: uniform temperature in the reactor, good heat transfer, high catalyst and reactor productivity and low cost (VI.6.1). In addition, the slurry phase FTS with iron catalysts enables hydrogen lean synthesis gas to be used because of the water-gas shift activity of iron and because the hydrogen mass transfer coefficient of hydrogen is higher than CO in the slurry phase. This is currently important because modern coal gasifiers typically produce synthesis gas with H₂/CO ratios of ~0.5-0.7.

Activation procedures have a major impact on the ultimate activity and selectivity of iron base Fischer-Tropsch catalysts. It is necessary to reduce fused magnetite catalysts to zero valent iron with H₂ in order to obtain a high surface area necessary for good activity; reduction in CO or CO/H₂ mixtures is completely ineffective (VI.6.2). In contrast, precipitated catalysts have been activated using H₂, CO and CO/H₂. Reduction in H₂ at low temperatures (<220°C) and high flow rates to

prevent sintering by water vapor can lead to active catalysts (VI.6.2). The Kaiser Wilhelm Institute favored pretreatment with CO or CO rich synthesis gas at subatmospheric pressure (VI.6.3). The Bureau of Mines also reported superior activity when precipitated iron catalysts were pretreated in CO or CO/H₂ (VI.6.3). Bukur reports that the best activity, selectivity and stability are achieved when catalysts are pretreated in CO at 280°C and atmospheric pressure (VI.6.4). At the CAER, we have found that activation with CO is the most consistent method for obtaining high activity. Pretreatment of a precipitate iron catalyst promoted with 4.4 atomic % Si and 0.7 atomic % K with CO at 270°C and 175 psig for 24 hr has resulted in runs with CO conversions consistently >90% for periods as long as one month. Herein are reported results of CO activation of an industrially prepared precipitated iron catalyst in laboratory scale CSTR and bubble column reactors. Our results are compared to the slurry phase CO activations conducted at the La Porte demonstration plant operated by Air Products and Chemicals, Inc.

VI.6.2. EXPERIMENTAL

A doubly promoted iron oxide catalyst prepared by United Catalysts, Inc. (Louisville, KY) and designated UCI 1185-78 was used in all runs of this study. Two batches of this catalyst with the following compositions were used: composite 1, 86.6% Fe₂O₃, 12.5% CuO, and 0.05% K₂O; composite 2, 86.4% Fe₂O₃, 12.0% CuO, and 0.05% K₂O. CO treatments of the catalyst were performed in one L autoclaves operated as continuous stirred tank reactors and a 6' bubble column reactor with a 2' i.d. Concentrations of CO and CO₂ in the exit stream of the reactors was monitored by a Carle gas analyzer.

LXU01- The 6' bubble column reactor was loaded with 1780 g of C₃₀ oil and 314.5 g of catalyst composite 1 was added to the oil with a low N₂ flow to ensure ebullation of the catalyst. The N₂ flow was set at 5 SCFH and the temperature was increased to 150°C at 175 psig after which a mixture of 75%CO/25%N₂ was started at a flow rate of 3.0 L/hr-g(Fe). The reactor was heated at 12°C/hr until CO₂ was detected in the exit stream and then heated at 7°C/hr up to 270°C. At approximately 4 hr into the temperature ramp, the pressure of the reactor was lowered to ~80 psig to increase the linear gas velocity by a factor of 2 (6.0 nL/hr-g(Fe)). CO treatment was continued at 270°C, 80 psig until approximately 95% of the theoretical amount of CO₂ had been produced to account for reduction of the catalyst to Cu and χ -Fe₅C₂.

LGX110- 32 g of catalyst composite 1 were mixed with 290 g of a ~C₃₀ Ethylflo polyalpha olefin oil (Ethyl Corporation) in a one L CSTR. The catalyst slurry was heated from 25°C to 150°C at 2°C/min under N₂ at 2.7 nL/hr-g(Fe) and 80 psig. After reaching 150°C, N₂ flow was stopped and a flow of 75% CO/25%N₂ was started at 2.6 L/hr-g(Fe). The temperature was ramped up to 270°C at 12°C/min and maintained until the amount of CO₂ generated was equivalent to the stoichiometric reduction of CuO and Fe₂O₃ to Cu and χ -Fe₅C₂, respectively.

