Title: Final Report: Sensitivity of Fischer-Tropsch synthesis and water-gas shift catalysts to poisons from high-temperature high-pressure entrained-flow (EF) oxygen-blown gasifier gasification of coal/biomass mixtures

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Abstract

There has been a recent shift in interest in converting not only natural gas and coal derived syngas to Fischer-Tropsch synthesis products, but also converting biomass-derived syngas, as well as syngas derived from coal and biomass mixtures. As such, conventional catalysts based on iron and cobalt may not be suitable without proper development. This is because, while ash, sulfur compounds, traces of metals, halide compounds, and nitrogen-containing chemicals will likely be lower in concentration in syngas derived from mixtures of coal and biomass (i.e., using entrained-flow oxygen-blown gasifier gasification gasification) than solely from coal, other compounds may actually be increased. Of particular concern are compounds containing alkali chemicals like the chlorides of sodium and potassium.

In the first year, University of Kentucky Center for Applied Energy Research (UK-CAER) researchers completed a number of tasks aimed at evaluating the sensitivity of cobalt and iron-based Fischer-Tropsch synthesis (FT) catalysts and a commercial iron-chromia high temperature water-gas shift catalyst (WGS) to alkali halides. This included the preparation of large batches of 0.5%Pt-25%Co/Al_2O_3 and 100Fe: 5.1Si: 3.0K: 2.0Cu (high alpha) catalysts that were split up among the four different entities participating in the overall project; the testing of the catalysts under clean FT and WGS conditions; the testing of the Fe-Cr WGS catalyst under conditions of co-feeding NaCl and KCl; and the construction and start-up of the continuously stirred tank reactors (CSTRs) for poisoning investigations.

In the second and third years, researchers from the University of Kentucky Center for Applied Energy Research (UK-CAER) continued the project by evaluating the sensitivity of a commercial iron-chromia high temperature water-gas shift catalyst (WGS) to a number of different compounds, including $KHCO_3$, $NaHCO_3$, HCl, HBr, HF, H_2S, NH_3, and a combination of H_2S and NH_3. Cobalt and iron-based Fischer-Tropsch synthesis (FT) catalysts were also subjected to a number of the same compounds in order to evaluate their sensitivities at different concentration levels of added contaminant.

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Executive Summary

At the project kickoff meeting, UK-CAER was requested to provide the four groups involved in the overall project with standard UK-CAER cobalt and iron Fischer-Tropsch (FT) synthesis catalysts. UK-CAER opted to provide a 0.5%Pt promoted 25%Co/Al_2O_3 catalyst supported on Sasol 150 m^2/g γ-Al_2O_3 for use at H_2/CO ratio of 2.0, and a precipitated/impregnated 100Fe: 5.1 Si: 3.0K: 2.0 Cu catalyst for use at H_2/CO ratios in the range of 0.7 – 0.8. Catalysts were prepared, calcined by Süd-Chemie, Inc., and furnished to the different groups (RTI, TDA, and DOE-NETL) during the third quarter. UK-CAER also procured a high temperature shift (HTS) catalyst from Süd-Chemie, Inc.

UK-CAER carried out catalyst characterization tests, and herein are included results of Brunauer, Emmett, and Teller (BET) surface analyses; Barrett, Joyner, and Halenda (BJH) pore size distributions (PSD), temperature programmed reduction (TPR), and hydrogen chemisorption/pulse reoxidation. UK-CAER is not permitted to carry out detailed characterization analyses on the commercial Süd-Chemie, Inc. HTS catalyst, since the catalyst is a proprietary formulation. For the cobalt-based FT catalyst, TPR and hydrogen chemisorption/pulse reoxidation tests are important for assessing the strength of the support interaction with cobalt species. Moreover, hydrogen chemisorption/pulse reoxidation provides a measure of the surface cobalt active site density, the extent of reduction of cobalt, and based on these two measurements an estimate of the average cobalt cluster size. The iron-based catalysts are very complex and difficult to characterize, since the working catalyst typically contains a mixture of different iron carbides, as well as a core of Fe_3O_4 iron oxide. Activation procedures for cobalt and iron catalysts are thus completely different. Cobalt catalysts are activated in hydrogen in order to form the active surface cobalt metal atoms, while iron-based catalysts are activated in CO in order to carburize the surface, the carbide being an important active surface for the synthesis. Attempts were made to analyze use catalysts by XANES spectroscopy carried out at Brookhaven National Laboratory. However, the results were inconclusive as to whether or not oxidation took place as little differences were observed between fresh and used catalysts. This is likely due to the fact that there is a significant amount of Fe that is not located on the surface, and it is difficult to obtain side-by-side comparisons of cobalt catalysts due to the stability issues associated with small cobalt particles supported on a strongly interacting support, alumina. We thus advocate that an alternative approach be used in the future, whereby model catalysts are developed specifically for synchrotron studies. Moreover, the studies should be carried out such that catalyst is withdrawn from the reactor before, during, and after poisoning so that the impact of poisoning can be assessed more transparently within a single run.

With the Sud-Chemie, Inc. high temperature shift Fe-Cr catalyst, little deactivation was observed with up to 200 ppb KCl, NaCl, up to 100 ppb $KHCO_3$, up to 1 ppm H_2S, and up to 5 ppm NH_3. With a combination of NH_3 and H_2S, little deactivation was observed with up to 0.6 ppm NH_3 in combination with up to 6 ppm H_2S. The only run in which measurable deactivation was observed was with 100 ppb $NaHCO_3$.

For the Fe-based Fischer-Tropsch synthesis catalyst (100Fe/5.1 SiO_2/2Cu/3K) tested, we observed a low impact on the deactivation rate with up to 100 ppm NaCl, 20 ppm KCl, 40 ppm $NaHCO_3$, 40 ppm $KHCO_3$, 0.75 ppm HCl, 0.6 ppm HBr, 0.1 ppm HF, 200 ppm NH3, 0.3 ppm H2S, and 1 ppm HCN. Moderate rates of deactivation were observed between 0.75 and 1.5 ppm of HCl and between 0.6 and 5.0 ppm HBr. High deactivation rates were observed between 20 and 40 ppm HCl, between 20 and 40 ppm HBr, with 20 ppm HF, with 800 ppm NH_3, and with just 1 ppm of H_2S.

With the Co-based Fischer-Tropsch synthesis catalyst (0.5%Pt-25%Co/Al_2O_3 using 150 m^2/g alumina), virtually no deactivation was observed with up to 1000 ppm $KHCO_3$ or 20 ppm HBr, only a slight deactivation of the catalyst was observed with up to 500 ppm KCl, up to 50 ppm NaCl, up to 1000 ppm $NaHCO_3$, up to 500 ppm HCl, and up to 100 ppm NH_4OH. However, a major impact was observed with H_2S in CSTR runs carried out with up to 5.4 ppm and 2.9 ppm.

Report Details –

A. Experimental methods

A.1 Catalyst Procurement or Preparation

A.1.1 Sud-Chemie, Inc. Iron-Chromia High Temperature Shift Catalyst

UK-CAER successfully procured a commercial Fe-Cr high temperature shift catalyst from Süd-Chemie, Inc. However, UK-CAER was not permitted to distribute the Süd-Chemie catalyst to other groups involved in the overall DOE project. Süd-Chemie, Inc. requested that the other groups contact Süd-Chemie, Inc. staff on an individual basis, in order to explain clearly their restrictions on usage. In a DOE web-meeting, group contacts for all groups indicated that they had successfully and independently procured the Süd-Chemie, Inc. catalysts.

A.1.2 Fe-Si-K-Cu Fischer-Tropsch Synthesis Catalyst

UK-CAER prepared, with the aid of Süd-Chemie, Inc., several kilograms of Fe-Si-K spray dried catalyst. Approximately 4-5 kilograms of uncalcined material were used. Precipitated iron catalysts were prepared using a ferric nitrate solution obtained by dissolving $Fe(NO_3)_3{\cdot}9H_2O$ (99.9 % purity) in distilled and deionized water, and then the amount of tetraethyl orthosilicate was added to provide the desired Fe/Si ratio. The mixture was stirred vigorously until the tetraethyl orthosilicate had hydrolyzed. A flow of the tetraethyl orthosilicate and iron nitrate mixture was added to a continuously stirred tank reactor (CSTR) precipitation vessel together with a stream of 30 % ammonium hydroxide that was added at a rate to maintain a pH of 9.5. By maintaining the slurry pH at 9 and an average residence time of 6 min, a base catalyst material containing iron and silicon (Fe: Si= 5:1) was obtained. The slurry from the CSTR was filtered with a vacuum drum filter and then washed twice with deionized water. The final filter cake was dried for 24 h in an oven at 110 °C with flowing air. The catalyst was calcined at 350 °C in an air flow for 4 h. For this study, the Fe/Si catalyst base powder was impregnated with the proper amount of aqueous KNO_3 (99.9 % purity) solution to produce the desired composition of Fe/Si/K = 100: 5.1: 1.25 (atomic ratios). The catalyst was dried at 110°C over night following impregnation. Three separate elemental analyses (Galbraith Laboratories) were carried out on the as-prepared catalyst and the amounts of KNO_3 and $Cu(NO_3)_2 \cdot 2.5\ H_2O$ (both 99.9 % purity) to be added to this base catalyst for preparing Fe/Si/K/Cu = 100: 5.1: 3.0: 2.0 were calculated using an average of the three analyses as a basis. Further loading of K and Cu was carried out sequentially using the IWI method whereby K was added first, followed by Cu. Between each step the catalyst was dried under vacuum in a rotary evaporator at 80 °C and the temperature was slowly increased to 95 °C. After the second impregnation/drying step, the catalyst was calcined by Süd-Chemie, Inc. researchers under air flow at 350 °C for 4 h. The catalyst was designated GJ457. Samples (~200 g) of catalyst GJ457 were shipped to Dr. Jason Trembly (RTI), Dr. Gokhan O. Alptekin (TDA), and Dr. Bryan Morreale (DOE) on June 8, 2009.

A.1.3 0.5%Pt-25%Co/Al_2O_3 Fischer-Tropsch Synthesis Catalyst

Two appropriate gamma alumina supports were procured from Sasol, including a 200 m^2/g support (i.e., Catalox Sba-200) and a 150 m^2/g support (i.e., Catalox Sba-150). Two separate 0.5%Pt-25%Co/Al_2O_3 catalysts, one using the 200 m^2/g support and one using the 150 m^2/g support, were prepared. To the support (previously calcined at 400°C in a muffle furnace for 4 hours), a slurry impregnation was utilized to load, in three impregnation and drying steps, enough cobalt nitrate to achieve between 2 and 3 kilograms of ~25% Co on Al_2O_3 after calcination. The catalysts were dried by rotary evaporation under vacuum at ~95°C. Prior to calcination, Pt promoter was added (to ~ 0.5% by weight) by aqueous incipient wetness impregnation (IWI) of tetraammine Pt(II) nitrate. The 200 m^2/g supported Co catalyst (GJ455) was calcined at Süd-Chemie, Inc. in February, 2009. The second batch on the 150 m^2/g support (GJ456) was calcined at Süd-Chemie, Inc. during May, 2009. Samples (~200 g) of catalyst GJ456 were shipped to Dr. Jason Trembly (RTI), Dr. Gokhan O. Alptekin (TDA), and Dr. Bryan Morreale (DOE) on June 8, 2009.

A.2 Catalyst Characterization

A.2.1 Elemental Analysis

Inductively coupled plasma (ICP) was used to obtain weight percentages of Pt, Co, Fe, Si, K and Cu in the samples. First, the catalyst powder was dissolved in a mixture of aqua-regia and HF. A nebulizer was used to introduce the sample to the plasma torch in Ar carrier. The torch is located in an induction coil, carrying high frequency AC. The electrically conducting ionized gas was thus heated by Joule’s effect to temperatures in the vicinity of 10,000 K. Under these conditions, the particles were atomized and partially ionized. When reverting to lower energy states, photons were emitted and detected for elemental analysis. The ICP analyses were conducted at Galbraith Laboratories.

A.2.2 BET Surface Area and BJH Porosity Measurements

The surface area, pore volume, and average pore radius of the supports and catalysts were measured by BET using a Micromeritics Tri-Star 3000 gas adsorption analyzer system. For each case, approximately 0.35 g of sample was weighed out and loaded into a 3/8″ sample tube. Nitrogen was used as the adsorption gas and sample analyses were performed at the boiling temperature of liquid nitrogen. Prior to a measurement, the sample was slowly ramped to 433K and evacuated overnight to approximately 6.7 Pa. Pore size distributions (PSD) of supports and catalysts were also quantified by the Barrett, Joyner, Halenda (BJH) method, which provides a relationship where the amount of adsorbate lost during a desorption step gives the average size of the pore emptied during that desorption step. Experimentally, the adsorption branches were employed, and PSDs, single point pore volumes, and pore radii with their corresponding BJH adsorption/desorption counterparts are provided.

A.2.3 Temperature Programmed Reduction

Temperature programmed reduction (TPR) profiles were recorded using a Zeton-Altamira AMI-200 unit which makes use of a TCD detector. The samples were first ramped to 350^{o}C in pure Ar to drive off any residual H_2O from the sample, prior to cooling to 50^{o}C to begin the TPR. The tests were performed using 10%H_2/Ar mixture referenced to Ar at a flow rate of 30 cm^3/min. The samples were heated to 1100^{o}C at a ramp rate of 10^{o}C per min.

A.2.4 Hydrogen Chemisorption with Pulse Reoxidation

Hydrogen chemisorption/pulse reoxidation [1] measurements were performed using a Zeton Altamira AMI 200 unit, which incorporates a thermal conductivity detector (TCD). The sample weight was ~0.2 g. The catalyst was activated at 350^{o}C for 10 h using 30 cm^3/min of 33%H_2, balance argon, and then cooled under flowing hydrogen to 100^{o}C. The sample was held at 100^{o}C under flowing argon to prevent physisorption of weakly bound species prior to increasing the temperature slowly to the activation temperature, 350^{o}C. At that temperature, the catalyst was held under flowing argon to desorb the remaining chemisorbed hydrogen so that the TCD signal returned to the baseline condition. The TPD spectrum was integrated and the number of moles of desorbed hydrogen determined by comparing to the areas of calibrated hydrogen pulses. Prior to experiments, the sample loop was calibrated with pulses of nitrogen in helium flow and compared against a calibration line produced from gas tight syringe injections of nitrogen under helium flow.

After TPD of hydrogen, the sample was reoxidized at the activation temperature by injecting pulses of pure oxygen in helium referenced to helium gas [1]. After oxidation of the cobalt metal clusters, the number of moles of oxygen consumed was determined, and the percentage reduction calculated assuming that the Co^0 reoxidized to Co_3O_4. While the uncorrected dispersions are based on the assumption of complete cobalt reduction, the corrected dispersions reported include the percentage of reduced cobalt as follows. A 1:1 ratio of H:Co site was assumed.

$\%D_{uncorr.}$ = (# of cobalt atoms on surface × 100%)/(total # cobalt atoms)

$\%D_{corr.}$ = (# of cobalt atoms on surface × 100%)/[(total # cobalt atoms)(fraction reduced)]

A.2.5 X-ray Absorption Near Edge Spectroscopy

In early December 2010, CAER researchers carried out X-ray absorption near edge spectroscopy (XANES) measurements over several used iron and cobalt Fischer-Tropsch synthesis catalysts, whereby the catalyst was solidified in the wax in its activated state. XANES measurements were recorded at Brookhaven National Laboratory (beamline X-18b), Upton, New York. Used catalysts (i.e., post-run) were evaluated at the cobalt K edge (7,709 eV) or Fe K edge (7,112 eV) in transmission mode. The beamline was equipped with a Si(1 1 1) channel cut monochromator. A crystal detuning procedure was used to help minimize glitches arising from harmonics. The X-ray ring at the NSLS has a flux of 1×10^{10} photons per second at 100 mA and 2.8 GeV, and the usable energy range at X-18b is from 5.8 to 40 keV. From reference compounds, sample thickness was determined by calculating the amount in grams per square centimeter of sample, w_D, by utilizing the following thickness equation: $w_D = \ln(I_o/I_t)/$ sum $\{(m/r)_j\ w_j\}$, where m/r is the total cross section (absorption coefficient / density) of element “j” in the sample at the absorption edge of the EXAFS element under study in cm^2/g, w_j is the weight fraction of element j in the sample, and $\ln(I_o/I_t)$ was taken over a typical range of 1 to 2.5. An average value of w_D from inputting both values was employed. Based on the calculation for w_D, and the cross-sectional area of the pellet, the grams were calculated. Boron nitride was utilized in some cases to dilute the sample, such that the wafer could be self-supported; for used catalysts, the wax provided support. Smooth self-supporting pellets, free of pinholes, were pressed and loaded into the in-situ XAS flow cell.

Data reduction and was carried out using the WinXAS [2] program. This included pre-edge and post-edge background subtraction, normalization of the height of the edge jump, and sectioning of the desired energy range.

A.3 Catalytic Testing

A.3.1 Sud-Chemie, Inc. Iron-Chromia High Temperature Shift Catalyst Testing

For the purpose of testing high temperature water gas shift (HTS) catalysts, a fixed bed reactor setup was constructed and calibrated. A dry gas mixture was used to mimic the outlet of the coal gasification processes. The gas compositions from the Texaco gasification process were used as a guideline for the input to the HTS reactor.

The fixed bed reactor (23” in length 3/8” diameter) (Figure 1) was constructed to allow for a gas mixture of CO_X, N_2, and H_2, to be mixed with water and passed through the Fe-Cr catalyst bed. The reactor was controlled by a three stage temperature controller, to monitor the changes in temperature throughout the fixed bed more accurately. The products were passed through a cold trap, cooled to 0ºC, set up to condense the liquids (mainly water, and its solutes) out from the gas. The liquids were extracted from the cold trap by opening a needle valve.

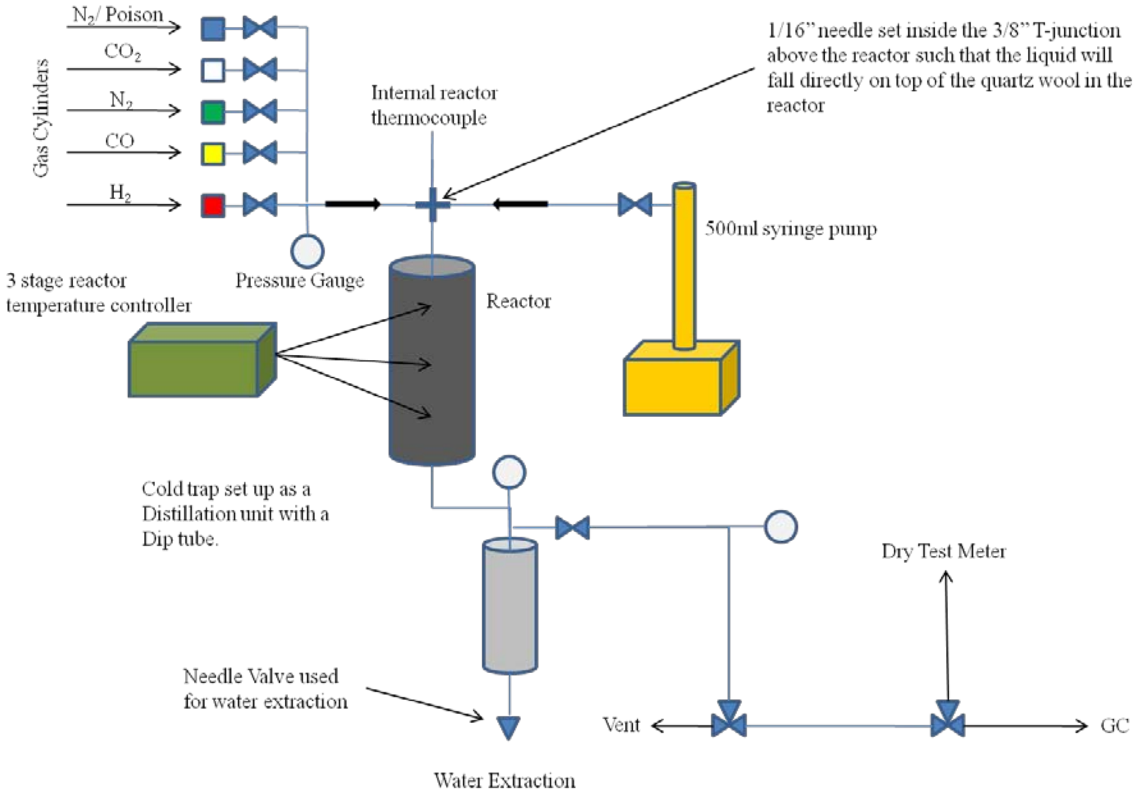


Figure 1: High-temperature shift reaction system.

After the gas was passed through the cold trap, an option was set up such that the gas was either directed to a vent, or allowed to pass through a dry test meter in order to obtain flow measurements, as well as be sent to a GC in order to analyze the exiting products.

In the case of liquid poisoning, the solution was pumped to the top of the reactor by a 500 ml high performance syringe pump, and mixed with the gas prior to the catalyst. The liquid was pumped through 1/8" heated stainless steel tubing, before passing into a 1/16" needle with a side port hole. The 1/16" needle was set inside the 3/8" T-junction above the reactor to allow the liquid to fall directly on top of the catalyst bed in the reactor. However, the liquid vaporizes before it drips into the reactor. For poisoning studies, the poison was pre-mixed with the water and pumped into the reactor.

A.3.2 Fischer-Tropsch Synthesis Catalyst Testing

The FTS experiments were conducted using 1 L CSTR equipped with a magnetically driven stirrer with turbine impeller, a gas-inlet line, and a vapor outlet line with a stainless steel (SS) fritted filter placed external to the reactor. A tube fitted with a SS fritted filter (2 µm opening) was extended below the liquid level of the reactor for withdrawing reactor wax in order to maintain a nearly constant liquid level in the reactor. Separate mass flow controllers were used to control the flow of hydrogen and carbon monoxide at the desired rate. The gases were premixed in a vessel before entering to the reactor. Carbon monoxide was passed through a vessel containing lead oxide-alumina to remove traces of iron carbonyl. The mixed gases entered the CSTR below the stirrer, which operated at 750 rpm. The reactor slurry temperature was maintained constant (±1°C) by a temperature controller.

The reaction products were continuously removed from the vapor space of the reactor and passed through two traps, a warm trap maintained at 100 ºC and a cold trap held at 0 ºC. The uncondensed vapor stream was reduced to atmospheric pressure through a letdown valve. The gas flow was measured using a wet test meter and analyzed by an online GC. The accumulated reactor liquid products were removed every 24 h by passing through a 2 µm sintered metal filter located below the liquid level in the CSTR. Conversion of CO was obtained by gas-chromatography analysis (i.e., using a micro-GC equipped with thermal conductivity detectors) of the reactor exit gas mixture. The reaction products were collected in three traps maintained at different temperatures – a hot trap (200°C), a warm trap (100°C) and a cold trap (0°C). The products were separated into different fractions (rewax, wax, oil and aqueous) for quantification. However, the oil and the wax fractions were mixed prior to GC analysis.

A.3.2.1 Fe-Si-K-Cu Catalyst Activation and Testing

The 100Fe/ 5.1Si/ 3.0K/ 2.0Cu catalyst GJ457 was activated in-situ in 2.0 Nl/g-cat/h CO at 270 ^{o}C and 1 atm for 24 h. During testing, the syngas H_2/CO ratio was approximately 0.77 [3]. The temperature was 270^{o}C and the pressure was 175 psig.

A.3.2.2 0.5%Pt-25%Co/Al_2O_3 Catalyst Activation and Testing

Prior to charging the CSTR, the calcined cobalt catalyst (~15 g of powder) was reduced ex-situ in a fixed bed reactor at 350 ºC for 10 h in 33% hydrogen (balance helium) at a flow rate of 1 L/min. The reactor temperature was increased from room temperature to 100 ºC at the rate of 2 ºC/min and held at 100 ºC for 1 h; then, the temperature was increased to 350 ºC at a rate of 1 ºC /min and kept at 350 ºC for 10 h. The catalyst was transferred pneumatically under the protection of helium to the CSTR, which contained 310 g of melted Polywax-3000 (polyethylene fraction with an average molecular weight of 3000). To facilitate the transfer, the fixed bed reactor was connected to the CSTR using a transfer tube fitted with a ball valve. The fixed bed reactor was pressurized with argon forcing the catalyst powder out of the reactor through the valve. The reactor was weighed before and after the transfer of the catalyst to ensure that all the catalyst powder was transferred to the CSTR. The catalyst was then reduced in situ with hydrogen at a flow rate of 60 SL/h at atmospheric pressure. With the temperature controller programmed in a ramp/soak mode, the reactor temperature was ramped to 280 ºC at a rate of 2 ºC /min and held at 280 ºC for 24 h.

After the activation period, the reactor temperature was decreased to 180 ºC, synthesis gas (H_2: CO = 2:1) was introduced to the reactor and the pressure was increased to the desired pressure. The reactor temperature was increased to the reaction temperature at a rate of 1 ºC /min.

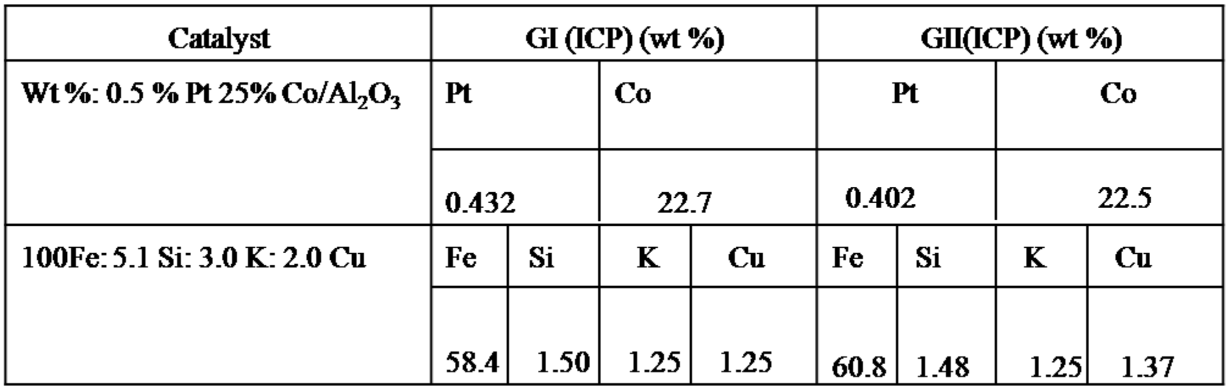
B. Results and Discussion

B.1 Catalyst Characterization

B.1.1 Elemental Analysis

Inductively coupled argon plasma (ICP) analysis was conducted at Galbraith Laboratories. In all cases, the measured loading was practically the same as the corresponding nominal loading, as shown in Tables 1 and 2.

Table 1. ICP analysis results of the Co and Fe catalysts; (GI and GII represents the two separate analysis results of the same sample.)



Catalyst	GI (ICP) (wt %)				GII(ICP) (wt %)			
Wt %: 0.5 % Pt 25% Co/Al_2O_3	Pt		Co		Pt		Co	
	0.432		22.7		0.402		22.5	
100Fe: 5.1 Si: 3.0 K: 2.0 Cu	Fe	Si	K	Cu	Fe	Si	K	Cu
	58.4	1.50	1.25	1.25	60.8	1.48	1.25	1.37

Table 2. Calculated and experimental wt% of elements in the Fe catalyst (GI and GII)

Element	Actual At (%)	Calculated Wt (%)	GI (Wt %)	GI (At %)	GII (Wt %)	GII (At %)
Fe	100	65.00989	58.4	100	60.8	100
Si	5.1	1.66715	1.50	5.108	1.48	4.8405
K	3.0	1.36521	1.25	3.058	1.25	2.9374
Cu	2.0	1.47925	1.25	1.881	1.37	1.9803

B.1.2 BET Surface Area and BJH Porosity

Below are the results for the BET surface area and BJH porosity measurements over the Fe/Si/K/Cu catalyst, GJ457, as well as both of the 200 and 150 m^2/g γ-Al_2O_3 supports and the corresponding supported 0.5%Pt-25%Co catalysts (labeled GJ455 and GJ456, respectively).

Table 3. BET surface area and porosity measurements.

Catalyst /support description	BET SA (m^2/g)	Single Point Pore Volume (cm^3/g)	BJH Adsorption/ Desorption Pore Volume (cm^3/g)	Single Point Pore Radius (nm)	BJH Adsorption/ Desorption Pore Radius (nm)
100 Fe: 5.1 Si: 1.25 K: 0.0 Cu (Calcined parent material)	119.4 119.3	0.1689 0.1687	0.1776 / 0.1767 0.1768 / 0.1759	2.83 2.83	2.54 / 2.18 2.52 / 2.16
100 Fe: 5.1 Si: 3.0 K: 2.0 Cu (**GJ457**)	107.1 106.9 107.0	0.1542 0.1530 0.1533	0.1631 / 0.1622 0.1616 / 0.1608 0.1607 / 0.1599	2.99 2.98 2.98	2.56 / 2.16 2.55 / 2.15 2.52 / 2.14
γ-Al_2O_3 (Catalox Sba 200)	197.0 202.2	0.4730 0.4847	0.4803 / 0.4797 0.4921 / 0.4915	5.00 5.00	3.79 / 3.37 3.80 / 3.36
γ-Al_2O_3 (Catalox Sba 150)	140.2 135.1	0.4357 0.4190	0.4434 / 0.4429 0.4241 / 0.4237	6.47 6.46	5.14 / 4.50 5.08 / 4.45
0.5%Pt-25%Co/Al_2O_3 (Sba 200, **GJ455**)	141.7 140.7	0.2515 0.2535	0.2783 / 0.2771 0.2789 / 0.2778	3.55 3.60	3.61 / 3.26 3.64 / 3.29
0.5%Pt-25%Co/Al_2O_3 (Catalox 150, **GJ456**)	97.8 99.1 96.5	0.2184 0.2217 0.2176	0.2249 / 0.2241 0.2283 / 0.2274 0.2242 / 0.2233	4.62 4.63 4.66	4.44 / 4.05 4.44 / 4.04 4.45 / 4.07

For the iron-based Fischer-Tropsch synthesis catalyst, adding an additional amount of K and adding Cu only slightly decreased the BET surface area from ~119 m^2/g to 107 m^2/g. Further addition of K and adding Cu did not significantly alter the PSD for the Fe-based catalyst (Figure 2).

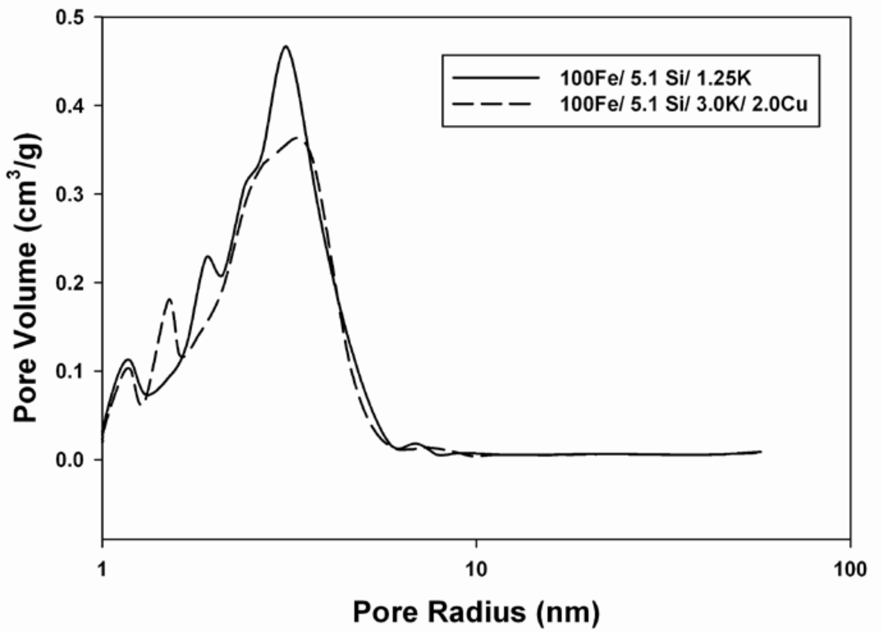


Figure 2: BJH adsorption pore size distributions for catalyst GJ457 before and after loading additional K and adding Cu.

Turning our attention to the cobalt catalysts, for catalyst GJ455, the BET surface area was close to 155 m^2/g. A wt. % loading of 25% metal is equivalent to ~33% by weight Co_3O_4. If the γ-Al_2O_3 (~200 m^2/g) is the only contributor to the area, then the area of the 0.5%Pt-25%Co/Al_2O_3 catalyst GJ455 should be 134 m^2/g. Because the average area of the catalyst is only slightly higher than this value, it is suggested that little if any pore blockage occurred with the addition of Co and Pt. Similarly, for catalyst GJ456, the BET surface areas was approximately 98 m^2/g. If the γ-Al_2O_3 (~138 m^2/g) is the only contributor to the area, then the area of the 0.5%Pt-25%Co/Al_2O_3 catalyst GJ456 should be 92 m^2/g. Again, because the area of the catalyst is only marginally above this range, little pore blockage was deemed to have occurred by addition of Co and Pt.

Pore size distributions (PSD) are reported in Figure 3. It is evident that adding Pt and Co to γ-Al_2O_3 did not significantly impact the PSD.

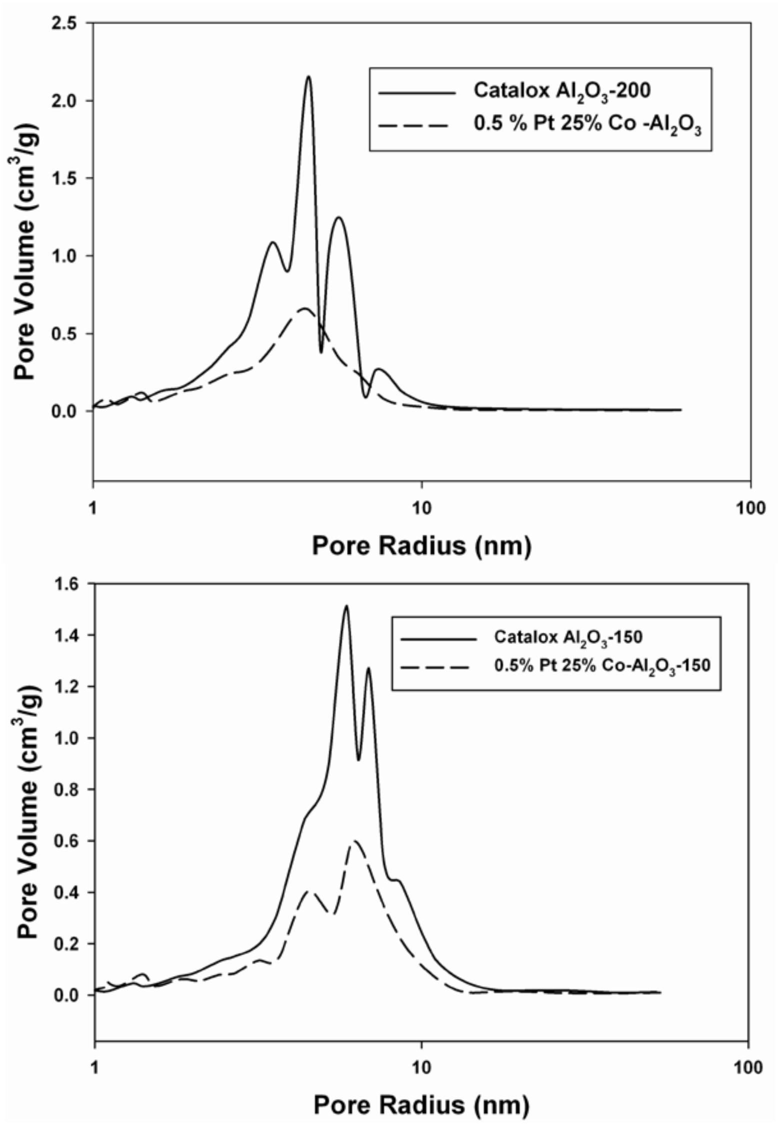


Figure 3: BJH adsorption PSD for (top) γ-Al_2O_3 200 m^2/g support and 0.5%Pt-25%Co/Al_2O_3 GJ455; (bottom) γ-Al_2O_3 150 m^2/g support and 0.5%Pt-25%Co/Al_2O_3 GJ456.

B.1.3 Temperature programmed reduction

The H_2-TPR profile showing the Fe_2O_3 to Fe_3O_4 and Fe_3O_4 to Fe metal transitions is given in Figure 4. However, the catalyst is typically activated in CO to carburize it [4] (not H_2).

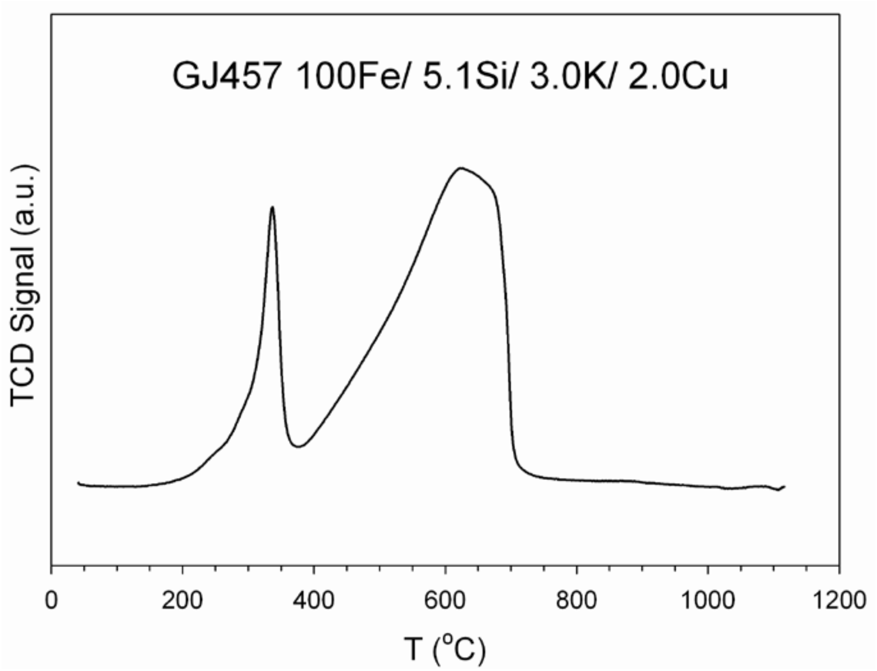


Figure 4: H_2-TPR of Fe/Si/K/Cu catalyst.

Temperature programmed reduction (TPR) profiles for the two 0.5%Pt-25%Co/Al_2O_3 catalysts GJ455 (supported on Catalox Sba 200) and GJ456 (supported on Catalox Sba 150) are displayed in Figure 5. Reduction of Co_3O_4 clusters is proposed to occur in two steps [5], with the second step consuming 3 times as much H_2 as the first. In general, for calcined catalysts of similar loading, we have found that, while the first step of reduction occurs at about the same temperature (~ 300-350^oC range), the second step strongly depends on the type of support. While Co oxides appear to have relatively weak interaction with silica, the TPR profiles of titania and alumina supported cobalt catalysts are much broader, with Co/Al_2O_3 extending

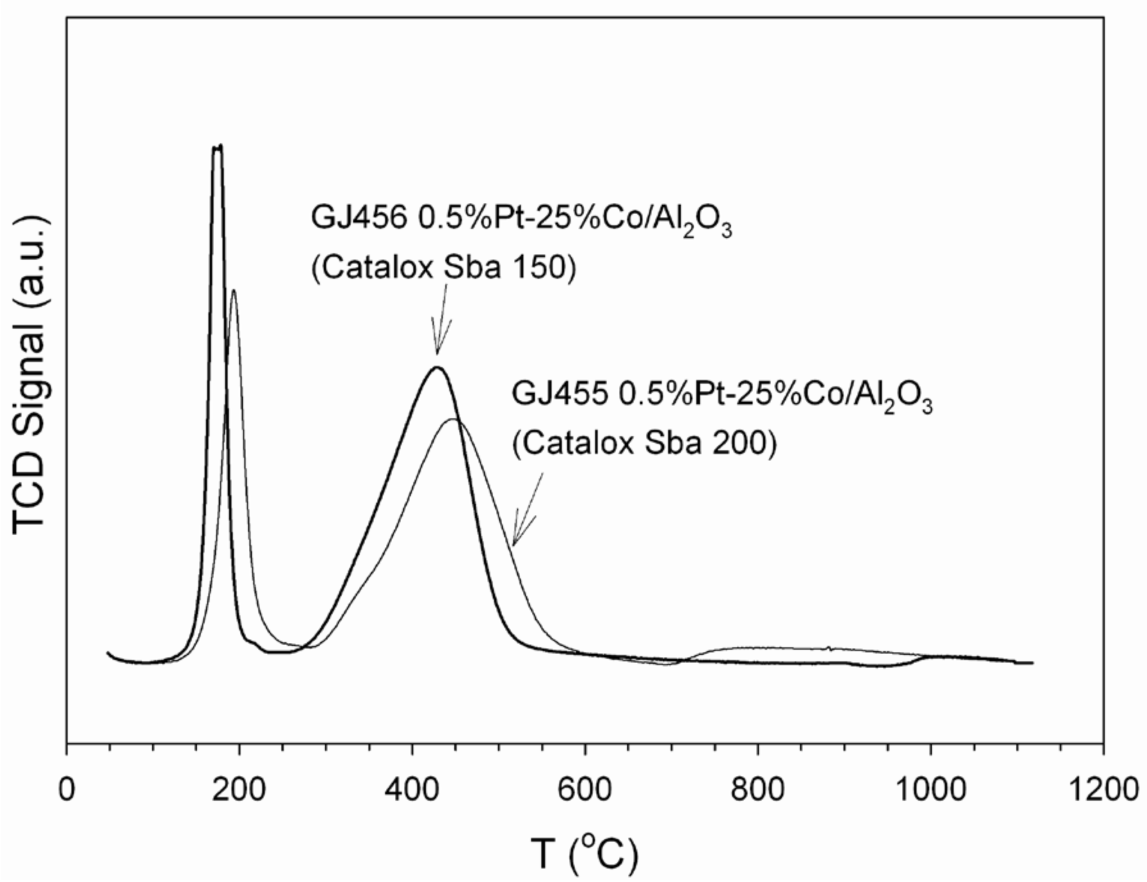


Figure 5: TPR profiles of the 0.5%Pt-25%Co/Al_2O_3 catalysts GJ455 and GJ456 supported on Catalox Sba 200 and 150, respectively.

all the way beyond 700°C. Extending the TPR beyond 800°C, there is typically a small peak for some cobalt which is sacrificed to the support as cobalt aluminate. It appears from the figure above that both steps of the reduction process have been promoted to significantly lower temperatures, possibly via a H_2 dissociation and spillover mechanism from the Pt clusters, which nucleate the formation of Co^0 in the CoO oxide, with the resulting nuclei then proceeding to the growth stage.

The results indicate that decreasing the surface area of the support from ~200 m^2/g to ~140 m^2/g while maintaining constant loading weakens somewhat the surface interaction between the γ-Al_2O_3 support and the Co_3O_4 clusters. This may be explained by a decrease in the interfacial surface contact area caused by a decrease in the surface area of the γ-Al_2O_3 support.

B.1.4 Hydrogen chemisorption with pulse reoxidation

Results of H_2 chemisorption / pulse reoxidation are summarized below. With the aid of the promoter, the extent of reduction increases to ~60-65% from ~40-45% (internal CAER results). The H_2 TPD provides a measurement of the active site density of surface cobalt atoms (though recall that H:Co = 1:1). The dispersion (fraction of metal that is dispersed) after correcting for the extent of cobalt reduction was ~11.9%. Taking these two measures into account, along with geometrical arguments, the corrected average diameter was approximately 8.6 nm.

<u>H_2 chemisorption / pulse reoxidation</u>
Catalyst ID: GJ455*
Composition: 0.5%Pt-25%Co/Al_2O_3 on Sba -200 (~200 m^2/g)
H_2 calibration: 6189.4
TPD H_2: 159.6 micromoles per g cat
O_2 calibration: 309.88
O_2 uptake: 1782.2 micromoles per g cat
Uncorrected dispersion: 7.52%
Uncorrected diameter: 13.7 nm
Extent of Reduction: 63.0%
Corrected dispersion: 11.94%
Corrected diameter: 8.3 nm
*note that the results are updated from a previous quarterly report.

The cluster size was quite small (e.g., < 10 nm) and using the catalyst, there were difficulties in obtaining reproducible extents of reduction during catalyst activation. Therefore, UK-CAER opted to prepare the 0.5%Pt-25%Co/Al_2O_3 catalyst using the lower surface area 150 m^2/g support – GJ456. The particle size was slightly larger, slightly more reducible (i.e., in agreement with TPR data), and deemed to be more robust.

