APPENDIX A

Improved Catalyst Activation Tests in Laboratory

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One of the objectives of the methanol/fluid dynamics run in the AFDU at LaPorte was to demonstrate new technology proposed for Kingsport. To simplify the process equipment and procedure for catalyst reduction in the Liquid Phase Methanol plant design for Eastman, a new reduction procedure for the standard baseline catalyst was investigated in the lab. The goal of the new reduction procedure was to eliminate H_2O production during reduction by using H_2-free reduction feed gas, decrease the time required for reduction, and simplify the temperature ramping procedure. To this end, reduction of the baseline catalyst was carried out in the lab autoclave using CO in N_2 feed gas (H_2-free). The activity and life of the catalyst were also tested.

Background

The current design for the Liquid Phase Methanol plant at the Eastman Chemical Company complex includes a catalyst reduction vessel from which slurry containing fresh, reduced catalyst will be supplied to the process. The heretofore established reduction procedure for the baseline catalyst involves an empirically established temperature ramping protocol and the use of H_2-containing reduction gases (either 2% H_2 in N_2 or 4% Texaco syngas in N_2). The use of H_2 as a reductant results in the production of H_2O via CuO reduction:

$$H_2 + CuO \rightarrow Cu + H_2O.$$

However, H_2O production during reduction complicates downstream processing since slurry mineral oil vaporized and entrained during reduction and H_2O may form two phases and the H_2O produced must be processed as waste water.

To investigate the possibility of simplifying the process equipment and operating procedure for catalyst reduction, a new reduction procedure was investigated in the 300 cc lab autoclave. The goal of the new reduction procedure is to minimize water production during reduction, decrease the time required for reduction, and simplify the temperature ramping procedure. In this experiment, a nominal 2% CO in N_2 reduction gas was used. Thus, CuO is reduced by CO:

$$CO + CuO \rightarrow Cu + CO_2,$$

which eliminates H_2O as a direct product of reduction.

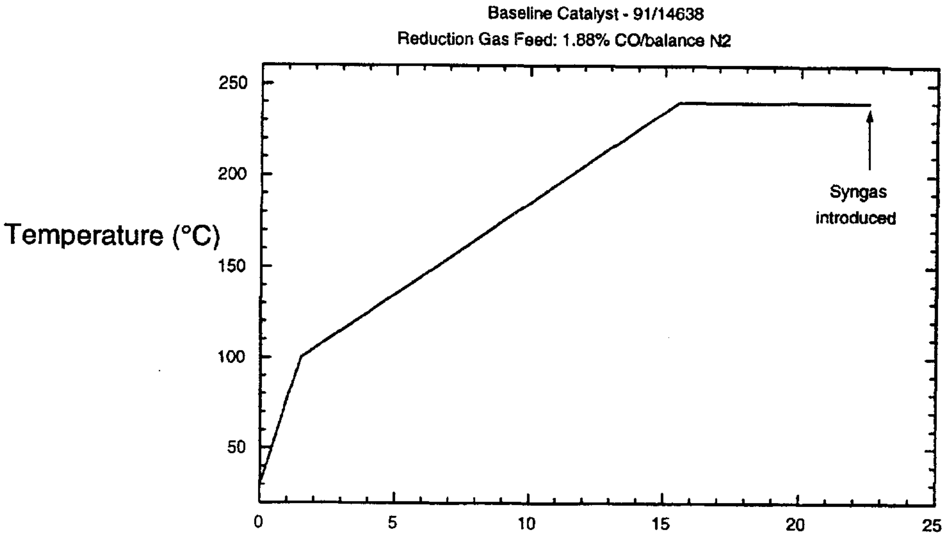
Experimental

The time-temperature ramp was simplified. The previously established procedure involved a 12 hr temperature hold at 200°C during the overall increase from 100°C to 240°C. For the present experiment, the temperature was increased from 100°C to 240°C at 10°C/hr continuously, thereby saving 12 hr in the reduction procedure. A feed flow rate of 1500 std.lit./kg-hr and a pressure of 50 psig were chosen.

Reduction with 2% CO-98% N_2

Figure A.1 shows the time temperature profile used for this experiment.