LXU02, LXU03 and LXU04- 314.5 g of catalyst composite 1 and 1780 g of C₃₀ oil were loaded into the 6' bubble column reactor. Similar CO treatment conditions were used for these runs as in the LGX110 run. The reactor was purged with N₂ at a flow of 5.0 SCFH and heated to 150°C at 85 psig. The temperature was then ramped to 270°C at 12°C/hr under a mixture of 75%CO/25%N₂ at 20 SCFH (6.0 nL/hr-g(Fe)).

These conditions were maintained until enough CO₂ had been evolved to account for approximately 95% catalyst reduction.

LGX149- 118.4 g of a mixture of 19.3% composite 1 and 80.7% composite 2 were loaded into a one L CSTR with 290 g of melted polyethylene wax at 100°C. The reactor was purged with N₂ at 2.0 nL/hr-g(Fe) and heated to 220°C at 2°C/min. The catalyst slurry was then treated with a 75%CO/25%N₂ gas mixture at 2.0 nL/hr-g(Fe) and heated to 270°C at 17°C/hr. The reactor was held at these conditions until enough CO₂ had been detected to account for reduction of 50% of the catalyst to Cu and χ -Fe₅C₂.

LGX150- Identical conditions and procedures were followed as for LGX149; however, CO treatment was carried out until enough CO₂ was detected to account for 100% reduction of the catalyst.

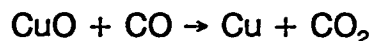
LGX151- The same procedure was used as for LGX150 except C₃₀ oil was substituted for the polyethylene wax.

Two runs were conducted at the La Porte Alternative Fuels Development Unit operated by Air Products and Chemicals, Inc. In the first run, 996 lb of catalyst composite 2 was loaded with 1132 lb of Fischer-Tropsch wax (46.8% catalyst) and treated similarly to that described for LXU01. The catalyst slurry was heated from 93°C to 150°C under N₂ at a rate of 9°C/hr. After reaching 150°C, the catalyst was treated with a 75%CO/25%N₂ mixture at a flow rate of 20,883 SCFH (2.2 L/hr-g(Fe)). The catalyst was heated to 270°C at 7°C/hr and held there until the CO₂ produced was equivalent 128% catalyst reduction.

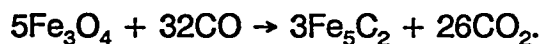
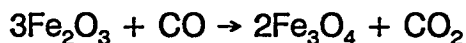
The second run, designated LPFT IIA, used a 29% catalyst slurry with Drakeol-10 start-up oil. Similar run conditions were used as described for LGX149, LGX150 and LGX151. The reactor was heated to 220°C under N₂ and then heated to 270°C at 17°C/hr under a 75%CO/25%N₂ mixture with a space velocity of 2.1 L/hr-g(Fe). These conditions were maintained for approximately 12 hr, ~80% of theoretical CO₂ production.

VI.6.3. RESULTS

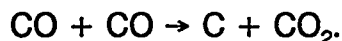
Plots of the concentration of CO₂ in the reactor effluent versus time of CO treatment for the various runs are shown in Figures VI.6.1, VI.6.2 VI.6.and 3.- A small peak corresponding to the reduction of CuO to metallic Cu,



is seen initially, followed by a much larger and broader peak corresponding to the reduction of Fe₂O₃ to Fe₃O₄ and χ -Fe₅C₂



The reduction of the catalyst to Fe₃O₄ and χ -Fe₅C₂ has been verified by Mössbauer spectroscopy. The CO₂ concentration decreases rapidly; however, it never reaches 0 due to production of CO₂ by the Boudouard reaction



Differences in the intensities of the CO₂ peaks in Figures VI.6.1-VI.6.3 can be attributed mostly to differences in the space velocity of the activation gas. Essentially the same amount of CO₂ is liberated per unit weight of Fe for each run, so at high space velocity the CO₂ was diluted by unreacted activation gas as compared to the

low space velocity runs. In Figure VI.6.1, the CO₂ concentration peaked at ~ 4.5 mol% for the La Porte FTII run and 1.5 mol% for the LXU01 run because the La Porte FTII run used a much lower space velocity. This is seen likewise in Figure VI.6.2 where the CSTR run (LGX110, 2.6 L/hr-g(Fe)) had a more intense CO₂ peak than the bubble column reactor runs (6.0 L/hr-g(Fe)). In Figure VI.6.3, the CO₂ peak was substantially higher for the CSTR runs, LGX149, LGX150 and LGX151 than the second La Porte run, despite having similar space velocities. This implies that gas mixing with the catalyst was more efficient in the CSTR runs than in the La Porte demonstration plant which allowed the catalyst reduction to occur more quickly in the CSTR.