H_2 chemisorption / pulse reoxidation
Catalyst ID: GJ456
Composition: 0.5%Pt-25%Co/Al_2O_3 on Sasol-150 (~150 m^2/g)
H_2 calibration: 6439.9
TPD H_2: 114.1 micromoles per g cat
O_2 calibration: 307.53
O_2 uptake: 1812.4 micromoles per g cat
Uncorrected dispersion: 5.38%
Uncorrected diameter: 19.2 nm
Extent of Reduction: 64.1%
Corrected dispersion: 8.40%
Corrected diameter: 12.3 nm

B.1.5 X-ray Absorption Near Edge Spectroscopy

Some preliminary X-ray absorption near edge spectroscopy (XANES) results were obtained over the used catalyst samples post-run, as well as reference compounds of interest. For iron catalysts, comparing the edge data and the white line intensities, the results are inconclusive (Figure 6). Here, the problem is that there is so much Fe in the catalyst, that the contribution from bulk Fe masks the minor contribution from surface Fe atoms that are exposed to possible poisoning by added compounds. It should be noted that the results for cobalt are suggestive, but not conclusive (Figure 7). One reason is that cobalt catalysts may undergo changes in oxidation state during a run. In some studies, whereby cobalt catalysts are not significantly reduced, the cobalt continues to reduce in the reducing environment of the FTS feed [6]. On the other hand, if significant H_2O is produced (e.g., high conversion), very tiny cobalt crystallites may undergo oxidation during FTS [7,8]. CAER recommends that more detailed investigations be planned and executed, whereby catalyst samples are retrieved from the reactor and solidified in the wax to maintain their in-situ-like state during a single FTS test. In this way, differences in oxidation state could be assessed prior to, during, and after poisoning by a specific

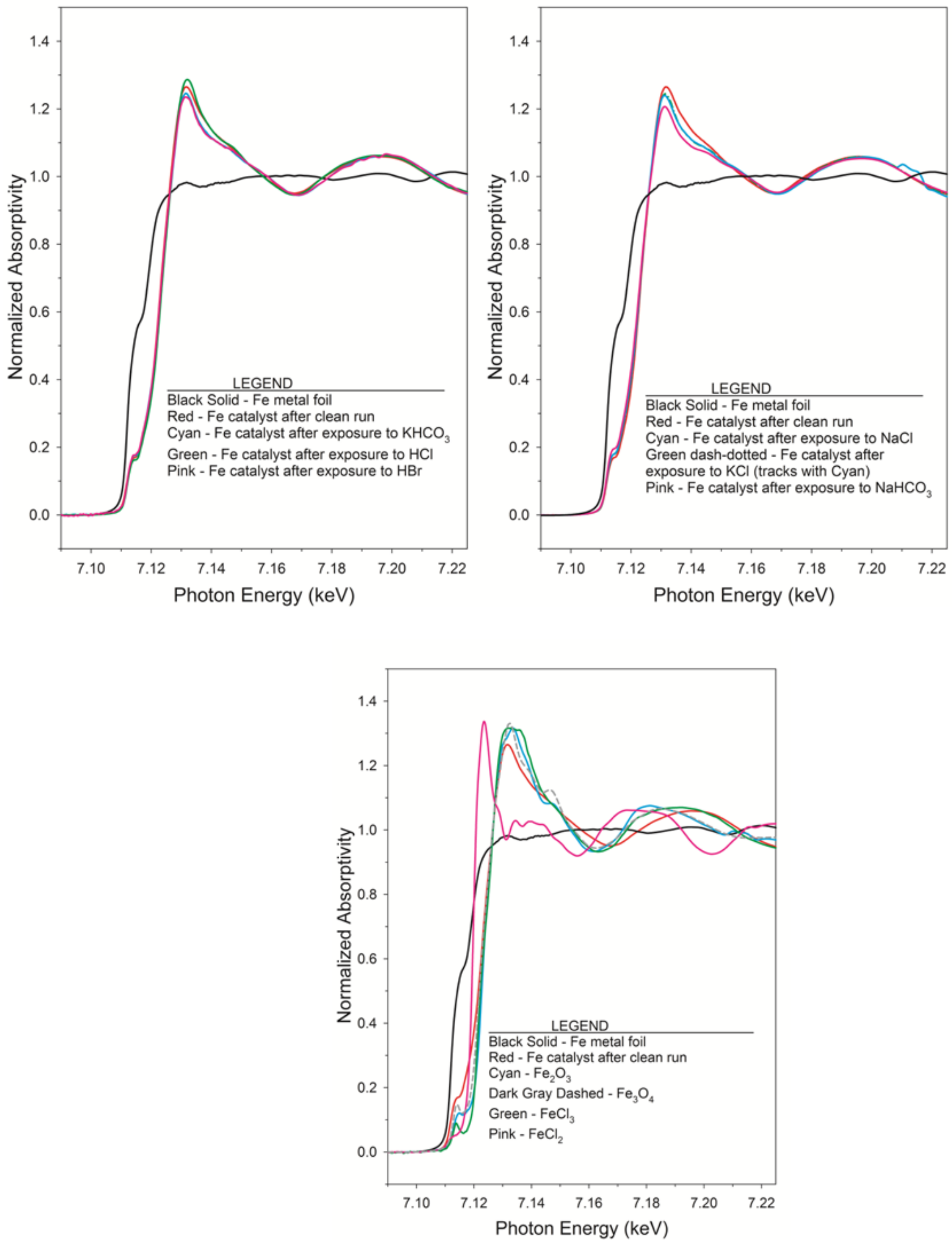


Figure 6: (upper left) Fe-Si-K-Cu catalyst GJ457 after running under clean conditions and after exposure of up to 400 ppb NaCl or KCl, or 40 ppm of $NaHCO_3$. (upper right) Fe-Si-K-Cu catalyst GJ457 after exposure to 40 ppm HCl, HBr, or $KHCO_3$. (bottom) reference compounds. No discernible oxidation above that of the clean reference run can be observed for the case of poisoning. This is likely due to the significant presence of bulk Fe that masks the surface Fe.

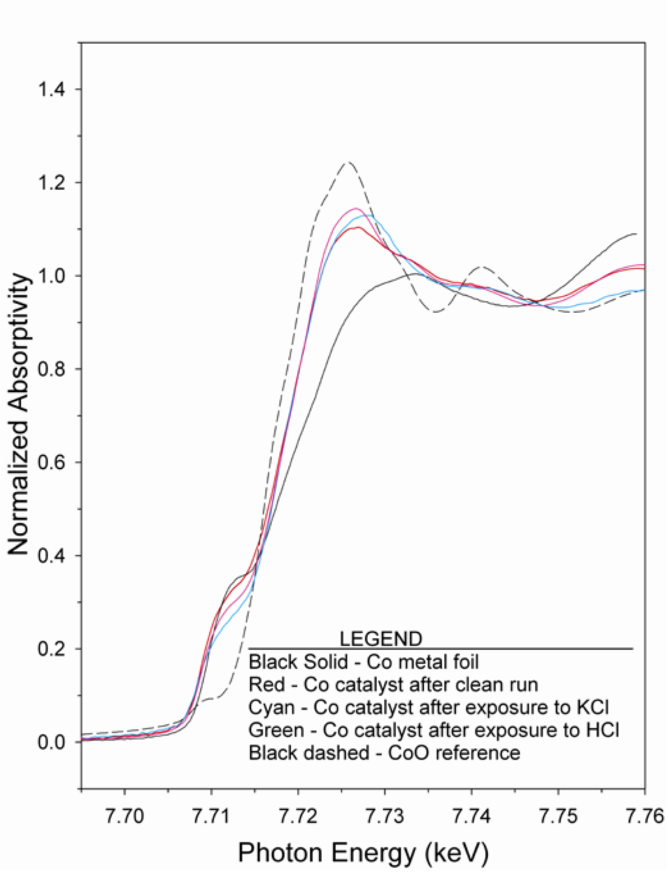


Figure 7: (upper left) 0.5%Pt-25%Co/Al_2O_3 catalyst GJ456 after running under clean conditions and after exposure of up to 500 ppm KCl and of up to 10 ppm of HCl, including reference compounds for Co metal foil and CoO. Only slight oxidation is suggested by the results. However, as with iron previously, this is likely due to the significant presence of Co located within the core of particles that masks the surface Co.

component at a concentration of interest. This would remove systematic errors that may occur in comparing multiple runs, where there could exist slight inherent differences due to catalyst pretreatment, catalyst charging, etc. Moreover, CAER recommends that tests be carried out on model catalysts, where Fe catalysts are used that exhibit higher surface areas of the active component relative to the bulk, such that the signal for the surface iron carbides are not below detection limits. Similarly, model cobalt catalysts might also be developed to improve the contribution of the surface to the cobalt signal in XANES.

B.2 Catalytic Testing Results and Discussion

B.2.1 Süd-Chemie, Inc. Iron-Chromia High Temperature Shift Catalyst Testing

B.2.1.1 Clean Feed

Before starting with the stability studies (clean and poisoned) on the HTS commercial catalyst for the WGS reaction, UK-CAER studied the effect of gas hourly space velocity (GHSV) on WGS activity (i.e., CO conversion) in order to carry out stability studies under conditions that are far from equilibrium influences. The test conditions were as follows:

- The dry gas compositions were chosen to mimic the outlet of the coal gasification process from the Texaco gasifier (H_2/CO = 0.75, N_2/CO = 0.4). A steam to dry gas ratio of unity (1:1) was used for WGS activity tests.
- Catalyst particle sizes were between 355 and 600 µm.
- The catalyst was activated prior to testing using the same feed conditions indicated above.
- Tests were carried out at 350°C and 460 psi.

The effect of GHSV on CO conversion was examined after stabilizing the catalyst for 5 days on stream. It was not possible to continue lowering the GHSV to find out the point where the slope starts changing from the effect of equilibrium. This was due to (i) minimum flow rate restrictions from the mass flow controllers (MFCs) and (ii) limitations on the catalyst bed length (i.e., catalyst weight) where a reliable controlled temperature could be achieved. The results of space velocity tests are shown in Figure 8. CO conversion decreases with increasing GHSV by a linear correlation. A conversion of 80% (GHSV ~ 3250 hr^{-1}) was chosen for stability tests. At this conversion level, there was no significant effect from equilibrium on CO conversion and the conversion is high enough for the poisoning studies such that clear deactivation patterns could, if present, be observed.

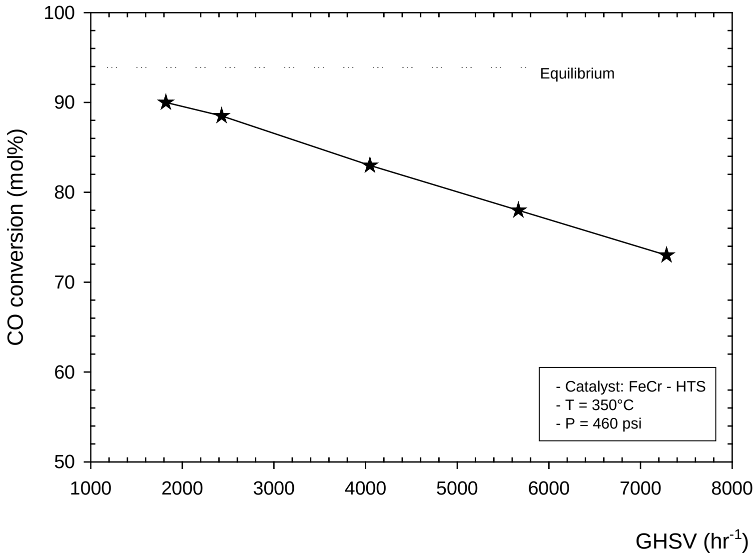


Figure 8: Effect of GHSV on WGS activity (CO conversion) over FeCr – HTS catalyst.

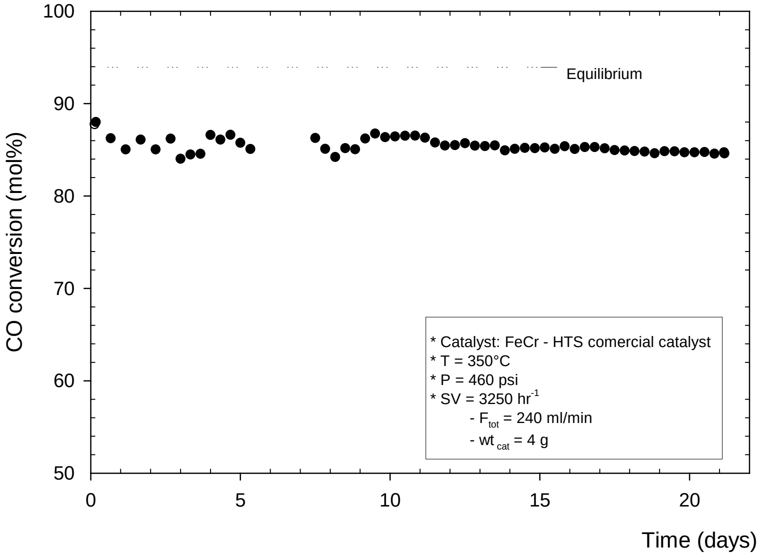


Figure 9: WGS activity (CO conversion) with time on stream over the Fe-Cr HTS commercial WGS catalyst.

A clean stability test of the Fe-Cr catalyst was carried out for 21 days under HTS conditions, and the results are displayed in Figure 9. The catalyst was stable during the period of testing and the CO conversion was about 78 mol% at 350ºC, 460 psi, 3250 hr^{-1} space velocity, with unity steam/dry gas ratio, where the dry gas compositions was 46.5%CO, 34.9%H_2 and 18.6%N_2. This result serves as the basis for poisoning studies.

B.2.1.2 Feed Containing Contaminants

B.2.1.2.1 KCl and NaCl

The effect of co-feeding KCl and NaCl on the activity and stability of the HTS catalyst during WGS was investigated. KCl or NaCl were added via the water feed pump as KCl or NaCl solutions. The concentrations of KCl were calculated based on the total wet feed gas rate. In all tests, glass wool was not added to the top of the catalyst bed in order to reduce the chance of losing some of the added contaminants by adsorption onto the surface of the glass wool.

Figure 10 displays the activity and stability of the HTS catalyst for the WGS reaction as a function of TOS under different KCl concentrations. Three different KCl concentrations were tested (50, 100, and 200 ppbw KCl). From these results, the catalyst displayed little, if any, deactivation during 21 days TOS for all the different KCl concentrations. Moreover, a slight increase in CO conversion was observed. This increase may be attributed to the role of K^+ in enhancing water activation on the catalyst surface. Similar observations regarding the effect of alkali promoters on the activity of iron-silica catalysts in FT and WGS were also reported by Ngantsoue-Hoc et al. [9].

In a separate study, we have tested the role of K^+ in enhancing the WGS activity of iron-silica based catalysts by comparing the activity of K^+ promoted and unpromoted iron-silica

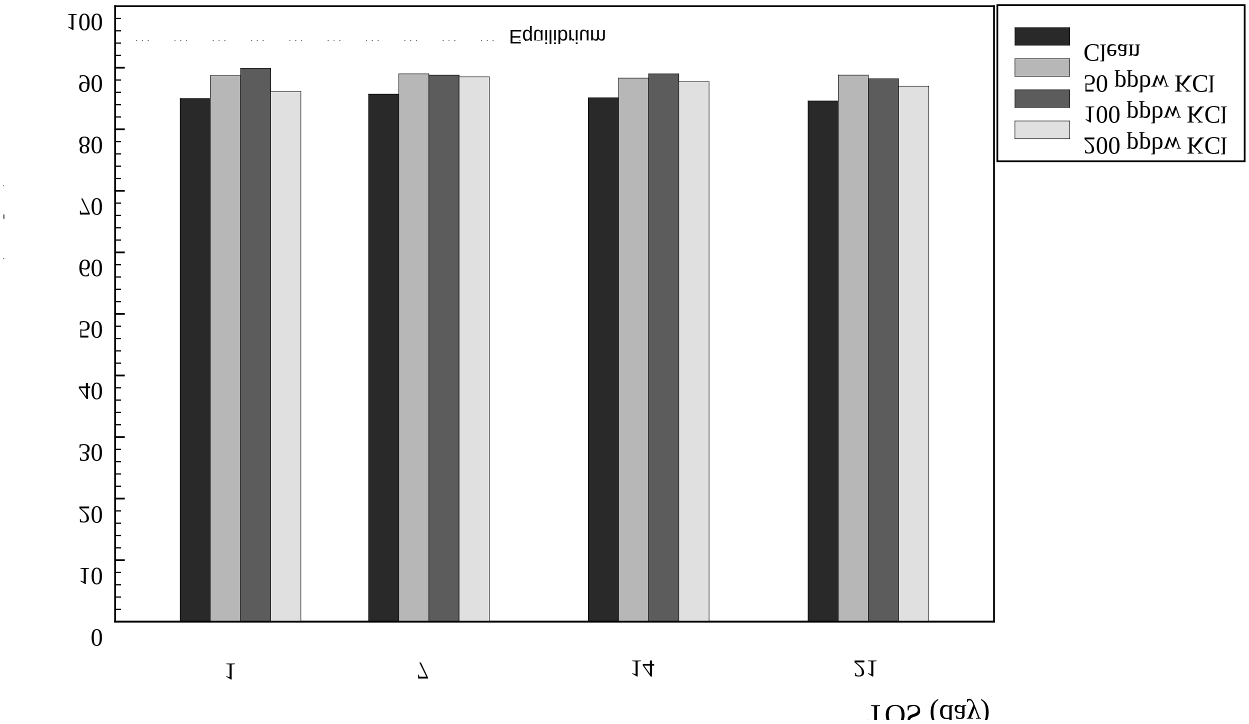


Figure 10: KCl concentration effect on the activity and stability of Süd-Chemie HTS catalyst during the WGS reaction versus TOS. Test conditions: 350ºC, 460 psi, 3250 hr^{-1}, 240 ml/min (steam/dry gas ratio of 1), catalyst weight of 4 g.

catalysts for the WGS reaction (results not shown here) and observed that K^+ increases the WGS activity of iron based catalysts.

At the highest KCl concentrations tested in this study (i.e., 200 ppbw), the concentration of Cl^- was about 95 ppbw in the gas feed mixture. The catalyst showed excellent stability against this chlorine concentration, as shown in Figure 10.

Based on the results from the KCl study, NaCl co-feeding was carried out at the higher concentration of 200 ppbw NaCl and results are provided in Figure 11. As with KCl, the catalyst was found to display excellent resistance to NaCl. Therefore, it was unnecessary to investigate the stability of the catalyst at the lower concentrations of NaCl. The results also indicated that

Na^+ does not enhance the activity of the catalyst as did K^+ since the catalyst exhibited an activity comparable to the clean test.

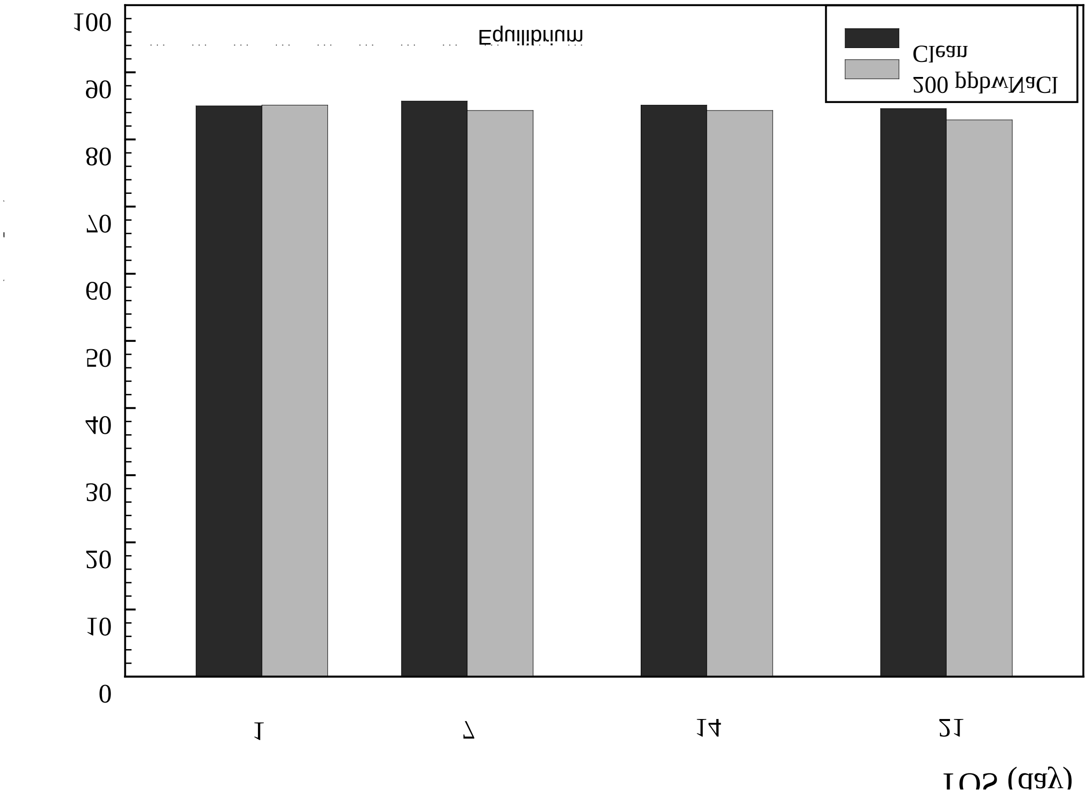


Figure 11: NaCl concentration effect on the activity and stability of Süd-Chemie HTS catalyst during WGS versus TOS. Testing conditions: 350ºC, 460 psi, 3250 hr^{-1}, 240 ml/min (steam/dry gas ratio of 1), catalyst weight of 4 g.

Although the Süd-Chemie HTS catalyst was found to exhibit good resistance to KCl and NaCl poisons in the range of concentrations tested (i.e., up to 200 ppbw) over the time interval examined, since the tests were conducted using a fixed bed reactor, there remains the question as to whether the contaminants contacted the entire catalyst bed or rather accumulated only on the top layer. To investigate this, several downstream water samples, collected from the cold trap during the 200 ppbw KCl poisoning test, were analyzed for K^+ and Cl^- and results are displayed in Table 4. By comparing the concentrations of K^+ and Cl^- in the feed with those collected from the cold trap at different times on-stream (TOS), results indicate that almost all Cl^- and most of the K^+ adsorbed on the catalyst. Examining the mass balance over the catalyst after 21 days TOS, an average of 153 ppmw K^+ (based on catalyst weight) and 139 ppmw Cl^- should be accumulated on the catalysts if all the K^+ and Cl^- ions adsorbed. In order to check if there is a distribution of K^+ and Cl^- ions in the catalyst bed, the 200 ppbw KCl poisoning test was repeated and the catalyst bed was divided into three layers, with each layer separated by a small volume of glass wool between layers. The catalyst was stable for 21 days of TOS. After that, each catalyst bed was mixed very well and three representative samples from each bed were analyzed for K^+ and Cl^-. The fresh catalyst was also analyzed to quantify any impurities of K^+ and Cl^- already present in the catalyst prior to poisoning.

Table 5 shows the results of accumulated K^+ in each catalyst bed after 21 days of TOS. The fresh catalyst was found to contain K^+ impurities with an average value of about 29 ppmw, so this value was subtracted from the measured values obtained for each bed following poisoning. After 21 days of TOS, K^+ accumulated significantly in both the top and middle beds, but little was found to be accumulated in the bottom bed. Considering the 95% confidence interval (CI) calculations, both the calculated CI_{upper} and CI_{lower} values of the top and middle beds (see Table 5) were found to be greater than those calculated for the fresh catalyst, consistent with K^+ accumulation in both beds. In the case of the bottom bed, the CI_{lower} was found to be even less than that of the CI_{lower} value of the fresh catalyst; thus, one cannot say with certainty that K^+ accumulated in this bed. More datasets for this bed would be required in order to draw a firm conclusion that there was no K^+ accumulation, because the 95% confidence interval calculations are more accurate when the datasets contain more data. Nevertheless, the results of Table 5 indicate that K^+ does accumulate in the top and middle beds.

Table 4: K^+ and Cl^- in recovered water from the HTS reaction after co-feeding 200 ppbw KCl.

Sample #	Time (day)	Cl^- (ppmv)	K^+ (ppmv)
1[a]	-	**0.04**	**0.05**
2[b]	-	**0.27**	**0.188**
3	8	0.02	0.087
4	15	0.01	0.081
5	19	0.03	0.078
6	21	0.02	0.077

a: distilled water,
b: Feed, 400 ppb KCl soln (equivalent to 200 ppbw in the wet gas phase).

In the case of Cl^- (Table 6), it is difficult to draw a conclusion regarding the distribution of Cl^- in the three beds. This is due to the fact that the three samples for the fresh catalyst have a wide variation so the average is unreliable. The calculated standard deviation for the results of the three catalyst beds is high. The CI values for the three catalyst beds (CI_{upper} and CI_{lower}) overlap with the ones of the fresh catalyst; therefore, a firm conclusion regarding the distribution of Cl^- is not possible. Two reasons for these results are considered: (1) it is possible that the Cl^- impurity in the fresh sample is not uniform or (2) the analysis technique (ICP) is not accurate. Additional investigation would be required to form a definitive conclusion on this point.

Table 5: Analysis of K^+ (ppmw) in fresh and spent HTS-WGS (Süd-Chemie) catalyst.

							95% Confidence interval calculations	
Table A	K^+ (ppmw)							
Sample	S1 (ppmw)	S2 (ppmw)	S3 (ppmw)	Average (X)	bed_{avg}-$fresh_{avg}$	σ	CI_{upper} = X+t*σ/(n)^0.5	CI_{lower} = X-t*σ/(n)^0.5
Fresh	34	30.2	22.4	28.9	0.0	5.9	35.6	22.2
Bed - top	**96**	**51.8**	**64.1**	**70.6**	**41.8**	22.8	96.4	44.8
Bed - middle	**88**	**60.4**	**72.4**	**73.6**	**44.7**	13.8	89.3	57.9
Bed - bottom	**46**	**22.2**	**26.2**	**31.5**	**2.6**	12.7	45.9	17.0

Table 6: Analysis of Cl^- (ppmw) in fresh and spent HTS-WGS (Süd-Chemie) catalyst.

							95% Confidence interval calculations	
Table B	Cl^- (ppmw)							
Sample	S1 (ppmw)	S2 (ppmw)	S3 (ppmw)	Average (X)	bed_{avg}-$fresh_{avg}$	σ	CI_{upper} = X+t*σ/(n)^0.5	CI_{lower} = X-t*σ/(n)^0.5
Fresh	52	86.6	123.4	87.3	0.0	35.7	127.7	46.9
Bed - top	**114**	**170**	**102**	**128.7**	**41.3**	36.3	169.7	87.6
Bed - middle	**237**	**197**	**100**	**178.0**	**90.7**	70.4	257.7	98.3
Bed - bottom	**99**	**12.6**	**19.6**	**43.7**	**-43.6**	48.0	98.0	-10.6

B.2.1.2.2 $KHCO_3$, $NaHCO_3$, HCl, HBr, and HF

The next aim was to decouple the effect of the alkali from that of the halide and thus, alkali bicarbonates and acid halides were introduced with the HTS feed. First, alkali bicarbonates were investigated in order to assess the impact of alkali. Figure 12 displays the activity and stability of the Süd-Chemie Fe-Cr catalyst during HTS as a function of time on stream (TOS) under 100 ppbw levels of $KHCO_3$ or $NaHCO_3$. With 100 ppbw $KHCO_3$, the catalyst displayed little deactivation during 21 days of TOS, with CO conversion dropping from 85 to 81%. However, in the case of 100 ppbw $NaHCO_3$, the deactivation was slightly more pronounced, with CO conversion dropping from 85 to 78%. Earlier, it was shown that K^+ ions enhance the WGS activity when KCl solution was used. However, this enhancement was not observed with $KHCO_3$. It is possible that the HCO_3^- ions somehow influence the stability of the catalyst because when extents of deactivation with co-feeding $KHCO_3$ and $NaHCO_3$ were compared, deactivation was more severe in case of $NaHCO_3$. The Na^+ ions did not enhance the WGS activity when NaCl was utilized. Thus, it is possible that K^+ ion enhances activity but that the positive effect may be compensated by deactivation from HCO_3^- ions.

In the case of halide decoupling, the impact of Cl^- ions on catalyst stability, by way of co-feeding 100 ppbw HCl, on catalyst stability, was investigated separately. Figure 13 displays the activity and stability of the HTS catalyst for the WGS reaction as a function of time on stream (TOS) under 100 ppbw concentration levels of HCl, HBr, or HF. No significant deactivation of the HT-WGS Süd-Chemie catalyst was observed during the three week interval of testing under the conditions used (e.g., with HCl, CO conversion dropped only slightly, from 85 to 82%). The results suggest that the commercial HTS catalyst is relatively resistant to the different halide poisons within concentrations of up to 100 ppbw in the syngas. However, longer testing times would be required to prove this beyond any doubt. Thus, at the concentrations tested, 100 ppbw of the contaminants tested induced little deactivation to the Süd-Chemie HTS catalyst over the time interval studied.

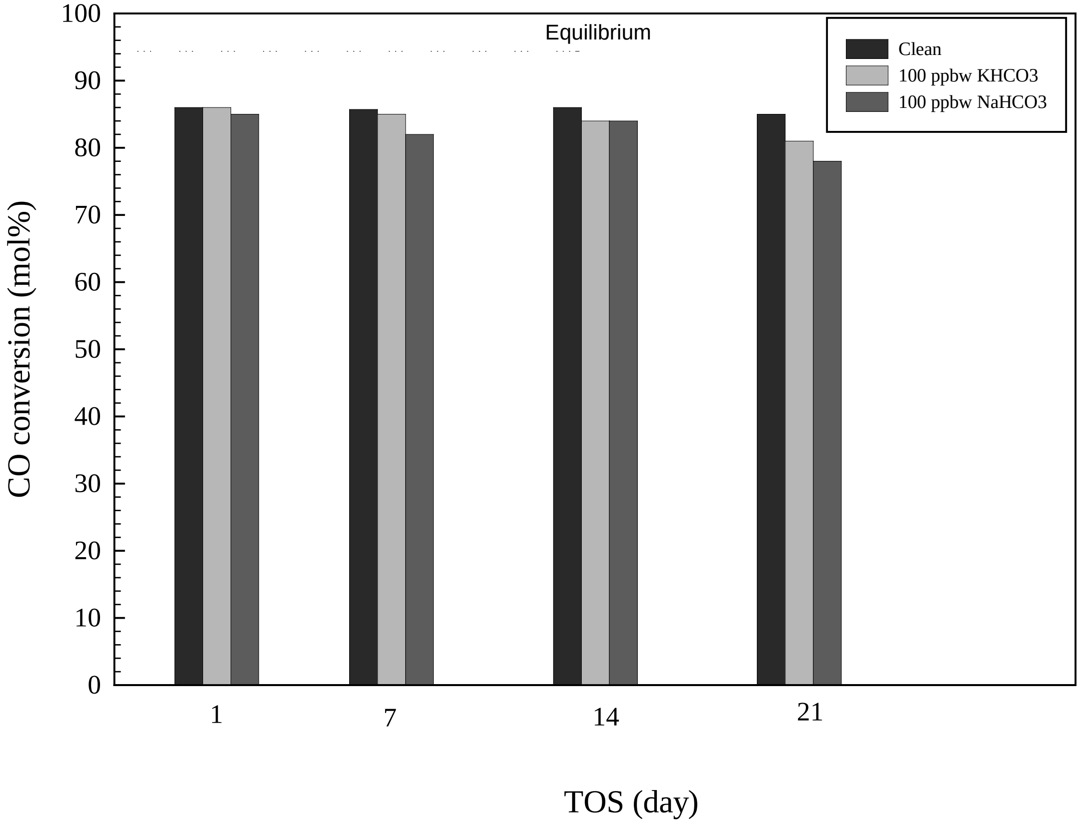


Figure 12: Effect of $KHCO_3$ and $NaHCO_3$ on the activity and stability of Süd-Chemie Fe-Cr catalyst during HTS as a function of TOS. Conditions: 350°C, 460 psi, 3250 hr^{-1}, 240 ml/min (steam/dry gas ratio of 1), catalyst weight of 4 g.

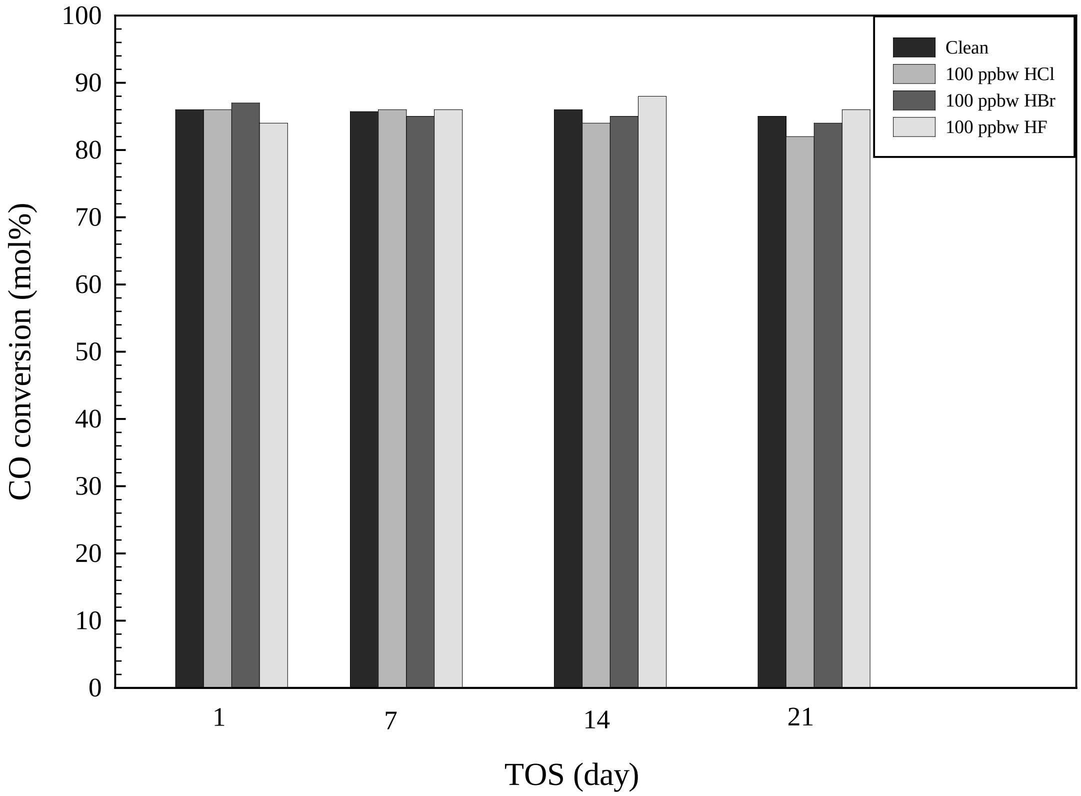


Figure 13: Effect of HCl, HBr, and HF on the activity and stability of Süd-Chemie Fe-Cr catalyst during HTS as a function of TOS. Conditions: 350°C, 460 psi, 3250 hr^{-1}, 240 ml/min (steam/dry gas ratio of 1), catalyst weight of 4 g.

B.2.1.2.3 H_2S, NH_3, and H_2S combined with NH_3

Figure 14 shows the effect of 1 ppmv H_2S poisoning levels on the performance of the HTS catalyst. Again, no significant deactivation was observed during a time interval of three weeks.

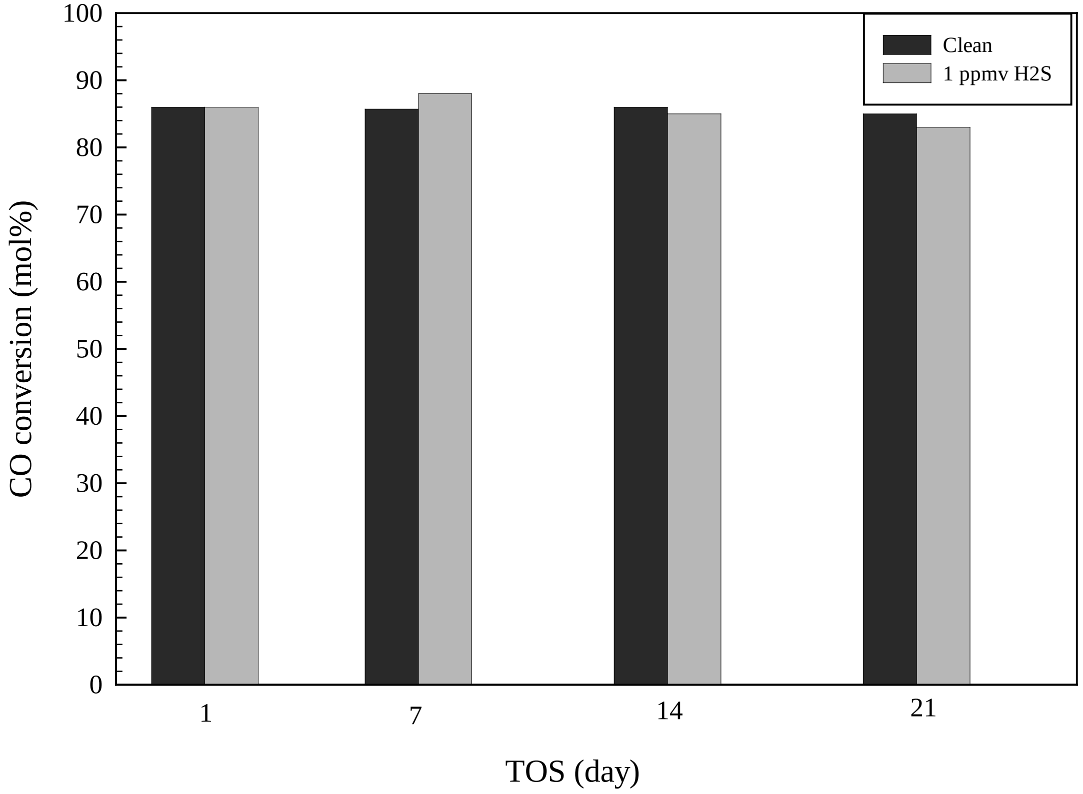


Figure 14: Effect of H_2S addition on the activity and stability of the Süd-Chemie HTS catalyst during WGS as a function of TOS. Conditions: 350°C, 460 psi, 3250 hr^{-1}, 240 ml/min (steam/dry gas ratio of 1), catalyst weight of 4 g.

Next, the effect of NH_3 and a combination of NH_3 and H_2S poisoning on the stability of the Süd-Chemie catalyst during HTS was investigated. The concentrations of NH_3 used were 2, 5, 10 and 12 ppm, whereas that of NH_3 and H_2S were varied as described in Table 7.

Table 7. Concentrations of NH_3 and H_2S utilized.

NH_3 (ppm)	H_2S (ppm)
2	0.2
2	0.4
4	0.4
4	0.6
6	0.6
6	0.8

The conditions used were as follows: temperature, 350°C; pressure, 460 psi; and space velocity, 3250 hr^{-1}.

Figure 15 shows the activity and stability of the HTS catalyst for the WGS reaction as a function of time on stream (TOS). The concentration levels of NH_3 used were: 2, 5, 10 and 12 ppm, respectively. The results imply that the commercial HTS catalyst is somewhat resistant to NH_3 poisoning within the concentration levels of up to 5 ppm of testing under the conditions used. However, in examining the effect of NH_3 poisoning at higher concentration levels (e.g., 12 ppm in the syngas), a slight decrease in catalytic activity was observed from 88% to 85% as displayed in Figure 15, although longer testing times and higher concentrations would be required to explore further the poisoning effect on the HTS catalyst.

Figure 16 investigates the effect of a combination of (NH_3 and H_2S) poisoning levels on the performance of the HTS catalyst. No significant deactivation was observed during a time interval of three weeks. A slight decrease in catalytic activity was observed at concentration levels of 6 ppm NH_3 and 0.6 ppm H_2S from 88% to 87%.

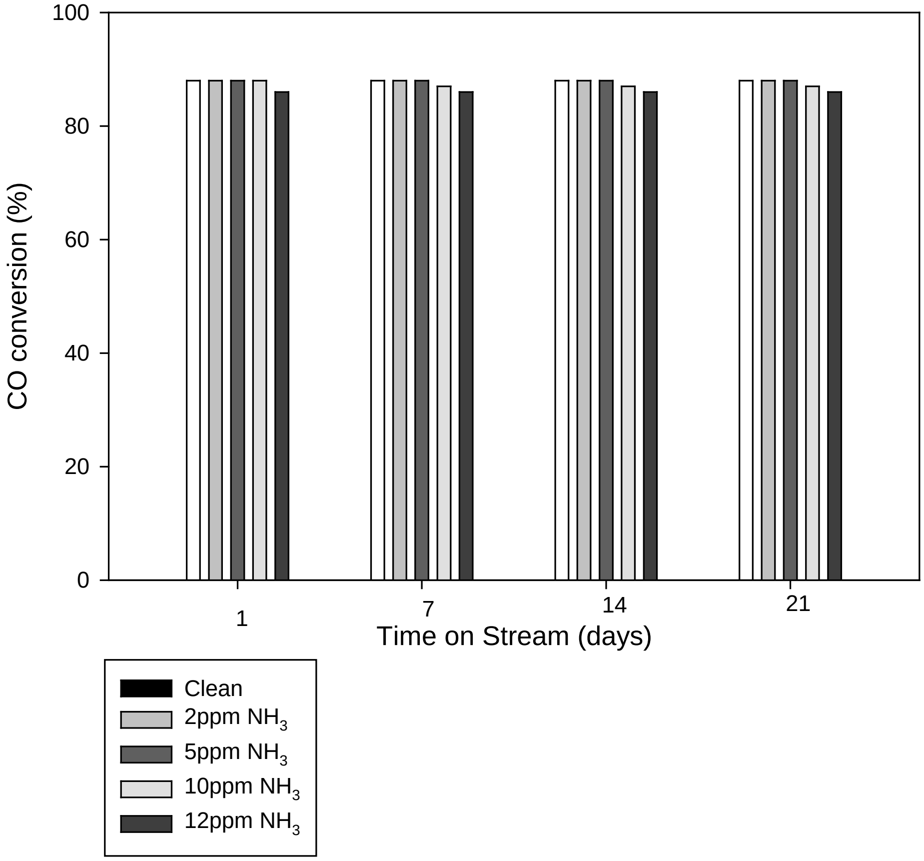


Figure 15: Effect of NH_3 addition on the activity and stability of Süd-Chemie HTS catalyst during WGS showing CO conversion (%) vs. TOS (days). Conditions: 350°C, 460 psi, 3250 hr^{-1}, 240 ml/min (steam/dry gas ratio of 1), catalyst weight of 4 g.

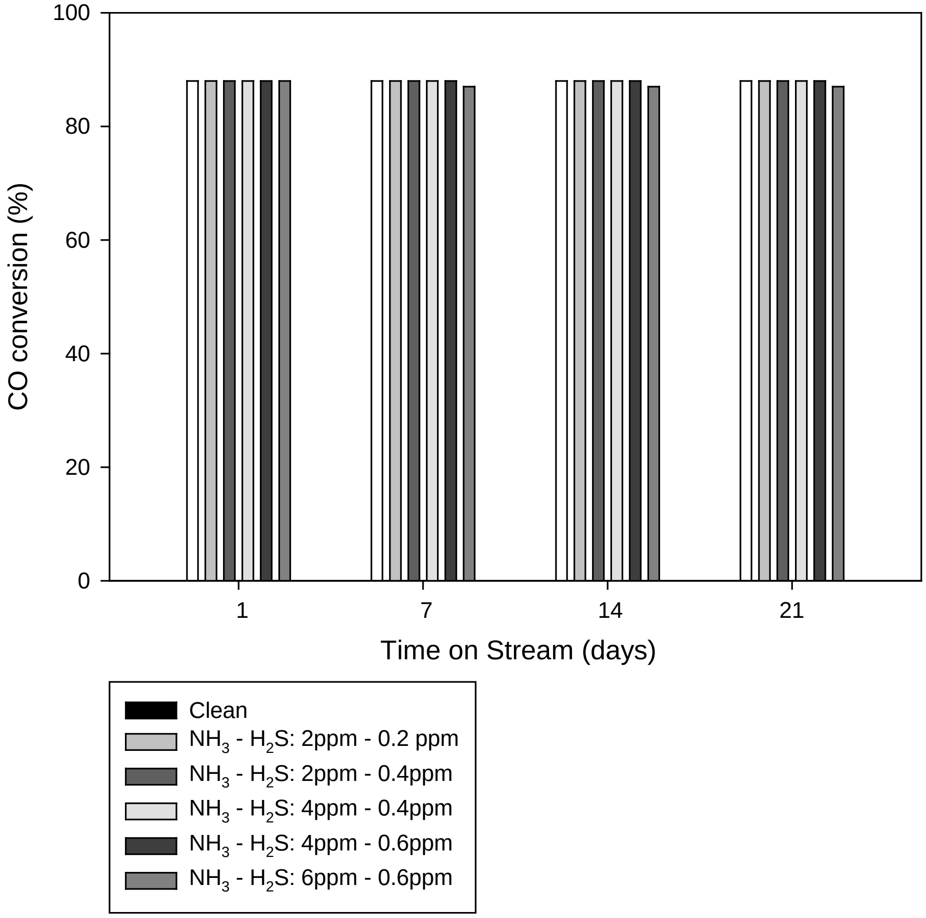


Figure 16: Effect of NH_3 and H_2S addition on the activity and stability of the Süd-Chemie HTS catalyst during WGS as a function of time on stream. Conditions: 350°C, 460 psi, 3250 hr^{-1}, 240 ml/min (steam/dry gas ratio of 1), catalyst weight of 4 g.