Figure A.1. Temperature Ramp Used for Catalyst Reduction

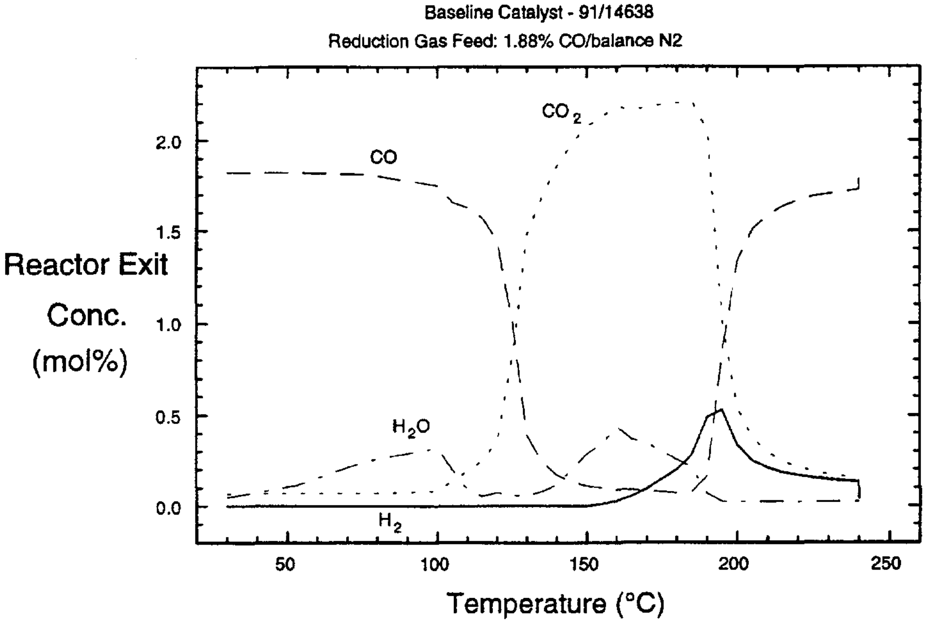


Syngas introduction was delayed for several hours after 240°C was reached so that the feed could be switched during normal working hours. As shown below, very little occurs during the 240°C hold. In practice, the feed could be switched as soon as the reactor temperature reaches 240°C.

The reactor effluent concentrations of CO, CO_2, H_2O, and H_2 during reduction were obtained by GC. The GC was calibrated for H_2O using a controlled temperature and pressure H_2O saturator. For low concentrations, a sub-0°C condenser (freezer) was used downstream of the H_2O saturator. Water concentration was calculated from the vapor pressure of liquid or solid H_2O at the saturator or freezer temperature. The GC response was slightly non-linear, necessitating the use of a calibration curve. Quantitation accuracy for H_2O was ±10% (relative) for H_2O concentrations greater than 0.1 mol%, but the detection limit was about 0.025 mol%.

Figure A.2 shows the reactor effluent concentrations of CO, CO_2, H_2O, and H_2 during reduction plotted as a function of the reduction temperature.

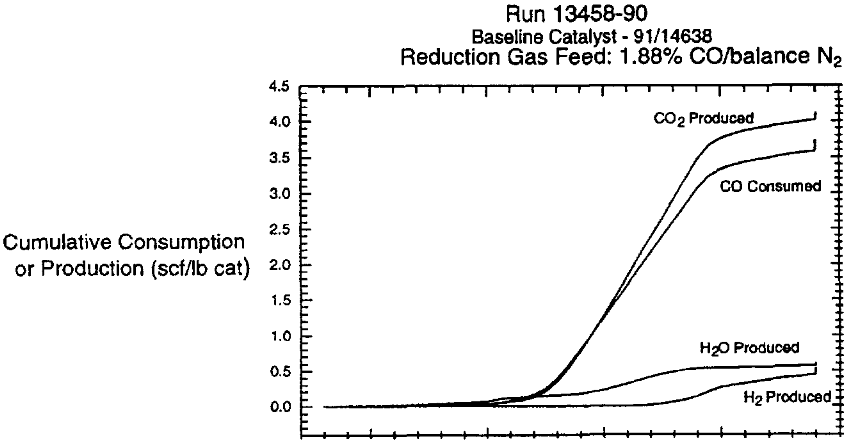
Figure A.2. Reactor Exit Concentration versus Reduction Temperature



Clearly, CO is consumed, while CO_2, H_2O, and H_2 are produced during reduction.

