APPENDIX C

CHRONOLGY OF RUNS IN SLURRY BUBBLE COLUMN REACTORS

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CHRONOLOGY OF RUNS MADE IN THE SLURRY BUBBLE COLUMN REACTORS DURING THE FIRST QUARTER OF 1995

Task 2.0 -- Catalyst Testing

Subtask 2.2 - Slurry Bubble Column Testing

Run No. 35 in the M3-SBCR was started on January 3rd with a charge of 26.0 gm of Catalyst No. Co.041 to attempt another high CO conversion test. This catalyst contained 20% Co plus 8.5% Zr and 0.5% Ru on silica support. The CO conversion was 35.7% at startup conditions which is about 10% higher than obtained with a 15 gm charge (Run 20 in M3-SBCR). The conversion increased to 42.1% at 250°C and 45.1% at 260°C reaction temperature. Lowering the total gas feed rate from 905 SLH to 544 SLH resulted in a slight increase in CO conversion to 46.7%. Lowering the feed gas rate to 403 SLH increased conversion to 49.6%. Reducing the N_2 feed rate to 40% of total with a corresponding increase in H_2 and CO rates reduced the conversion to 47.9%. Reducing the N_2 feed rate to 25% increased the conversion back up to 49.7%. The reactor was returned to startup conditions for a catalyst activity check. The CO conversion was only 19.6%, about one half of the initial activity. The activity loss probably occurred at the higher temperatures. A run will be made with a larger charge of catalyst with a higher loading of cobalt.

Run No. 28 in the M4-SBCR was started on Jaunary 6th with a charge of 15.8 gm of Catalyst No. Co.057. This catalyst contained 20% Co plus 1.0% Re metal, and 1.0% La promoter on silica support. The CO conversion at startup conditions was 18.7%, which is similar to that obtained with an unpromoted silica supported catalyst, Co.011. The CO conversion increased to 25.3% at 250°C, and 29.7% at 260°C. The conversion dropped to 13.8% at the final rate check conditions, about a 25% loss over the entire run.

Run No. 36 in M3-SBCR was started on January 16th with a charge of 15.9 gm of Catalyst No. Co.032. This catalyst contained 20% Co and 8.5% Zr on alumina support with aqueous IW co-impregnation. The CO conversion at startup conditions was 24.0%. This was about 3.5% lower than obtained with Catalyst No. Co.034 which was prepared in multiple steps, aqueous IW, with Zr pre-impregnation. The latter catalyst preparation method appears to increase the final catalyst activity.

Run No. 29 in M4-SBCR was started on January 23rd with a charge of 45.4 gm of Catalyst No. Co.061 to attempt another high CO conversion test. This catalyst contained 30% Co with 0.5% Ru on alumina catalyst support. The initial CO conversion started at 42% and slowly diminished to 29% over a 24-hour period. Catalyst was found in the overhead product for the next three days. Synfluid was stopped after the first day, but this did not stop the catalyst carryover. It appears that the reactor slowly filled up with slurry as indicated by the slow decrease in CO conversion until it began to overflow. The run was shut down after three days and the reactor was drained without flushing. The reactor walls and internal filter were clean on the surfaces. The internal filter pores

were filled with wax and catalyst which was easily removed by steaming. It appears that the internal filter could not function properly with the 45 gm catalyst charge. Additional experiments will be made to determine the optimum catalyst loading that can be used in the existing SBCR's without catalyst carryover.

Run No. 37 in the M3-SBCR was started on January 30th with a charge of 15.9 gm of Catalyst No. Co.045. This catalyst contained 20% Co and 4% Zr on silica support (similar to Co.025 which had 8.5% Zr added). Conversion was only 14.77% at startup conditions, which was considerably lower than obtained with similar catalysts containing 0.0, 0.7, 8.5, and 15% Zr. The CO conversion reached a maximum of 27.4% at 260°C and dropped to 13.7% at startup conditions after 207 hours of operation. The catalyst activity was fairly stable and appeared to be unaffected at the higher temperatures.

Run No. 30 in the M4-SBCR was started on February 6th with a charge of 15.9 gm of Catalyst No. Co.011, an unpromoted 20% Co on silica support catalyst. The CO conversion was only 8% at startup conditions compared to 18.5% in Run 9 in M3 with the same catalyst. The reaction temperature was increased to 280°C where the CO conversion reached 28.5%. Lowering the total gas feed rate from 900 to 540 SLH increased conversion to 36.0%. Lowering the gas rate to 400 SLH increased conversion to 38.5%. Lowering the N_2 concentration from 60% to 25% resulted in a lower CO conversion at 36.0%. After returning to startup conditions, the CO conversion leveled out at 4.4%, a 45% drop from the initial startup conversion. This run will be repeated at a higher catalyst charge level, probably 30 gm (approximately 15 wt% of slurry).