B.2.2 Fe-Si-K-Cu FTS Catalyst Testing

Tests on Fe-based FTS catalysts were conducted at two different temperatures, 260^{o}C and 270^{o}C; for this reason, logs of the runs at the two different temperatures are presented, with the 260^{o}C log given in Table 8 and the 270^{o}C log furnished in Table 9.

B.2.2.1 Clean Feed

For the purpose of comparison, a clean reference run was first carried out at 270^{o}C. Results of CO conversion are provided in Figure 17. Catalyst GJ457 displayed an induction period, since the active catalyst should exist as a mixture of Fe carbides and Fe_3O_4 oxide and time is required to achieve a steady state partitioning of the two phases. The catalyst exhibited excellent stability over 300 hours, with CO conversion between 70 and 75%, C_1 selectivity below 5%, and C_5+ selectivity at close to 80% (Figure 17).

B.2.2.2 Feed Containing Contaminants

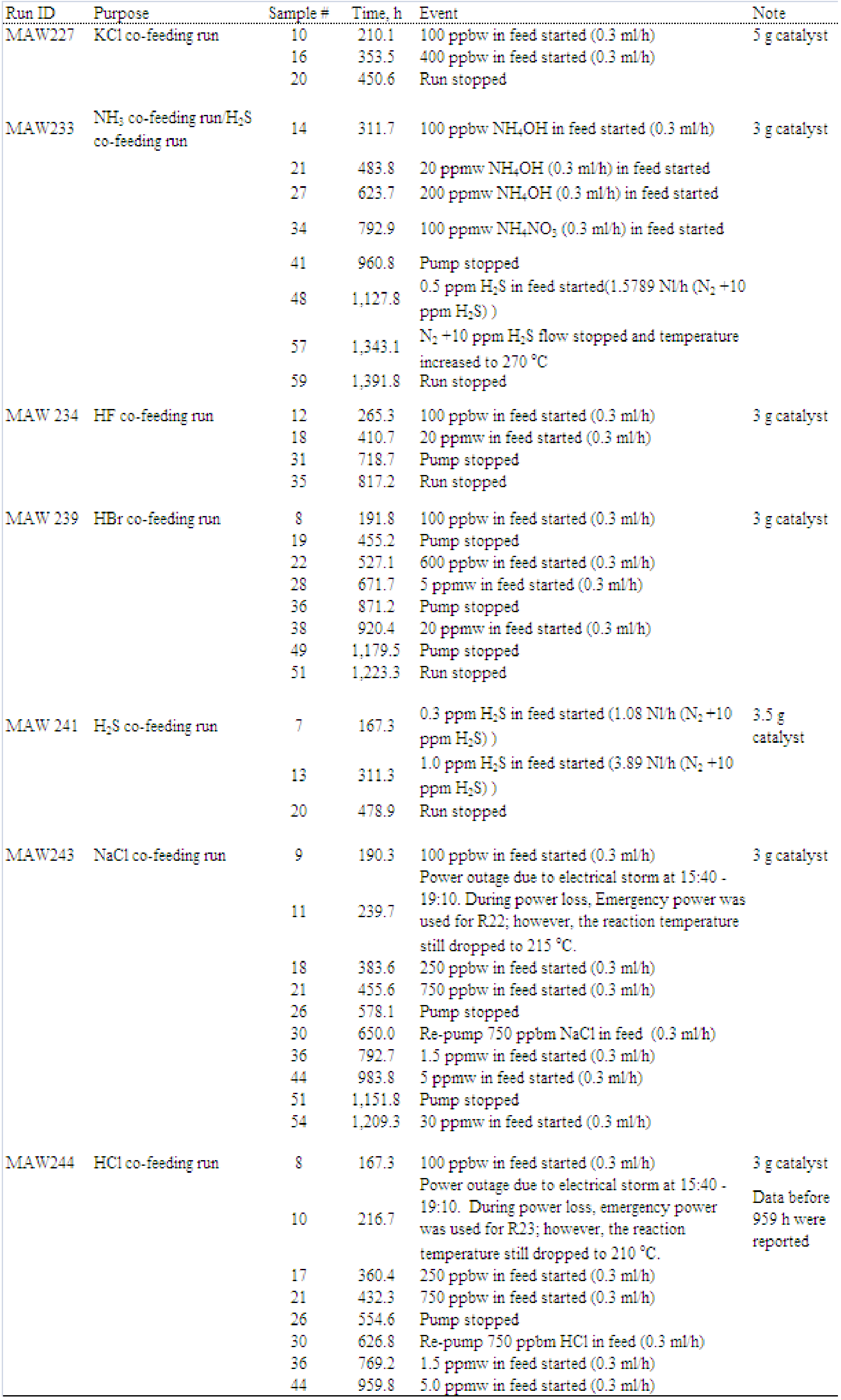
B.2.2.2.1 HCl and NaCl

The sensitivity of CAER high alpha iron catalyst to contaminant concentrations of up to 400 ppbw KCl and, in a separate study, 400 ppbw NaCl in syngas feed, were evaluated at 270 ^{o}C. No significant impact on the catalyst behavior over the high alpha iron catalyst was found. CO conversion (Figure 18a) displayed some decreases during feeding of the contaminant-containing solutions, but the slopes of the curves following contaminant addition were essentially the same as the baseline catalyst deactivation during the first 5-7 days. The catalyst selectivities to CH_4, C_{5+}, C_4 olefin and 1-C_4 olefin, reported in Figures 18b and 19b, were nearly identical before and after adding 100 ppbw and 400 ppbw poisons. CO_2 selectivity (Figure 19a) increased slightly after feeding KCl or NaCl solutions.

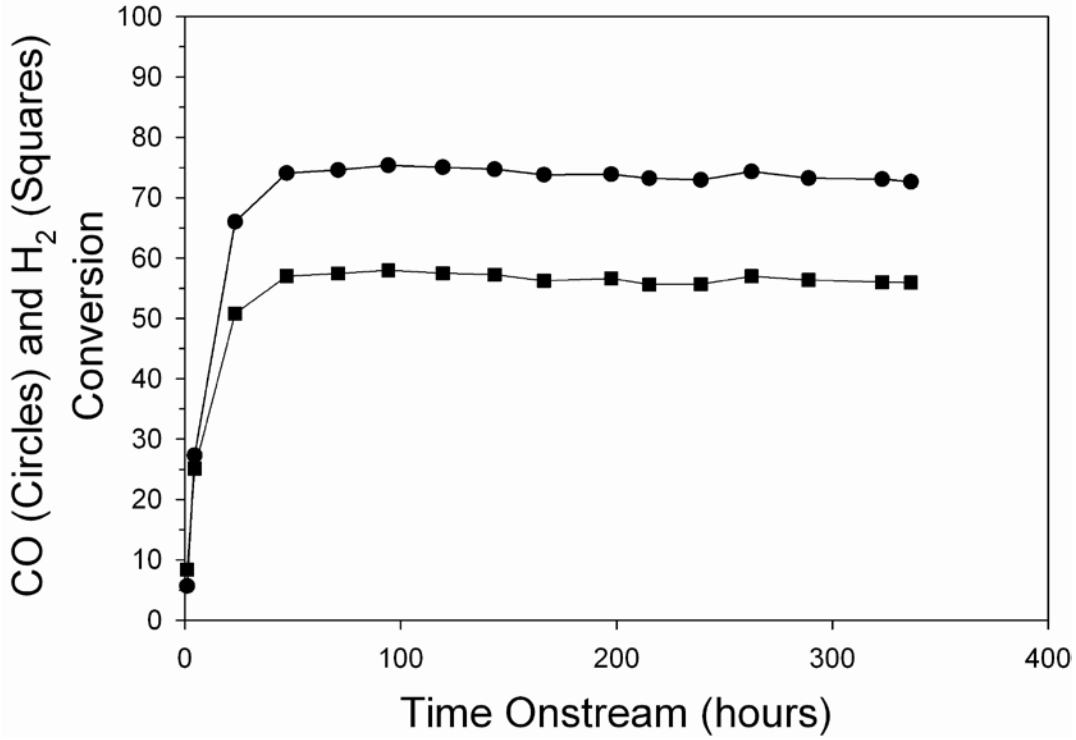
Table 8. Experimental log-1(test conditions: 270 ^{o}C, H_2/CO = 0.77, 175 psig, 10 Nl/g-cat/h).

Run ID	Purpose	Sample #	Time, h	Event	Note
MAW153	Fe clean run	16	336.0	Run stopped	5 g catalyst
MAW169	KCl co-feeding run	8	166.8	100 ppbw KCl in feed started (1ml/h)	5 g catalyst
		14	310.4	400 ppbw KCl in feed started (1ml/h)	
		18	406.0	Run stopped	
MAW174	NaCl co-feeding run	5	95.9	100 ppbw (0.3 ml) in feed started	using Paul Corp. filter, 5 g catalyst
		9	192.8	400 ppbw (1.2 ml) in feed started	
		12	265.5	Run stopped	
MAW177	$NaHCO_3$ co-feeding run	7	143.6	100 ppbw (0.3 ml) in feed started	5 g catalyst
		11	240.9	400 ppbw (1.2 ml) in feed started	
		14	312.3	40 ppmw (1.2 ml) in feed started	
		16	361.0	Run stopped	
MAW188	$KHCO_3$ co-feeding run	6	99.3	100 ppbw (0.3 ml) in feed started	5 g catalyst
		9	168.4	400 ppbw (1.2 ml) in feed started	
		13	263.4	40 ppmw (1.2 ml) in feed started	
		18	392.0	Run stopped	
MAW191	HCl co-feeding run	4	97.0	100 ppbw (0.3 ml) in feed started	5 g catalyst
		7	176.8	400 ppbw (1.2 ml) in feed started	
		10	240.0	40 ppmw (1.2 ml) in feed started	
		24	552.0	Run stopped	
MAW196	HBr co-feeding run	6	121.3	100 ppbw (0.3 ml) in feed started	5 g catalyst
		9	193.5	400 ppbw (1.2 ml) in feed started	
		12	265.0	Pump stopped	
		15	312.8	re-started 400 ppbw (1.2 ml) in feed	
		20	431.6	40 ppmw (1.2 ml) in feed started	
		25	562.1	Pump stopped	
		29	647.5	Run stopped	
MAW204	NH_3 co-feeding run 1	6	143.8	100 ppbw (0.3 ml) in feed started	5 g catalyst, using NH_4NO_3 solution
		10	239.5	400 ppbw (1.2 ml) in feed started	Data only before 500 h
		19	432.6	1 ppmw (1.2 ml) in feed started	were reported here
		25	599.5	Measuring NH_4 conc. in outlet gas using NH_3 testing tubing. No color change after flowing 1204 ml gas, suggesting no NH_3 in outlet gas.	
		44	1,128.0	10 ppmw (1.2 ml) in feed started	
		52	1,321.3	40 ppmw (1.2 ml) in feed started	
		58	1,465.2	Meauring NH_4 conc. in outlet gas using NH_3 testing tubing. No color change after flowing 1059.1 Nml gas, suggesting no NH_3 in outlet gas.	
		60	1,515.1	Power failure; pump stopped; power back next day	
		68	1,762.1	40 ppmw (1.2 ml) in feed re-started	
		73	1,872.9	Pump stopped	
		76	1,929.9	40 ppmw (1.2 ml) in feed re-started	
		88	2,207.8	Run stopped	
MAW215	NH_3 co-feeding run 2	6	145.0	40 ppmw (1.2 ml) in feed started	5 g catalyst
		12	288.8	400 ppmw (1.2 ml) in feed started	
		22	529.1	Run stopped	
MAW222	H_2S co-feeding run	8	197.3	1 ppm H_2S in feed started (5.556 Nl/h (N_2+10 ppm H_2S))	5 g catalyst
		14	335.0	N_2+H_2S flow stopped	
		19	407.5	Run stopped	

Table 9. Experimental log-2 (test conditions: 260 °C, H_2/CO = 0.67, 175 psig, 10 Nl/g-cat/h).



Run ID	Purpose	Sample #	Time, h	Event	Note
MAW227	KCl co-feeding run	10	210.1	100 ppbw in feed started (0.3 ml/h)	5 g catalyst
		16	353.5	400 ppbw in feed started (0.3 ml/h)	
		20	450.6	Run stopped	
MAW233	NH_3 co-feeding run/H_2S co-feeding run	14	311.7	100 ppbw NH_4OH in feed started (0.3 ml/h)	3 g catalyst
		21	483.8	20 ppmw NH_4OH (0.3 ml/h) in feed started	
		27	623.7	200 ppmw NH_4OH (0.3 ml/h) in feed started	
		34	792.9	100 ppmw NH_4NO_3 (0.3 ml/h) in feed started	
		41	960.8	Pump stopped	
		48	1,127.8	0.5 ppm H_2S in feed started(1.5789 Nl/h (N_2 +10 ppm H_2S))	
		57	1,343.1	N_2 +10 ppm H_2S flow stopped and temperature increased to 270 °C	
		59	1,391.8	Run stopped	
MAW 234	HF co-feeding run	12	265.3	100 ppbw in feed started (0.3 ml/h)	3 g catalyst
		18	410.7	20 ppmw in feed started (0.3 ml/h)	
		31	718.7	Pump stopped	
		35	817.2	Run stopped	
MAW 239	HBr co-feeding run	8	191.8	100 ppbw in feed started (0.3 ml/h)	3 g catalyst
		19	455.2	Pump stopped	
		22	527.1	600 ppbw in feed started (0.3 ml/h)	
		28	671.7	5 ppmw in feed started (0.3 ml/h)	
		36	871.2	Pump stopped	
		38	920.4	20 ppmw in feed started (0.3 ml/h)	
		49	1,179.5	Pump stopped	
		51	1,223.3	Run stopped	
MAW 241	H_2S co-feeding run	7	167.3	0.3 ppm H_2S in feed started (1.08 Nl/h (N_2 +10 ppm H_2S))	3.5 g catalyst
		13	311.3	1.0 ppm H_2S in feed started (3.89 Nl/h (N_2 +10 ppm H_2S))	
		20	478.9	Run stopped	
MAW243	NaCl co-feeding run	9	190.3	100 ppbw in feed started (0.3 ml/h)	3 g catalyst
		11	239.7	Power outage due to electrical storm at 15:40 - 19:10. During power loss, Emergency power was used for R22; however, the reaction temperature still dropped to 215 °C.	
		18	383.6	250 ppbw in feed started (0.3 ml/h)	
		21	455.6	750 ppbw in feed started (0.3 ml/h)	
		26	578.1	Pump stopped	
		30	650.0	Re-pump 750 ppbm NaCl in feed (0.3 ml/h)	
		36	792.7	1.5 ppmw in feed started (0.3 ml/h)	
		44	983.8	5 ppmw in feed started (0.3 ml/h)	
		51	1,151.8	Pump stopped	
		54	1,209.3	30 ppmw in feed started (0.3 ml/h)	
MAW244	HCl co-feeding run	8	167.3	100 ppbw in feed started (0.3 ml/h)	3 g catalyst
		10	216.7	Power outage due to electrical storm at 15:40 - 19:10. During power loss, emergency power was used for R23; however, the reaction temperature still dropped to 210 °C.	Data before 959 h were reported
		17	360.4	250 ppbw in feed started (0.3 ml/h)	
		21	432.3	750 ppbw in feed started (0.3 ml/h)	
		26	554.6	Pump stopped	
		30	626.8	Re-pump 750 ppbm HCl in feed (0.3 ml/h)	
		36	769.2	1.5 ppmw in feed started (0.3 ml/h)	
		44	959.8	5.0 ppmw in feed started (0.3 ml/h)	



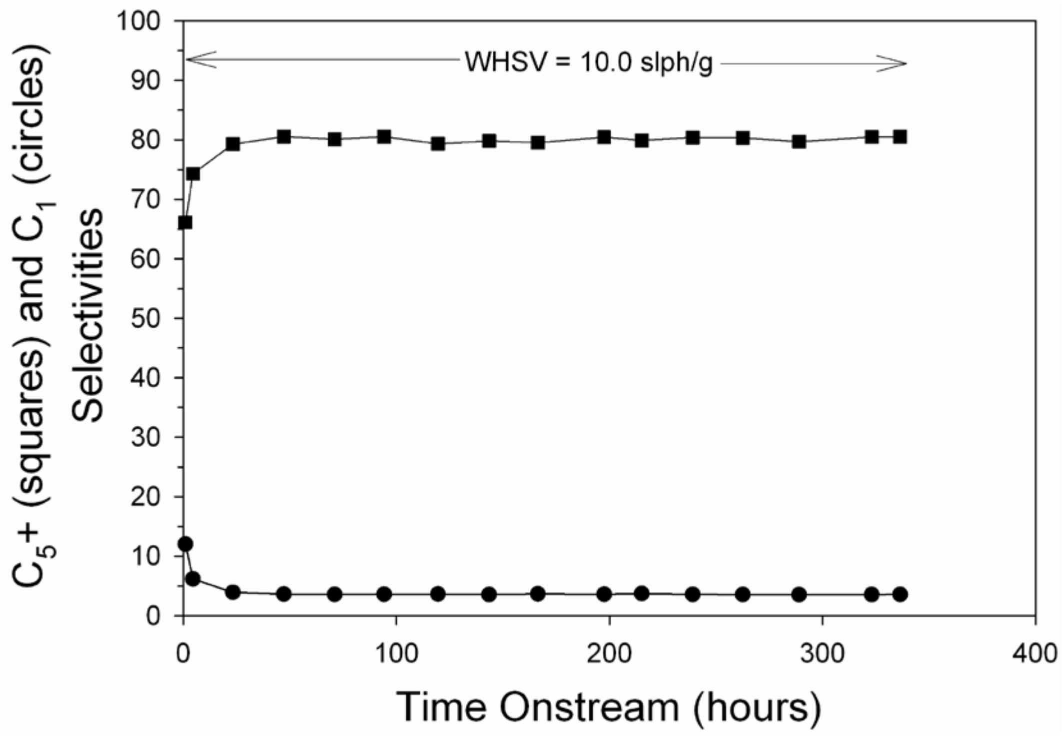


Figure 17: Change in (top) CO and H_2 conversion and (bottom) HC selectivity with time on stream over 100Fe/ 5.1Si/ 3.0K/ 2.0Cu (GJ457).
Test conditions: 270 ^oC, 175 psig, $H_2/CO = 0.77$, SV: 10 Nl/g-cat/h.

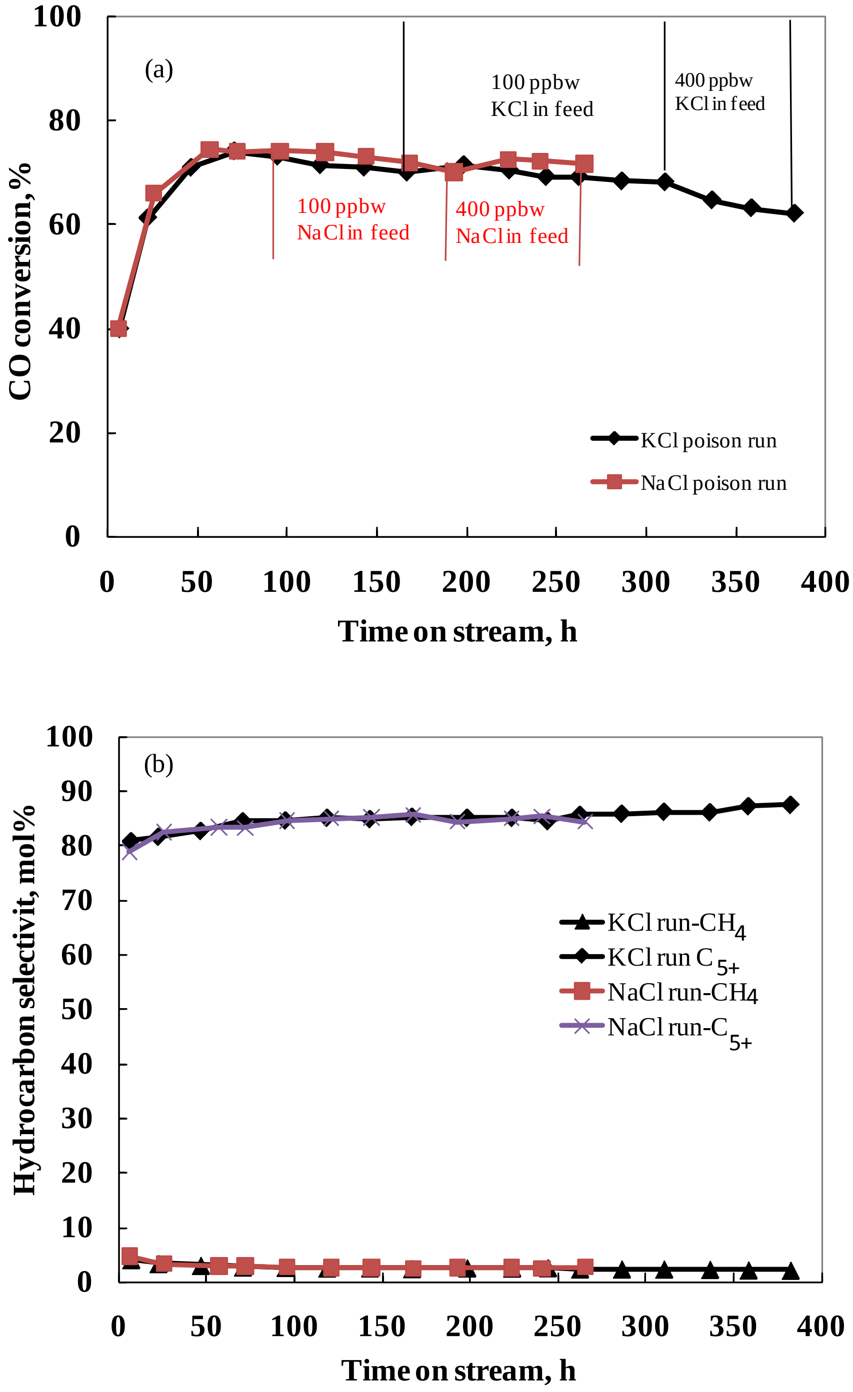
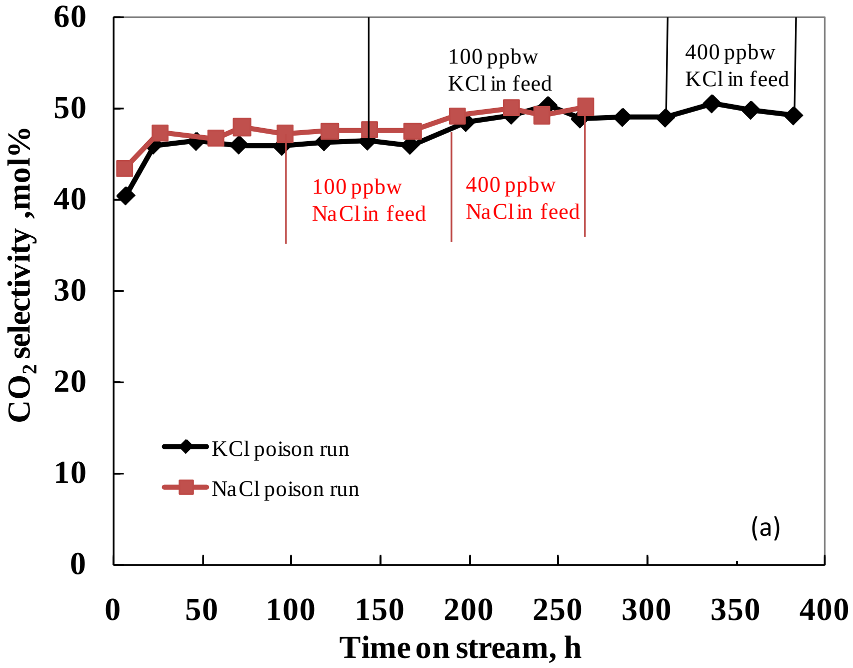


Figure 18: Effect of alkali halides (KCl and NaCl) on (a) CO conversion, (b) CH_4 and C_{5+} selectivities for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 270 °C, 175 psig ($CO+H_2$), $H_2/CO = 0.77$, SV_{CO+H2}=10 Nl/g-cat/h.



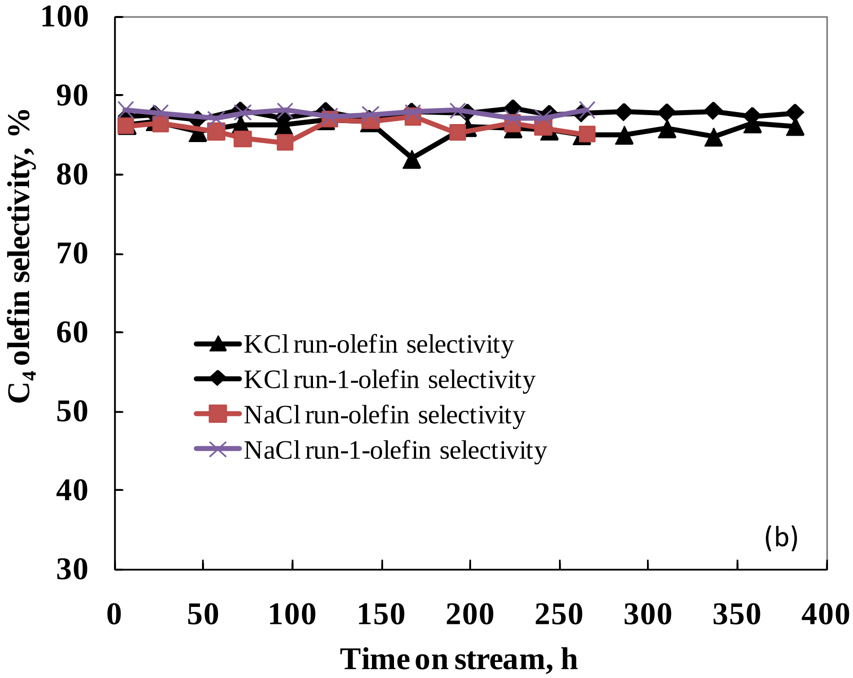


Figure 19: Effect of alkali halides (KCl and NaCl) on (a) CO_2 selectivity, and (b) C_4 olefin selectivity for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 270 ^oC, 175 psig (CO+H_2), H_2/CO = 0.77, SV_{CO+H2}=10 Nl/g-cat/h.

B.2.2.2.2 $KHCO_3$ and $NaHCO_3$

The sensitivity of the CAER high alpha iron catalyst to up to 40 ppmw $KHCO_3$ or, separately, 40 ppmw $NaHCO_3$ in syngas feed was evaluated at 270 ^oC. Comparing the slopes (Figure 20) obtained at different contaminant levels, co-feeding 400 ppbw $KHCO_3$ or 400 ppbw $NaHCO_3$ with the syngas feed did not measurably impact FTS behavior over the high alpha iron catalyst. However when the concentration was increased to 40 ppm for both poisons, catalyst activity decreased slightly; however, the decreases observed were essentially in line with the activity slopes prior to feeding the salt solutions (Figure 20). This implies that 40 ppm $KHCO_3$ or $NaHCO_3$ added to the feed also does not significantly change or diminish catalytic activity over the 13 days of addition.

The catalyst selectivities to CH_4, C_{5+}, C_4 olefin and 1-C_4 olefin were nearly identical before and after adding 100ppbw, 400 ppbw, and 40 ppm concentration levels of $KHCO_3$ or $NaHCO_3$ contaminants (Figure 20, bottom and Figure 21, bottom). Slightly higher C_4 olefin selectivity at the end of both runs might be as a result of rewax accumulation in the reactor. CO_2 selectivity increased only slightly after feeding $KHCO_3$ or $NaHCO_3$ solutions (Figure 21, top).

Based on the FTS reaction data before and after adding NaCl, KCl $NaHCO_3$ and $KHCO_3$ (100ppb-40 ppm) solutions, it appears that alkali compounds, including chloride salts and bicarbonates, do not adsorb significantly onto active Fe catalyst surfaces (e.g., Fe_xC and Fe_3O_4) or react with these active sites at the FTS reaction conditions, to result in deleterious changes in catalyst activity or selectivity. Note that:

C_4 olefin sel, % = 100 * C_4 olefins/(C_4 olefins+C_4 paraffins)

1-C_4 olefin sel, % = 100 * 1-C_4 olefin/C_4 olefins (1- olefin and internal olefin)

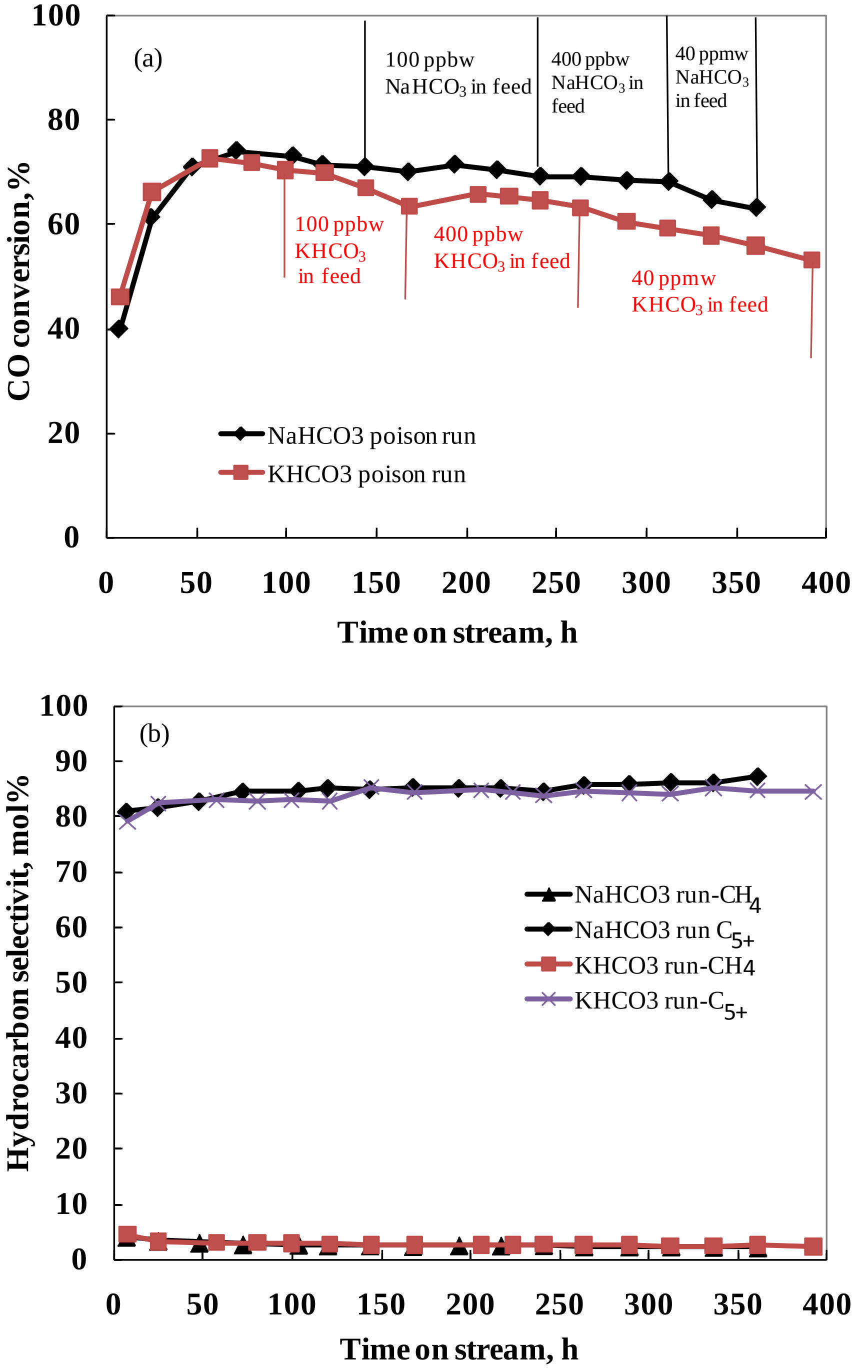


Figure 20: Effect of alkali bicarbonate ($KHCO_3$ and Na HCO_3) on (a) CO conversion, (b) CH_4 and C_{5+} selectivities for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 270 ^oC, 175 psig (CO+H_2), H_2/CO = 0.77, SV_{CO+H2}=10 Nl/g-cat/h.

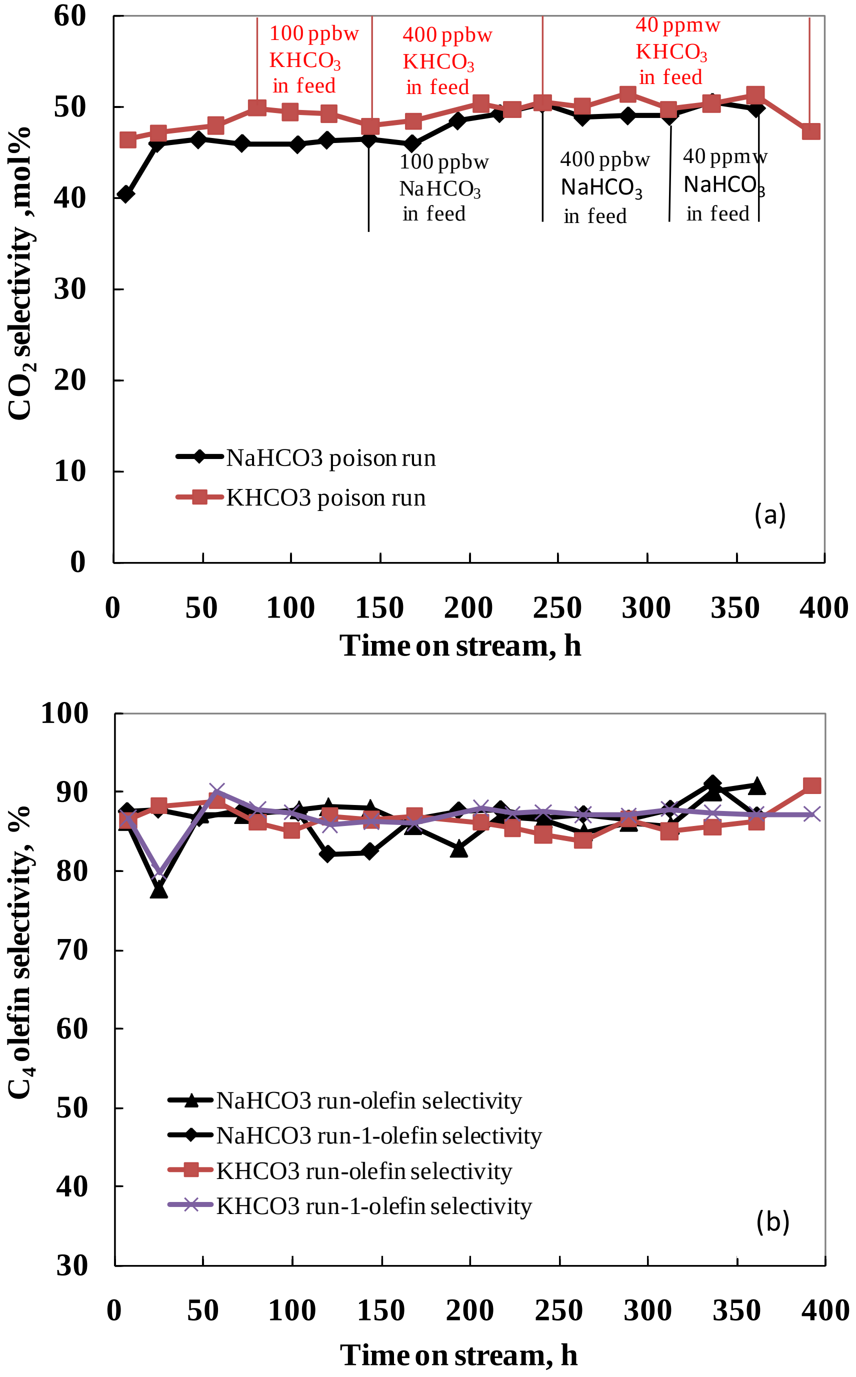


Figure 21: Effect of alkali bicarbonate ($KHCO_3$ and $NaHCO_3$) on (a) CO_2 selectivity and (b) C_4 olefin selectivity for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 270 °C, 175 psig ($CO+H_2$), $H_2/CO = 0.77$, SV_{CO+H2}=10 Nl/g-cat/h.

B.2.2.2.3 HCl or HBr

The sensitivity of the CAER high alpha iron catalyst to up to 40 ppmw HCl or 40 ppmw HBr in the syngas feed was evaluated at 270 ^{o}C. Adding 100 ppbw or 400 ppbw HCl into the feed for about 72 h did not result in measurable losses in activity at 270 ^{o}C over the high alpha iron catalyst. However when the concentration of either contaminant in the feed was increased to 40 ppm, catalyst activity declines were observed (Figure 22, top).

With co-feeding HBr, deactivation was observed on the Fe catalyst after feeding 100 ppbw and 400 ppbw HBr at 120-265 h (Figure 22, top). However, one uncertainty was whether the deactivation was due to the relatively low concentration of HBr added, or if it was the result of an un-steady state condition established prior to adding the solution or if water was perhaps involved in oxidizing some fine Fe particles (e.g., decreased C_{5+} selectivity was observed). When a new steady state was reestablished between 265-312 h without pumping any solution, catalyst activity was quite able after re-feeding 400 ppbw HBr for about 120 h. This suggests that up to 400 ppbw HBr did not greatly impact catalyst activity under the conditions used. However, when the HBr concentration increased to 40 ppm, CO conversion dropped from 51 to 30% within 130 h. CO conversion became stable (30%) after the HBr pump was switched off.

Catalyst deactivation after feeding 40 ppm HCl or HBr also led to a significant decrease in C_{5+}, selectivity (Figure 22, bottom), but an increase in the CH_4 selectivity. Selectivities to C_4 olefin and 1-C_4 olefin depended on the contaminant added (Figure 22, bottom and Figure 23). Increases in selectivities to C_4 and 1-C_4 olefin in both runs were observed by the end of two tests, which could be due to higher amounts of rewax accumulated in the reactor, and a slight pressure variation at the end of the runs.

CO_2 selectivity increased slightly after feeding HCl and HBr solutions and remained stable during addition of 100 ppbw and 400 ppbw HCl or HBr. However, it decreased significantly after feeding 40 ppm HCl or HBr.

Figures 24 and 25 show the fraction of the CO conversion that is lost relative to the accumulated acid (HCl or HBr). It appears that there is a threshold level where the added acid does not have a measurable effect. Above the threshold level the activity loss is about 6-7 surface sites for each acid molecule added.

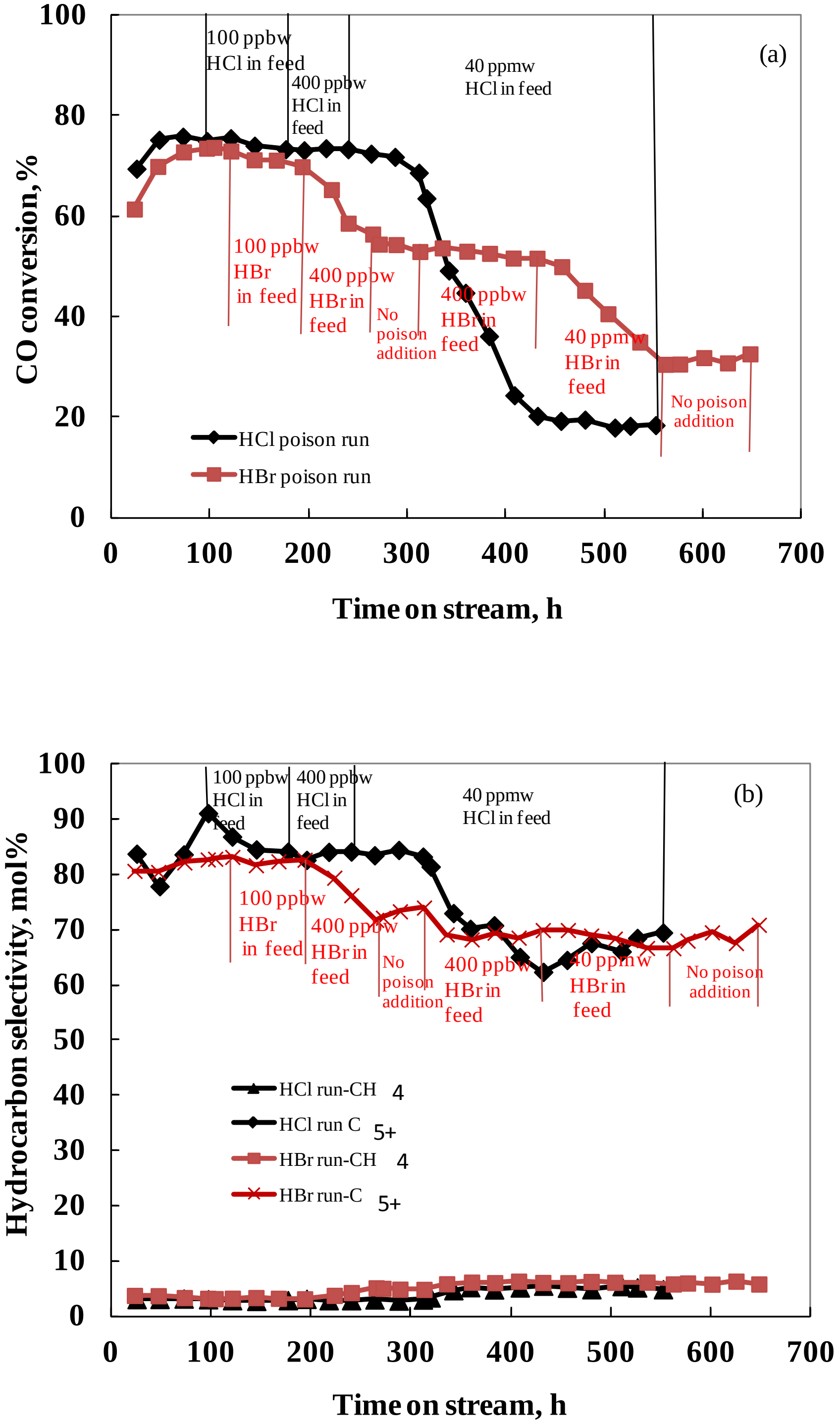


Figure 22: Effect of Halides (HCl and HBr) on (a) CO conversion, (b) CH_4 and C_{5+} selectivities for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 270 ^oC, 175 psig (CO+H_2), H_2/CO = 0.77, SV_{CO+H2}=10 Nl/g-cat/h.

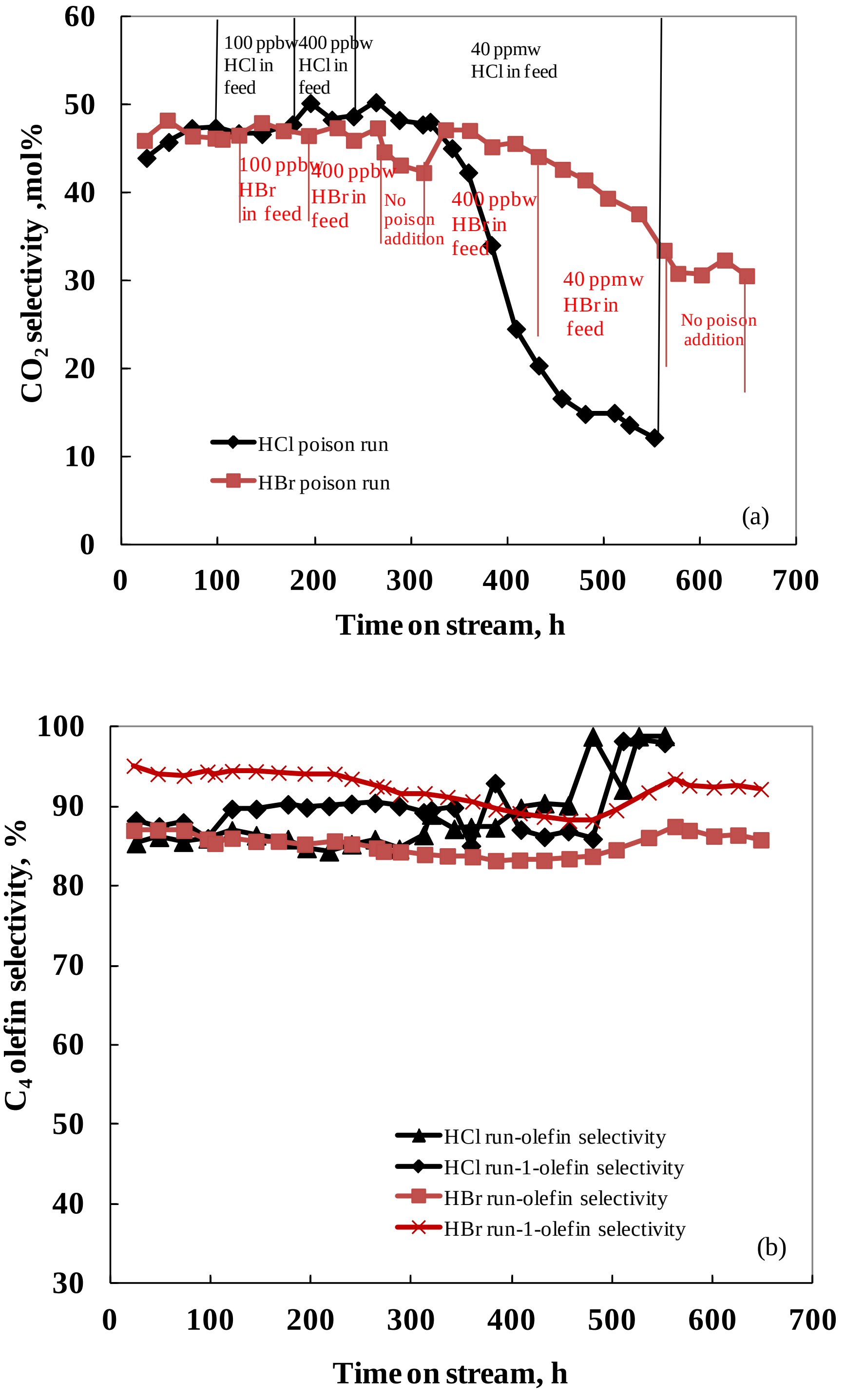


Figure 23: Effect of Halides (HCl and HBr) on (a) CO_2 selectivity and (b) C_4 olefin selectivity for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 270 ^{o}C, 175 psig ($CO+H_2$), $H_2/CO = 0.77$, SV_{CO+H2}=10 Nl/g-cat/h.