Figure A.3 shows the cumulative consumption of CO and the cumulative production of CO_2, H_2O, and H_2 versus reduction temperature.

Figure A.3. Cumulative Consumption/Production versus Reduction Temperature



The use of the CO/N_2 feed gas did not completely eliminate H_2O production during reduction. Approximately 0.55 scf of H_2O/lb of as-received catalyst was produced during reduction. This detection of unexpected H_2O was examined in detail.

The presence of two peaks in the water concentration profile in Figure A.2 suggests that H_2O is derived from two different sources during reduction. The low temperature peak probably corresponds to the loss of physically adsorbed H_2O that has been retained after calcination or adsorbed during handling after calcination. The second peak is probably produced from decomposition of the "hydroxy-carbonate" precursor that constitutes the as-received catalyst. This hydroxy-carbonate precursor eliminates hydroxide groups as H_2O during heat-up.

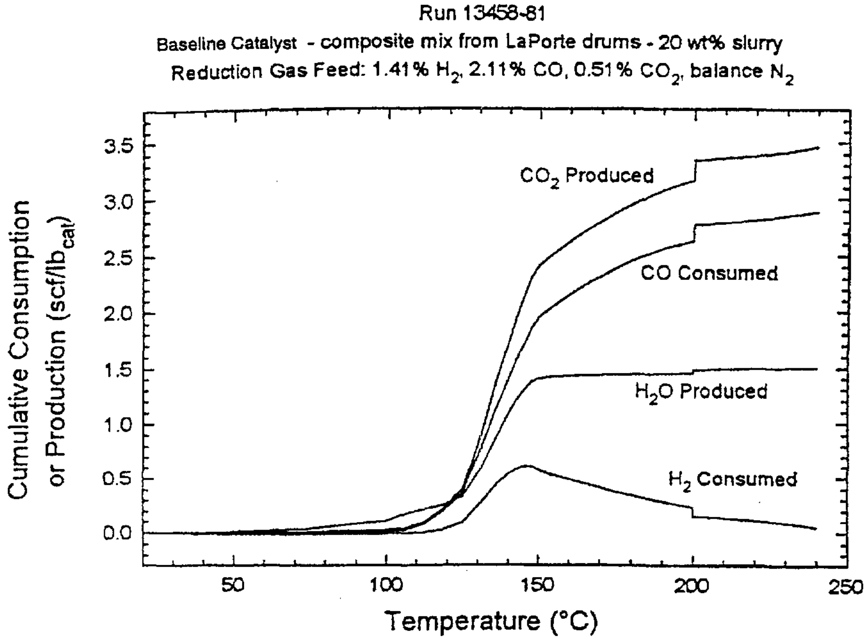
The H_2 produced in the later stage of reduction results from H_2O reacting with CO via the water-gas shift reaction:

$$CO + H_2O \leftrightarrow H_2 + CO_2.$$

Thermodynamic equilibrium for the exothermic shift reaction lies very far to the right for the temperature range of reduction, thereby representing a possible "sink" for H_2O during reduction. The equilibrium constant, Kp, ranges from 3600 at 100°C to 105 at 240°C. However, the data show that the shift reaction was far from equilibrium at any point during reduction up to 190°C. At temperatures greater than 190°C, the H_2O concentration was below the detection limit, so it was impossible to determine whether the shift reaction was close to equilibrium.

Comparison of the present results with results from a "standard" reduction using 4% syngas in N_2, for which a slower temperature ramp was also used, reveals corroborating evidence. Figure A.4 shows the cumulative consumption of CO and H_2 (H_2 is first consumed and then produced during reduction with syngas) and the cumulative production of CO_2 and H_2O.