Plots of the cumulative CO₂ production for each run are shown in Figures VI.6.4 and 5. Typically the CO₂ production was low until a temperature of ~ 250°C was reached after which it rose rapidly corresponding to iron reduction. Comparing the CO₂ production for runs LXV02, LXU03 and LXU04 (Figure VI.6.4) shows that the catalyst activations were reproducible in the 6' bubble column reactor. Examination of Figure VI.6.4 indicates that activations in the CSTR and 6' bubble column reactor were very similar during the first 13 hr of CO exposure, when operated under the same conditions. It is clear from Figure VI.6.4 that CO₂ production slowed dramatically and asymptotically approached 100% of the theoretical value in the bubble column reactor while the CO₂ production slowed only slightly as it approached the theoretical value in The CSTR. This could indicated that the Boudouard reaction was more active in the CSTR. The CO₂ production for the La Porte FTII run and the 6' bubble column reactor are also compared under similar conditions in Figure VI.6.4. In general the two reactors gave similar results during the first 19 hr of the activations;

however, the La Porte reactor produced CO_2 more quickly during the last 12 hr of the run. This also probably indicates that excessive amounts of elemental carbon was deposited on the catalyst in the La Porte reactor due to the Boudouard reaction. The La Porte FTII run used a very high catalyst loading of >46% which caused the slurry to be too viscous to allow for adequate mixing of the CO with the catalyst. As a result, channeling and slugging occurred which may have caused coking of the catalyst.

In Figure VI.6.5 the CO_2 production for the La Porte FTIIA repeat run is compared to various runs using CSTR's under identical operating conditions. - The La Porte FTIIA run utilized a Drakeol-10 start-up oil which was somewhat lighter than the C_{30} start-up oil used in LGX151. LGX 149 and LGX150 used a heavy polyethylene wax with a carbon number greater than C_{50} . LGX149 was stopped after reaching 50% of the theoretical CO_2 production; however, it was identical to that obtained for LGX150 up to the point the activation was stopped. Comparing LGX150 and LGX151 shows that the CO_2 production was faster when the lighter C_{30} start-up oil was used. This probably was due to a less viscous slurry which allowed for better gas mixing with the catalyst. Comparing LGX151 with the La Porte FTIIA run indicates that the CO_2 production was faster in the CSTR than in the demonstration plant.

In general, it can be concluded that CO activation of the unsupported UCI 1185-78 catalyst in the slurry phase proceeds similarly in laboratory scale CSTR, and bubble column reactors and that these laboratory scale reactors give similar results to an industrial scale bubble column reactor. Differences in the rate of reduction and the amount of carbon deposition are probably due to better mixing of reactants in the laboratory scale reactors as compared to the industrial reactor at La Porte.

VI.6.4. REFERENCES

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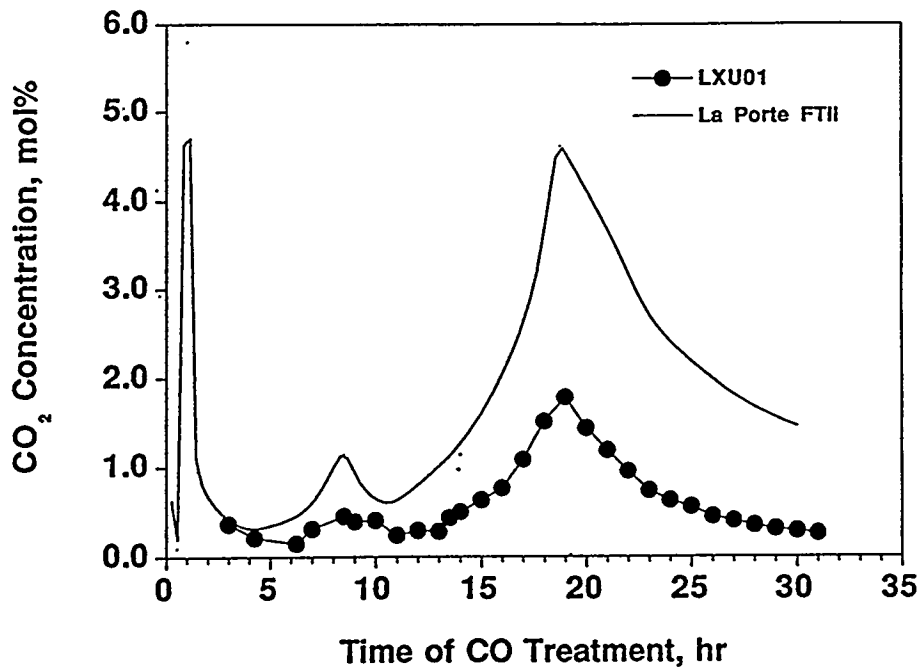


Figure VI.6.1. Concentration of CO₂ in the reactor effluent versus time of CO pretreatment for LXU01 (●) and the LaPorte FT II run (—).