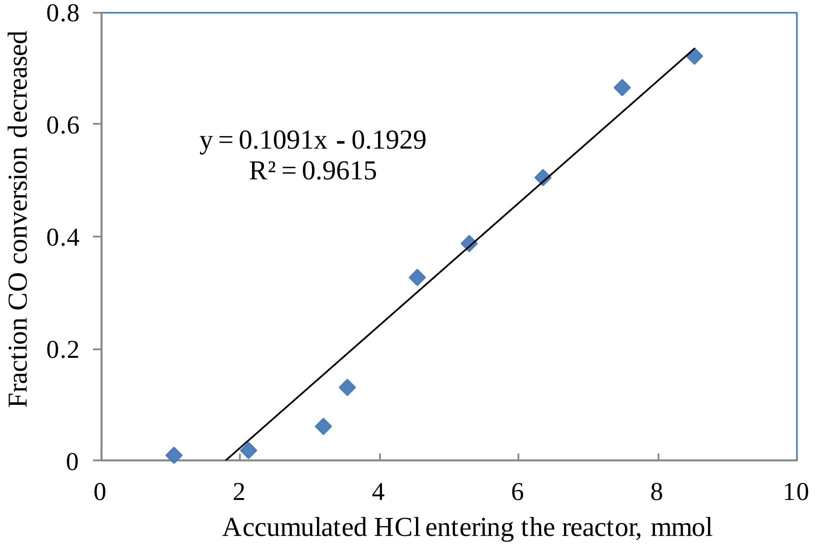


Figure 24: Fraction of CO conversion decreased versus accumulated HCl entering the reactor. Test conditions: 270^{o}C, 175 psig (CO+H_2), H_2/CO = 0.77, SV_{CO+H2}=10 Nl/g-cat/h.

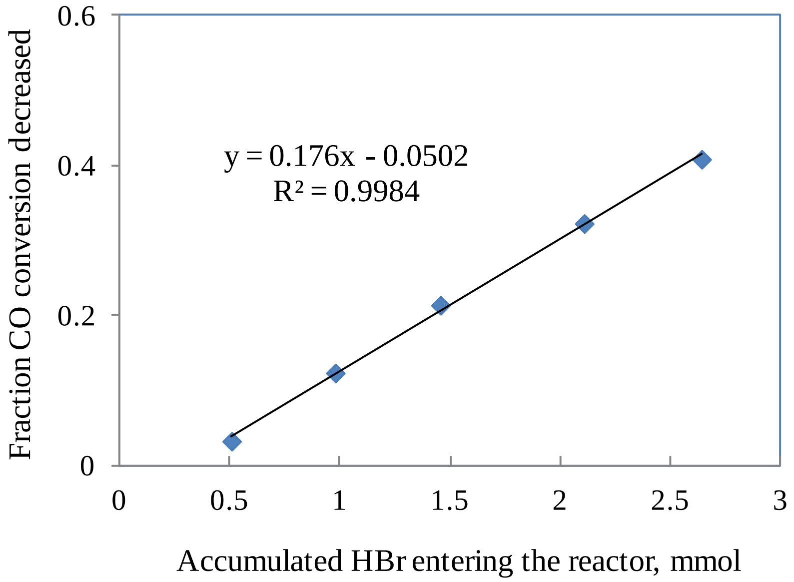


Figure 25: Fraction of CO conversion decreased versus accumulated HBr entering the reactor. Test conditions: 270^{o}C, 175 psig (CO+H_2), H_2/CO = 0.77, SV_{CO+H2}=10 Nl/g-cat/h.

B.2.2.2.4 NH_3

Two test runs were undertaken to examine the Fe catalyst sensitivity to four different NH_3 concentrations in the range of 200 ppbw – 800 ppmw added to the feed. In the first test run (run1), 100 ppbw and 400 ppbw $NH_4NO_{3.}$ addition were examined for 96 h, respectively. The changes in CO conversion and selectivities (CH_4, C_{5+}, and CO_2, C_4 olefin selectivity) with time and NH_3 concentration at 270 ^oC are shown in Figure 26. In the first 340 h of testing, 100 ppbw NH_4NO_3 and 400 ppbw NH_4NO_3 essentially did not significantly alter catalyst conversion and selectivities (Figure 26 and 27), although a small increase was observed in CO_2 selectivity (due to the WGS reaction, Figure 27). In this run, 1 ppm, 10 ppm and 40 ppm NH_4NO_3 were also tested between 430-2200 h, but the catalyst experienced an unexpected deactivation after 430 h. So, the data after this time is not summarized in the final report since it was not possible to identify what the cause for the decrease was.

In the 2nd test run (run 2), much higher concentrations of NH_4NO_3 were used in the feed, 40 ppmw and 400 ppmw, and their impact on catalyst behavior was examined. The effect of high NH_3 concentrations on catalyst activity and selectivity are shown in Figures 28 and 29. The catalyst steady state was established before 145 h in this run, and 40 ppmw NH_4NO_3 were added at this time. During 144 h of continuous feeding of the NH_4NO_3 solution, CO conversion remained stable (~73%, Figure 28), suggesting that the iron catalyst was very resistant to NH_3 (at least 80 ppm (40*2) in feed) at the test conditions. This was also indicated by nearly unchanged selectivities to CH_4, and C_{5+} and C_4 olefins (Figure 28, bottom and Figure 28, bottom). CO_2 selectivity increased slightly after feeding the NH_4NO_3 solution due to an increase in the WGS activity of the Fe catalyst due to the added water. Subsequently, the NH_4NO_3 concentration was increased to 400 ppm, which gave 800 ppmw NH_3 in the feed. This NH_3 concentration led to significant decreases in catalyst activity and C_{5+} and CO_2 selectivities, an increase in the selectivity of C_1, but little impact on C_4 olefin selectivity. CO conversion dropped to 40 from 73% after adding 400 ppmw NH_4NO_3 between 288-529 h. 1-C_4 olefin select ivies decreased between 400-530 h, and this is likely attributable to deactivation of the catalyst during in this period.

A calculation of the fraction of CO conversion decreased versus the accumulated NH_4 ions entering the reactor was made using the 288-529 h data obtained in run 2. The result is shown in Figure 30. The data suggest that one NH_4NO_3 eliminates about 9 surface sites. It appears that NH_4^+ and NO_3 have different impacts as catalyst poisons.

According to the results achieved, CAER high alpha Fe catalyst is not sensitive to ammonia. However, when the ammonia concentration is high enough, the effect on the Fe catalyst behavior is measurable.

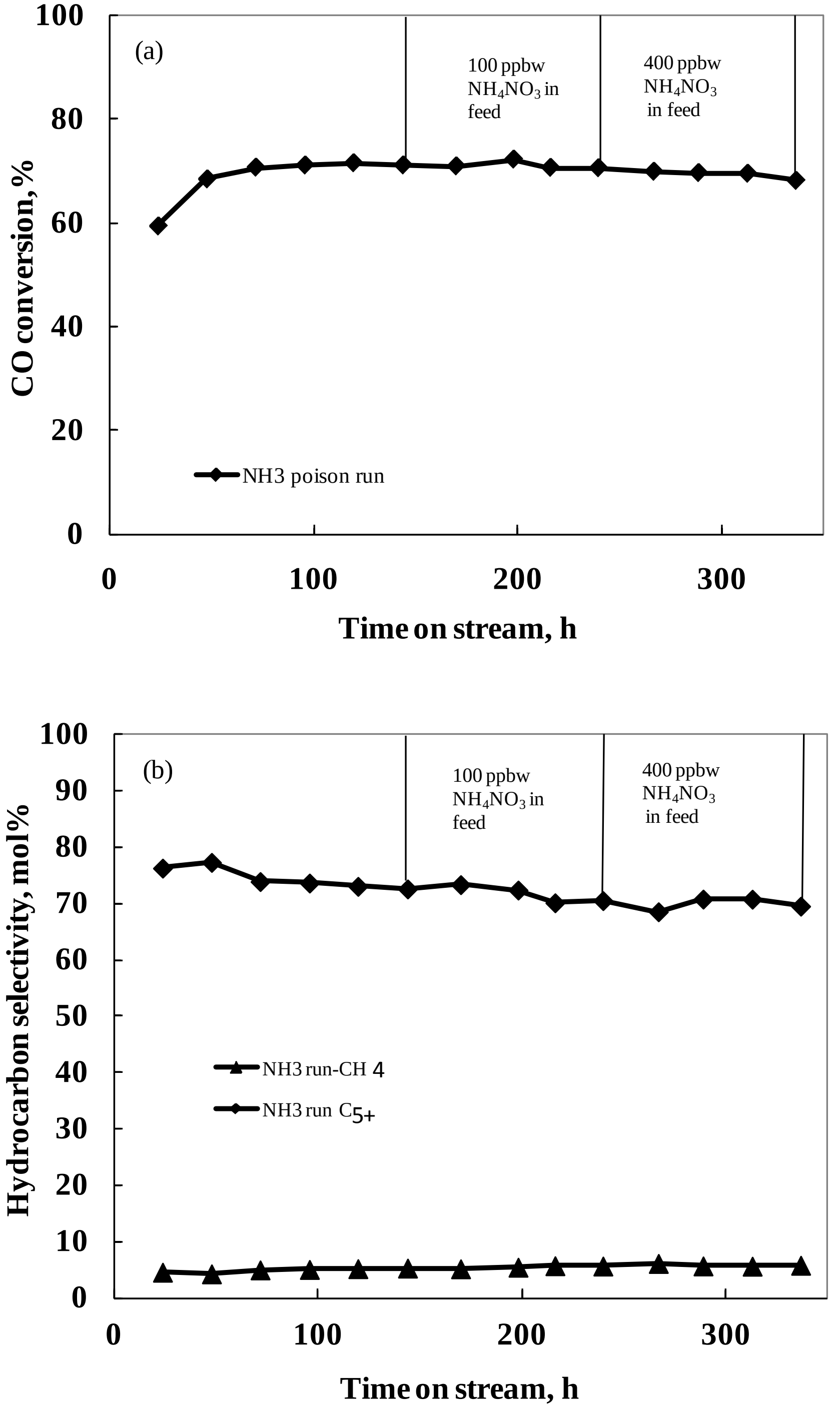


Figure 26: Effect of 100 and 400 ppbw NH_4NO_3 on (a) CO conversion and (b) CH_4 and C_{5+} selectivities for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 270 ^{o}C, 175 psig (CO+H_2), H_2/CO = 0.77, SV_{CO+H2}=10 Nl/g-cat/h.

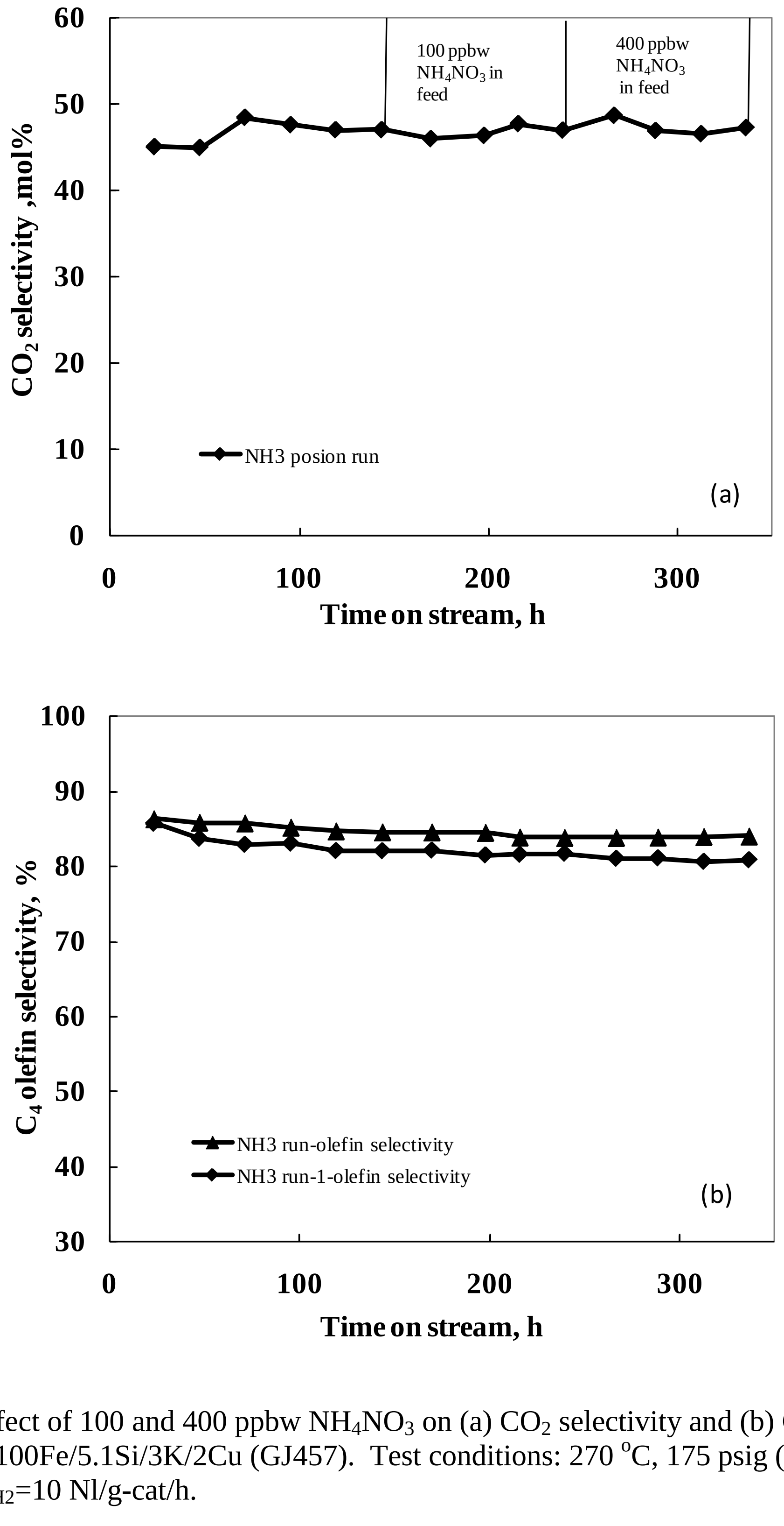


Figure 27: Effect of 100 and 400 ppbw NH_4NO_3 on (a) CO_2 selectivity and (b) C_4 olefin selectivity for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 270 ^oC, 175 psig (CO+H_2), H_2/CO = 0.77, SV_{CO+H2}=10 Nl/g-cat/h.

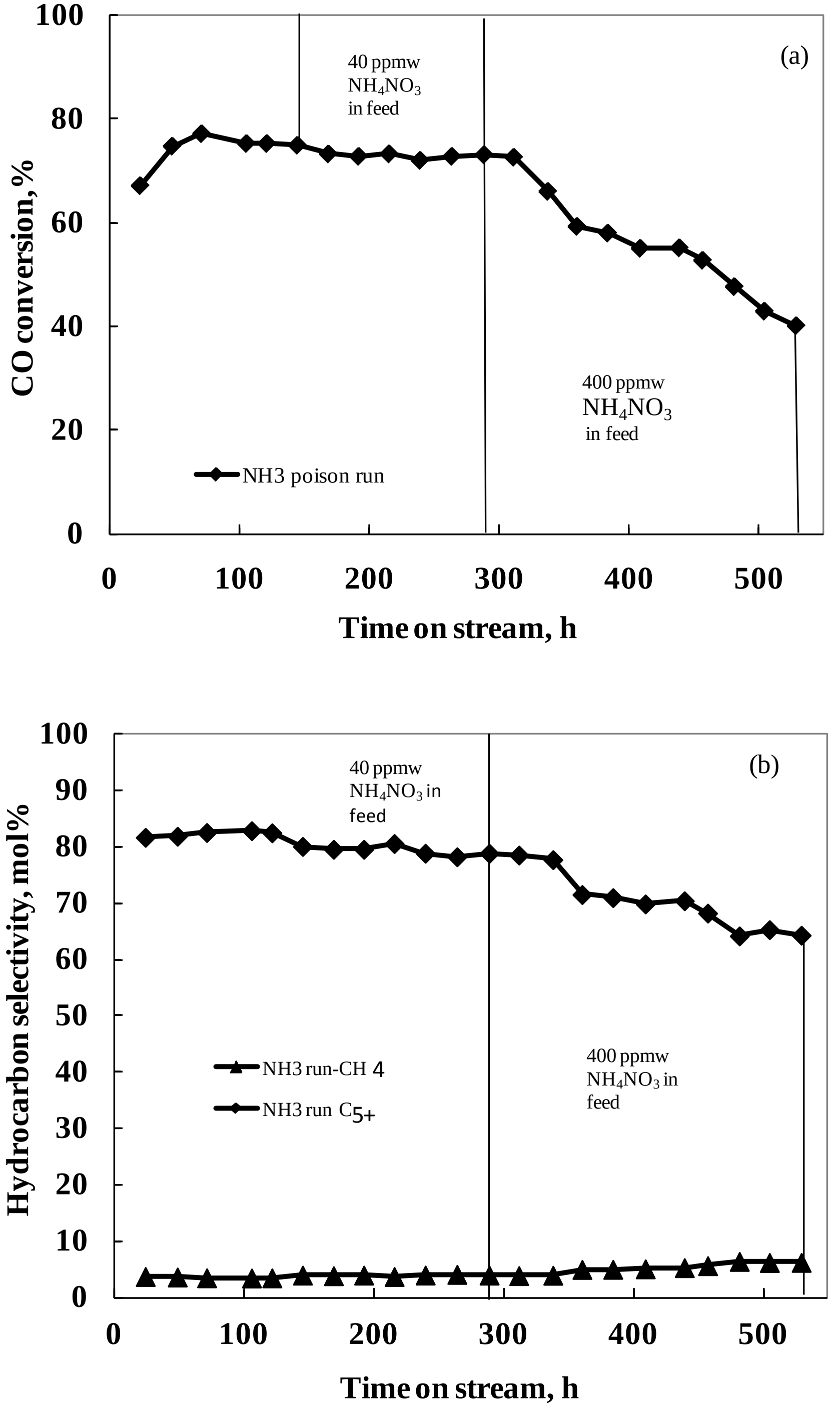


Figure 28: Effect of 40 and 400 ppmw NH_4NO_3 on (a) CO conversion and (b) CH_4 and C_{5+} selectivities for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 270 ^oC, 175 psig ($CO+H_2$), $H_2/CO = 0.77$, SV_{CO+H2}=10 Nl/g-cat/h.

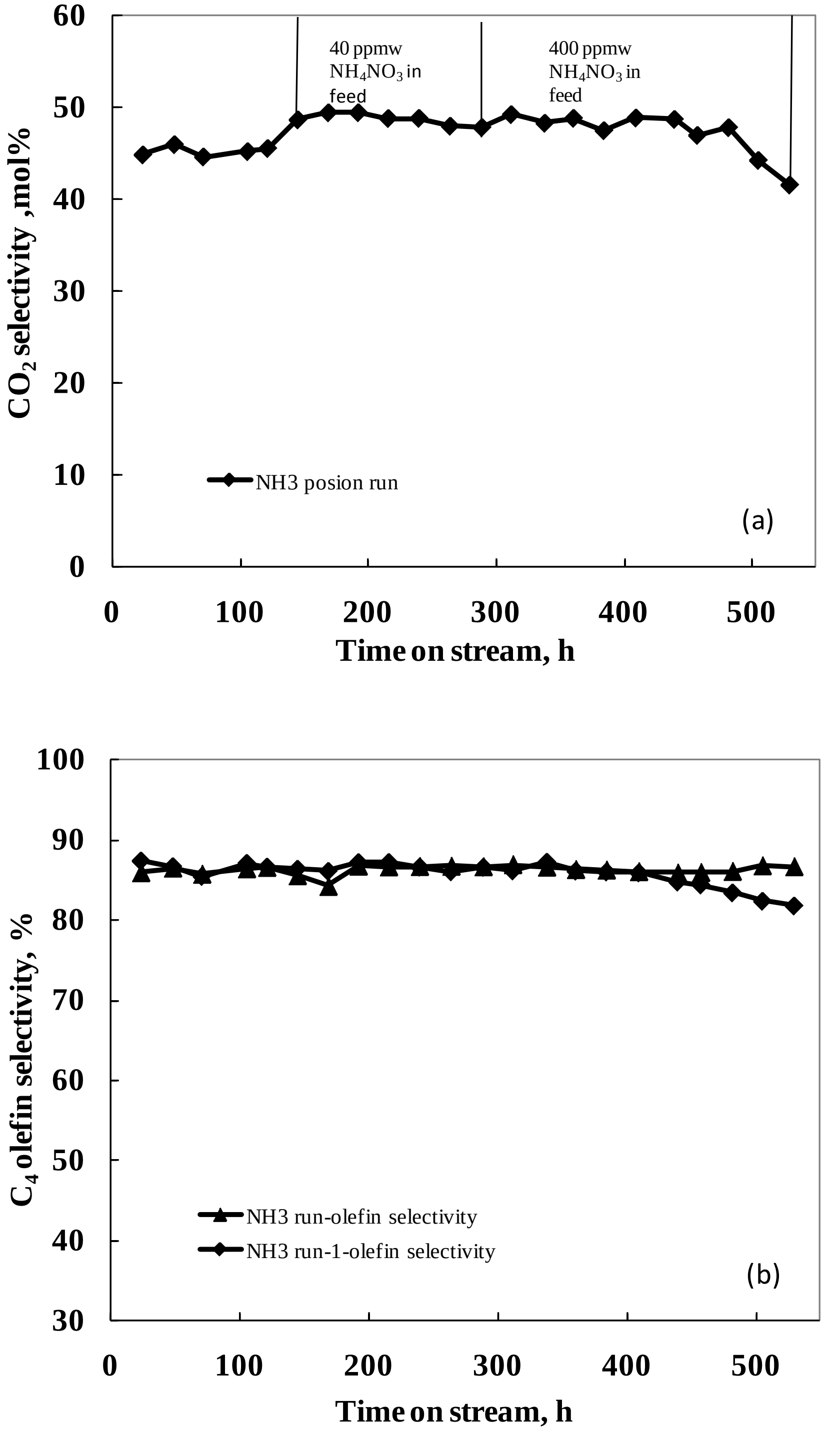


Figure 29: Effect of 40 and 400 ppmw NH_4NO_3 on (a) CO_2 selectivity and (b) C_4 olefin selectivity on 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 270 ^oC, 175 psig ($CO+H_2$), $H_2/CO = 0.77$, SV_{CO+H2}=10 Nl/g-cat/h.

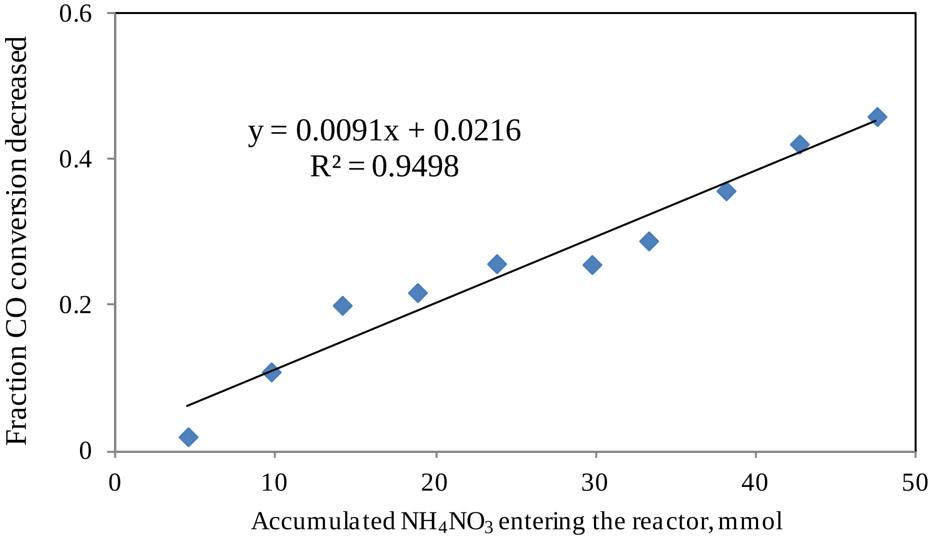
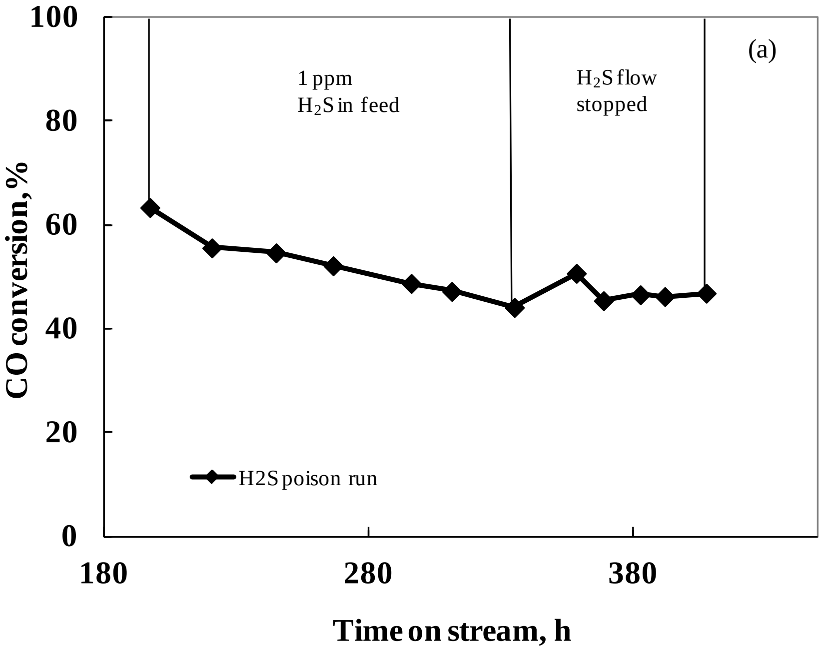


Figure 30: Fraction of CO conversion decreased versus accumulated ammonia fed in reactor using the FTS data after adding 400 ppmw NH_4NO_3. Test conditions: 270°C, 175 psig ($CO+H_2$), $H_2/CO = 0.77$, SV_{CO+H2}=10 Nl/g-cat/h.

B.2.2.2.5 H_2S

Figure 31a shows that adding 1 ppm 1H_2S resulted in steadily decrease of CO conversion between 170-335 h. When H_2S gas flow was stopped, the CO conversion was stable between 335-410 h (Figure 31a). Selectivities of the catalyst did not change before and after feeding 1ppm H_2S in feed (Figures 31b and 32). Figure 33 shows the change in the fraction of CO conversion decrease with accumulated H_2S entering the reactor. Assuming all Fe atoms are active sites and all sulfur is adsorbed as a poison, the fraction of CO conversion reduced is about 671 times of moles of H_2S that entered in the reactor. This shows that H_2S has a greater impact on deactivating the Fe catalyst as compared to halide acids and ammonia, as discussed previously.



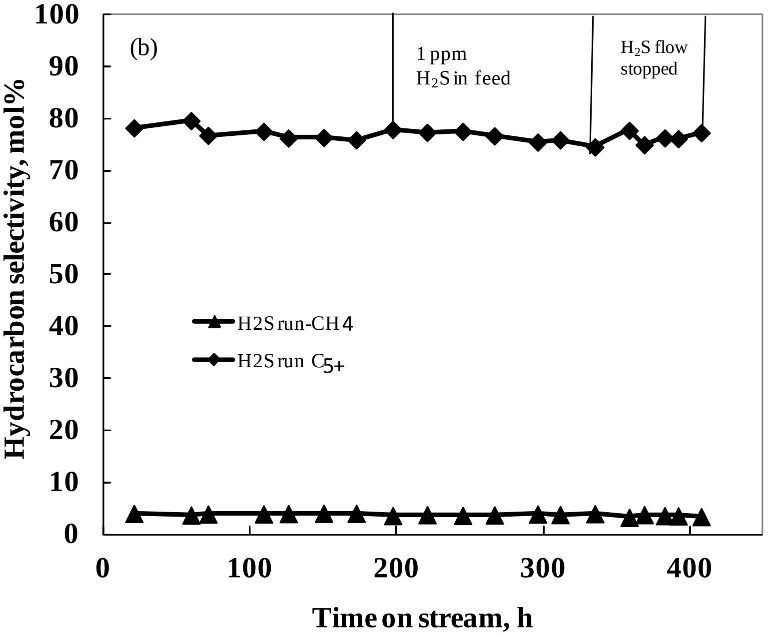


Figure 31: Effect of 1 ppm H_2S on (a) CO conversion and (b) CH_4 and C_{5+} selectivities for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 270 ^oC, 175 psig ($CO+H_2$), $H_2/CO = 0.77$, SV_{CO+H2}=10 Nl/g-cat/h.

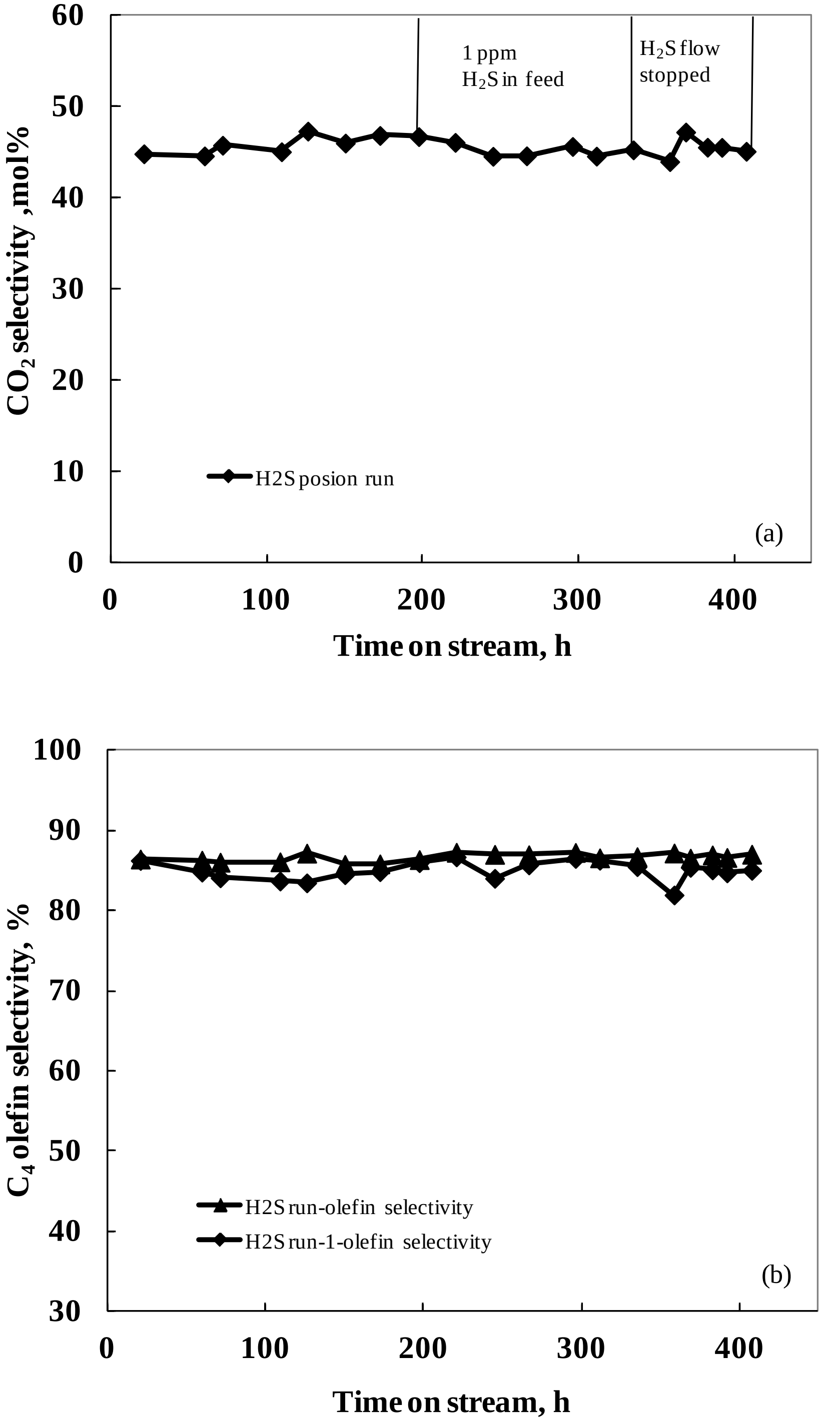


Figure 32: Effect of 1 ppm H_2S on (a) CO_2 selectivity, and (b) C_4 olefin selectivity for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 270 ^oC, 175 psig ($CO+H_2$), $H_2/CO = 0.77$, SV_{CO+H2}=10 Nl/g-cat/h.

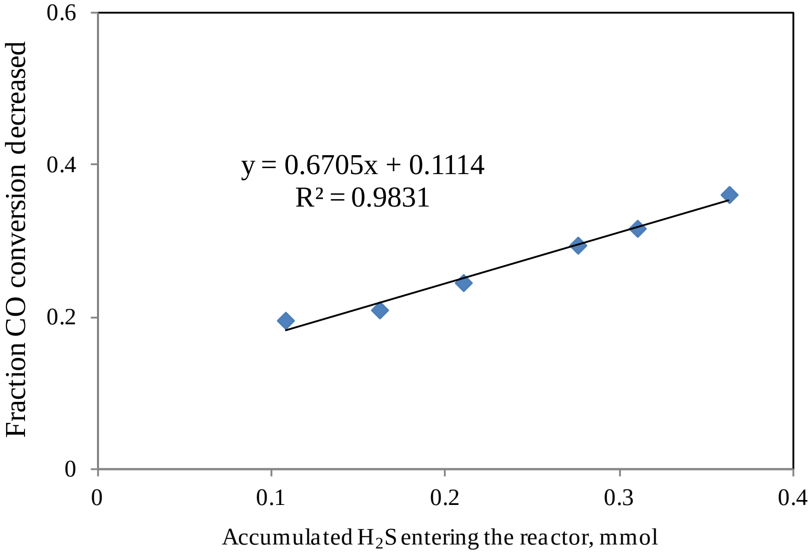


Figure 33: Fraction of CO conversion decreased versus accumulated H_2S entered. Test conditions: 270 °C, 175 psig ($CO+H_2$), $H_2/CO = 0.77$, SV_{CO+H2}=10 Nl/g-cat/h.

B.2.3 Fe-Si-K-Cu FTS Catalyst Testing at 260°C

B.2.3.1 NaCl and KCl

The sensitivities of CAER high iron catalyst to the contaminants discussed above (e.g., KCl, NaCl, $KHCO_3$, $NaHCO_3$, HCl, HBr, H_2S and NH_4NO_3) were previously tested at 270 °C. However, due to the very high productivity of the CAER high alpha Fe catalyst, each run lasted less than 400-500 h due to fast rewax accumulation in the CSTR reactor even though only 5 g of catalyst were used, a small amount for CSTR testing. This limited testing to only 2-3 concentrations for each test. Thus, the difference in contaminant concentration must sometimes be very large in order to observe a clear effect on the FTS reaction rate prior to shutdown. Also, the iron catalyst appears to be not as stable as expected at 270 °C. In order to get more information about the Fe catalyst sensitivity to more and higher contaminant concentration levels, longer test runs were deemed to be needed. In 2011, we adjusted baseline testing temperature, H_2/CO ratio, and catalyst amount, decreasing them to 260 °C, 0.67, 3 g, respectively. This allowed each test run to last more than 1000 h without our encountering a rewax removal problem. We finished re-examining the sensitivities of CAER iron catalyst to KCl, NaCl, HCl, HBr, HF, H_2S, NH_3 and HCN at 260 ^oC. The effect of $KHCO_3$, $NaHCO_3$ or NH_3+H_2S at 260 ^oC remains incomplete, but should be finished within 2-3 months after the reporting period.

The sensitivities of CAER high alpha iron catalyst to alkali halides (KCl and NaCl) were tested at 260 ^oC. KCl concentrations of up to 20 ppm were examined in a run that lasted about 460 h. At the time of reporting, a 30 ppm NaCl run was completed that lasted 1350 h (this run is ongoing to test 100 ppm NaCl). Each concentration was tested about 120-144 h. Adding 20-30 ppm KCl and NaCl into the feed did not result in significant deactivation (Figure 34a), or changes in catalyst selectivities (CO_2, CH_4, C_{5+}, C_4 olefin), as shown in Figures 34b and 35. In the NaCl test run, the catalyst displayed slight deactivation between 456-578 h when feeding 0.75 ppm NCl. However, it disappeared when co-feeding was stopped and a new baseline re-established at 578-650 h. The reason for the deactivation is not well known, but may not be due to the 0.75 ppm NaCl because retesting 0.75 ppm NaCl (650-793 h) did not lead to any measurable catalyst deactivation. A slight activity drop observed earlier in the testing period could be related to a power failure at about 240 h or other unknown factors. This result is consistent with the results obtained at 270 ^oC, confirming that the Fe catalyst is not sensitive to KCl and NaCl in the concentrations tested.

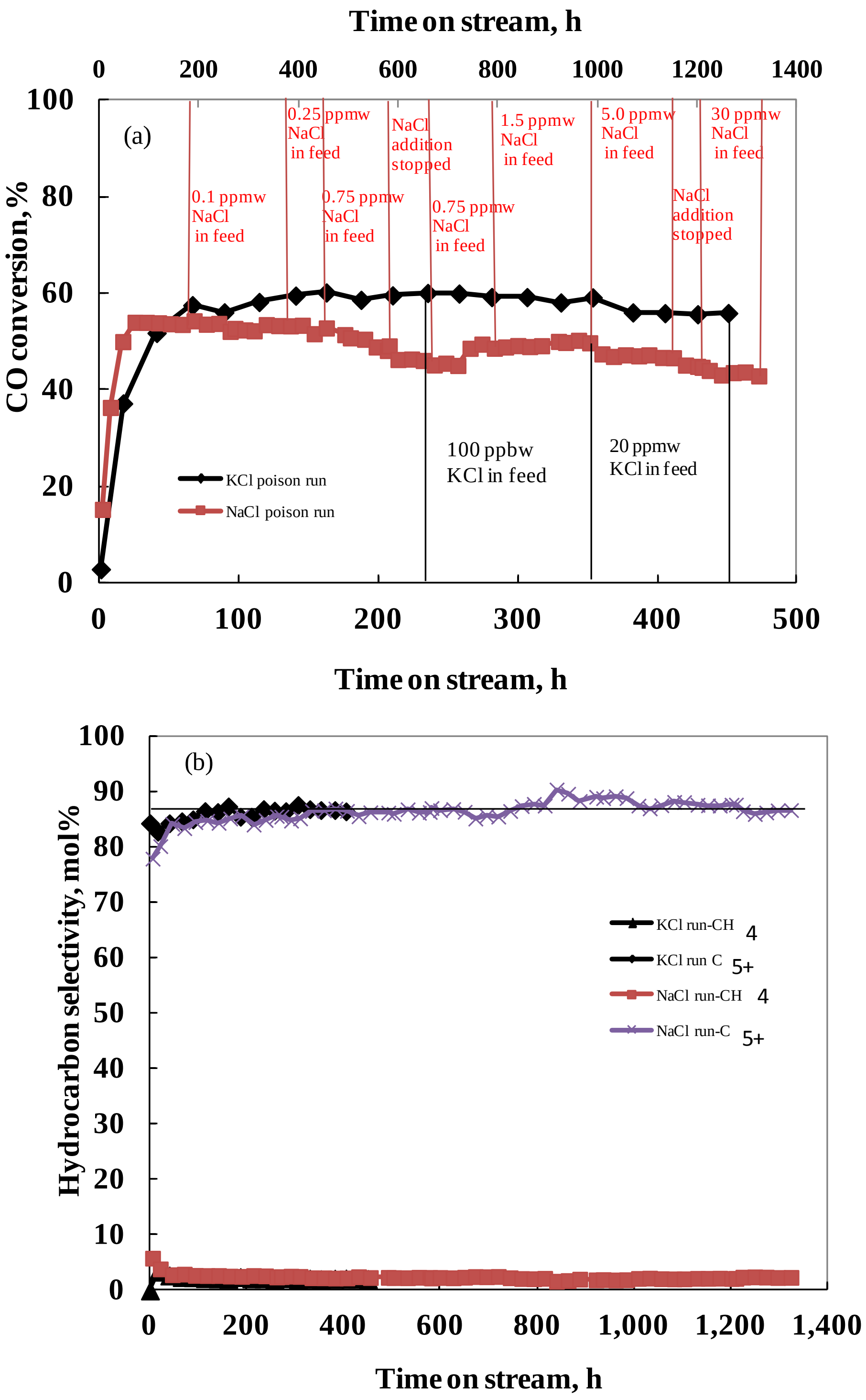


Figure 34: Effect of alkali halides (KCl and NaCl) on (a) CO conversion and (b) CH_4 and C_{5+} selectivities for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 260 ^{o}C, 175 psig ($CO+H_2$), $H_2/CO = 0.67$, SV_{CO+H2}=10 Nl/g-cat/h.

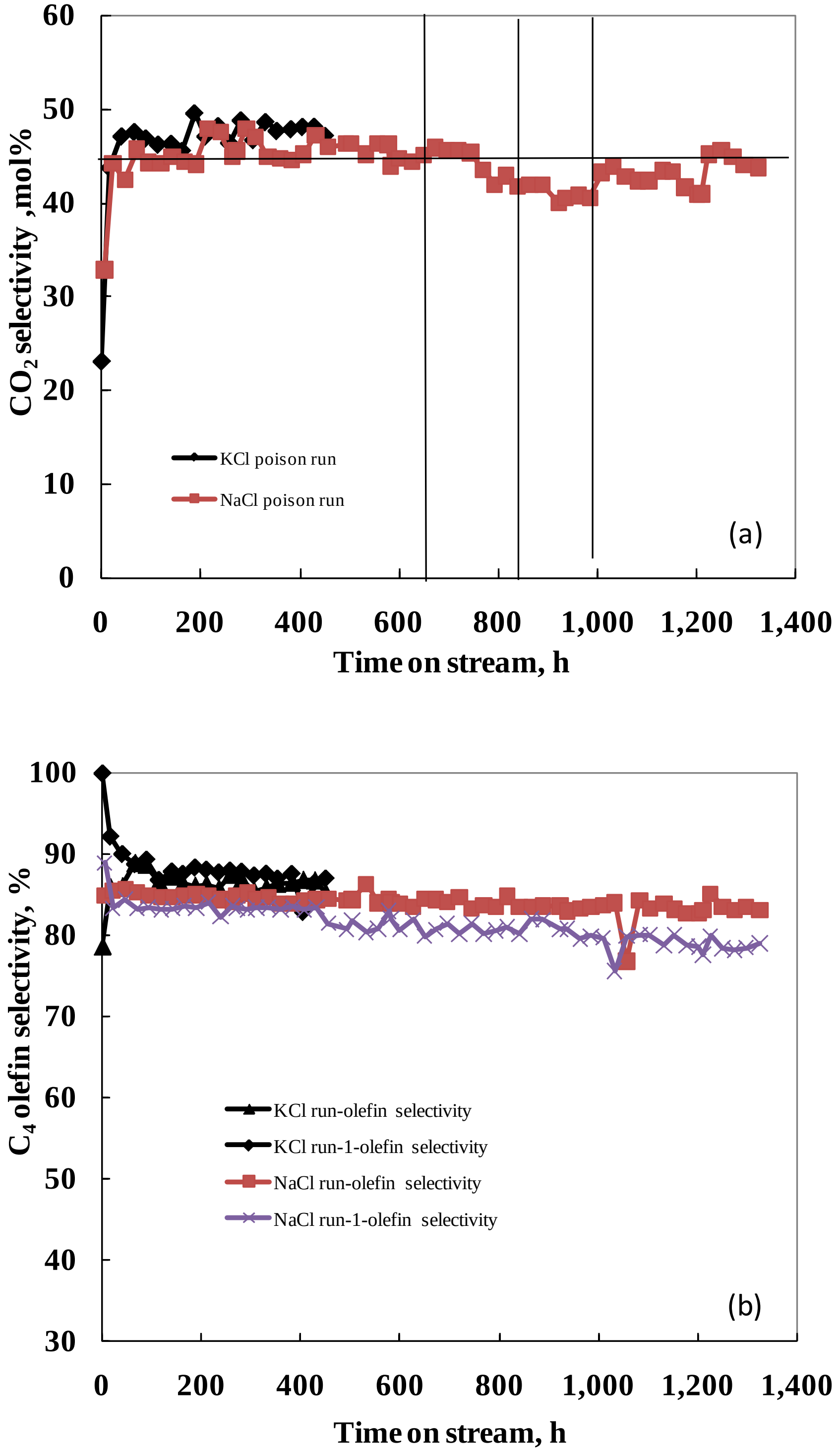


Figure 35: Effect of alkali halides (KCl and NaCl) on (a) CO_2 selectivity, and (b) C_4 olefin selectivity for 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 260 °C, 175 psig ($CO+H_2$), $H_2/CO = 0.67$, SV_{CO+H2}=10 Nl/g-cat/h.