Figure A.4. Cumulative Consumption/Production versus Temperature for Reduction Using 4% Syngas in N_2

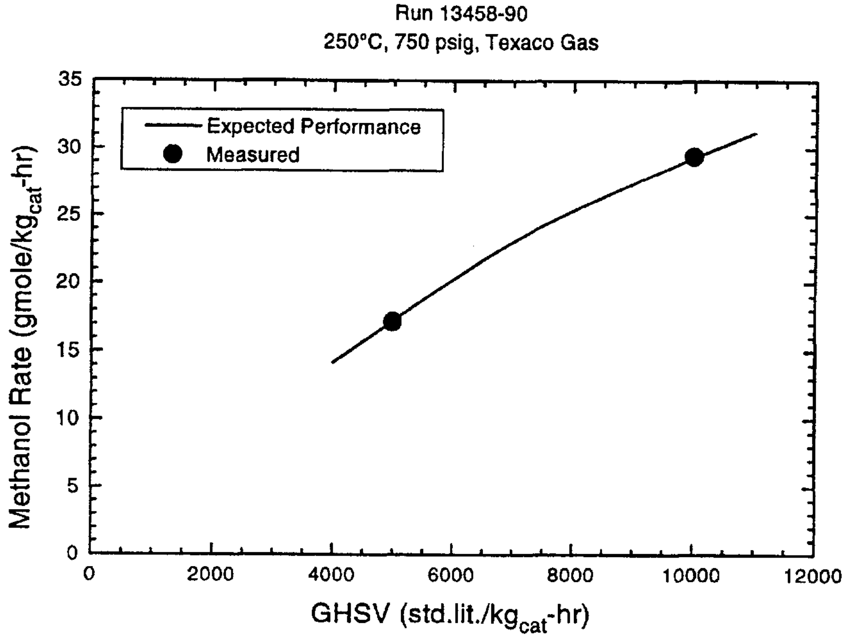


As expected, the H_2O produced for the H_2-containing reduction feed gas is higher: 1.5 scf of H_2O/lb versus 0.55 scf of H_2O/lb for the 2% CO/N_2 reduction gas. Again, the shift reaction is far from equilibrium for data points where the H_2O concentration was above the detection limit.

Activity of CO-Reduced (2% CO in N_2)

The catalyst activity after reduction using 2% CO/N_2 was measured at 250°C and 750 psig using Texaco syngas feed (35% H_2/51% CO/13% CO_2/1% N_2) at GHSVs of 5,000 and 10,000 std.lit./kg-hr. The expected performance and the results for the activity tests after reduction using 2% CO/N_2 are shown in Figure A.5.

Figure A.5. Performance of Catalyst After Reduction Using 2% CO in N_2



The expected performance curve was established by previous lab data for the baseline catalyst after reduction in 4% syngas in N_2 or 2% H_2 in N_2 using slower temperature ramps. Clearly, reduction using 2% CO/N_2 and the faster temperature ramp produced a catalyst with the same performance as that obtained using the H_2-containing reduction gases.

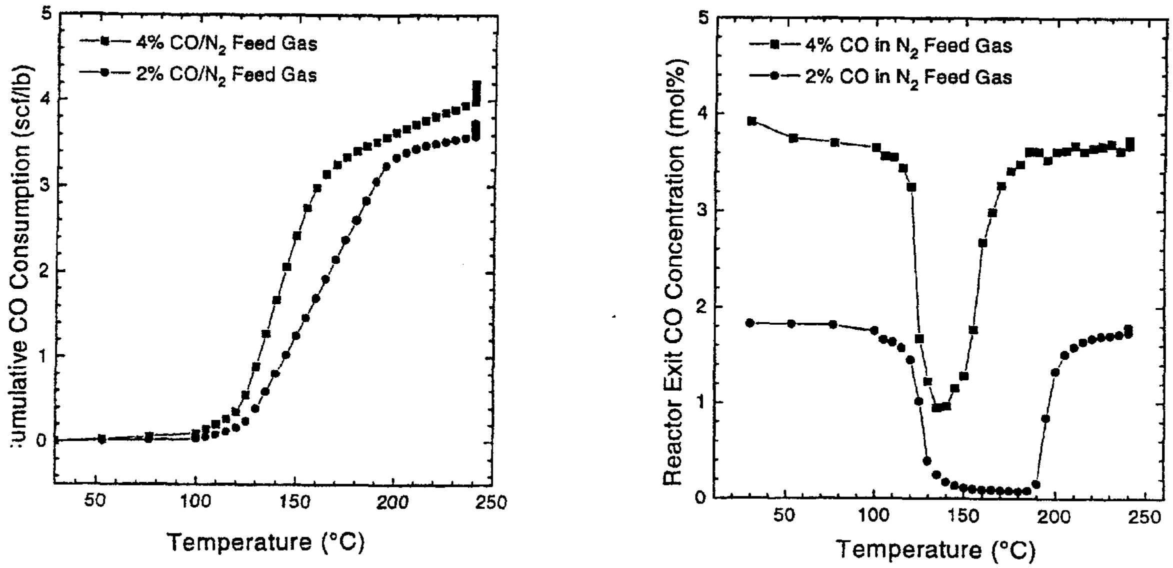
Reduction and Performance Using 4% CO (Balance N_2)