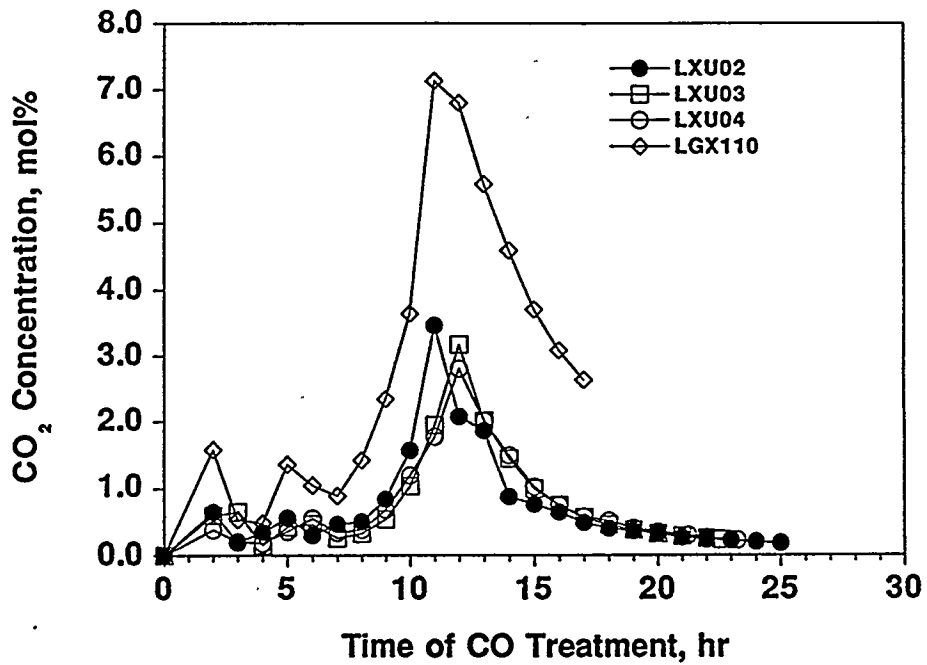


Figure VI.6.2. Concentration of CO₂ in the reactor effluent versus time of Co pretreatment for LXU02 (●), LXU03 (□), LXU04 (○) and LGX110 (◇).

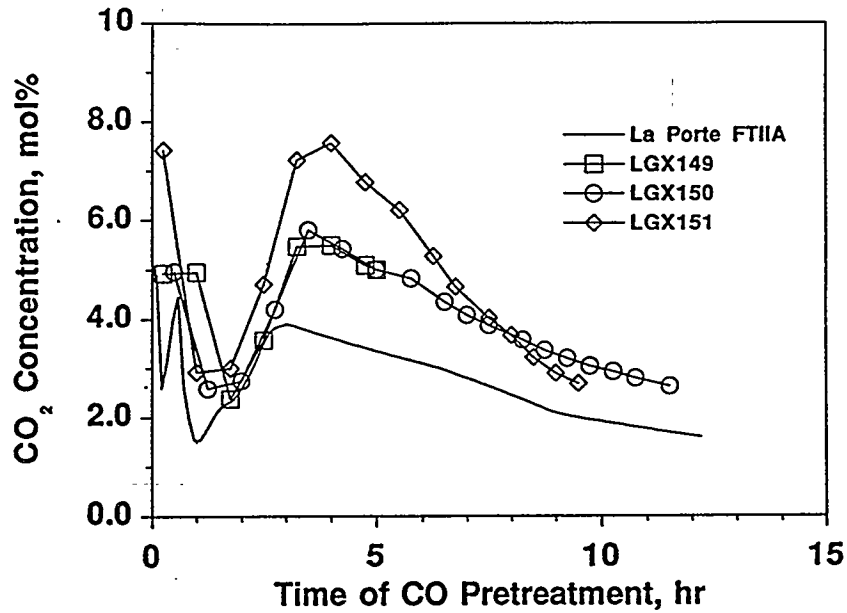


Figure VI.6.3. Concentration of CO_2 in the reactor effluent versus time of Co pretreatment for the LaPorte FT IIA run (—), LGX149 (\square), LGX150 (\circ) and LGX151 (\diamond).