B.2.3.2 HF, HCl, and HBr

The sensitivities of CAER high alpha iron catalyst to halide acids (HF, HCl and HBr) at 260 ^{o}C were evaluated and the results are plotted in Figures 36 and 37. Up to 20 ppm contaminants were tested and the results suggest halide acids do poison Fe catalysts. Two HF concentrations (i.e., 0.1, 20 ppm), four HBr concentrations (i.e., 0.1, 0.6, 5.0 and 20 ppm), and four HCl concentrations (i.e., 0.1, 0.25, 0.75, and 1.5 (at the time of reporting)) were used. In all cases, up to 0.75 ppm concentrations did not significantly alter catalyst activity and selectivity during 120-144 h of testing. For HBr (red line in Fig 36a) and HCl (green line in Fig 36a), 1.5-5.0 ppm led to a drop in activity, but it occurred only in the first 2 days. The Fe catalyst became stable in the next 4-6 days of testing. This suggests that a saturation adsorption state was reached. 20 ppm HF and HBr led to a significant decrease in catalyst activity and selectivity during co-feeding at 410 h and 920 h, respectively. These marked changes in activity and selectivity strongly suggest that the halide acids (HF, HCl and HBr) poisoned catalysts, and are consistent with the corresponding results at 270 ^{o}C. Results of calculations based on 20 ppm HF and 20 ppm HBr data at 260 ^{o}C are shown in Figures 38 and 39. They suggest that the fraction of CO conversion decreased are about 108 to 374 times the amount of HF that entered the reactor, consistent with the values (109-176) obtained using 40 ppm HCl and HBr data at 270 ^{o}C.

The question about whether H^+ ion or halide ions (F^-, Cl^- and Br^-) or both play roles in deactivating Fe catalyst is interesting. Based on the test results, halide ions adsorbed to a lesser extent on Fe catalyst surface since adding 20-30 ppm NaCl and KCl did not result in significant changes in catalyst activity. In this case, the acid ion (i.e., H^+) likely plays a dominate role in deactivating the Fe catalyst. One sign that halide acids played a role in deactivating the Fe catalyst is that the Fe catalyst activity and selectivity became stable when the feed of these solutions was switched off (see HF run (260 ^{o}C) and HCl run (270 ^{o}C)).

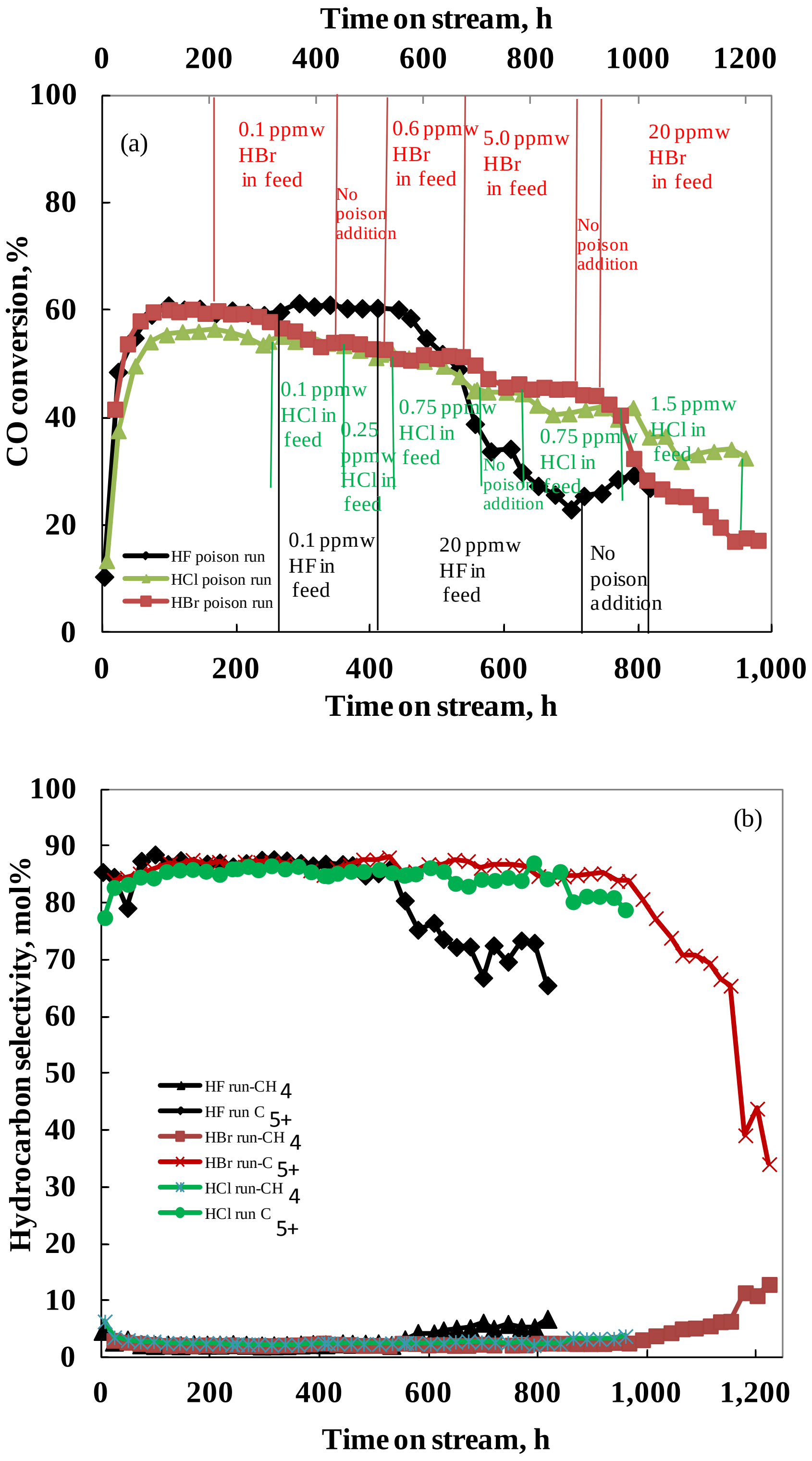


Figure 36: Effect of alkali bicarbonate ($KHCO_3$ and Na HCO_3) on (a) CO conversion, (b) CH_4 and C_{5+} selectivities. Test conditions: 260°C, 175 psig (CO+H_2), H_2/CO = 0.67, SV_{CO+H2}=10 Nl/g-cat/h.

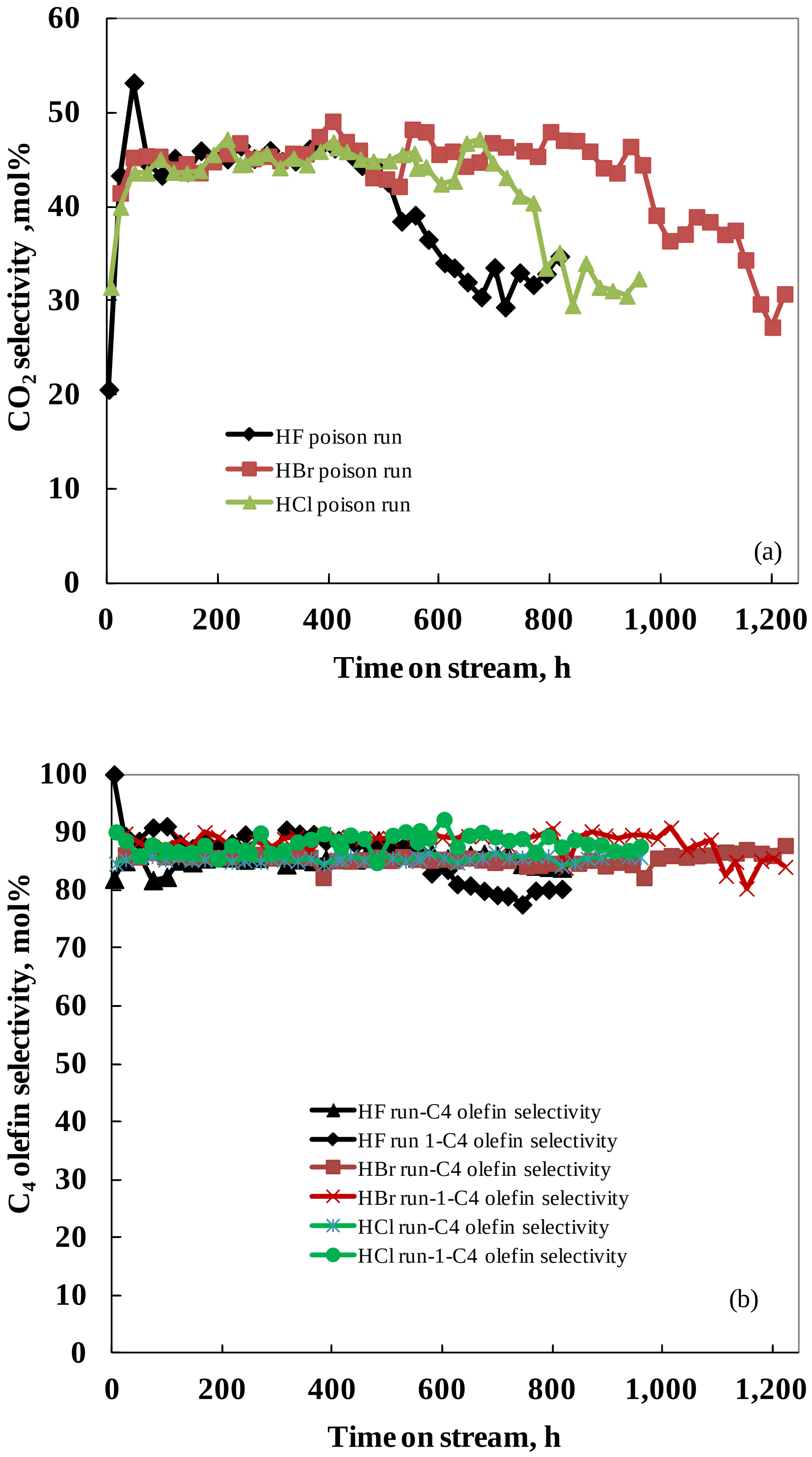


Figure 37: Effect of alkali bicarbonate ($KHCO_3$ and Na HCO_3) on (a) CO_2 selectivity, and (b) C_4 olefin selectivity on 100Fe/5.1Si/3K/2Cu (GJ457). Test conditions: 260°C, 175 psig ($CO+H_2$), $H_2/CO = 0.67$, SV_{CO+H2}=10 Nl/g-cat/h.

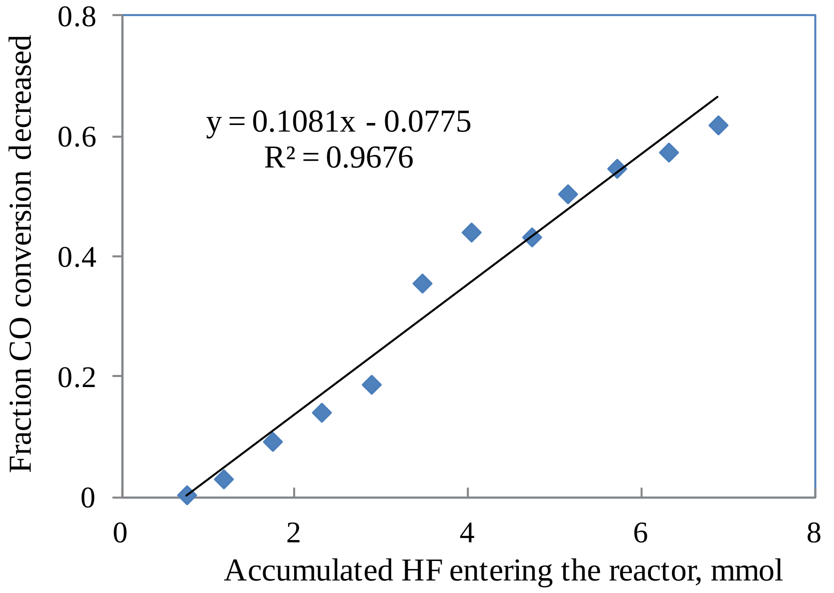


Figure 38: Fraction of CO conversion decreased versus accumulated HF entered reactor. Test conditions: 260°C, 175 psig ($CO+H_2$), $H_2/CO = 0.67$, SV_{CO+H2}=10 Nl/g-cat/h.

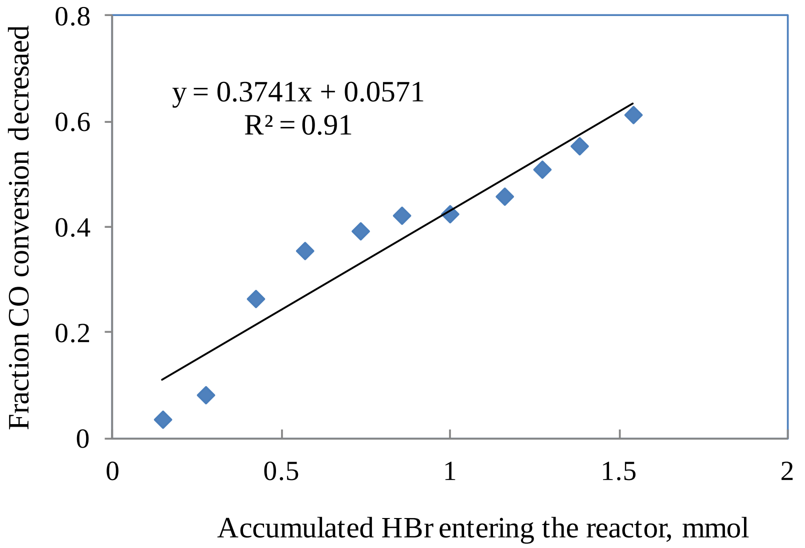


Figure 39: Fraction of CO conversion decreased versus accumulated HBr entered. Test conditions: 260°C, 175 psig ($CO+H_2$), $H_2/CO = 0.67$, SV_{CO+H2}=10 Nl/g-cat/h.

B.2.3.3 NH_3 or H_2S

In this run, up to 200 ppm NH_3 in feed and 0.5 ppm H_2S were examined at 311-1128 h and 1127-1343 h, respectively, at 260 ^oC. Although this run had an interruption in the 2nd day (at ~31 h), it recovered quickly. The ammonia added to the syngas came from concentrated ammonia and an ammonia nitrate solution. Three concentrations of ammonia in the syngas feed (i.e., 100 ppbw, 20 ppmw and 200 ppmw) were employed to examine the sensentivty of the iron catalyst to NH_3 at 260 ^oC. The examination of the impact of each NH_3 concentration on CAER iron catalyst FTS performance lasted for 144 to 168 h. The results indicate that the iron catalyst was quite resistant to NH_3 poisoning at the FTS conditions used (Figure 40). During 1200 h of testing, no changes in the catalyst selectivities to CH_4, C_{5+}, and CO_2 (Figure 40 a,b), the selectivities to C_4 olefin and paraffin (Figure 41), and the selectivities to straight C_4 olefin and internal C_4 olefin (Figure 41) were observed. The catalyst activity displayed a slight increase while adding 100 ppbw of solution in the first four days, which might be partly due to a slight increase in the water gas shift activity of the catalyst. Afterwords, the catalyst displayed a stable CO conversion (~56.3%) regardless of the concentration of NH_3 used.

0.5 ppm H_2S was co-fed at 1128 h, and a constant conversion drop was obtained. However, selectivity remained rather stable (not reported here), which is consistent with the conclusion obtained at 270 ^oC in MAW222 run, and with the results obtained at 260^oC shown in Figures 42b-43 (MAW241 run). The fraction of CO conversion decreased versus accumulated H_2S entering the reactor in this run is given in Figure 44. The slope was determined to be 2634 (Figure 44), close to the value (1873) determined in another run MAW241 (Figure 45).

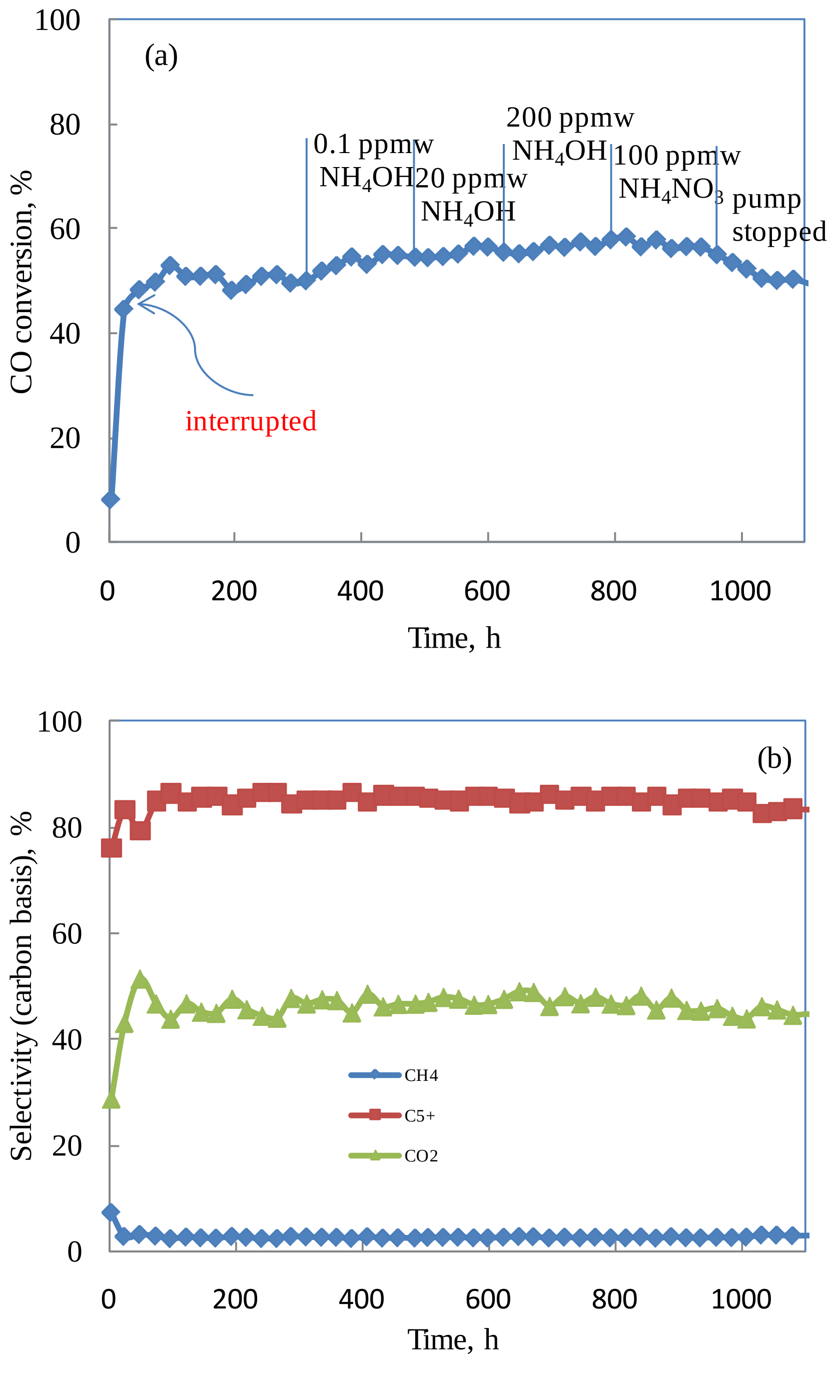


Figure 40: Run ID = MAW233 Effect of NH$_4$OH (0.1-200 ppm in feed) on (a) CO conversion, (b) CH$_4$, C$_{5+}$ selectivities and CO$_2$ selectivity for 100Fe/5.1Si/3K/2Cu (GJ457, 3.0 g). Test conditions: 260 ^{o}C, 175 psig (CO+H$_2$), H$_2$/CO = 0.67, SV$_{CO+H2}$=10 Nl/g-cat/h.

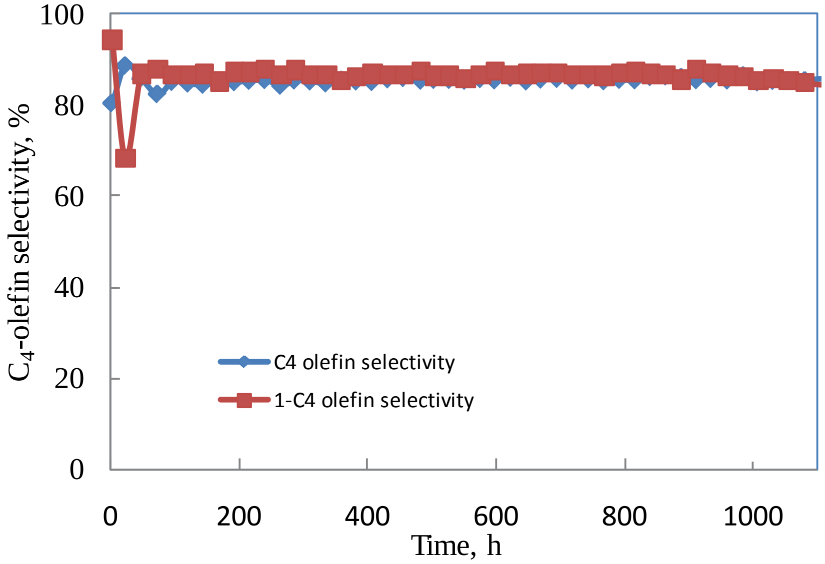


Figure 41: Run ID = MAW233 Effect of NH_4OH (0.1-200 ppm in feed) on (a) C_4 olefin selectivity, 1-C_4 olefin selectivity for 100Fe/5.1Si/3K/2Cu (GJ457, 3.0 g). Test conditions: 260 °C, 175 psig (CO+H_2), H_2/CO = 0.67, SV_{CO+H2}=10 Nl/g-cat/h.

The sensitivity of CAER high alpha iron catalyst to H_2S was tested at 260 °C in two separate runs, MAW 233 (1128-1343 h) and MAW241. In MAW 233, 0.5 ppm H_2S in feed was examined, while in MAW241 RUN, 0.3 ppm and 1 ppm H_2S in feed were examined. Even though the initial time for feeding H_2S containing gas was different between the two runs, they were very consistent. As shown in Figures 44 and 45, accumulated Fe activity lost versus accumulated H_2S entering the reactor gave very straight lines, and Fe/H_2S comes to 1.87 in MAW241 run and 82.63 in MAW233, which are in a good agreement. Also hydrocarbon selectivities and CO_2 selectivity during feeding different amounts of H_2S were essentially the same in the two runs, but only the selectivity data in MAW241 run is reported here (Figure 42).

Figure 42 shows that adding 0.3 ppm (167-311 h) slowly deactivated the catalyst, and 1 ppm H_2S in feed (311-479 h) resulted in faster catalyst deactivation. However, it is interesting that selectivities to CH_4, C_{5+}, C_4 olefin/1-C_4 olefin did not change significantly before and after feeding 0.3-1.0 ppm H_2S into the feed, consistent with the conclusion obtained at 270 ^{o}C.

It seems that high temperature decreases the impact of S since the Fe/H_2S values at 270^{o}C (0.67) was only about 45% of the values at 260^{o}C (1.87-2.63). Further study is needed to confirm this conclusion.

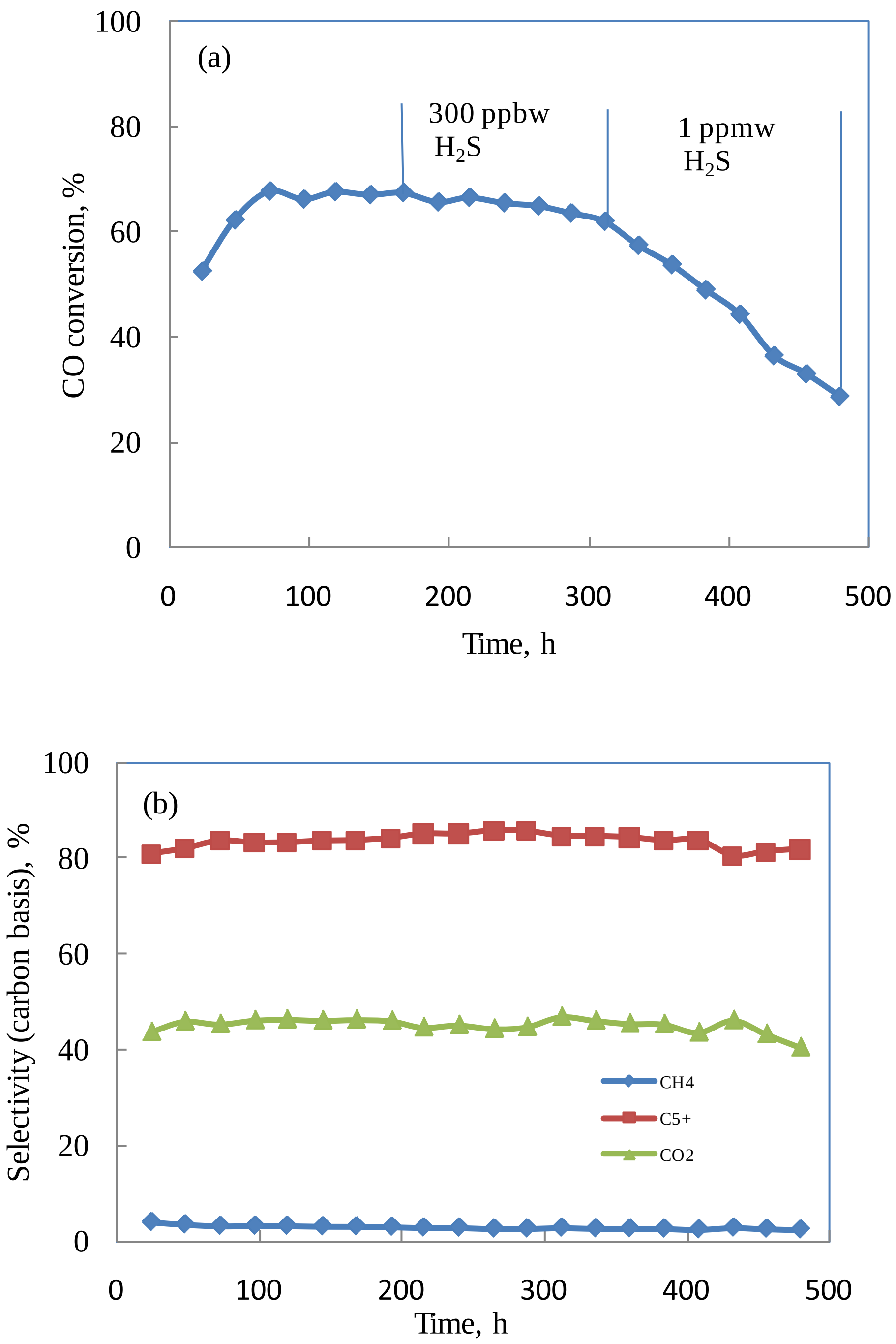


Figure 42: Run ID = MAW241 Effect of H_2S (0.3-1.0 ppm in feed) on (a) CO conversion and (b) CH_4, C_{5+} selectivities and CO_2 selectivity.Test conditions: 260 ^oC, 175 psig ($CO+H_2$), H_2/CO = 0.67, SV_{CO+H2}=10 Nl/g-cat/h.

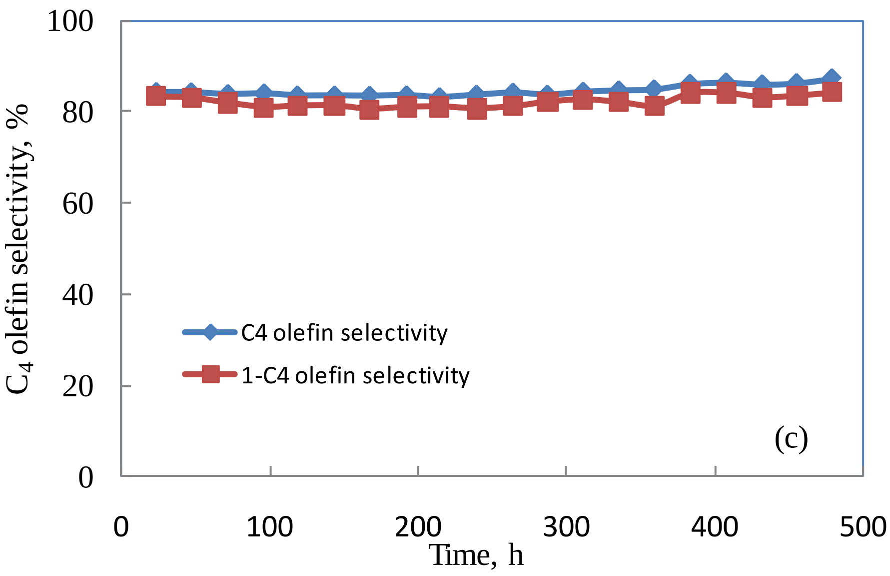


Figure 43: Run ID = MAW241 Effect of H_2S (0.3-1.0 ppm in feed) on C_4 olefin selectivity and 1-C_4 olefin selectivity over 100Fe/5.1Si/3K/2Cu (GJ457, 3.5 g).Test conditions: 260 °C, 175 psig ($CO+H_2$), H_2/CO = 0.67, SV_{CO+H2}=10 Nl/g-cat/h.

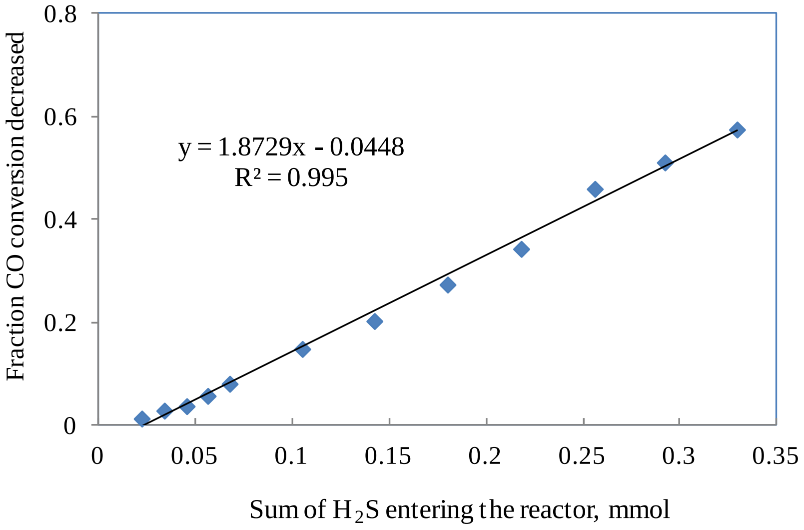


Figure 44: Fraction of CO conversion decreased versus accumulated H_2S entered reactor. Test conditions: 260 °C, 175 psig ($CO+H_2$), H_2/CO = 0.67, SV_{CO+H2}=10 Nl/g-cat/h.

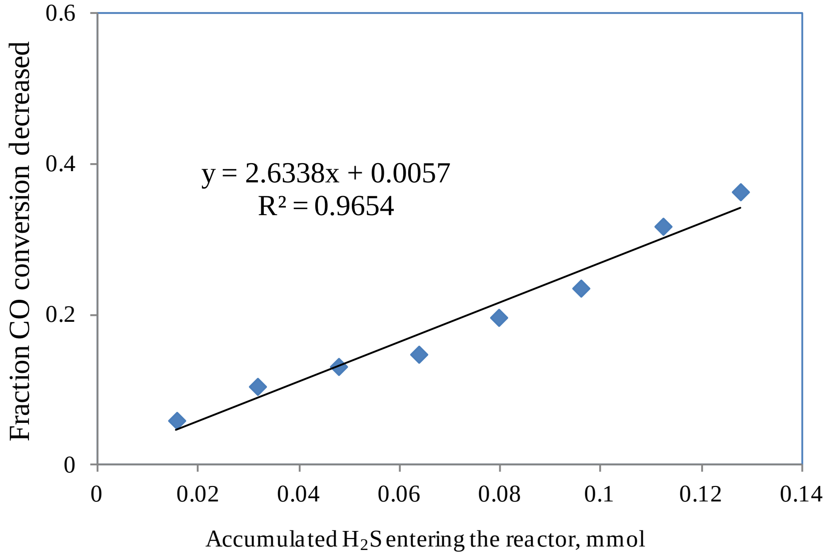


Figure 45: Fraction of CO conversion decreased versus accumulated H_2S entered reactor determined in run Maw233. Test conditions: 260 ^{o}C, 175 psig ($CO+H_2$), $H_2/CO = 0.67$, SV_{CO+H2}=10 Nl/g-cat/h.

In summary, very consistent results of the sensitivity of CAER high alpha iron catalyst at 260 and 270 ^{o}C to various poisons which are usually present in bio-mass/coal-derived syngas were obtained in this study. The Fe catalyst is not sensitive to alkali halide, alkali bicarbonates, or ammonia. Even up to 40-200 ppm of these contaminants in the feed did not significantly change Fe catalyst activity and selectivity, with each concentration being tested for 72-144 h. The Fe catalyst was found to be sensitive to halide acids and much more sensitive to sulfur (e.g., H_2S). The impact of small amounts of halide acids (e.g., < 400 ppbw in the feed) was unnoticeable, but higher concentrations of halide acids (e.g. > 20 ppm) can lead to faster catalyst deactivation. In our test, 0.3 ppm of H_2S in the feed was observed to slowly deactivate the catalyst. Sulfur is more effective at poisoning the Fe catalyst at low temperature than at high temperature.

H^+ plays a dominant role in poisoning the Fe catalyst relative to Br, Cl, and F. NH_3 had a weak and negative impact on Fe catalyst. Only when the NH_3 concentration in the feed was sufficiently high (>200 ppm) could it change Fe catalyst activity and HC selectivity. S resulted in significant catalyst deactivation but catalyst selectivity remained relatively unchanged. Alkali compounds (e.g., salts and bicarbonates) adsorbed to a lesser extent, and according to the data obtained thus far, less than 40 ppm of alkali compounds in the feed did not alter Fe catalyst behavior.

B.2.4 0.5%Pt-25%Co/Al_2O_3 Catalyst Testing

B.2.4.1 KCl and NaCl

Run AWP031 (reactor #R21, 24 Nov 2009 – 05 Mar 2010) was carried out to study the poisoning effect of KCl. 2 ml/ hr of seven different aqueous solutions of KCl with increasing concentrations were added to the reactor to produce KCl concentrations in the total feed (H_2 + CO + H_2O) ranging from 100 ppb (wt) to 500 ppm (wt).

Starting with a relatively high feed rate of 10 slph/g, the initial conversion was acceptable at 45+%. Somewhat atypically, the conversion stabilized sooner than expected at ~31% after only four days. During the next five days a baseline was established and the first poisoning test started at 216 hours (Figure 46). The conversion fell by about three percent during the first day of the test (possibly due to the start of the water injection) and then remained constant over the course of the remaining five days of this first test, indicating no poisoning.

The feed rate was halved to 5 slph/g and the conversion was monitored to produce a new baseline (Figure 47). After almost 200 hours at this new feed rate, and with the conversion still slowly declining, a second test was started. The KCl concentration for this second test was nearly doubled to 190 ppb (wt), and after five days there was almost no loss of conversion.

A new KCl solution was prepared, raising the concentration in the total feed to 600 ppb (wt) for the third test (Figure 48). After a week of erratic performance, the conversion stabilized and then showed a slow smooth decline for another week. A straight line fit for the data from both tests at this SV shows a combined average loss of CO conversion of 0.193% per day.

The GC retention time for propylene slowly shifted during this third test, causing the peak to be mis-identified. The resulting incorrect high values for the propylene content skewed the C_2-C_4 and C_5+ values in the hydrocarbon product distribution plot. In attempting to correct this, the propylene peak was then missed altogether in subsequent GC shots, falsely depressing the reported C_2-C_4 content and increasing the reported C_5+ percentages. This was corrected early in the 4th test.

After the third test the feed rate was reduced to 3.49 slph/g. A baseline and three consecutive poisoning tests were performed, with the KCl concentration of the total feed increasing from 2 ppm (wt) for test #4, to 20 ppm (wt) for test #5 and to 100 ppm (wt) for test #6. A straight line fit for all of the data from the baseline and the three tests shows an average loss of conversion of 0.425% per day, with no discernible decreases attributable to the changing KCl concentration (Figure 49).

The apparent step change in the C_2-C_4 and C_5+ selectivity midway through the fourth test as shown in Figure 49 is due to the belated correction of error in the GC's propylene peak identification. After the sixth test, the reactor's feed rate was again reduced, dropping it to 2.50 slph/g. Six days of operation established a new baseline performance, with an average loss of CO conversion of 0.473% per day.

For the seventh and final test period of this run, a 2 ml/hr feed of an aqueous KCl solution was again started, with the concentration adjusted to provide 500 ppm (wt) in the total feed. This is equivalent to a volume or molar concentration of 77 ppm of the total feed (H_2 + CO + H_2O).

Conversion fell by 3.5% the first day, and then continued to decline at a slower rate (Figure 50). A straight line fit for the data from the next nine days indicates that this rate was 0.714%. Subtracting the two gives a loss rate of 0.241% per day that may be attributable to the KCl present in the feed. Hydrocarbon product distribution was not affected (Figure 51).

Calculations

Starting with a total charge of 8.6 grams of reduced catalyst in the reactor, and with the chemisorption data indicating 228.2 x 10^{-6} moles of active cobalt per gram of reduced catalyst, the starting inventory of active cobalt in the reactor during the first moments of operation at FT synthesis conditions would have been 1.9625 x 10^{-3} moles.

A straight line passing through the conversions obtained from the first two gas samples (taken at 6 and 25 hours on stream) indicate that at the beginning of the run the CO>HC rate was 0.60328 mol/hr, or 307.403 moles/hr per mole of active cobalt (note: this was ignored in the first six tests, which did not show discernible poisoning).

Using the straight line linear regression fit for the six samples taken during the baseline period of 1772-1892 hours, the CO > HC rate was 143.524 x 10^{-3} mol/hr at 1892 hours. Dividing by 307.403 indicates that there were 0.46689 x 10^{-3} moles of active cobalt remaining at the start of test #7, or only about a quarter of the original amount of active cobalt at the start of the run.

Extrapolating this baseline rate out to the end of the seventh poisoning test at 2158.5 hours, the expected CO > HC rate would have been 136.942 x 10^{-3} mol/hr if the KCl had not been added to the feed, or 0.44548 x 10^{-3} moles of active cobalt.

But by the end of the test, the straight line fit for the test period indicates that the CO > HC rate had fallen to 108.591 x 10^{-3} moles/hr, so that there was now only 0.35325 x 10^{-3} moles of active cobalt remaining.

So the loss in the total amount of active cobalt that can be attributed to the poisoning effect of the KCl was (0.44548 x 10^{-3}) – (0.35325 x 10^{-3}), or 92.23 x 10^{-6} moles.

The KCl feed rate during this last test was 82.1 x 10^{-6} moles/hr, with the feed starting at 1901.5 hours and ending shortly after the sample 093 at 2158.5 hours. So the total amount of KCl added during the test was (82.1 x 10^{-6} moles/hr) x (257 hours), or 21.100 x 10^{-3} moles.

(92.23 x 10^{-6} moles cobalt poisoned) / (21.100 x 10^{-3} moles KCl added) =

4.37 x 10^{-3} moles cobalt poisoned per mole KCl added (at a KCl concentration of 500 ppm (wt), or 77 ppm (vol) of the total feed, including the water of the KCl solution.

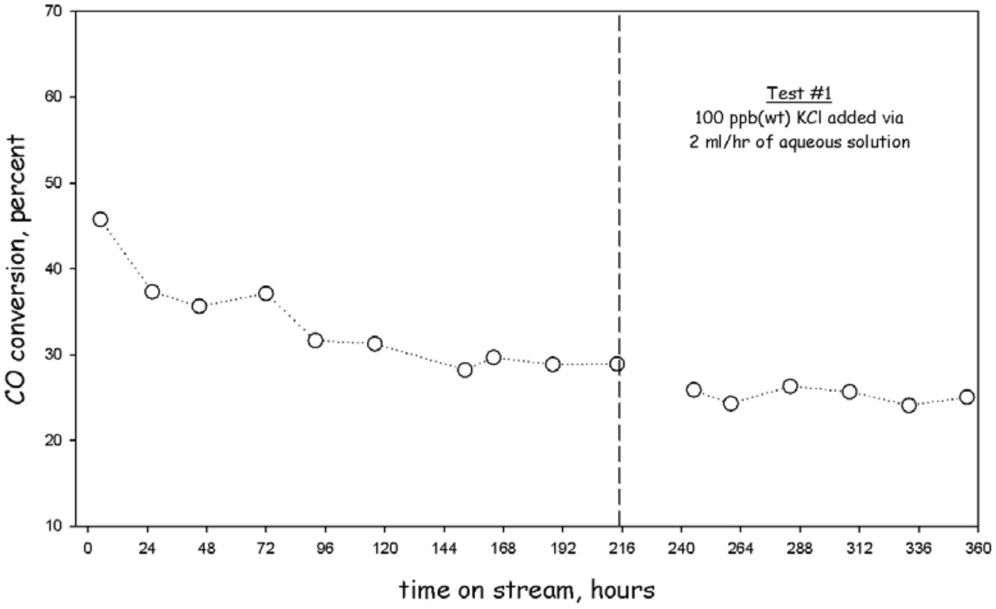


Figure 46. Reactor #21, Run #AWP031. CO conversion versus time on-stream. Startup and 1st KCl test using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 10.0 slph/g, $H_2/CO = 2.0$, T = 220°C, and P = 280 psig.

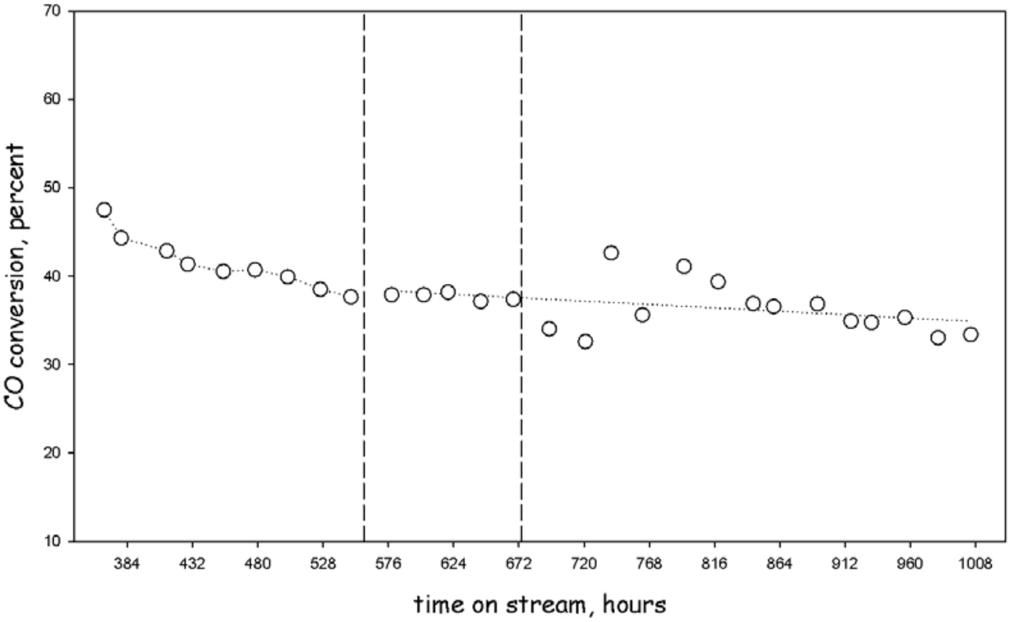


Figure 47 Reactor #21, Run #AWP031. CO conversion versus time on-stream. 2nd and 3rd KCl tests using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 5.0 slph/g, $H_2/CO = 2.0$, T = 220°C, and P = 280 psig.