H_2O production during reduction was not entirely eliminated but reduced by 63% compared to reduction by 4% syngas in N_2 (contains H_2). Even though the 2% CO reduction gas was H_2-free, H_2O was still produced from thermal desorption of physically adsorbed H_2O and dehydroxylation of the hydroxy-carbonate catalyst precursor. Also evident in this experiment was that the CO concentration was nearly zero during a portion of the temperature ramp, indicating almost complete consumption of the reductant.

In an attempt to avoid the complete consumption of reductant and to further reduce the production of H_2O during reduction, in situ reduction was done in the lab autoclave using a feed gas with a higher CO content (4% CO in N_2). The hypothesis was that the higher CO concentration may drive the water-gas shift reaction, $CO + H_2O = CO_2 + H_2$, to the right, thereby reducing H_2O production during reduction. Moreover, the use of higher CO concentration may avoid complete consumption of reductant, a situation that has an unknown, but possibly deleterious, effect on catalyst activation.

In situ reduction of the baseline catalyst was carried out using the 300 cc autoclave system. The temperature ramp, pressure, and feed flow rate were the same as those used for the 2% CO in N_2 reduction experiment. Figure A.6 compares the CO uptake and reactor exit CO concentration as a function of temperature for reduction using 2% CO and 4% CO. The final consumption of CO is slightly higher for the 4% CO case, but probably not significantly different within the accuracy of the measurements. Also, the rate of CO consumption is faster for the 4% CO case, indicating a positive dependence of reduction rate on CO concentration. Note also that the lowest reactor exit CO concentration for the 4% CO feed case dropped to a minimum of 1 mol%, in contrast to the 2% CO feed case in which the reactor exit CO concentration fell nearly to zero.

Figure A.6. The Effect of CO Feed Concentration on CO Consumption and Reactor Exit CO Concentration

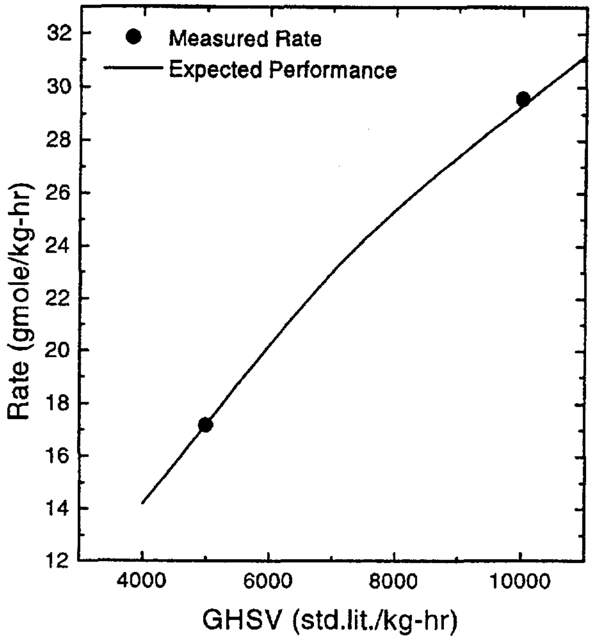


The fact that the CO concentration in the reactor was higher for 4% CO reduction apparently had no effect on the H_2O produced. The cumulative H_2O produced for the

4% CO reduction was estimated to be 0.65 scf/lb, which is comparable (within the experimental accuracy of the GC measurements) to the 0.55 scf/lb measured for the 2% CO reduction. Of course, these values are much lower than the 1.5 scf/lb measured for reduction using 4% Texaco gas in N_2. Evidently, the higher reactor CO concentration did not have a measurable effect on H_2O conversion via the water-gas shift reaction.

