APPENDIX C

CHRONOLOGY OF RUNS IN SLURRY BUBBLE COLUMN REACTORS

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

Task 2.0 -- Catalyst Testing

Subtask 2.2 - Slurry Bubble Column Testing

Run No. 40 in the M3-SBCR was started on April 13th with a charge of 15.0 gm of Catalyst No. Co.063. This catalyst contained 20% Co plus 8.5% La_2O_3 on alumina support. The CO conversion at startup conditions was only 8.7% which is considerably lower than 28% CO conversion obtained with Catalyst No. Co.058 that contained 1.0% La_2O_3. Too much La_2O_3 had a negative effect on catalyst activity.

Run No. 41 in the M3-SBCR was started on April 19th with a charge of 15.0 gm of Catalyst No. Co.062. This catalyst contained 30% Co with 0.5% Ru metal and 1.5% K promoter on alumina support. The CO conversion at startup conditions was only 6.6% which is considerably lower than that obtained with similar catalysts containing 0.5, 0.3, and 0.1% K. Apparently, the amount of K added was too high.

Run No. 42 in the M3-SBCR was started on April 26th with a charge of 15.9 gm of Catalyst No. Co.065. This catalyst contained 20% Co with 0.5% Ru, 8.5% Zr, and 0.3% K promoters on alumina support. The CO conversion at startup conditions was 27.6%, the total hydrocarbon production rate was 1.25 g C_1+/g cat/hr, and the CH_4 selectivity was 7.85%. These results were almost identical to those obtained with Catalyst No. Co.047 which contained 0.5% Ru and 0.3% K, but no Zr. The addition of Zr to alumina supported catalysts has little or no effect on the catalyst activity.

Run No. 43 in the M3-SBCR was started on May 8th with a charge of 9.1 gm of Catalyst No. CoW.12. This catalyst contained 10% Co, 10% Fe, with 0.5% Ru on silica support. The CO conversion at startup conditions was 6.1%, the THC production rate was 0.47 g C_1+/g cat/hr, the CH_4 selectivity was 20.3%, and the CH_2 selectivity was 7.3%. Unfortunately, there was only 60% of the normal catalyst charge amount available which resulted in lower CO conversion. The presence of Fe in the catalyst, however, yielded low CO conversion and higher CH_4 selectivity increased to 32.4%.

Run No. 44 in the M3-SBCR was started on May 17th with a charge of 15.6 gm of Catalyst No. CoW.11. This catalyst contained 10% CO_2, 10% Fe, with 0.5% Ru and 0.5% K on alumina support. The CO conversion at startup conditions was quite low, 4.7%, with a CH_4 selectivity of 8.4%. The CO conversion increased to 24.5% at 280°C reaction temperature while the CH_4 selectivity increased to 25.6%.

Run No. 45 in the M3-SBCR was started on May 24th with a charge of 15.9 gm of Catalyst No. Fe.01. This was the only iron catalyst without Co that has been tested. It contained 30% Fe plus 1.5% Cu on silica support. The CO conversion at startup conditions was quite low, 3.4%, while the CH_4 selectivity was too low to detect. The CO conversion increased to 14.5% at 280°C and 19.0% at 300°C reaction temperature. The CH_4 and CO_2 product selectivities at 300° C were 23.3% and 26.7% respectively. In general, the iron catalysts had much lower activity and produced more CH_4 and CO_2 than cobalt catalysts in the slurry bubble catalytic reactors.

Run No. 46 in the M3-SBCR was started on June 1st with a charge of 15.7 gm of Catalyst No. CoW.05. This catalyst contained 20% Co, 5.0% Cu, and 4.0% Zr on alumina support. The CO conversion at startup conditions was quite low, 4.87%, with a CH_4 selectivity of 10.9%. The CO conversion increased to 14.0% at 280°C reaction temperature while the CH_4 selectivity increased to 44.2%. At 300°C, the CO conversion peaked at 19.4% and the CH_4 selectivity reached 54.4%.

Run No. 47 in the M3-SBCR was started on June 21st with a charge of 15.6 gm of Catalyst No. Co.070. This catalyst contained 13% Co on alumina support with no promoters. The CO conversion at startup conditions was 22.8% with a CH_4 selectivity of 10.93%. The CO conversion dropped to 8.6% at 220°C reaction temperature and increased to 19.8% later in the run when the temperature was raised back to 240°C. The CO conversions, CH_4 selectivities, and production rates with 13% Co catalyst were lower than those obtained with 20 and 30% Co catalysts, but not proportional to the Co concentration. The catalyst activity was higher than expected.

Subtask 2.3 - CSTR Testing

Three catalysts, CAL.13, Co.005, and Co.041, were taken by Bill Gall to the Center for Applied Energy Research of the University of Kentucky at Lexington, Kentucky to be run in their one liter autocalve reactor. The purpose was to obtain kinetic rates and high syngas conversion data. High CO conversions were attained with a maximum of 99% for Catalyst No. CAL.13. The complete run results will be available next month. Results for Catalyst Nos. Co.005, Co.041, plus one more catalyst will be available in a few weeks.

Task 4.0 - Catalyst Aging Studies

Run No. 34 in M4-SBCR was started on June 8th with a charge of 15.8 gm of Calsicat Catalyst No. CAL.13 to attempt an aging run at lower temperatures. The CO conversion was only 1.0% at 210°C reaction temperature, so the temperature was increased to 220 C. When the CO conversion reached only 2.5%, it was decided to terminate the run. The reactor was disassembled and most of the catalyst was found inside the internal filter and in the heavy product tank. Apparently, there was a crack or defect in the filter, so a new filter was installed.

Run No. 35 in the M4-SBCR was started on June 14th with a charge of 25.0 gm of Calsicat Catalyst No. CAL.13 to repeat Run No. 33. The CO conversion at 220°C was too high, 17.2%, so the reaction temperature was held at 212°C where the initial CO conversion was 8.87%. After 240 hours on-stream the CO conversion leveled out at 7.4% for the remainder of the run, a total of 524 hours on-stream. The average rate of deactivation of the catalyst was about 5.96 gm CO/Kg catalyst/hr per Kg CO converted. The deactivation rate at 240°C was 30 gm CO/Kg catalyst/hr per Kg CO converted; thereby, demonstrating that catalyst deactivation is dependent on temperature rather than on total syngas consumed.