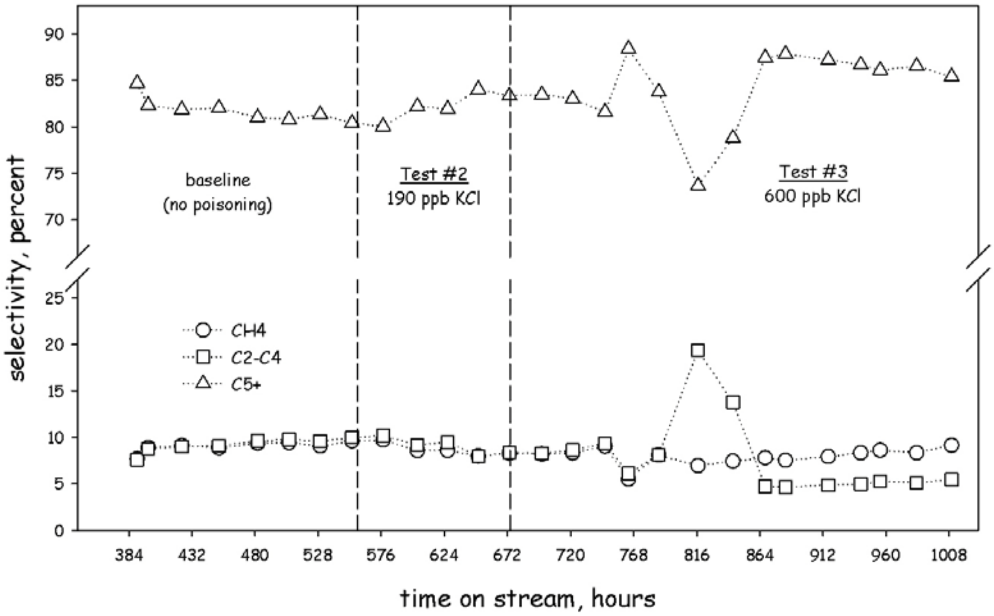


Figure 48: Reactor #21, Run #AWP031. Selectivity versus time on-stream. 2nd and 3rd KCl tests using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 5.0 slph/g, $H_2/CO = 2.0$, T = 220°C, and P = 280 psig.

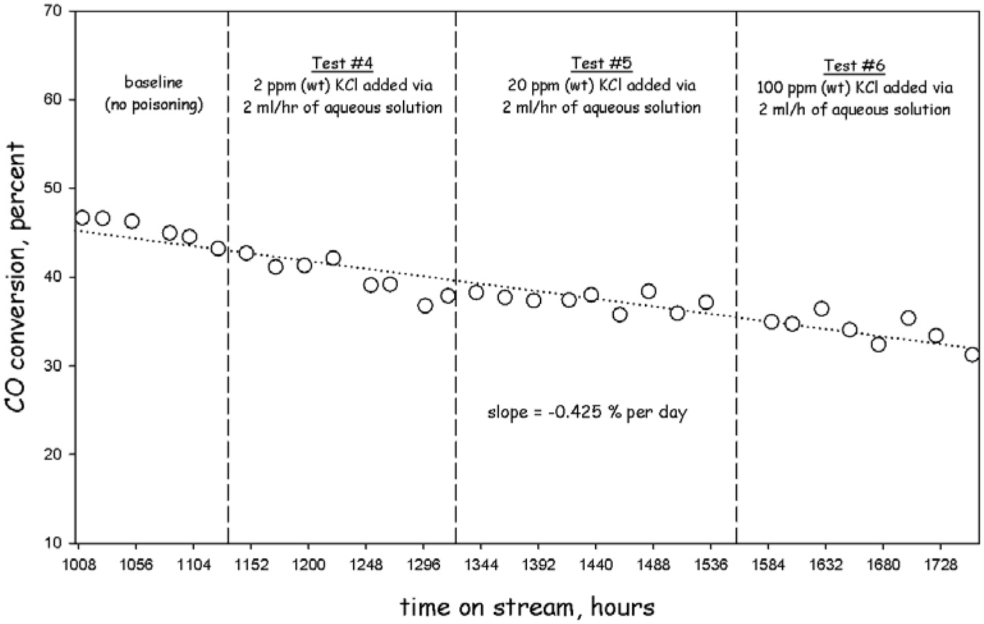


Figure 49: Reactor #21, Run #AWP031. CO conversion versus time on-stream. 4th through 6th KCl tests using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 3.49 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

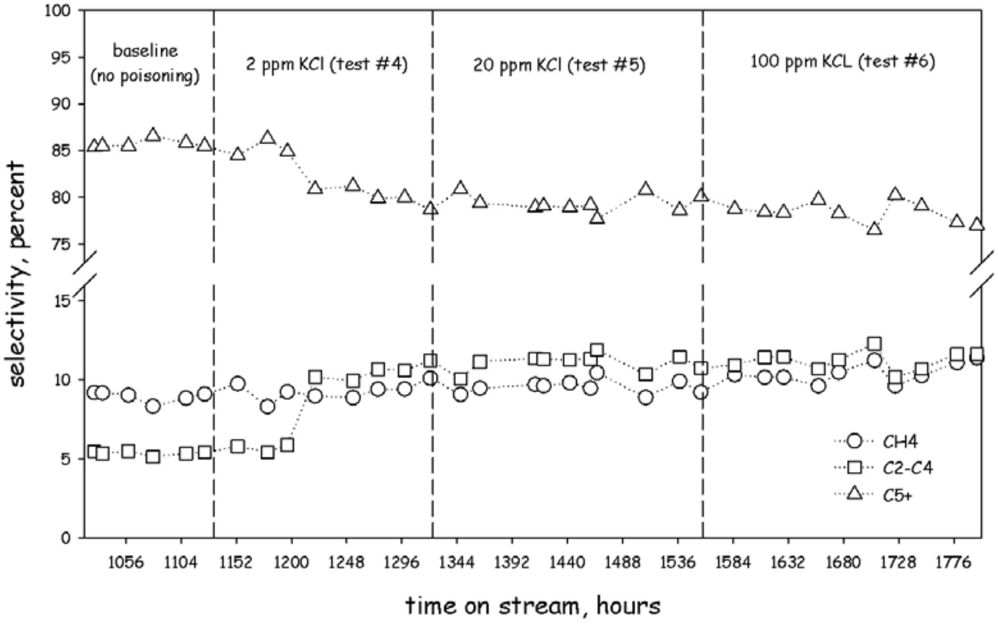


Figure 49: Reactor #21, Run #AWP031. Selectivity versus time on-stream. 4th through 6th KCl tests using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 3.49 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

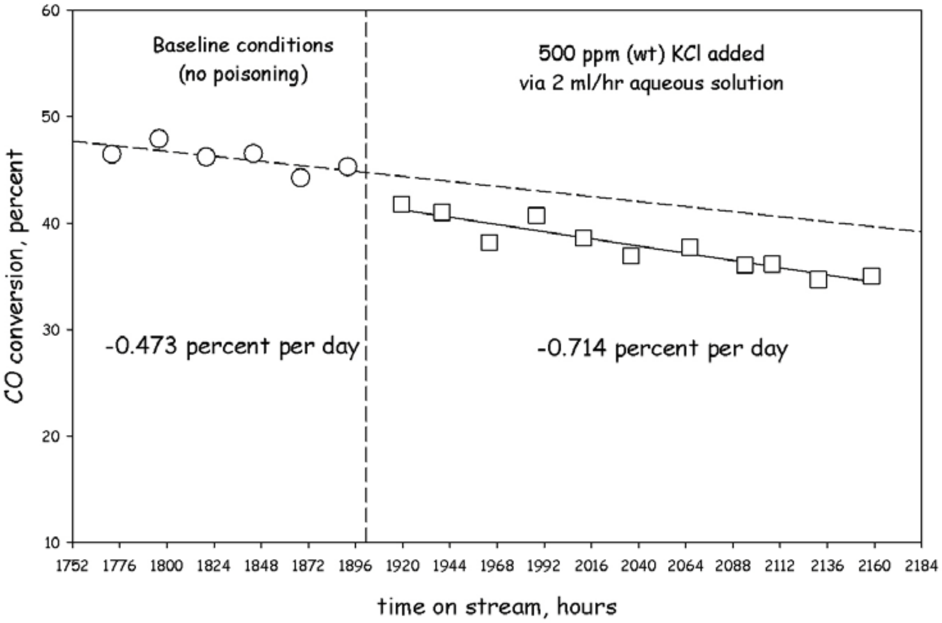


Figure 50: Reactor #21, Run #AWP031. Conversion versus time on-stream. 7th KCl tests using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2.50 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

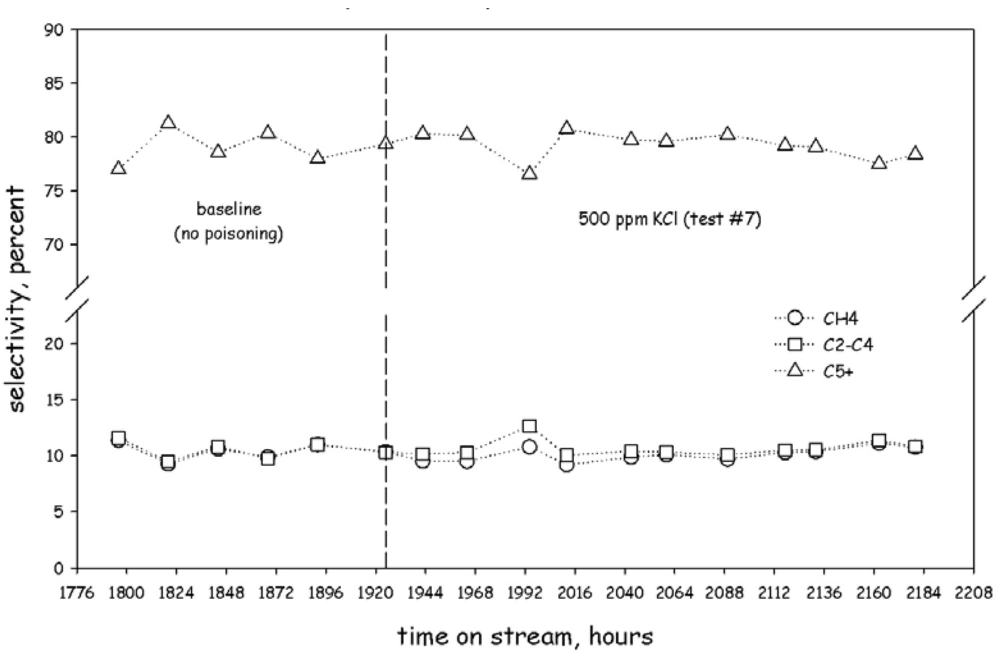


Figure 51: Reactor #21, Run #AWP031. Selectivity versus time on-stream. 7th KCl tests using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2.50 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

Run number AWP036 was conducted in Reactor #23 from 07 Jan-11 to Mar-11. This run tested three concentrations of NaCl (100 ppb, 1 ppm, 50 ppm), which was supplied via 2 ml/hr of aqueous solutions of different NaCl concentrations.

Following transition to F-T conditions (220°C, 280 psig), the initial feed rate of 10.0 slph/g (H_2/CO = 2) was maintained for four days while the CO conversion fell from 54 to 36% (Figure 52). The SV was then reduced to 7.5, which brought the conversion back up to 50%, but with little actual increase in the amount of hydrocarbon products being produced (10.736 slph vs. 11.142 slph).

Conversion slowly decreased to ~45% over the next week. A straight line fit for the last five days of that period indicate an average loss of 0.534% per day, and this was used as the baseline for the first test (Figure 52).

The first test period started at 293 hours, when the syringe pump was started, delivering 2.0 ml/hr of a solution containing 1.686 x 10^{-6} g/ml of NaCl. This was sufficient to produce a concentration of 100 ppb (wt) NaCl in the total feed (H_2 + CO + H_2O). Note that 100 ppb (wt) = 19 ppb (mol) (Figure 52).

This first test was continued for nine days (293-509 hours), with the conversion showing no clear evidence of poisoning, as the conversion and selectivities (Figure 53) roughly matched the values predicted by the baseline projection. After a total of about 400 hours on stream, the conversion curve began to flatten out.

The syringe pump was flushed and refilled with a stronger NaCl solution (1.686 x 10^{-5} g/ml) to increase the concentration in the total feed to 1 ppm (wt) [148 ppb (vol)] in the total (H_2 + CO + H_2O) feed while using the same 2.0 ml/hr liquid feed rate. This second test also ran for nine days (509-725 hours), and also failed to show any evidence of poisoning. A straight line linear regression fit for the data for the last five days of the first test plus the 1 ppm test (a total of 405-723 hours) indicated an average loss of CO conversion of 0.072 % per day (Figure 54).

After 725 hours, the syringe pump was again stopped, flushed and refilled with a stronger solution, and once again restarted at 2.0 ml/hr. The NaCl concentration of the aqueous solution was increased to provide 50 ppm (wt) in the total feed. For five days (725-837 hours), the loss of CO conversion continued to match that of the second test. A straight line fit for the conversions of test # 2 plus the first five days of test #3 indicate an average loss of 0.176% per day (Figure 55). Hydrocarbon selectivities did not display a significant change (Figure 56).

But sometime during the evening after taking sample #36 (at 837 hours) there was a suspected mechanical or procedural problem, as the conversion plummeted from 41% to 13% by the next sample.

The only physical clue was that the amount of rewax collected for sample 36 was 65.82 grams, which was larger than expected ~10 grams. At this point, liquid product samples were being collected every 2-3 days, and for samples #25-33 (555-770 hrs), the average rewax catch was 3.9 g/day. The rewax collected during sample 36 was from the previous three days and the rewax catch rate increased to 21.3 g/day.

The run was continued for four more days at these same feed rates, but the conversion did not recover.

Calculations

8.9 grams of reduced GJ456 catalyst was injected into the reactor. Chemisorption indicates that it contains 228.2×10^{-6} moles of active cobalt per gram of catalyst, for a total starting reactor inventory of 2.031×10^{-3} moles of active cobalt.

The first sample (taken after 4 hours on stream) showed a conversion of 16.094 slph of CO>HC, or 0.71804 mol/hr. Dividing by the amount of active cobalt, the initial conversion is 353.54 mol/hr of CO>HC per mole cobalt.

By the end of the first baseline period at 285 hours, the conversion was still 10.221 slph of CO>HC, or 0.45601 mol/hr. With the assumption that the initial conversion figure of 353.54 mol/hr per mole of cobalt is a constant, this means that 1.2898×10^{-3} moles of active cobalt remain at this point. This is more than 63% of the starting amount, higher than the 40-50% that's usually noted.

Using this same assumption, the amount of active catalyst after 285 hours (prior to the first test) was 1.2898×10^{-3} moles, and at 837 hours (the end of the third test) it was 1.1428×10^{-3} moles. So the total amount of active cobalt that had been poisoned during all three tests was 0.147×10^{-3} moles, a figure that includes both the normal rate of decay and any poisoning effect.

Assuming that all of this loss was due to the poisoning effect of NaCl can at least provide a worst case figure.

The total amount of NaCl added during the first test was:

(1.686 x 10^{-6} g NaCl / ml) x (2 ml/hr) x (216 hours) = 0.7284 x 10^{-3} grams

For the second test, this total rose to:

(1.686 x 10^{-5} g NaCl / ml) x (2 ml/hr) x (216 hours) = 7.284 x 10^{-3} grams

And finally, for the third test, the total amount of NaCL added rose to:

(8.430 x 10^{-5} g NaCl / ml) x (2 ml/hr) x (112 hours) = 18.883 x 10^{-3} grams

for combined total of 26.895 x 10^{-3} grams of NaCl, or 0.4602 x 10^{-3} moles

(0.147 x 10^{-3} moles of cobalt poisoned) / (0.4602 x 10^{-3} moles NaCl fed) =

0.3194 moles of cobalt poisoned per mole of NaCl (worst case scenario)

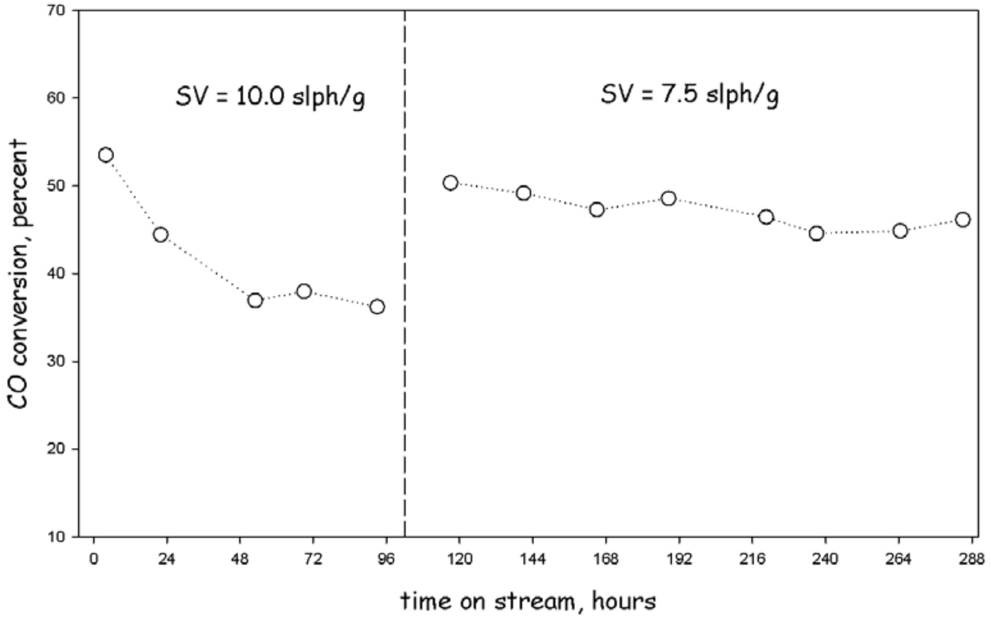


Figure 52: Reactor #23, Run #AWP036. CO conversion versus time on-stream. Startup using 8.9 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 10.0 and 7.5 slph/g, $H_2/CO = 2.0$, T = 220°C, and P = 280 psig.

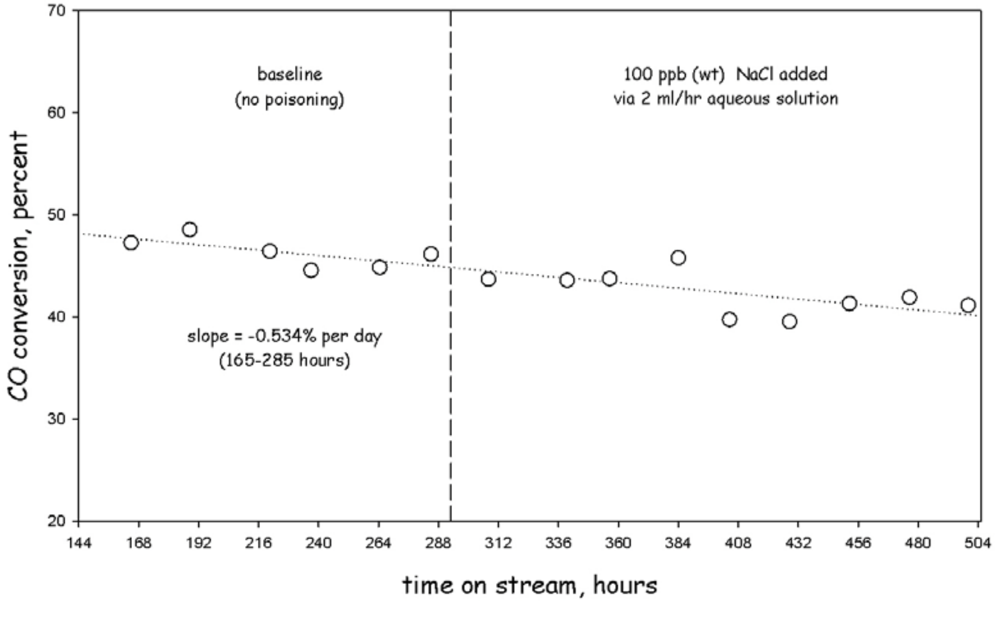


Figure 52: Reactor #23, Run #AWP036. CO conversion versus time on-stream. NaCl test #1 using 8.9 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 7.52 slph/g, $H_2/CO = 2.0$, T = 220°C, and P = 280 psig.

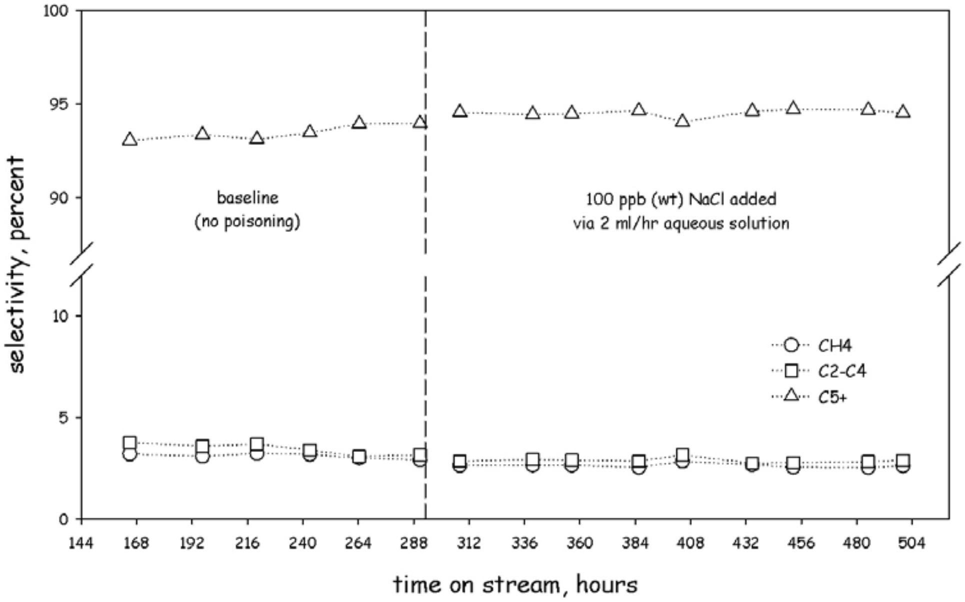


Figure 53: Reactor #23, Run #AWP036. Selectivity versus time on-stream. NaCl test #1 using 8.9 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 7.52 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

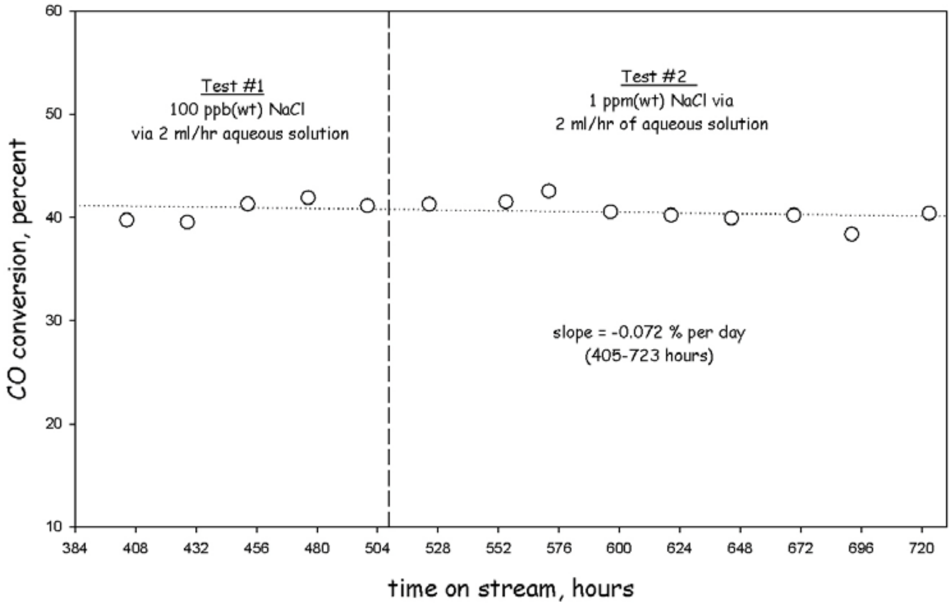


Figure 54: Reactor #23, Run #AWP036. CO conversion versus time on-stream. NaCl test #2 using 8.9 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 7.52 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

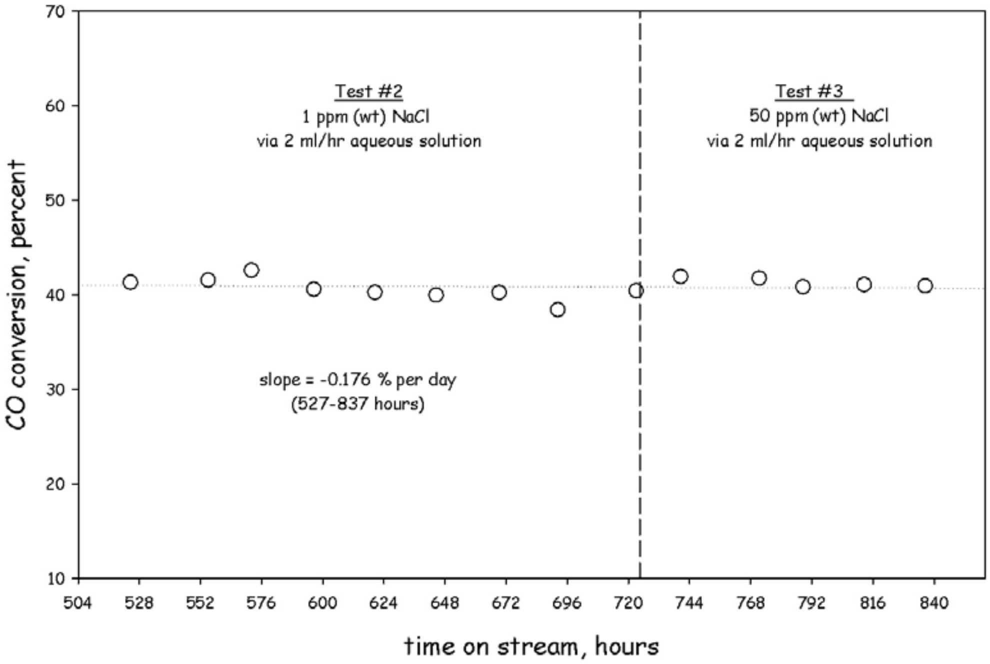


Figure 55: Reactor #23, Run #AWP036. CO conversion versus time on-stream. NaCl tests #2 and 3 using 8.9 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 7.52 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

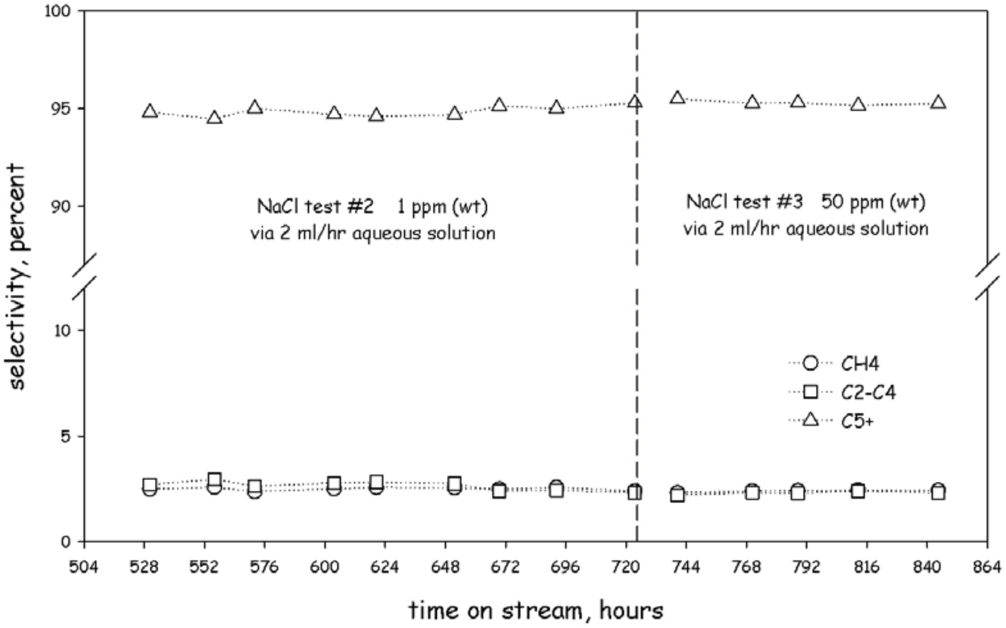


Figure 56: Reactor #23, Run #AWP036. Selectivity versus time on-stream. NaCl tests #2 and 3 using 8.9 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 7.52 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

B.2.4.2 $KHCO_3$ and $NaHCO_3$

Run #AWP042 was tested in Reactor #21 from 06 May to 13 Jul 2010. This run tested five levels of $KHCO_3$ in the total feed, ranging from 100 ppb (wt) to 1000 ppm (wt). These tests were followed by two tests using $NaHCO_3$, at 100 ppb and 1.0 ppm. Due to the low conversion seen following the startup and initial operation, all of the tests were performed at a SV of only 1.5 slph/g, and all were performed by injecting 1.0 ml/hr of aqueous solutions.

Starting with a SV of 8.0 slph/g, the conversion fell from 37% to 15% during the first two days of operation. Decreasing the SV to 3.0 boosted the conversion to only about 22%, so the SV was further cut to 1.5 slph/g after four days (Figure 57). For four more days (96-188 hours) the conversion remained at about 35%, but then slowly began climbing before leveling off at about 48% (332-452 hours) (Figure 57). Although the data showed some scatter owing in part to the difficulty of accurately measuring the relatively small amount of product gas exiting the reactor, this was deemed satisfactory for a baseline conversion.

Starting at 459 hours, a syringe pump was used to deliver 1.0 ml/hr of a dilute $KHCO_3$ solution, with the concentration adjusted to provide 100 ppb (wt) $KHCO_3$ in the total feed (H_2 + CO + H_2O). The seven samples collected before the end of this test at 600 hours, while again showing some scatter, showed no evidence of a poisoning effect at this concentration (Figures 58 and 59).

The syringe pump was stopped, flushed and refilled with a second $KHCO_3$ solution, with the concentration increased tenfold to provide 1.0 ppm in the total reactor feed. This second test ran five days (600-723 hours) and also failed to indicate any catalyst poisoning. A linear regression straight line fit for the data from 500-720 hours (encompassing most of the first test and all of the second) shows a loss rate of only 0.001 % per day (Figures 58 and 59).

Three more $KHCO_3$ tests were made, with the concentration in the total feed rising to 10, 100 and finally 1000 ppm (wt), and all showed no catalyst poisoning (Figure 60). In fact, the straight line fit for the data from all three tests combined shows that the CO conversion actually increased by an average of 0.154 % per day. Also, the selectivity for methane decreased modestly during these three tests, falling from about 17 down to 13% (Figure 61).

Following the last $KHCO_3$ test, the syringe pump was again flushed and refilled, this time with a dilute $NaHCO_3$ solution. Injecting the solution at 1.0 ml/hr provided a concentration of 138 ppb (wt) for the one week test (988-1155 hrs) (Figures 62 and 63).
The test was repeated with a $NaHCO_3$ solution with a concentration 1000x stronger, to produce 138 ppm $NaHCO_3$ in the total feed (H_2 + CO + H_2O). This was followed by another week with no liquid feed to serve as an end-of-run baseline (Figures 62 and 63).

A straight line fit using the data from the last $KHCO_3$ test, both $NaHCO_3$ tests and the final week of baseline shows an average loss of conversion for this entire time period (1007-1632 hrs) of 0.194 % per day, with no discernible poisoning effect during any of the tests.

Calculations

This run used 7.8 g of catalyst, so based on the chemisorption figure of 228.2×10^{-6} moles of active cobalt per gram of catalyst, the starting amount of active cobalt was 1.780×10^{-3} moles.

Using a straight line through the conversions obtained from the first two data points (at 8.5 and 20.5 hours) to estimate the conversion at time zero yields 7.763 slph CO>HC, or 0.34634 mol/hr. Dividing by the amount of active cobalt present at time zero gives a rate of 194.57 mol/hr of CO>HC per mole of active cobalt.

Since these two data points did not show the typical large decrease in conversion, I've also estimated the initial conversion rate using a straight line through the first and third data points (8.5 and 47.25 hours). This produces a 12% higher initial conversion of 8.711 slph CO>HC, equivalent to 218.343 mol/hr CO>HC per gram of active cobalt.

Even this larger estimate is low compared to the initial conversions for other three successful runs that used this same starting SV of 8 slph/g. These other three ranged from 243-293, with an average value of 267 mol/hr CO>HC per gram of active cobalt.

After four days on stream, only about 1.4 slph of the 3.9 slph of CO being fed to the reactor was being converted to hydrocarbons, and about 17% of this was methane. In retrospect, this run should probably have been aborted, but as it was following on the heels of a string of unsuccessful runs, the decision was made to press on with a poisoning test. Fortunately, after about 200 hours on stream the conversion had increased to about 50%, or about 1.8 slph of CO>HC, with the methane selectivity falling to 13-14%. The last 120 hours (332-452 hrs) of this extended startup period was selected as the baseline for the first test.

Due at least in part to the difficulties of accurately measuring the low product gas rate, there is no clear trend to allow calculation of an average daily loss of conversion rate, but the average conversion during this baseline period was 1.823 slph CO>HC, or 0.08134 mol/hr. Using the assumption that the initial conversion rate per mole of cobalt is a constant, this means that 0.378 x 10^{-3} moles of active cobalt remained, or only about 21% of the original amount.

This is using the higher estimate of 218.343 mol/hr CO>HC per gram of active cobalt. Substituting the lower estimate of 194.57 instead yields 0.418 x 10-3 moles of active cobalt remaining, or about 23% of the original value. Both are rather less than half of the typical value.

With no further loss of activity in five successive $KHCO_3$ tests and two $NaHCO_3$ tests, it's impossible to calculate any poisoning effect. But since there wasn't even any normal decay (i.e., without poisoning, normal catalyst aging) either, perhaps the catalyst was already at or near the point where it was difficult to poison any further. In other runs, this point seems to be at perhaps 0.5-0.8 slph CO>HC a similarly low SV, but the selectivity for methane on these runs usually ran to 20% or more, while this run still showed CH_4 selectivities of 10-12%.

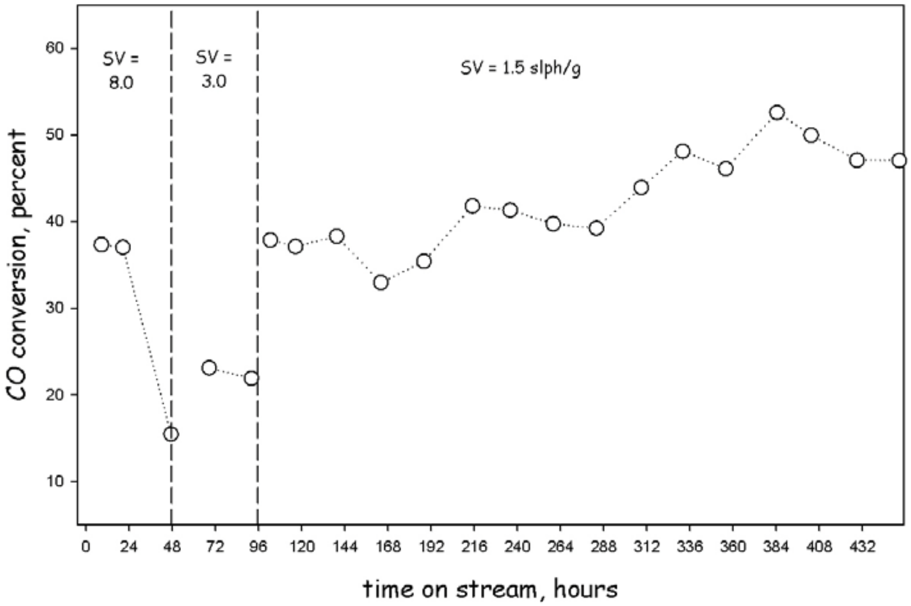


Figure 57: Reactor #21, Run #AWP042. CO conversion versus time on-stream. Startup using 7.8 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 8.0, 3 and 1.5 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

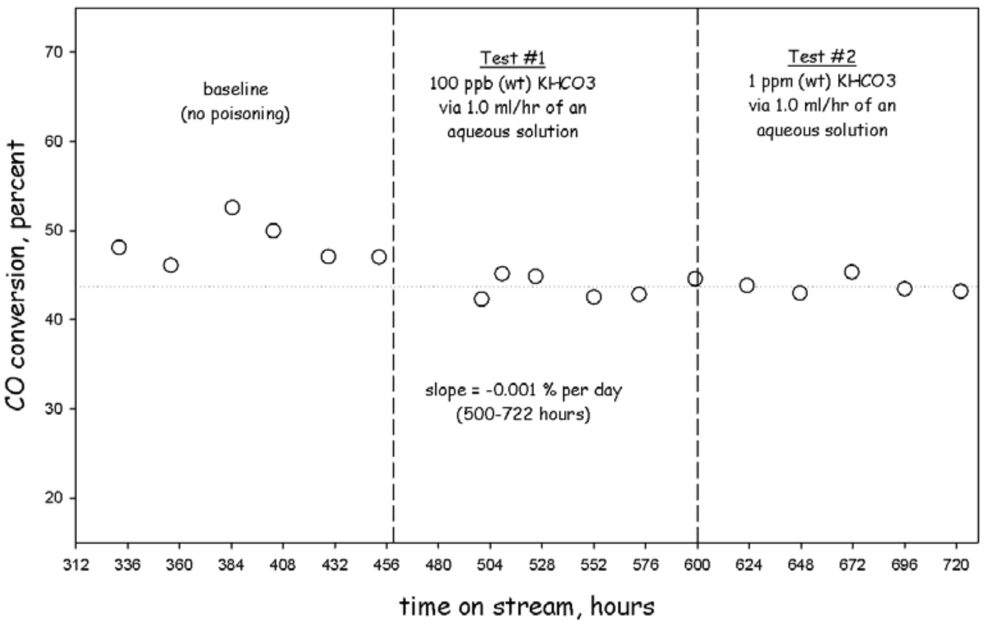


Figure 58: Reactor #21, Run #AWP042. CO conversion versus time on-stream. $KHCO_3$ tests #1 and 2 using 7.8 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.5 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

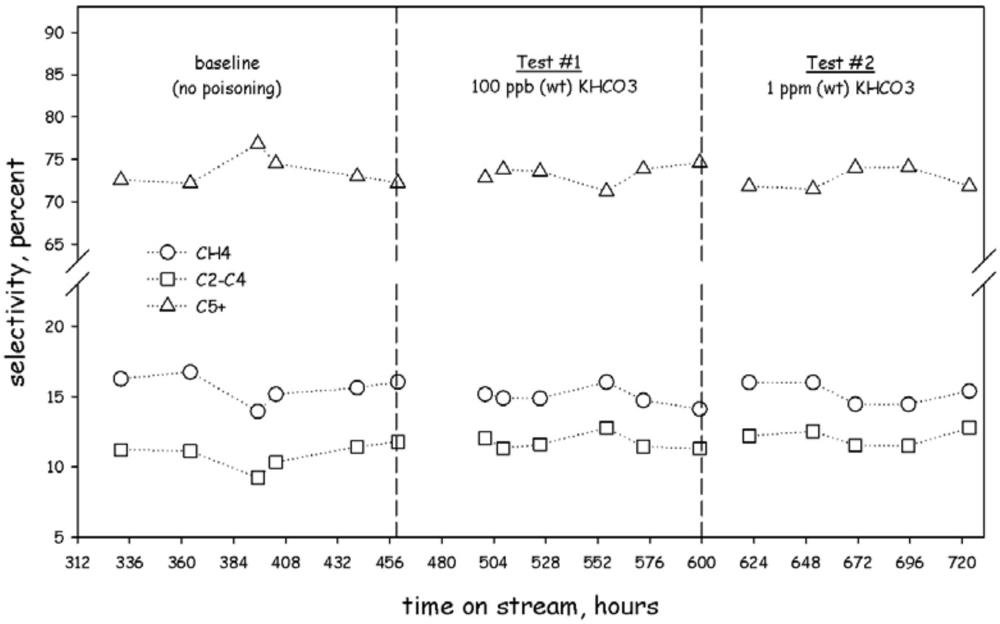


Figure 59: Reactor #21, Run #AWP042. Selectivity versus time on-stream. $KHCO_3$ tests #1 and 2 using 7.8 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.5 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

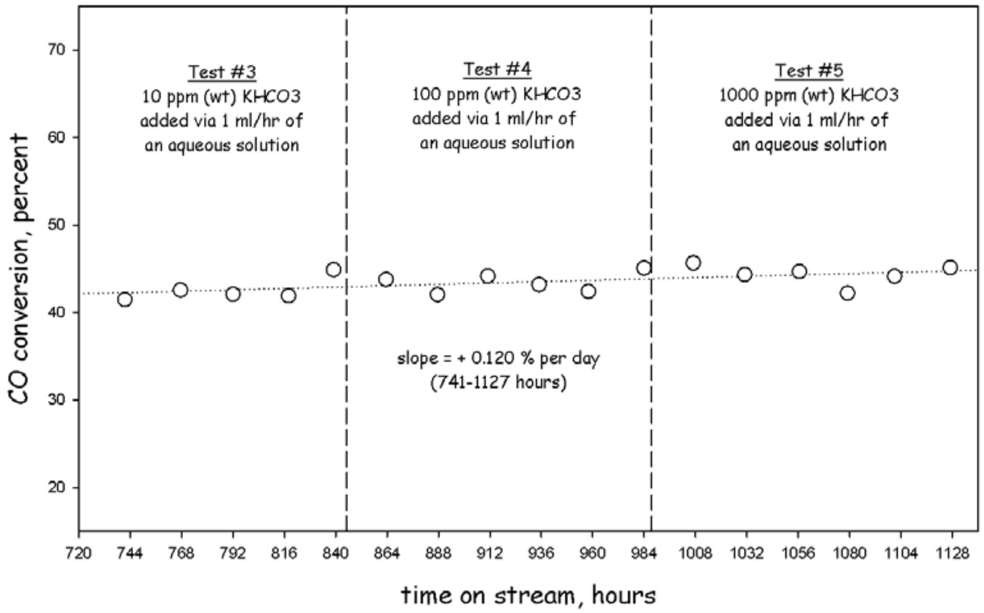


Figure 60: Reactor #21, Run #AWP042. CO conversion versus time on-stream. $KHCO_3$ tests #3-5 using 7.8 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.5 slph/g, $H_2/CO = 2.0$, T = 220^oC, and P = 280 psig.

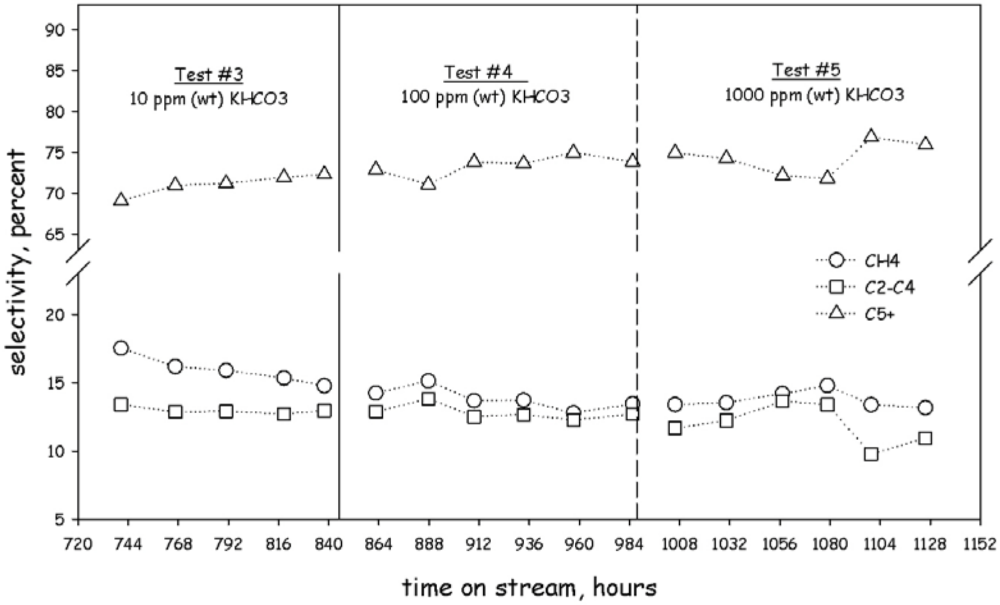


Figure 61: Reactor #21, Run #AWP042. Selectivity versus time on-stream. $KHCO_3$ tests #3-5 using 7.8 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.5 slph/g, $H_2/CO = 2.0$, T = 220^oC, and P = 280 psig.

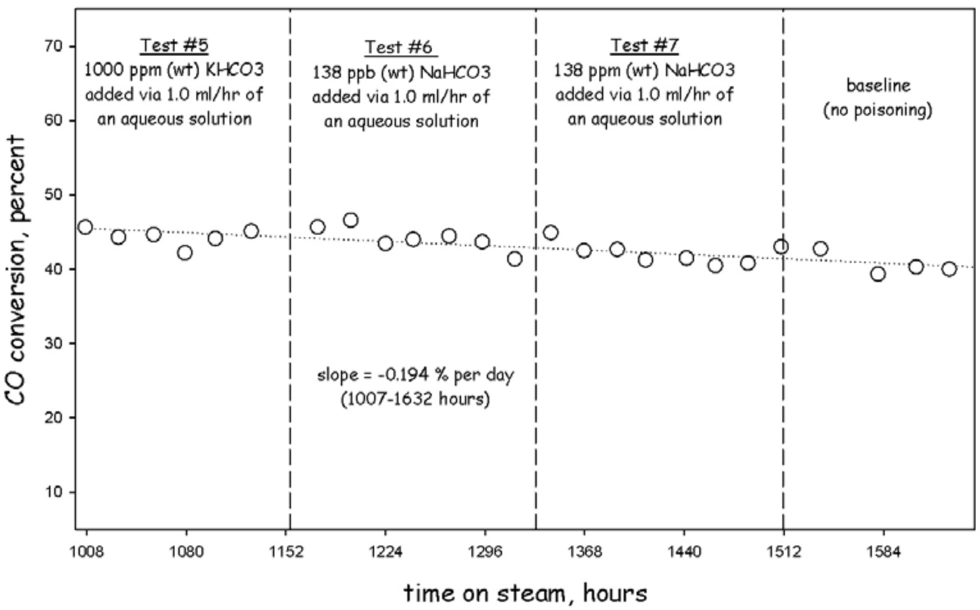


Figure 62: Reactor #21, Run #AWP042. CO conversion versus time on-stream. Test #5-7 using 7.8 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.5 slph/g, $H_2/CO = 2.0$, T = 220°C, and P = 280 psig.