Reduction with 4% CO resulted in a catalyst with the same methanol synthesis activity as that obtained after reduction using the standard H_2-containing reduction gases. Figure A.7 shows the measured performance after reduction with 4% CO and the expected performance curve after reduction using previously established reduction procedures and H_2-containing reduction gases. Clearly, the performance of the catalyst after the new reduction procedure equals that obtained for the previously established reduction procedure. Thus, in situ reduction of the baseline catalyst with 4% CO in N_2 is a viable way of activating the catalyst.

Figure A.7 Methanol Synthesis Rate after 4% CO Reduction
250°C, 750 psig, Texaco Gas



A new procedure that was changed slightly from the initial procedure to conserve CO was implemented. The data for the run are summarized in Figures A.8-A.11. The heating rate and gas flow rate have been slightly modified from the initial run (Run 8--Figure A.8). Gas uptake rate and product generation (Figs. A.9-11) were satisfactory for all runs. The new procedure is substantially similar to the old procedure.

Figure A.8 Reduction Temperature Profiles
4% CO/Balance N_2;
SV: 1,500 sl/kg-hr for 14191-50, 1,600 for 14045-08

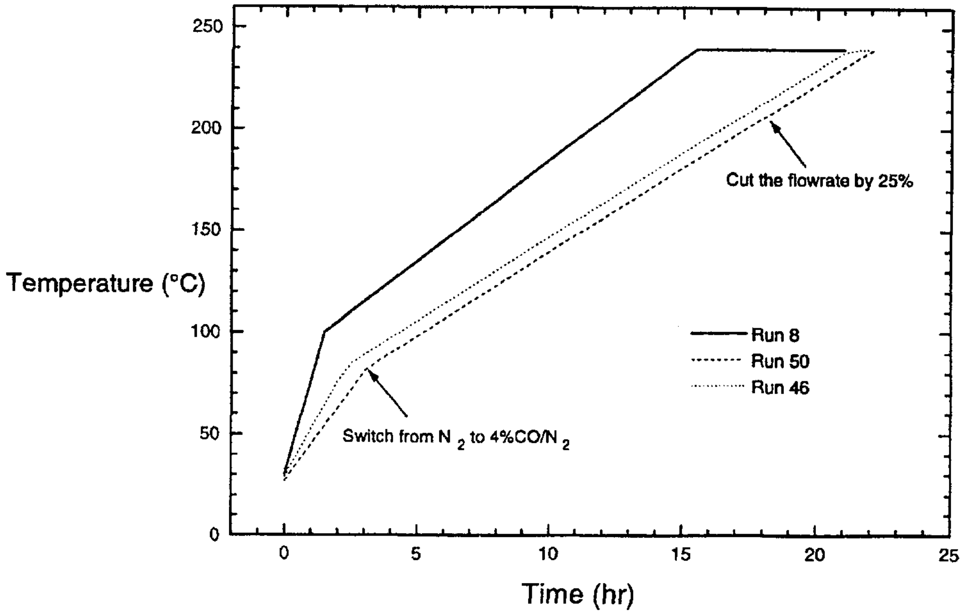


Figure A.9 Runs 14191-50 and 14045-08
Reduction Gas Feed: 4% CO/Balance N_2;