A special test run was made in the M3-SBCR to determine whether slugging or plugging occurred in the reactor system at higher solids loading. A charge of 50 wt% inactive catalyst in synfluid was charged to the M3 reactor. The reactor was brought up to 240°C, 450 psi, and 900 SLH nitrogen gas feed rate. No catalyst carryover was observed. The gas rate was increased to 1300 SLH with still no solids carryover. Finally, synfluid was fed at 30 ml/hr and no overhead slugging and no plugging occurred in the internal heavy product filter. The reactor system can handle high solids loading. However, the reactor cannot handle high heat generation because there is no capability for removing the heat of reaction except by lowering the inlet gas temperature and by adding more nitrogen in the feed gas.

Run No. 38 in the M3-SBCR was started on March 15th with a charge of 15.9 gm of Catalyst No. Co.058. This catalyst contained 20% Co plus 1% La_2O_3 on alumina support. The CO conversion at startup conditions was 28.0%, the total hydrocarbon production rate was 1.28 g/g/hr, and the CH_4 selectivity was 11.9%. A similar catalyst, Co.005, which consisted of 20% Co and no additives on alumina support produced similar results; 27.1% CO conversion production rate of 1.34 g/g/hr, and 7.9% CH_4 selectivity. The addition of La_2O_3 had no effect on catalyst activity.

Run No. 39 in the M3-SBCR was started on March 22nd with a charge of 15.9 gm of Catalyst No. Co.064. This catalyst contained 20% Co with 0.5% Ru and 8.5% Zr on alumina support. This catalyst is similar to Catalyst No. Co.034, but has 0.5% Ru added. The CO conversion was considerably higher with the added Ru, 34.2% vs. 27.5%, but the CH_4 selectivity was also much higher, 13.6% vs. 10.4%. Similar CO conversion and CH_4 selectivity was obtained with Catalyst No.

Co.053 which contained 0.5% Ru and no Zr. The addition of Zr to promoted or unpromoted alumina supported catalysts has little or no effect on catalyst activity.

Subtask 3.1 - Reproducibility of Catalyst with Low Methane Selectivity

Three 1 Kg samples were obtained from Calsicat for reproducibility and aging tests. Each catalyst contained 20% Co, 0.5% ruthenium, and 0.3% potassium on Vista Catapal B alumina.

Run No. 31 in the M4-SBCR was started on February 20th with a charge of 15.9 gm of Catalyst No. CAL.12. The initial CO conversion at startup conditions was 27.6%. The total hydrocarbon production rate was 1.26 g/g/hr and the CH_4 selectivity was 7.9%. These values are very similar to those obtained with two previously formulated Calsicat catalysts, CAL.04 and CAL.05. They are also similar to the reference catalyst prepared by Pitt, Catalyst No. Co.047.

Run No. 32 in the M4-SBCR was started on February 27th with a charge of 15.9 gm of the second batch of catalyst from Calsicat, No. CAL.11. The initial CO conversion was slightly higher at startup conditions, 30.6%. The THC was slightly higher, 1.40 g/g/hr, but the CH_4 selectivity was the same, 7.8%. This catalyst contained a little more ruthenium than CAL.12.

Run No. 33 in M4-SBCR was started on March 6th with a charge of 15.9 gm of the third batch of catalyst from Calsicat, No. CAL.13. The initial CO conversion at startup conditions was 28.1%, very similar to the first batch of catalyst, CAL.12. The total hydrocarbon production rate was similar, 1.28 g/g/hr vs. 1.26 g/g/hr, but the CH_4 selectivity was a little lower, 6.4% vs. 7.9%. This run will be extended up to 1000 hours at the same run conditions as the catalyst aging test of the low methane selectivity catalyst prepared by Calsicat. At 111 hours into the run, the CO conversion had dropped to 25.12% and the THC to 1.145 g/g cat/hr. For the next 300 hours, the CO conversion slowly dropped at 0.58%/day and the THC production rate dropped at 1.1 g/g cat/hr. This run will be continued to 1000 hours on stream or terminated earlier if deemed necessary.