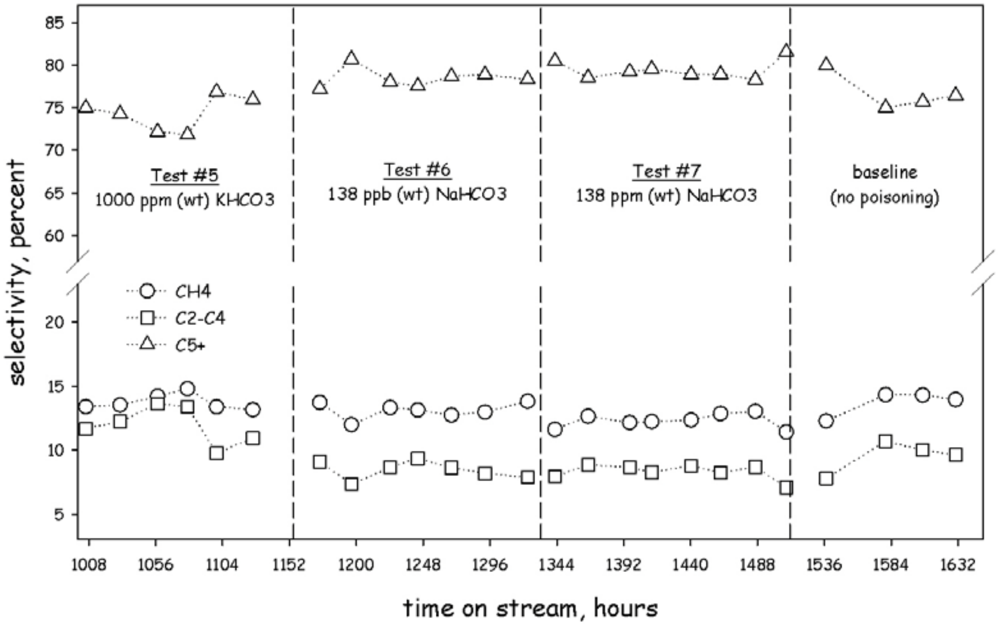


Figure 63: Reactor #21, Run #AWP042. Selectivity versus time on-stream. Test #5-7 using 7.8 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.5 slph/g, $H_2/CO = 2.0$, T = 220°C, and P = 280 psig.

Run #AWP044 was carried out in Reactor #23 between June 4th and July 20th, 2010. This run tested $NaHCO_3$ as a poisoning agent at concentrations at the two extremes of the testing range, 100 ppb (wt) and 1000 ppm (wt) in the total reactor feed. Two other $NaHCO_3$ tests [at 138 ppb (wt) and 138 ppm (wt)] were added at the end of run AWP042 (in reactor R21), which was running concurrently.

8.5 grams of reduced GJ456 was added to the reactor on 03 June 2010 and treated with the usual flowing hydrogen at $230^{o}C$ overnight before transitioning to FT synthesis the following day. Using an initial feed rate of 8 slph/g, the reactor was at $220^{o}C$ and 280 psig at 15:00 on 04 June. The CO conversion after two hours was 49.9%, but this fell rapidly. After 41 hours, the conversion was 22.8%, so the SV was reduced to 4.0 slph/g (Figure 64).

After about 160 hours on stream, the conversion began to level off, with the samples taken during the next five days (169-283 hours) selected as the baseline for the first test (Figure 65). Starting at 285 hours, 2 ml/hr of an aqueous solution containing 0.905×10^{-6}g/ml of $NaHCO_3$ was injected using a syringe pump, an amount sufficient to produce a concentration of 100 ppb (wt) of $NaHCO_3$ in the total feed (H_2 + CO + H_2O).

Over the course of the 143 hours (283-426 hours) of this first test the CO conversion fell from 39.4% to 26.6%, for an average loss of 2.148% per day (Figure 65). Moreover, a seemingly adverse impact on selectivity was also observed (Figure 66). The $NaHCO_3$ feed was then discontinued to return to the baseline conditions for four days (426-524 hours). During this time the conversion increased to about 30% and selectivity improved (Figures 65 and 66).

Since the $NaHCO_3$ seemed to demonstrate a poisoning effect, the test was repeated in R21's run AWP042, which had recently finished a series of tests with $KHCO_3$. The same

$NaHCO_3$ solution was used, but with the feed rate reduced to only 1.0 ml/hr. With the lower SV in use in R21, this yielded an $NaHCO_3$ concentration in this reactor of 138 ppm (wt).

When this 138 ppb test and a following test in R21 at 138 ppm (wt) showed no poisoning effect, the 100 ppb test was repeated in R23/AWP044. The feed rate was reduced to 2.5 slph/g to improve the percent CO conversion (which had no effect on the total slph of CO being converted to hydrocarbons) and a new baseline conversion of about 48% was established during five days of operation (524-649 hours) (Figure 67).

At 649 hours, the syringe pump was restarted, delivering the same $NaHCO_3$ solution. The pump's feed rate was reduced to 1.2 ml/hr to provide a concentration of 97 ppb (wt) $NaHCO_3$ to the total feed. This second $NaHCO_3$ test in AWP044 ran for 8 days (649-840 hours), and showed no poisoning effect (Figures 67 and 68).

The pump was then flushed and refilled with a much stronger $NaHCO_3$ solution (0.01104 g/ml). When injected at a rate of 1.0 ml/hr, this produced a concentration in the total feed of 1000 ppm (wt). This third test ran for five days (840-979 hours) and also failed to demonstrate any poisoning effect (Figures 67 and 68). For the entire period at this SV (baseline + 97 ppb test + 1000 ppm test), the CO conversion lost an average of 0.127 % per day.

Calculations

Based on the chemisorption estimate of 228.2×10^{-6} moles of active cobalt per gram of freshly reduced catalyst, there were 1.9397×10^{-3} moles of active cobalt present at the start of the run.

The first sample was taken only two hours after reaching FT synthesis conditions. With a gas product rate of 36+ slph and an estimated gas holdup in the reactor and traps of about 30 std. liters, this means that there were only about 2.3 gas turnovers before this sample was taken, less than the desired 4-6 turnovers to ensure a good sample. Fortunately, the conversions obtained during the next two samples (at 22.5 and 41.5 hours) form a good straight line passing through the first sample, indicating that the first sample was probably a valid sample. Extrapolating this line back to time zero provides an estimate of 10.544 slph of CO>HC during the first moments of operation. Using the ideal gas value of 22.414 std. liters per mole, this is equivalent to 0.47042 mol/hr.

(0.47042 mol/hr CO>HC) / (1.9397 x 10^{-3} moles of active cobalt) =

242.522 mol/hr of CO>HC per mole of active cobalt at the start of the run

Since the first test during this run appears to have been an anomaly (disagreeing with both a repeated test later in this run and another concurrent test in a second reactor), I'm skipping this first test entirely and going on to the second and third tests.

A straight line linear regression fit for the baseline period (546-643 hours) prior to the second test shows a very slight positive slope, indicating the conversion was actually increasing by 0.015 slph of CO>HC per day, so the decision was made to use the average conversion of 3.351 slph, or 0.14950 mol/hr CO>HC. Assuming that the initial rate is a constant, this means that (0.14950) / (242.522), or 616.44 x 10^{-6} moles of active cobalt remain prior to the start of the second test, which is about 32% of the original amount.

Both the second and third tests show very little loss of conversion. Over the course of both tests (667-979 hours), a straight line fits shows an average loss of 0.0096 slph CO>HC per day. The fit predicts that the conversion rate at 979 hours would be 3.187 slph CO>HC, and the data from this last sample shows a conversion of 3.188 slph, or 0.14223 mol/hr.

From this, the amount of active cobalt present at the end of the third test is estimated to be 586.46 x 10^{-6} moles, for a loss of only 29.98 x 10^{-6} moles over the course of both tests.

For the second test, the pump delivered 1.2 ml/hr of a solution containing 0.9053 x 10^{-6} g/ml $NaHCO_3$ for a period of 190.5 hours, for a total of 0.20695 x 10^{-3} grams.

For the third test, at 1000 ppm(wt), or 131 ppm(vol) of $NaHCO_3$ in the total feed (H_2+CO+H_2O), the pump delivered 1.0 ml/hr of a solution containing 11.04 x 10^{-3} g/ml for a period of 140 hours, for a total of 1545.6 x 10^{-3} grams.

The total amount of $NaHCO_3$ added for both tests was 1.5458 grams. At a formula weight of 84.0066 g/mol, the total was 0.01840 moles.

(29.98 x 10^{-6} moles of cobalt poisoned) / (0.01840 moles of $NaHCO_3$ added) =

1.6296 x 10^{-3} moles of cobalt poisoned per mole of $NaHCO_3$ (worst case scenario)

At the end of the third test, the conversion was still 3.188 slph CO>HC, out of a 7.026 slph of CO fed, or about 46% conversion, and the selectivity for methane was still very low at 5.2%. A fourth test was started with the $NaHCO_3$ concentration increased to 4000 ppm (wt), but the feed line plugged after one day, ending the run.

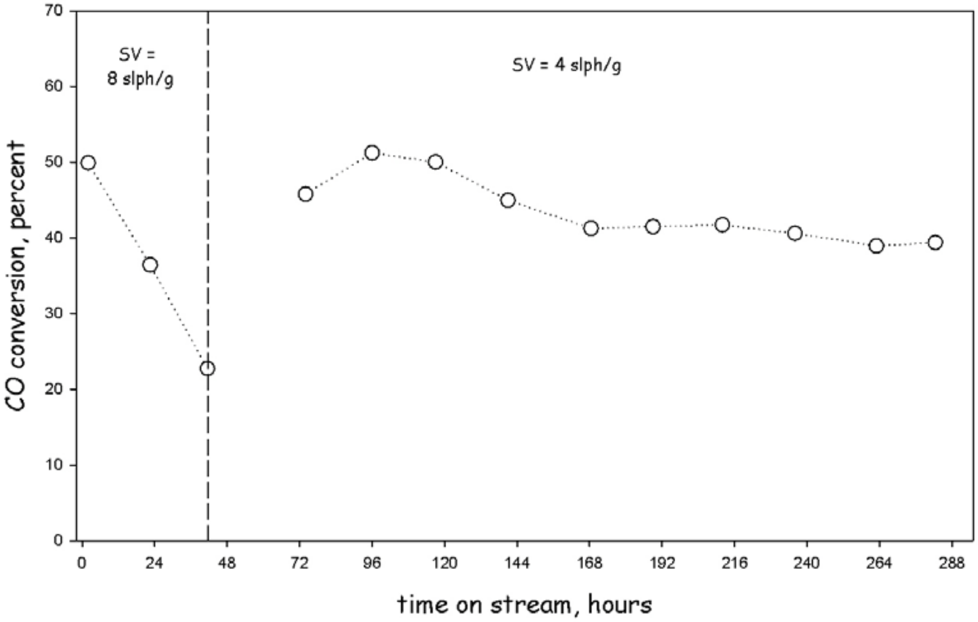


Figure 64: Reactor #23, Run #AWP044. Conversion versus time on-stream. Startup using 8.5 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 8.0 and 4.0 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

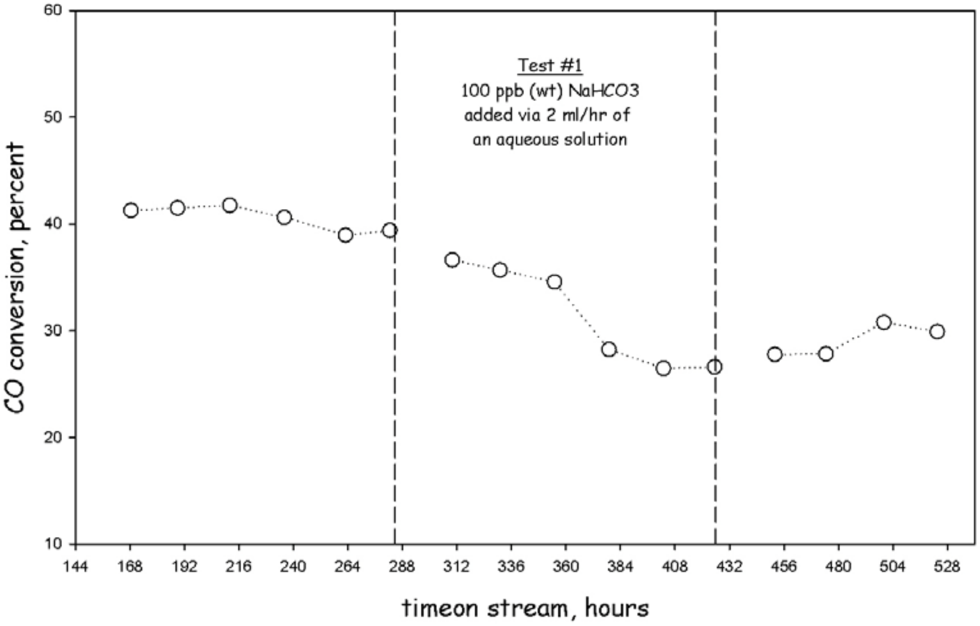


Figure 65: Reactor #23, Run #AWP044. Conversion versus time on-stream. Test #1 using 8.5 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 4.0 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

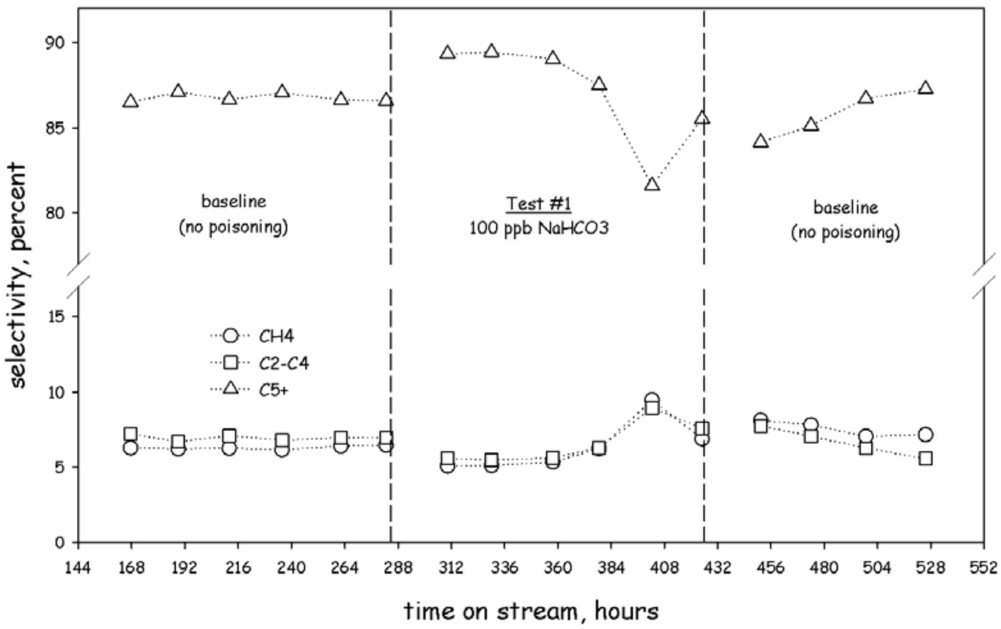


Figure 66: Reactor #23, Run #AWP044. Selectivity versus time on-stream. Test #1 using 8.5 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 4.0 slph/g, H_2/CO = 2.0, T = 220^oC, and P = 280 psig.

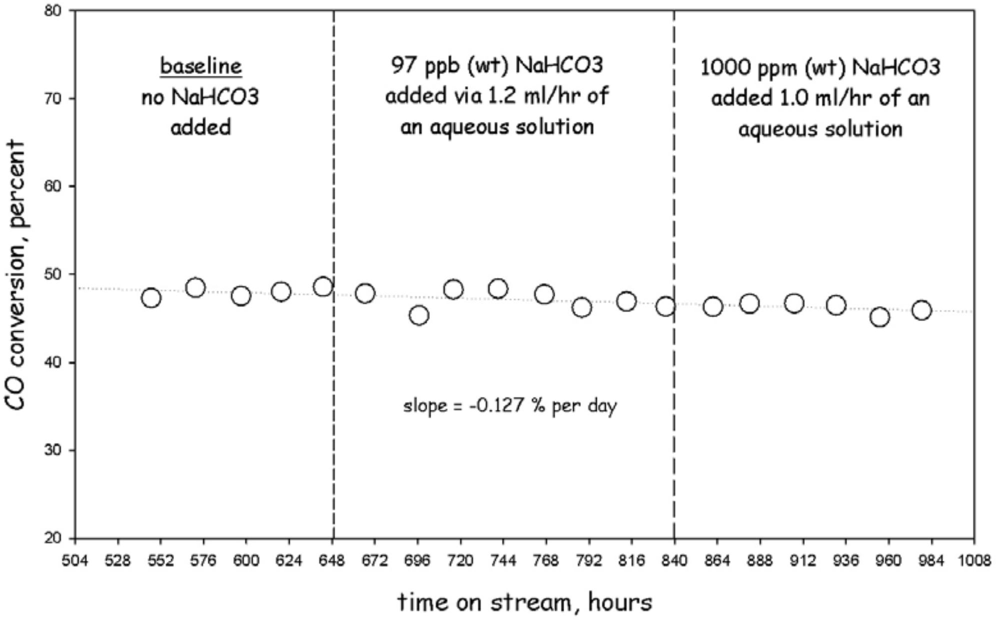


Figure 67: Reactor #23, Run #AWP044. CO conversion versus time on-stream. Tests #2 and 3 using 8.5 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2.5 slph/g, H_2/CO = 2.0, T = 220^oC, and P = 280 psig.

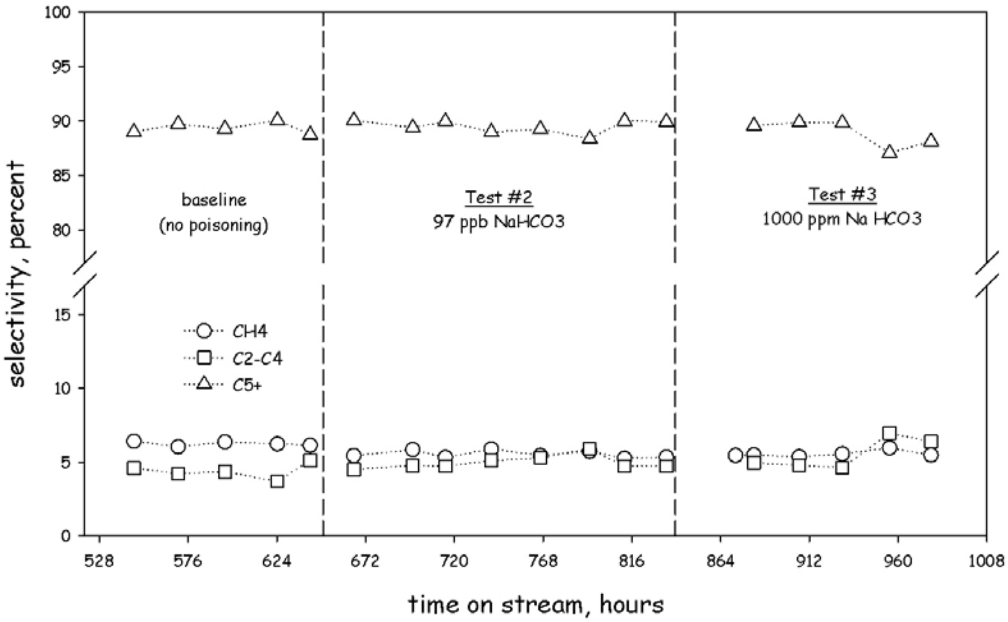


Figure 68: Reactor #23, Run #AWP044. Selectivity versus time on-stream. Tests #2 and 3 using 8.5 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2.5 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

B.2.4.3 HCl and HBr

HCl Trial #1

Run number AWP046was carried out in Reactor #21 from 30 Jul to 23 Sep, 2010. This run used aqueous HCl solutions to test the poisoning effect at 100 ppb (wt) and 10 ppm (wt) in the total feed (H_2 + CO + H_2O). A third test at 50 ppm (wt) was underway for only two days before the CAER lost electrical power for several hours, ending the run.

A catalyst charge was reduced for 10 hours at 350°C using our usual ex-situ arrangement before being injected into reactor R21. After the 24 hours at 230°C under flowing H_2, the reactor transitioned to F-T synthesis at 12:00 on 30 July. Starting with a space velocity of 8.0 slph/g, the CO conversion was 56% after 3½ hours, but fell rapidly to 8% within the first day (Figure 69).

Decreasing the SV to 2.0 briefly increased the conversion to 32%, although the actual amount of CO going to HC was scarcely changed (rising from 1.810 slph to 1.830 slph). Conversion again decreased rapidly, falling to 17% by the third day (Figure 69).

But for no identifiable reason the conversion suddenly increased to 59% on the fourth day (Figure 69), which was then followed by a slow smooth decline over the next eight days. The average loss rate was 0.247 % per day for days 7-12 (166-286 hours), and this was chosen to serve as the baseline for the first test.

After 292 hours of FT operation, a syringe pump was used to begin injecting 1.0 ml/hr of a weak HCl solution, with the concentration sufficient to provide 100 ppb (wt) in the total feed. The conversion fell at an average rate of 1.204% per day over the next six days (309 – 452 hours), but after that the loss rate slowed.

The HCl pump was stopped after 28 days (672 hours), returning the reactor to the baseline operating conditions for four days. The average rate of loss of conversion for last eight days of the 100 ppb test plus the four day baseline (478-768 hours) was 0.202% per day, slightly less than the rate noted for the original baseline (Figure 70). The selectivity for methane remained constant at 12-13% for the entire baseline-test-baseline period (Figure 71).

At the end of this second baseline period, the 1.0 ml/hr HCl feed was restarted, with the concentration of the solution increased to provide 10 ppm (wt) in the total feed. The loss rate for CO conversion immediately increased, with a straight line fit for the test period indicating an average loss rate of 0.694% per day, a little over half of the rate seen in the first test (Figure 72). Hydrocarbon product selectivity was not affected (Figure 73), although the n-alkane / (1- + cis-2 + trans-2 alkenes) versus carbon number was lower for the highest poisoning level of 10 ppm (Figure 74).

A few hours after the end of this second test the CO MFC failed, with its set point climbing to add excess CO to the reactor. A new MFC was installed and calibrated and a new baseline was established. A third test at 50 ppm (wt) HCl was then started, but the run was ended two days later when the CAER lab lost all electrical power due a short in the conduit.

Calculations

Using the chemisorption value of 228.2 x 10-6 moles of active cobalt per gram of fresh reduced catalyst, multiplied by the catalyst charge of 8.7 grams, the amount of active cobalt in the reactor at time zero was 1.9853 x 10^{-3} moles.

Extrapolating the data from the first two samples (at 3.5 and 6.5 hours on stream) back to time zero gives an estimated 13.019 slph of CO>HC, or 0.58084 mol/hr, so the initial rate was 292.566 mol/hr CO>HC per mole of active cobalt.

At the end of the baseline period (286 hours), the conversion was 3.041 slph CO>HC, or 0.13567 mol/hr. Dividing by the initial conversion rate gives 463.72 x 10^{-6} moles of active cobalt remaining at this point, about 23% of the original amount.

100 ppb (wt) HCl was added to the feed at 292 hours. The conversion showed a sharp straight line loss from then until 452 hours, when the loss rate slowed to approximately that of the baseline rate until the HCl feed was discontinued at 672 hours.

Considering only the first part of the test (292-452 hours), the slope of the baseline predicts that at 452 hours the conversion would have been 2.905 slph CO>HC if the HCl had not been added. 2.095 slph = 0.12962 mol/hr, and dividing this by the initial rate of 292.566 mol/hr per mol of cobalt indicates that 443.04 x 10^{-6} moles of active cobalt would have remained with no poisoning.

The actual conversion at 452 hours was 2.596 slph CO>HC, or 0.11582 mol/hr, indicating that 395.88 x 10^{-6} moles of cobalt remained. So the amount of cobalt that had been poisoned by the HCl was 47.16 x 10^{-6} moles.

During this first test, the syringe pump delivered 1.0 ml/hr of an aqueous HCl solution containing 0.92864 x 10^{-6} g/ml of HCl for 160 hours, injecting a total of 148.582 x 10^{-6} grams. With a formula weight of 36.461 g/mol, this means that 4.0751 x 10^{-6} moles of HCl were added. (47.16 x 10^{-6} moles cobalt poisoned) / (4.0751 x 10^{-6} moles of HCl added) =

11.572 moles of cobalt were poisoned per mole of HCl added (292-452 hours)

But is this real? Might it not be the inverse of the odd sudden increase in conversion seen early in the run? Between the samples taken at 70 and 95 hours, the conversion increased from 0.954 slph CO>HC up to 3.572 for no reason that could be determined. Since the conversion is based on the product gas rate, this would have suggested that a large leak developed somewhere between 70 and 95 hours to give the appearance of a large increase in conversion. The presumed leak would then have needed to have partially stopped at the moment HCl injection was started at 292 hours. And it would need to be only "partially stopped", as the conversion at the end of the poisoning test was still significantly higher than during the first part of the run.

Turning to the second test, at 10 ppm HCl (<u>note</u>: 10 ppm (wt) HCl = 3 ppm (vol)) a linear regression straight line fit was applied to the conversion .vs. time data from the last half of the 100 ppb test and baseline immediately prior to the 10 ppm test. Extrapolating this to the end of the 10 ppm test at 1030 hours indicated that if there had been no poisoning, the conversion would have been 2.341 slph CO>HC, or 0.10446 mol/hr. Dividing by the initial conversion rate of 292.566 mol/hr CO>H_2 per mole of cobalt suggests that 357.05 x 10^{-6} moles of active cobalt would have remained at this point.

But the actual conversion noted at 1030 hours was 2.067 slph, or 0.09222 mol/hr, indicating that only 315.21 x 10^{-6} moles of active cobalt remained. So the 10 ppm HCl in the syngas is presumed to have poisoned 41.84 x 10^{-6} moles of cobalt.

The HCl solution used was 100x stronger than what used for the first test, containing 0.92864 x 10^{-4} g/ml of HCl. The pumping rate was still 1.0 ml/hr and the test ran for 262 hours (768-1030 hours on stream), so the total amount of HCl added was 0.02433 grams. Dividing by the formula weight of 36.461 g/mol, this means that 667.30 x 10^{-6} moles of HCl were added.

(41.84 x 10^{-6} moles of cobalt poisoned) / (667.30 x 10^{-6} moles of HCl added) =

0.0627 moles of cobalt poisoned per mole of HCl added (768-1030 hours)

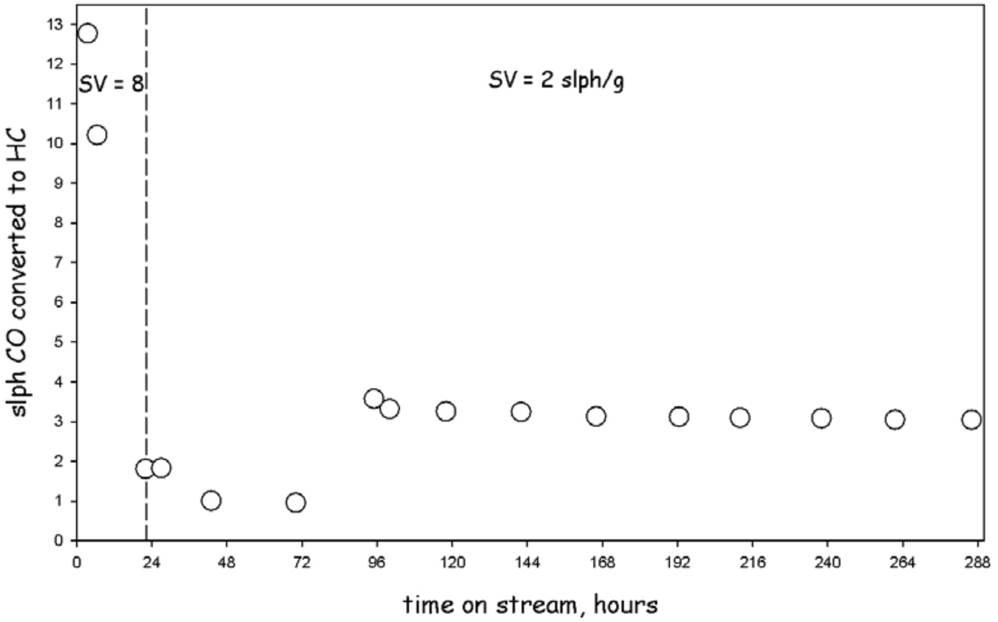


Figure 69: Reactor #21, Run #AWP046. slph CO converted versus time on-stream. Startup using 8.7 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 8 and 2 slph/g, H_2/CO = 2.0, T = 220^{o}C, and P = 280 psig.

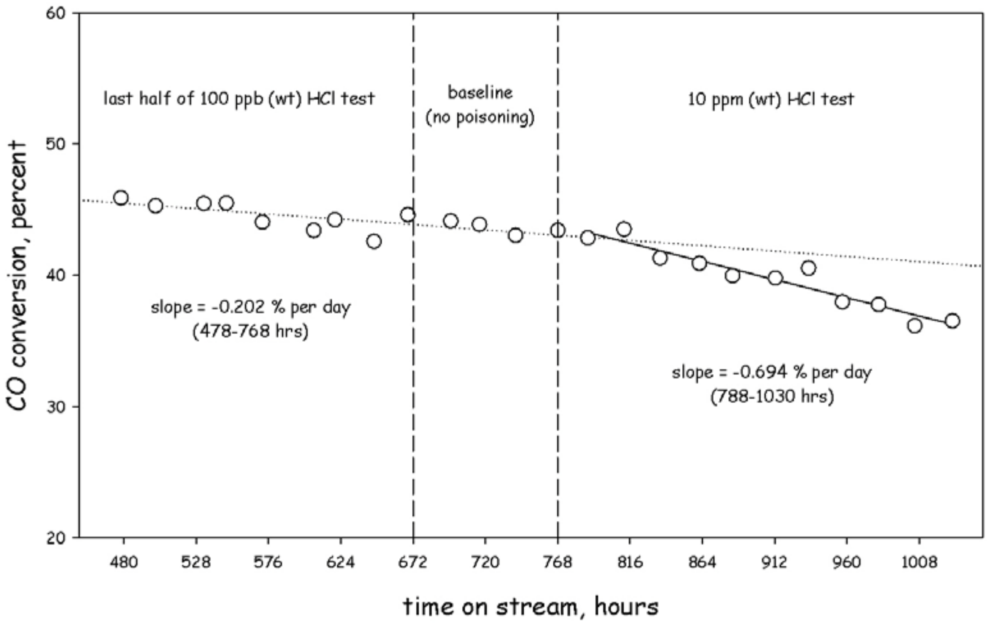


Figure 70: Reactor #21, Run #AWP046. CO conversion versus time on-stream. 100 ppb and 10 ppm tests using 8.7 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

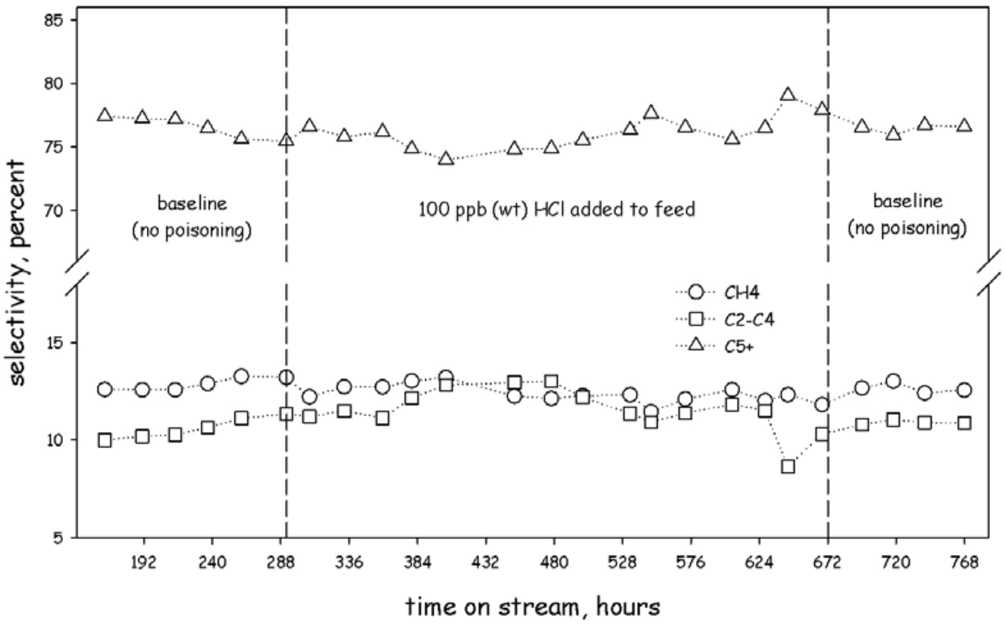


Figure 71: Reactor #21, Run #AWP046. Selectivity versus time on-stream. 100 ppb HCl test using 8.7 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

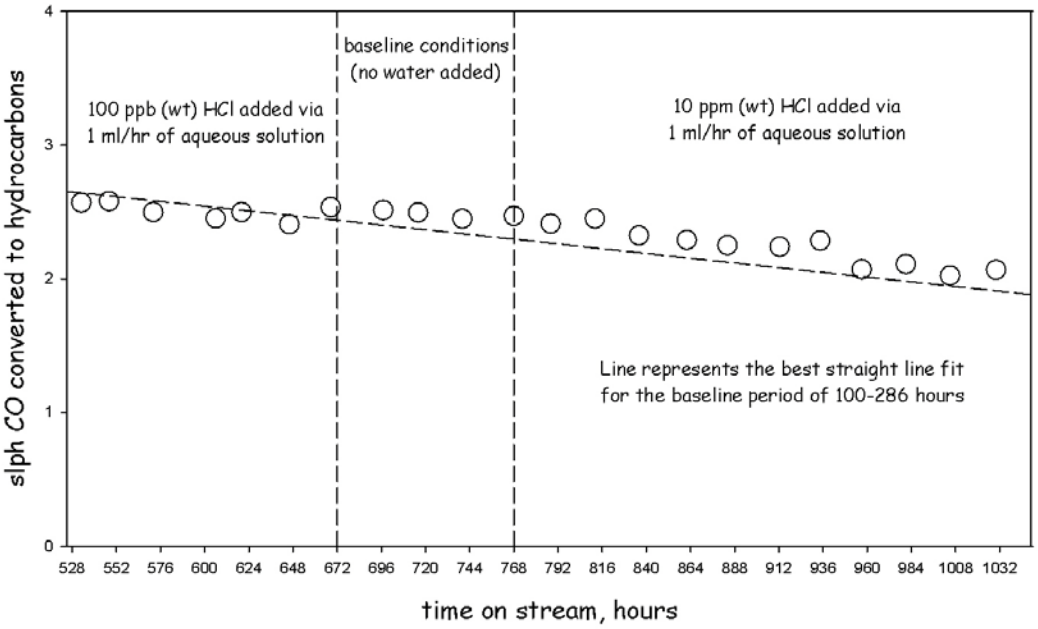


Figure 72: Reactor #21, Run #AWP046. slph CO converted versus time on-stream. 100 ppb and 10 ppm HCl tests using 8.7 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

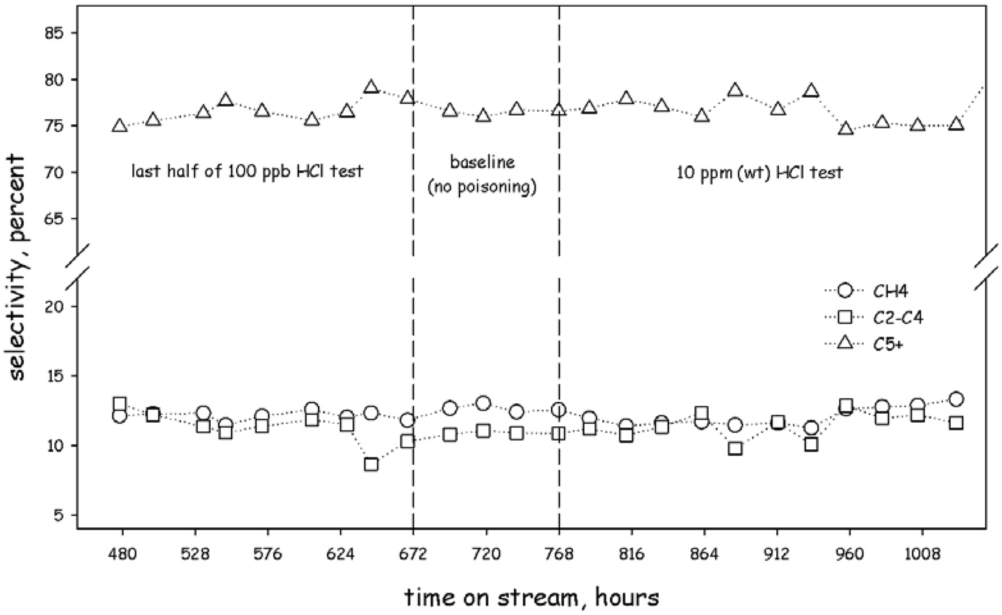


Figure 73: Reactor #21, Run #AWP046. Selectivity versus time on-stream. 100 ppb and 10 ppm HCl tests using 8.7 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

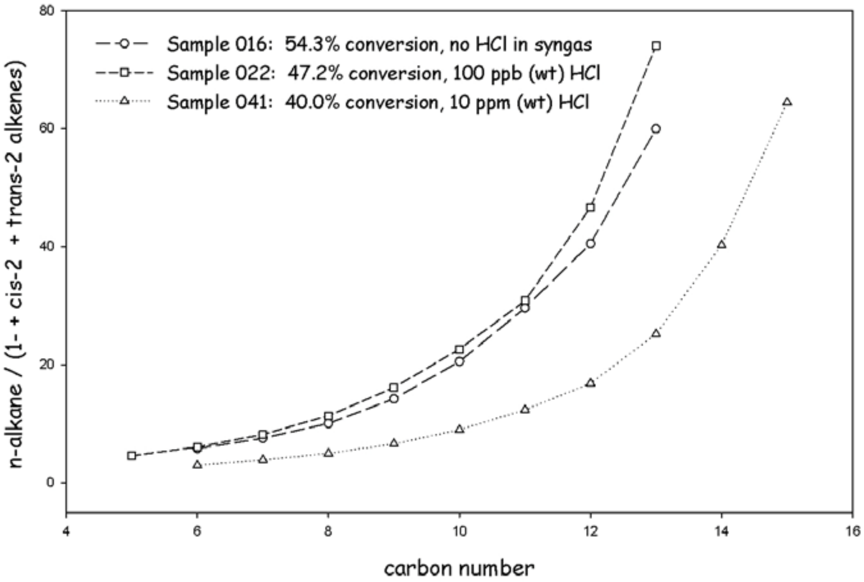


Figure 74: Reactor #21, Run #AWP046. n-alkane / (1- + cis-2 + trans-2 alkenes) versus carbon number. Clean, 100 ppb, and 10 ppm HCl tests using 8.7 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2 slph/g, H_2/CO = 2.0, T = 220^{o}C, and P = 280 psig.

HCl Trial #2

Run #AWP051 was conducted in Reactor #21 from 13 Oct to 09 Dec, 2010. This run continues the HCl testing started in Run AWP046. The first run tested the required minimum of 100 ppb (wt) and 10 ppm. A051 started with a nominal 50 ppm HCl, increased the concentration to 150 ppm, and ended with a test at 500 ppm.

Startup

310 grams of Polywax 3000 was added to R21 on 12 October 2010 and the reactor was heated to 140C under flowing nitrogen overnight. 8.4 grams of the large batch of GJ456 catalyst (25% Co, 0.5% Pt on 150 m^2/g alumina) was injected the following day. The nitrogen was replaced by ~20 slph of hydrogen and with the reactor pressure still at ~10 psig, the temperature was increased to 230^{o}C and held at these conditions overnight.

On the morning of 13 October, the temperature was decreased to 180C and a syngas feed was started. The temperature and pressure were then both slowly increased, reaching our standard operating conditions of 220^{o}C and 280 psig by noon.

I'd forgotten that the CO MFC had failed and been replaced midway through the previous run, and so at startup for this run, I mistakenly used the calibration for the failed unit. This caused the initial syngas feed to be deficient in CO, resulting in a syngas SV of 7.44 slph/g, but with a H_2/CO ratio of 2.871. I discovered my error after 22 hours and also reduced the feed rate to 3 slph/g at this same time, with the proper H_2/CO ratio of 2.0.

Baseline operation

The CO conversion continued to decline during an extended startup period. Decreasing the SV to 2 slph/g after 262 hours had no effect, and by 408 hours on stream, only 1.634 slph of CO was being converted to hydrocarbons, or a bit more than half of the conversion seen during the baseline period in run A046.

Adding HCl to the feed

1.0 ml/hr of a weak HCl solution was injected into the gas feed starting at 408.5 hours. The concentration of the solution was adjusted to provide 51.6 ppm (wt) HCl in the total feed, or 0.460 x 10^{-3} g/hr of HCl. This feed was continued for 406.5 hours, adding a total of 0.187 grams of HCl to the reactor. The CO conversion continued to fall at the same rate as the baseline for about the first two-thirds of this test, and then actually increased slightly and leveled off, which would indicate that there was no poisoning effect at this HCl concentration.

The HCl feed was discontinued after 815 hours to re-establish a baseline conversion. After maintaining this baseline conditions for 196 hours, the 1.0 ml/hr feed of an HCl solution was restarted, with the concentration now increased to provide 150 ppm (wt) HCl in the total feed, or 1.338 x 10^{-3} g HCl/hr.

This 150 ppm test ran for 164 hours. The CO conversion for both the baseline period (815-1011 hrs) and the test period (1011-1175 hrs) each show a mild rise and decline, but with no clear trend, so again, there was no evidence of poisoning. A linear regression straight line fit to the data from the baseline and this test indicates an average loss rate of 0.197% of CO conversion per day. A total of 0.219 grams of HCl was added to the reactor during this 150 ppm test.

Maintaining the same 1.0 ml/hr liquid feed rate, the strength of the HCl solution was once again increased, this time raising the concentration in the total feed to 500 ppm, or 4.460 x 10^{-3} g HCl/hr. A straight line fit indicates an average loss rate of 1.894% of conversion per day. A total of 0.7359 grams of HCl (0.020184 moles) were added to the reactor over the 165 hours of this final test. The run was terminated after a total of 1340 hours.

Calculations

From the chemisorption data for this catalyst, the reactor started with 1.917 x 10^{-3} moles of active cobalt. Based on the conversions calculated from samples taken at 11 and 22.5 hours on stream, the estimated initial conversion at time zero was 11.251 slph, or 0.50196 mol/hr of CO>HC. So the initial conversion rate per mole of active cobalt was 261.86 mol/hr.

Since the first two tests showed no clear indication of poisoning, I've only calculated the poisoning effect for only the third run, at 500 ppm (wt) HCl in the feed.

Using the conversions obtained during the second test and the intervening baseline period, a rather poor straight line fit can be made. Using this fit to estimate the conversion at 1340 hours if there had been no poisoning test, we would have seen 1.175 slph CO>HC, or

0.05240 mol/hr. Dividing by the initial rate gives an estimate of 200.11 x 10^{-6} moles of active cobalt remaining if no poisoning.

The actual observed conversion at this time was 0.451 slph, indicating that instead only 76.84 x 10^{-6} moles of active cobalt remain. So the amount that was poisoned was 123.27 x 10^{-6} moles.

(123.27 x 10^{-6} moles cobalt poisoned) / (20.184 x 10^{-3} moles HCl fed) =

6.107 x 10^{-3} moles of cobalt poisoned per mole of HCl fed (1175-1340 hours)

Alkane/alkene ratios

Three samples of the (oil + wax) product were submitted for GC analysis and the (n-alkane) / (1-alkene + cis- and trans-2-alkene) mole ratio was calculated for each carbon number. The first sample (A051-011) was the accumulation of all (oil + wax) product that was collected from time period of 74-148 hours on stream, before any HCl was added.

The second sample (A051-028) is from 409-532 hours on stream, or the first 123 hours of operation with 52 ppm HCl being added. Finally, the third sample (A051-032) was the (oil + wax) product collected from 532-623 total hours on stream, or 123-214 hours of the 52 ppm HCl addition.