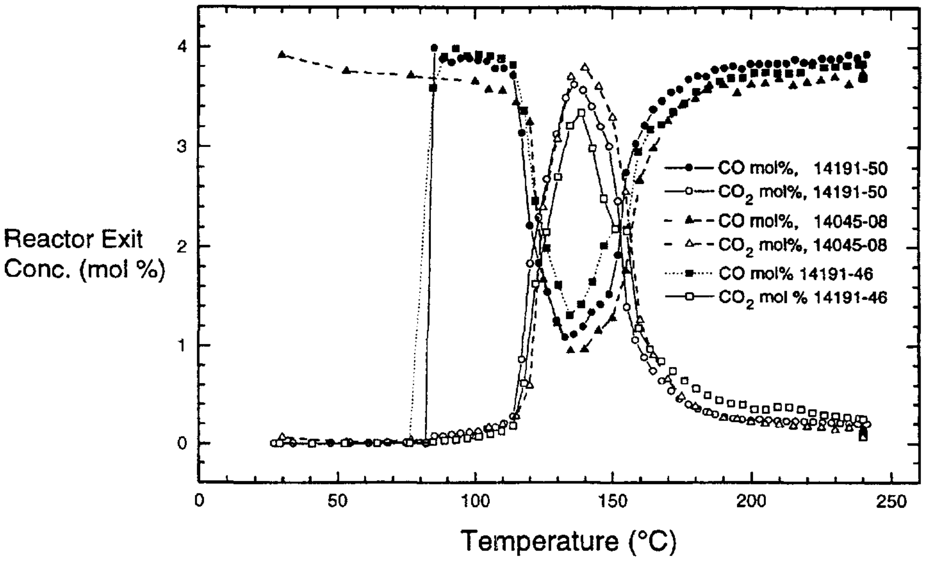


Figure A.10 Runs 14191-50, 14191-46, and 14045-08

Reduction Gas Feed: 4% CO/Balance N_2

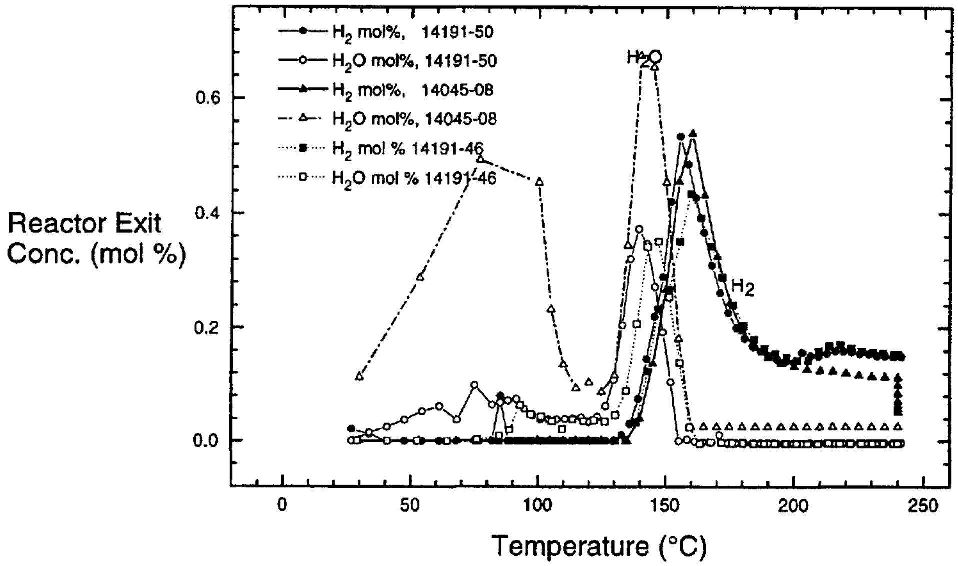
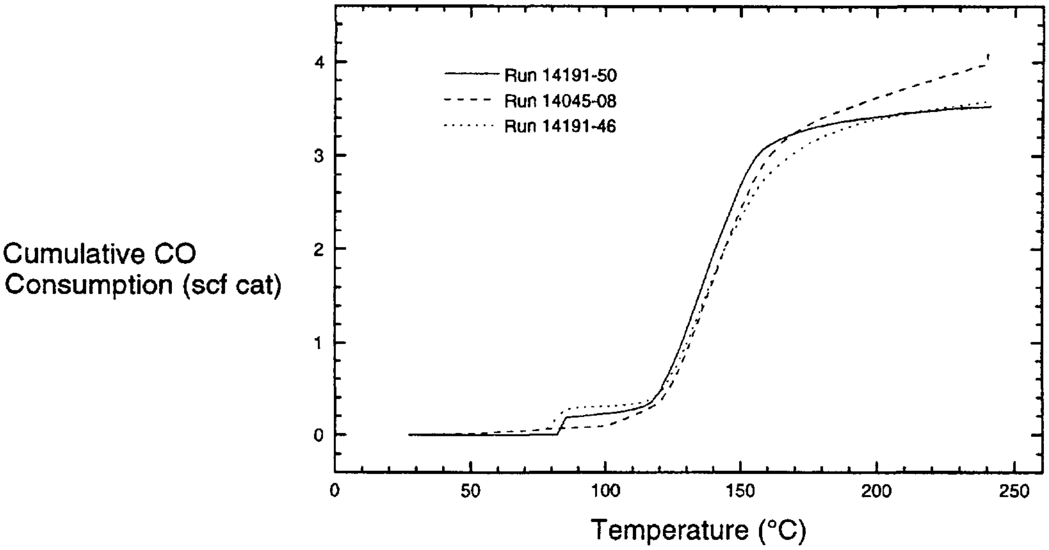