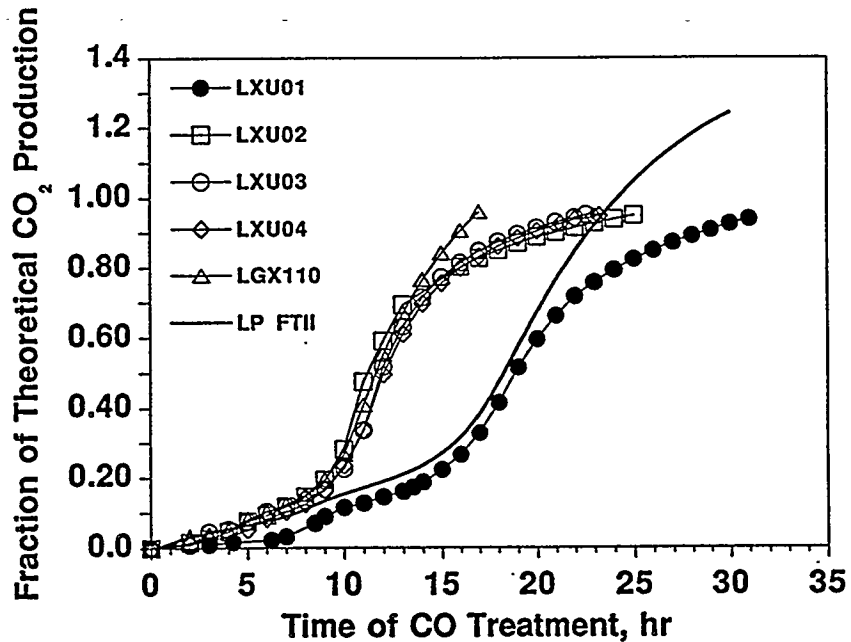


Figure VI.6.4. Cumulative CO_2 production relative to the theoretical CO_2 production for complete reduction to Fe_5C_2 and Cu^0 for LXV01 (\bullet), LVX02 (\square), LXV03 (\circ), LXV04 (\diamond), LGX110 (\triangle) and the LaPorte FT II run (—).

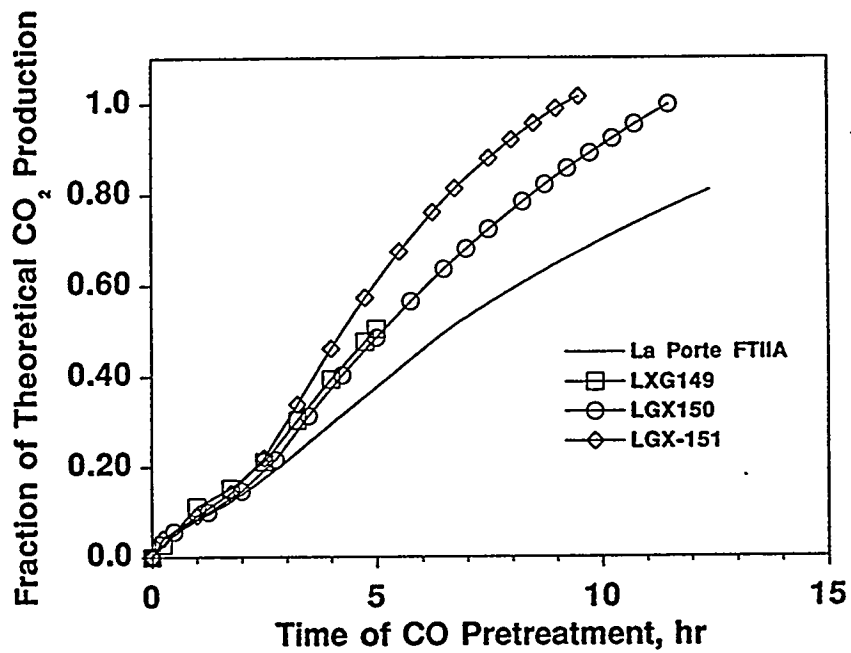


Figure VI.6.5.

Cumulative CO₂ production relative to the theoretical CO₂ production for complete reduction to Fe₅C₂ and Cu⁰ for the LaPorte FT IIA run (—), LGX149 (□), LGX150 (○), and LGX151 (◇).