Figure A.11 Comparison of Different Procedures

Runs 14191-50 and 14045-8 14191-46

Baseline Catalyst - 91/14638



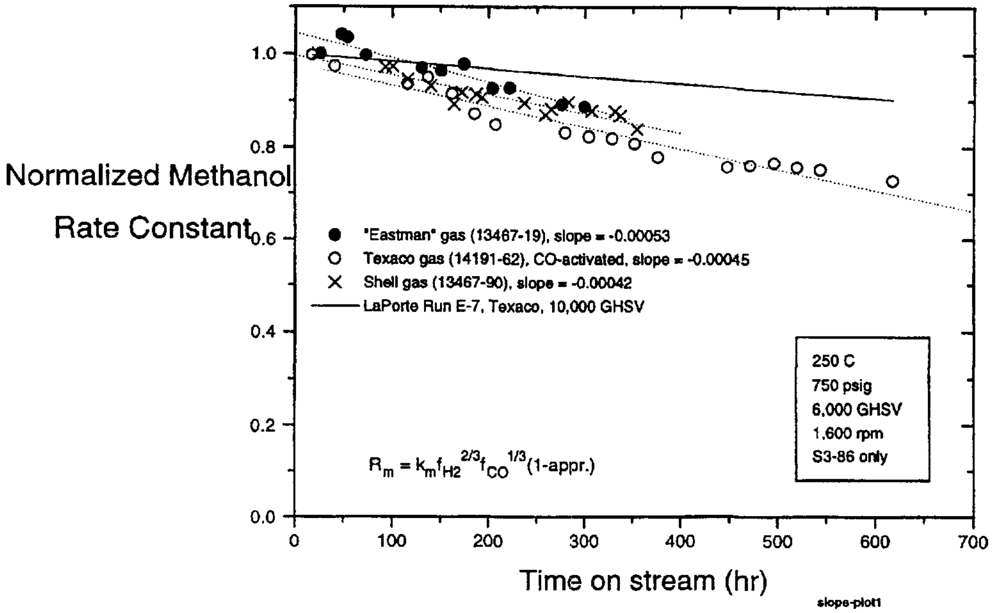
Life Test of Catalyst Activated Using CO

The final check on the CO activation procedure was to test the life of a CO-activated catalyst. Test results were analyzed by noting the change in specific rate constant with time. A decrease in rate constant translates to catalyst aging. To account for small differences in initial activity, aging is expressed as a % of the initial activity/unit time.

While the best kinetic expression available for methanol formation is not perfect, the correlation is good enough so that aging data can be compared. Since a CSTR is used for the rate measurement, the reaction conditions depend upon the activity of the catalyst. Using the rate expression allows comparison with experiments done at other conditions and accounts for small changes in operating conditions and catalyst activity.

Figure A.12 shows historical data of activation with H_2 taken for the baseline catalyst. The slope of the line is a direct measurement of aging. The laboratory tests always show a higher aging rate than measured in the LaPorte test. The reasons for this difference are not clear. The laboratory test gives a fairly constant value for aging and thus, may be used as an indication of the relative stability of the catalysts.

Figure A.12. Baseline Catalyst Deactivation in #1 300 cc Autoclave



The data for CO activated catalyst are shown in Figure A.13. The slope of the line from the laboratory data is about the same as for the laboratory data using the standard activation method. Therefore, we conclude that CO activation does not adversely affect the performance of the catalyst.

Figure 1.4.13. CO Reduction Comparison