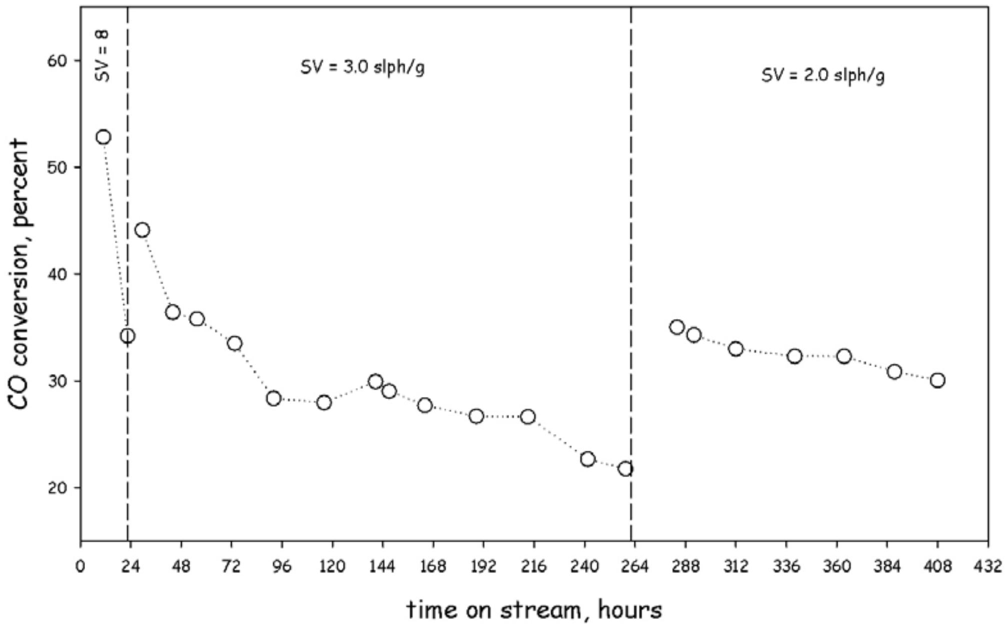


Figure 75: Reactor #21, Run #AWP051. CO conversion versus time on-stream. Startup using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 8, 3, and 2 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

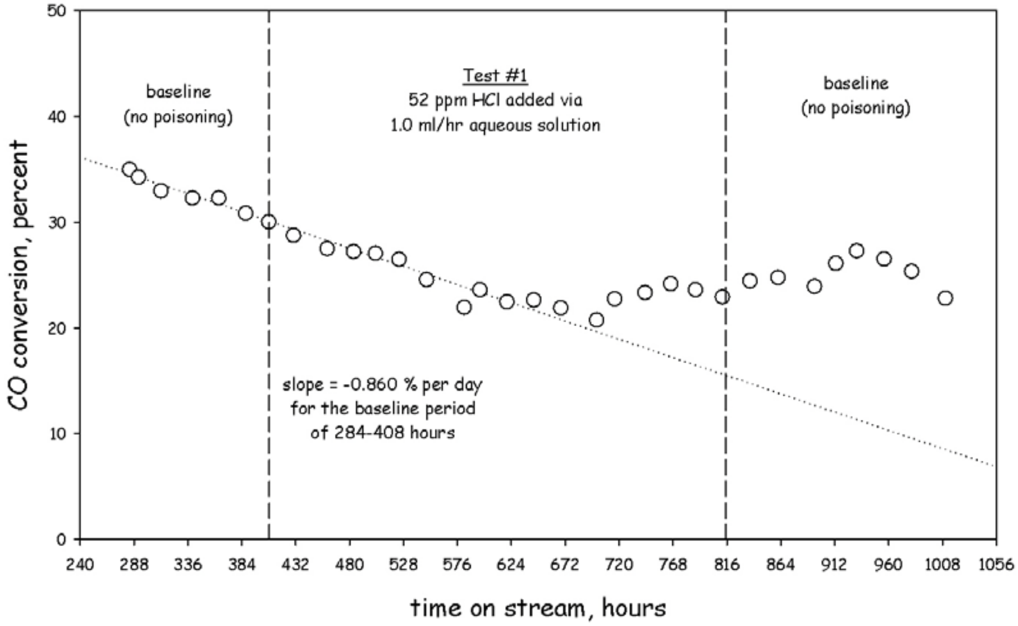


Figure 76: Reactor #21, Run #AWP051. CO conversion versus time on-stream. HCl test #1 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

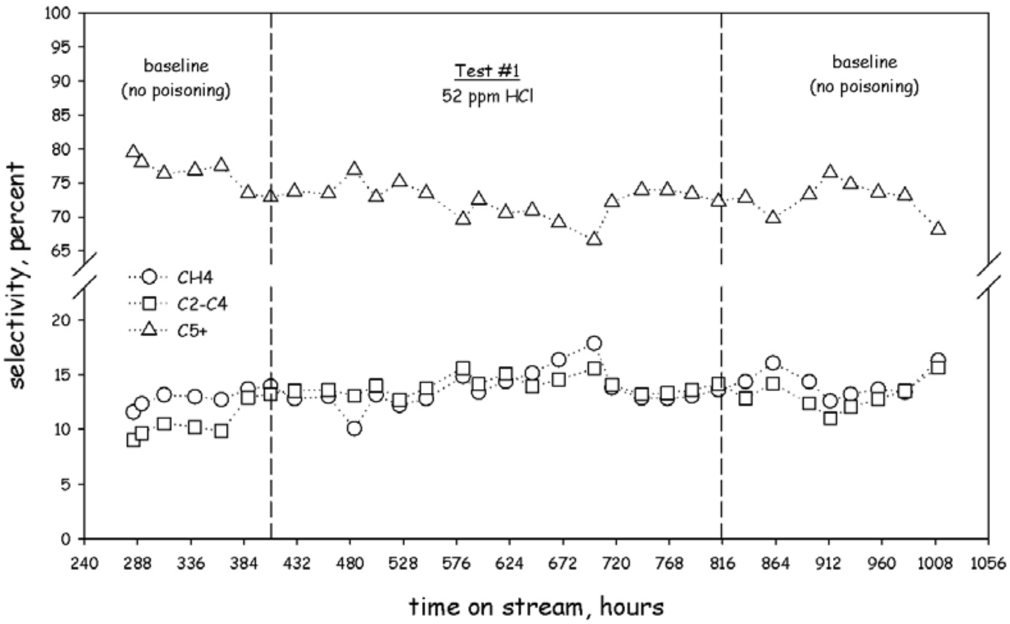


Figure 77: Reactor #21, Run #AWP051. Selectivity versus time on-stream. HCl test #1 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2 slph/g, $H_2/CO = 2.0$, T = 220°C, and P = 280 psig.

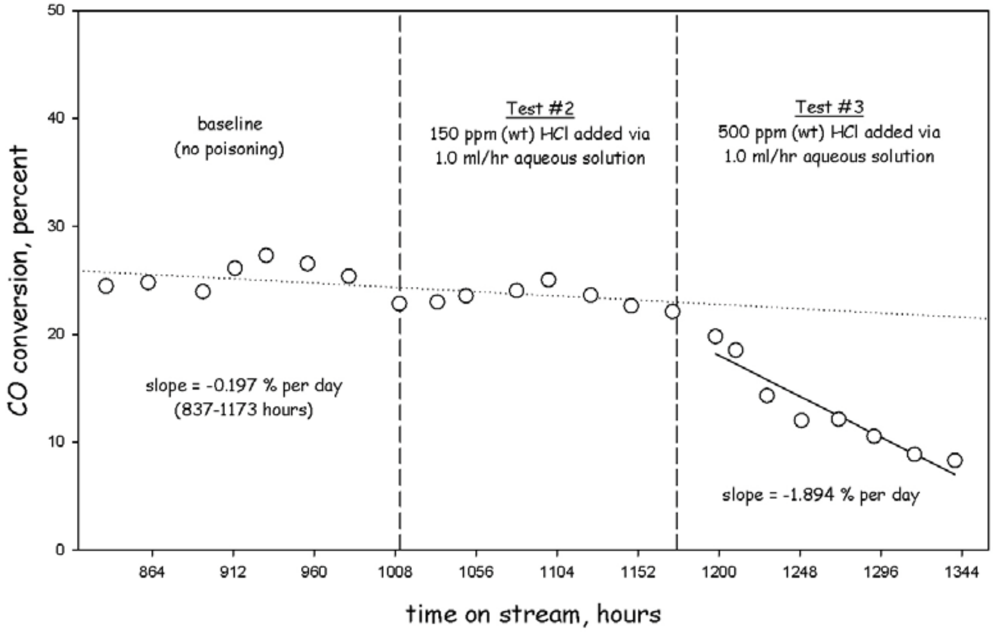


Figure 78: Reactor #21, Run #AWP051. CO conversion versus time on-stream. HCl tests #2 and 3 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2 slph/g, $H_2/CO = 2.0$, T = 220°C, and P = 280 psig.

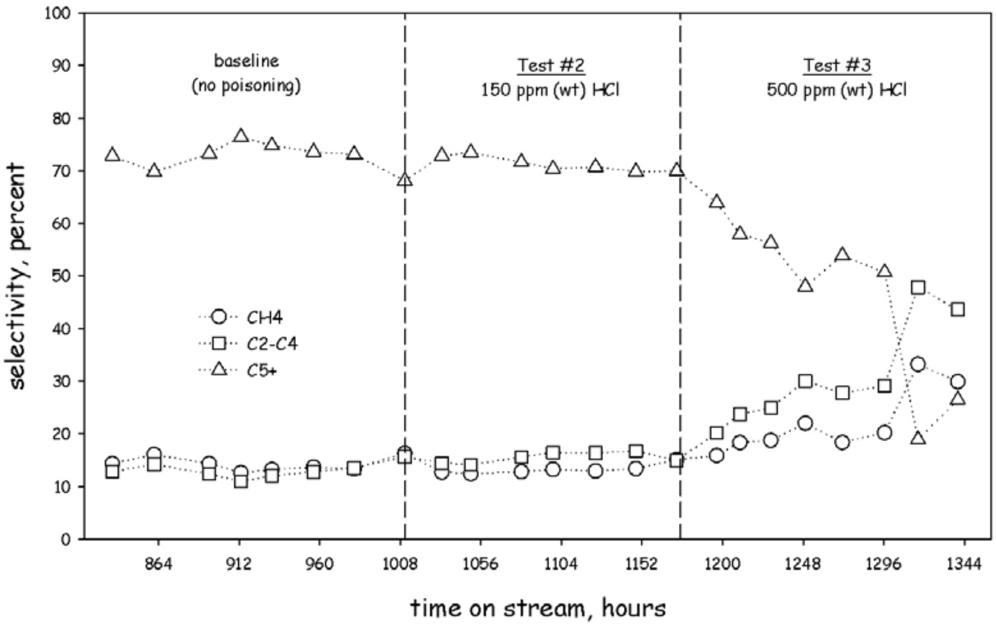


Figure 79: Reactor #21, Run #AWP051. Selectivity versus time on-stream. HCl tests #2 and 3 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

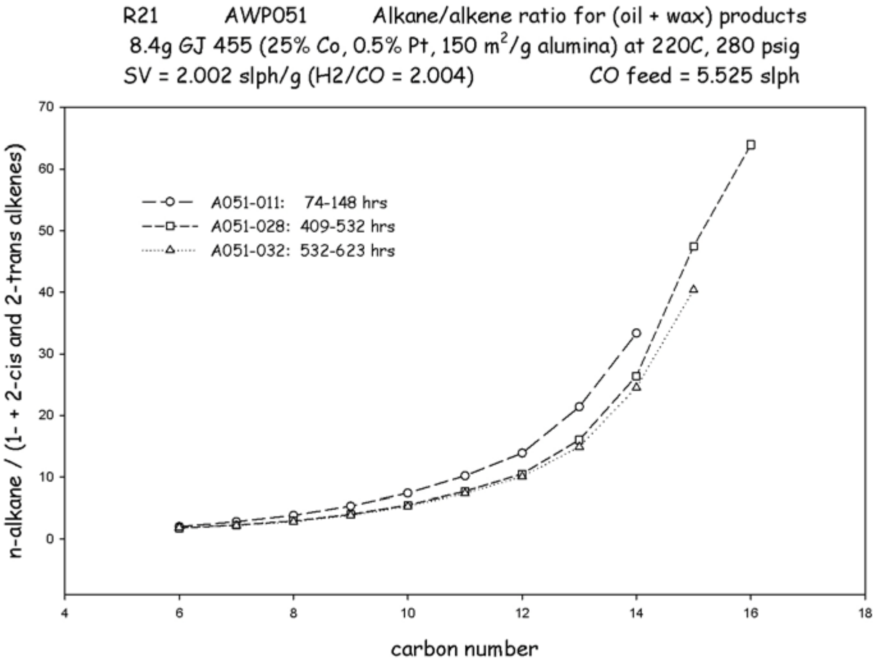


Figure 80: Reactor #21, Run #AWP051. n-alkane / (1- + cis-2 + trans-2 alkenes) versus carbon number. Clean (74 - 148 h) and 52 ppm HCl (initial addition during 409 - 532 h and later addition during 532 - 623 h) using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 2 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

HBr addition

Run #AWP050 was conducted in Reactor #23 between 09 Oct – 07 Dec, 2010. This run was used to conduct three tests of HBr poisoning. The first test was at the required 100 ppb (wt) HBr in the total feed, followed by 5 ppm and 20 ppm.

Startup

310 grams of Polywax 3000 was added to reactor R23 on 07 October 2010 and heated to 140°C under flowing nitrogen overnight. On the following day, 8.4 grams of GJ456 (25% Co, 0.5% Pt, 150 m^2/g alumina) was injected. The reactor was then heated to 230°C under ~20 slph flowing hydrogen and held at these conditions overnight. On the morning of 09 October, the reactor was first cooled to 180°C and then syngas (H_2/CO = 2) at a SV of 6 slph/g replaced the pure hydrogen feed. The reactor was then slowly pressurized to 280 psig and heated to 220°C, reaching these synthesis conditions by noon.

Operation

The first gas sample was taken after five hours of F-T operation, showing a CO conversion of ~49%, with 8.1 slph of CO being converted to hydrocarbons. After 19 hours, the CO conversion had fallen to 24%, so the SV was reduced from 6.0 to 3.0 slph/g. The conversion continued to fall, so the SV was reduced to the lowest acceptable minimum rate of 1.8 slph/g after 79 hours (Figure 83).

After fourteen days, a 1.0 ml/hr feed of an aqueous HBr solution was started (Figure 83), with the concentration of the solution adjusted to provide 100 ppb (wt) HBr in the total feed. HBr was added at a rate of 1.184 x 10^{-6} g/hr, or 0.01463 x 10^{-6} mol/hr for 219.25 hours (336.75 – 556 hours on stream), adding a total of 0.2596 x 10^{-3} grams, or 3.2076 x 10^{-6} moles of HBr to the reactor. With a charge of (8.4)(0.25) / (58.933), or 0.03563 moles of cobalt in the reactor, this means that 90.03 x 10^{-6} moles of HBr were added per mole of cobalt.

A linear regression straight line fit of the baseline period shows an average loss rate of CO conversion of 0.474 % per day (Figure 85) with little change in selectivities (Figure 86). After a rapid loss of 6% in conversion in the first two days, the conversion remained essentially unchanged for the next seven days.

The concentration of the HBr feed solution was increased after 556 hours on stream. Using the same 1.0 ml/hr feed rate, and with the syngas feed rate unchanged, the HBr concentration in the total feed rose to 5 ppm (wt). This stronger solution was added for 240 hours (556-796 hours on stream), adding an additional (240 hours)(59.191 x 10^{-6} g/hr), or 0.0142 grams of HBr to the reactor, or 0.1756 x 10^{-3} moles (Figures 85 and 86).

The cumulative total of HBr added to the reactor by the end of this second test was 0.1788 x 10^{-3} moles, or 5.017 x 10^{-3} moles HBr per mole of cobalt. There is no clear trend of decreasing activity (Figures 85 and 86). The scatter in the data is probably at least in part due to the increased difficulty of accurately measuring smaller gas product rates. To confirm that the water itself had no deleterious effect, 1.0 ml/hr of deionized water was injected for six days after ending the 5 ppm HBr test.

The syringe pump was refilled with a stronger HBr solution, sufficient to produce 20 ppm (wt) in the total feed (H_2 + CO + H_2O). These conditions were maintained for 13 days, again with no clear indications of a poisoning effect (Figures 87 and 88).

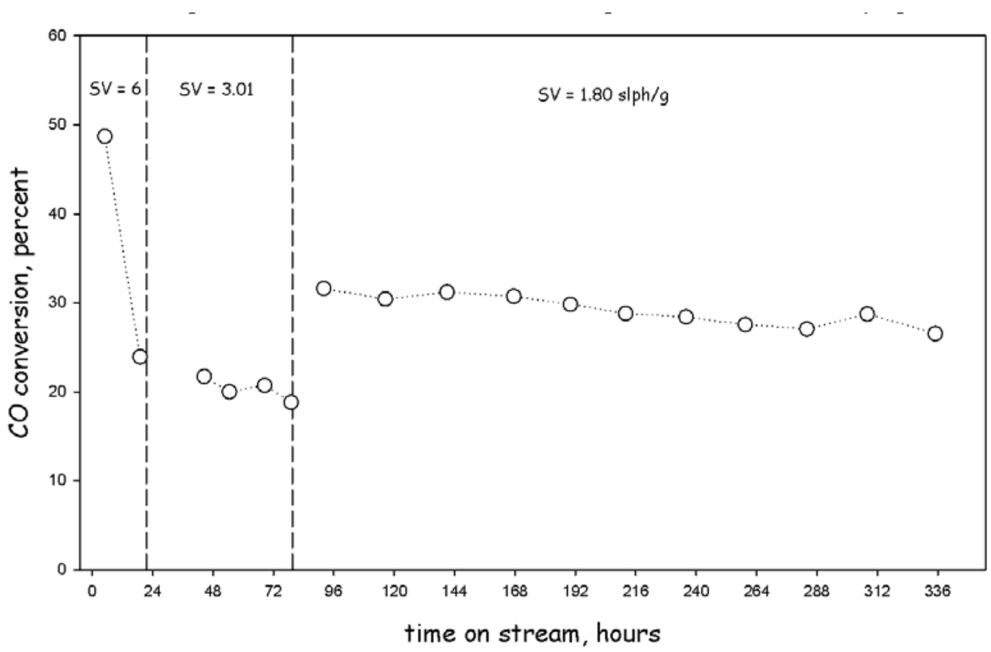


Figure 82: Reactor #23, Run #AWP050. CO conversion versus time on-stream. Startup using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 6, 3, and 1.8 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

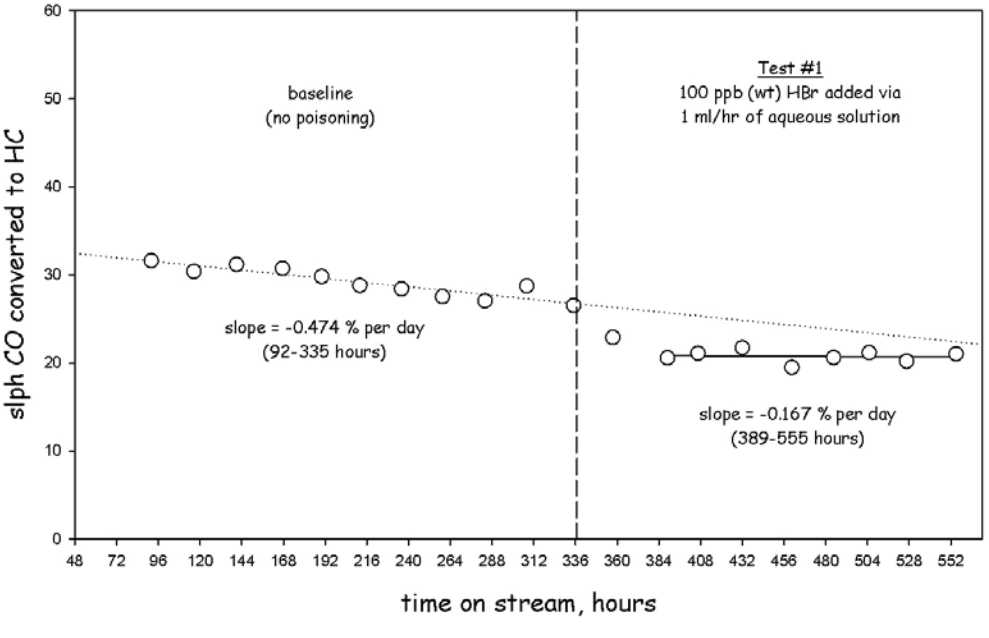


Figure 83: Reactor #23, Run #AWP050. slph CO converted versus time on-stream. HBr test #1 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.8 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

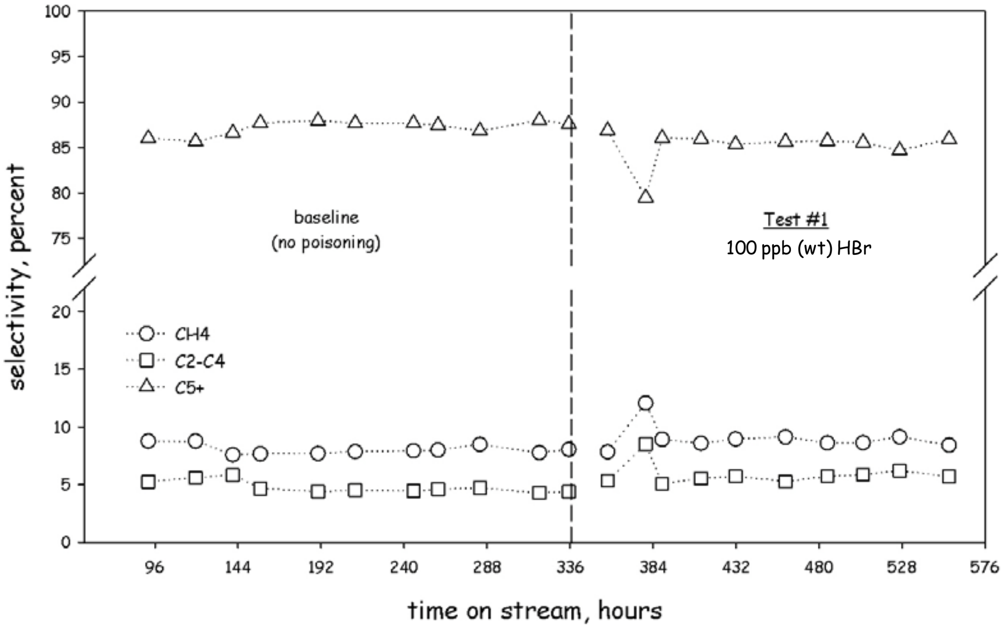


Figure 84: Reactor #23, Run #AWP050. Selectivity versus time on-stream. HBr test #1 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.8 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

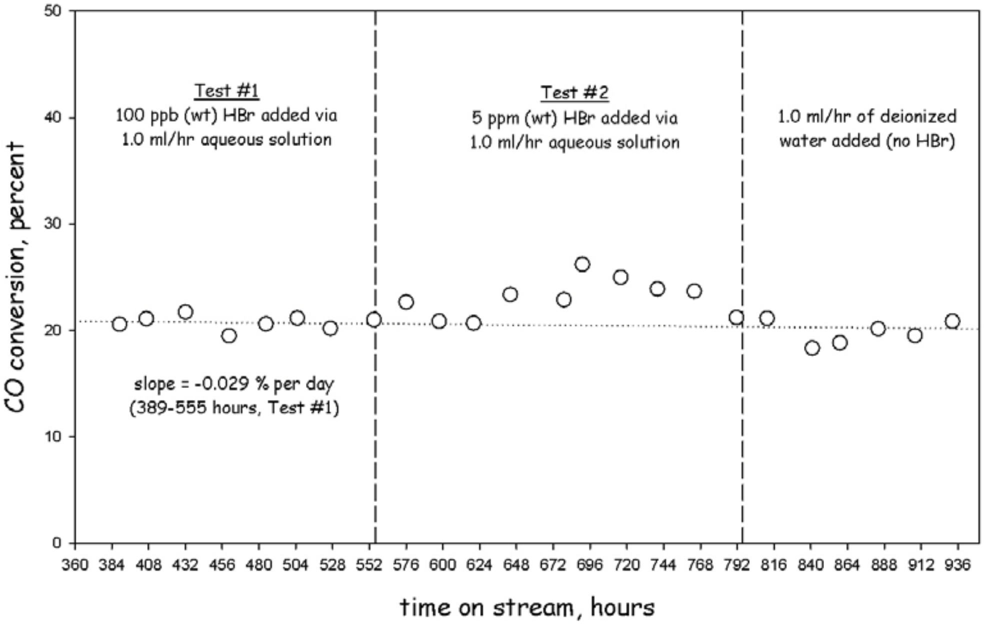


Figure 85: Reactor #23, Run #AWP050. CO conversion versus time on-stream. HBr tests #1 and 2 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.8 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

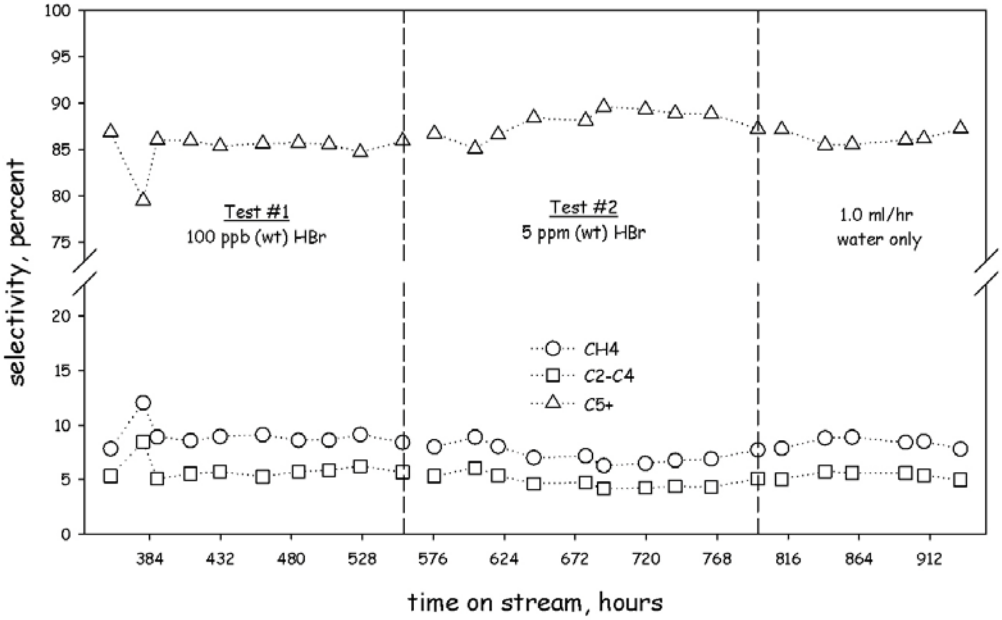


Figure 86: Reactor #23, Run #AWP050. Selectivity versus time on-stream. HBr tests #1 and 2 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.8 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

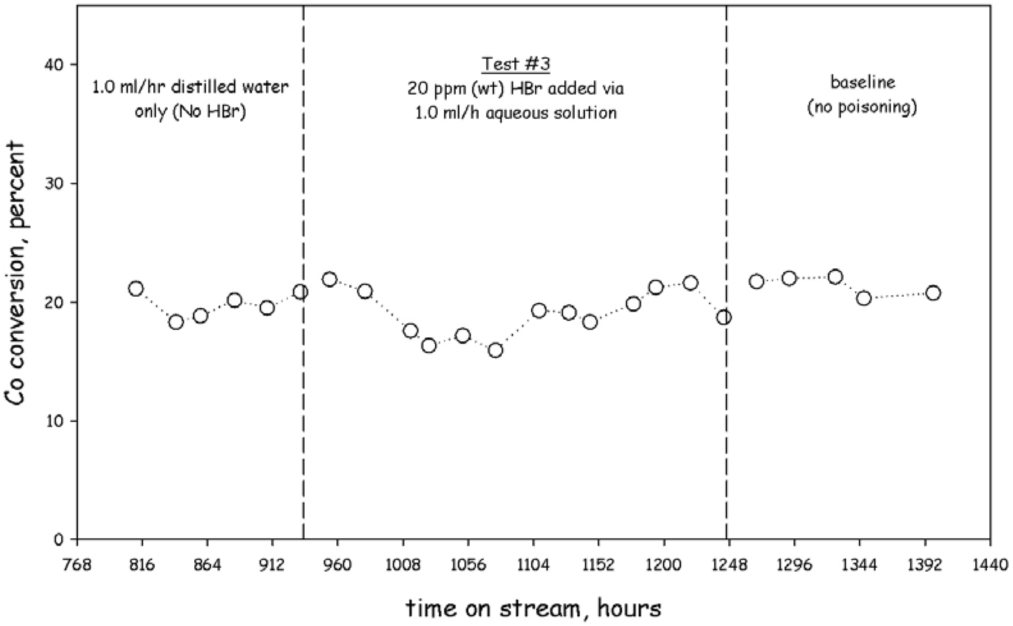


Figure 87: Reactor #23, Run #AWP050. CO conversion versus time on-stream. HBr test #3 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.8 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

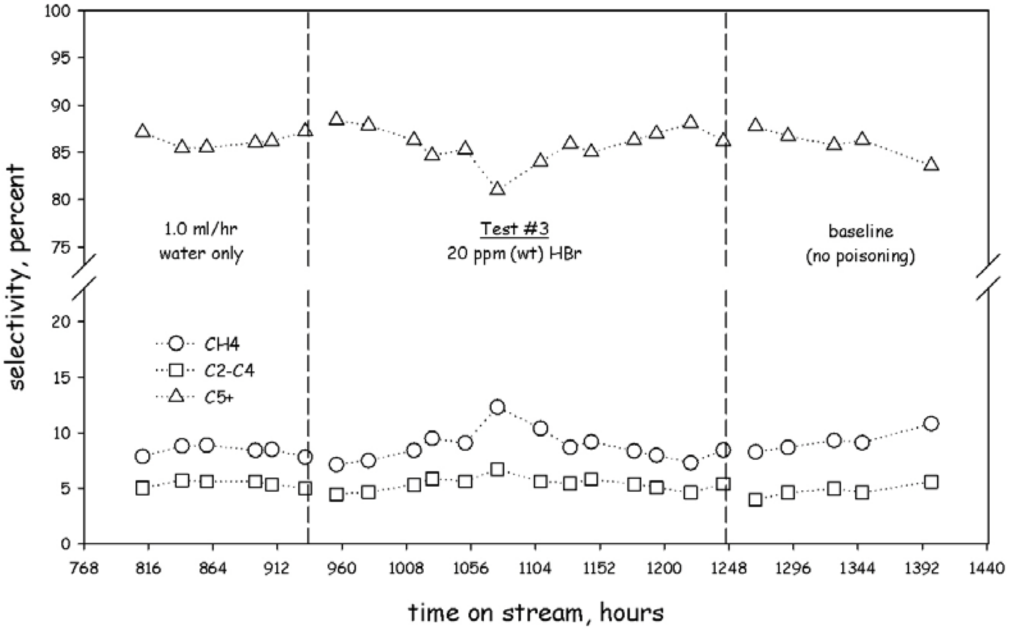


Figure 88: Reactor #23, Run #AWP050. Selectivity versus time on-stream. HBr test #3 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.8 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

B.2.4.4 H_2S or NH_3

H_2S Trial #1

Run #AWP049 was carried out in Reactor #R20 between 29 Sep-12 Nov 2010. This run used a cylinder containing 19.6 ppm H_2S/N_2 to add 5.4 ppm (wt) [2.0 ppm (vol)] to the total feed (H_2 + CO + N_2). A baseline was established with 10% (vol) nitrogen added to the syngas. The N_2 was then replaced by the same amount of the H_2S/N_2 mixture. The test was repeated later in the run with all of the feed rates reduced by 50%. The run was conducted with the assistance of Jessica Geddes and Christina Zhang, two students from Dunbar High School, who asked to use some of the data gathered as part of a national science fair entry.

Startup

310 grams of Polywax 3000 was added to reactor R20 on 27 September 2010 and heated to 140^{o}C under flowing nitrogen overnight. On the following day, 8.4 grams of reduced GJ456 (25% Co, 0.5% Pt, 150 m^2/g alumina) was injected. The reactor was then heated to 230^{o}C under ~20 slph flowing hydrogen and held at these conditions overnight. On the morning of 29 September, the reactor was first cooled to 180^{o}C and then syngas (H_2/CO = 2) at a SV of 6 slph/g replaced the pure hydrogen feed. The reactor was then slowly pressurized to 280 psig and heated to 220^{o}C, reaching these synthesis conditions by noon.

Operation

The first gas sample showed a conversion rate of about 50%, or ~8 slph of CO being converted to hydrocarbons. As expected, the conversion fell to about half of this value by the beginning of the second day, and so the SV was reduced to 3 slph/g after 30 hours on stream (Figure 89). The conversion began to level off at about 37% after four days (Figure 89). At this point 2.794 slph of pure nitrogen was added to the syngas, enough that the syngas now contained 10.0% N_2. The conversion fell slowly for about four more days and then leveled off to show a steady conversion of about 28% for an additional four days to yield a reasonable baseline conversion before adding H_2S (Figure 90). The selectivity for methane seemed a bit higher than normal, averaging 11-12% during this baseline (Figure 91).

After 285 hours on stream the pure N_2 feed was replaced by the same amount of a 19.6 ppm H_2S in nitrogen mixture to yield an H_2S concentration in the total feed of 5 ppm (wt), or 2 ppm (vol). The conversion fell sharply during the first 24 hours of H_2S addition and then began to decline much more slowly (Figure 90).

After 577 total hours on stream, and with the CO conversion at only about 10%, the H_2S/N_2 feed was replaced with the same amount of pure nitrogen. Holding at these conditions for 125 hours (577-702 hours on stream), a steady CO conversion averaging 9.8% was observed (Figure 76), with methane selectivity averaging 22.4% (Figure 91).

At 702 hours, the SV was reduced from 3 to 1.5 slph/g, with the pure N_2 feed proportionally reduced. The CO conversion doubled to 20%, leaving the CO > HC rate and methane selectivity unchanged (Figure 92).

After holding at these conditions for 137 hours, the H_2S/N_2 feed again replaced the pure N_2 at 839 total hours on stream, with the H_2S/N_2 also halved to maintain 5 ppm (wt) [2 ppm (vol)] H_2S in the total syngas feed. Over the next 143 hours, the CO conversion dropped only slightly (Figure 92), and the selectivity for methane remained at 22% (Figure 93).

To see of this was the lowest possible conversion (possibly due to an error in the assumed CO feed rate, for instance), the 19.6 ppm H_2S/N_2 feed was replaced after 982 total hours with a 1% H_2S/N_2 mixture. The feed rate of this mixture was only 0.382 slph, which still resulted in a very high 272 ppm H_2S in the total syngas feed. The conversion dropped very quickly to near zero, with essentially all of the small amount of hydrocarbon product that was formed being methane.

Calculations

Based on the results of the chemisorption test, the 8.4 gram catalyst load contained 1.917×10^{-3} moles of active cobalt. Extrapolating back to time zero from the first two samples collected (at 4.25 and 11.5 hours) yields an estimated initial conversion of 8.459 slph of CO>HC, or 0.37740 mol/hr. Dividing this by the amount of active cobalt present gives 196.881 mol/hr CO>HC per mole of active cobalt.

By the end of the first baseline period (164-284 hours), the conversion had decreased to 2.273 slph CO>HC, or 0.101410 mol/hr. Assuming that the rate per mole of active cobalt had remained constant, this means that the amount of active cobalt remaining at this point was (0.101410 mol/hr) / (196.881 mol/hr CO>HC per mole active cobalt), or 515.081 x 10^{-6} moles, or about 27% of the initial amount.

Extending the baseline straight line fit until the end of the first H_2S test at 576 hours, the expected conversion with no poisoning would have been 1.753 slph CO>HC, or 78.222 x 10^{-3} mol/hr. Dividing by 196.881 indicates that 397.31 x 10^{-6} moles of active cobalt would have been expected to remain.

But due to the poisoning effect of the H_2S, the actual conversion at the end of the first test was only 0.834 slph CO>HC, indicating that only 188.99 x 10^{-6} moles of active cobalt remained. So the amount of cobalt that was poisoned by H_2S in this first test was (397.31 x 10^{-6}) – (188.99 x 10^{-6}), or 202.32 x 10^{-6} moles.

The total syngas feed (H_2 + CO + N_2) for the first test was 27.951 slph, or 1.24703 mol/hr, and the H_2S concentration was 1.959 ppm (vol), so the H_2S feed rate was 2.4429 x 10^{-6} mol/hr. Multiplying this by the 117 hours of the test, the total amount of H_2S that was added to the reactor during this first test was 285.823 x 10^{-6} moles.

(202.32 x 10^{-6} moles cobalt poisoned) / (285.823 x 10^{-6} moles H_2S fed) =

0.708 moles of cobalt were poisoned per mole of H_2S fed (entire 117 hour test)

But this is only about 1/10 of the value obtained during some of the other H_2S tests. The problem is evident from the shape of the poisoning curve. Rather than showing a straight line loss of conversion during the entire test, a very steep drop in conversion was seen for the first 24 hours of the test (284-308 hours on stream). The conversion curve then flattened out and the slope approximated that of the baseline after about 56 hours.

So considering only this first 24 hours of the test, the amount of conversion predicted by the straight line of the baseline at 308 hours would be 2.2096 slph CO>HC if there had been no poisoning. However, the actual rate was 1.553 slph CO>HC, so 0.6566 slph of conversion was lost due to the poisoning effect of the H_2S, equivalent to a loss of 148.791 x 10^{-6} moles of active cobalt.

The H_2S feed rate of 2.4429 x 10^{-6} mol/hr, multiplied by 24 hours = 58.630 x 10^{-6} moles, so the loss rate per mole of H_2S fed is

(148.791 x 10^{-6} moles cobalt) / (58.630 x 10^{-6} moles H_2S) =

2.538 moles of cobalt poisoned per mole of H_2S fed (for first 24 hours of the test)

And if we consider only the first 56 hours of the test (284-340 hours), the amount of conversion at 340 hours on stream predicted by the straight line fit of the baseline would have been 2.155 slph CO>HC. But the actual value at this time was 1.327 slph, so a total of (2.155 – 1.327), or 0.828 slph of conversion was lost due to the poisoning effect of the H_2S that was added. This is 0.03694 mol/hr, which after dividing by 196.881 indicates that 187.63 x 10^{-6} moles of active cobalt have been poisoned.

The total amount of H_2S fed in this time period was (2.4429 x 10^{-6} mol/hr) x (56 hours), or 136.804 x 10^{-6} moles. So the poisoning rate per mole of H_2S fed is

(187.63 x 10^{-6} moles cobalt) / (136.804 x 10^{-6} moles H_2S) =

1.372 moles of cobalt poisoned per mole of H_2S fed (for first 56 hours of the test)

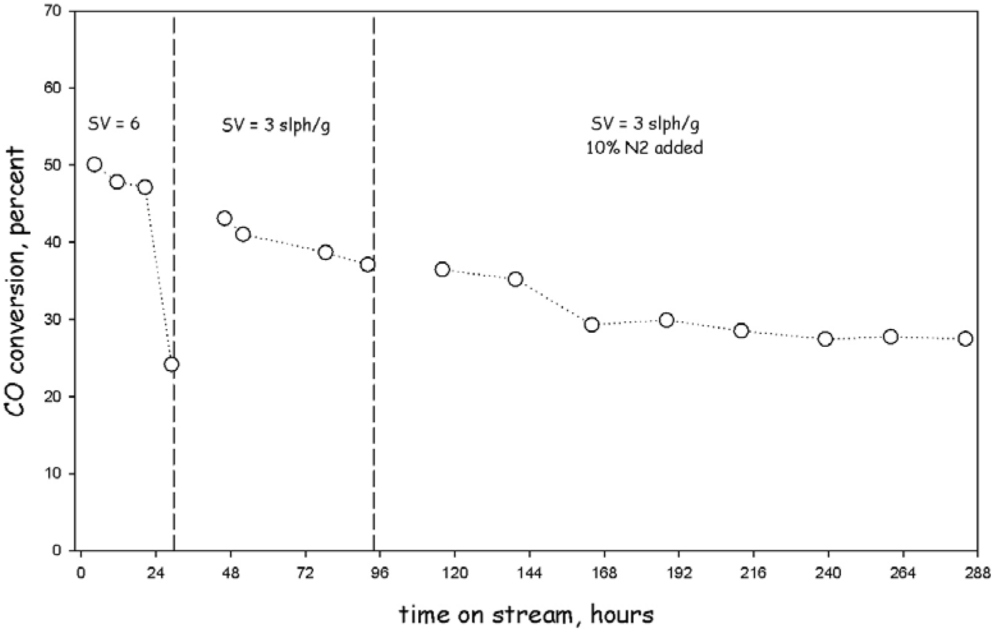


Figure 89: Reactor #20, Run #AWP049. CO conversion versus time on-stream. Startup using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 6 and 3 slph/g, H_2/CO = 2.0, T = 220^{o}C, and P = 280 psig.

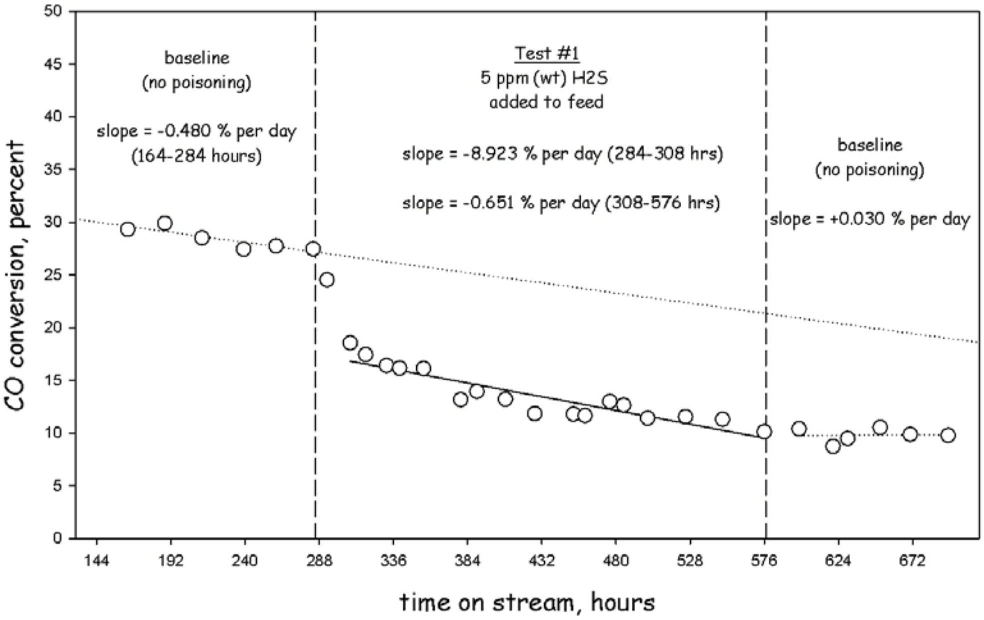


Figure 90: Reactor #20, Run #AWP049. CO conversion versus time on-stream. H_2S Test#1 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 3 slph/g, H_2/CO = 2.0, T = 220^{o}C, and P = 280 psig.

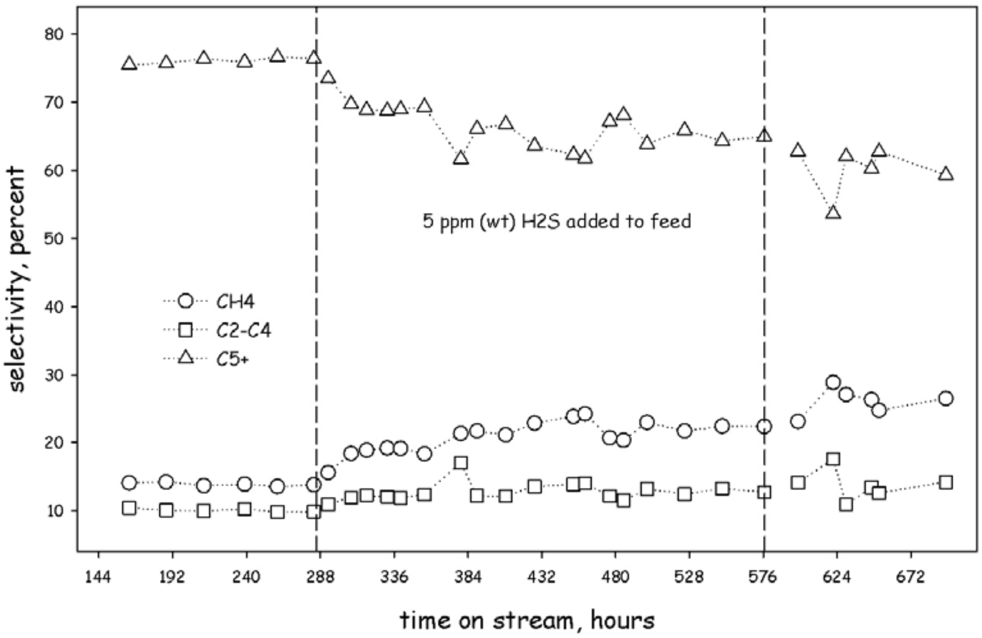


Figure 91: Reactor #20, Run #AWP049. Selectivity versus time on-stream. H_2S Test#1 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 3 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

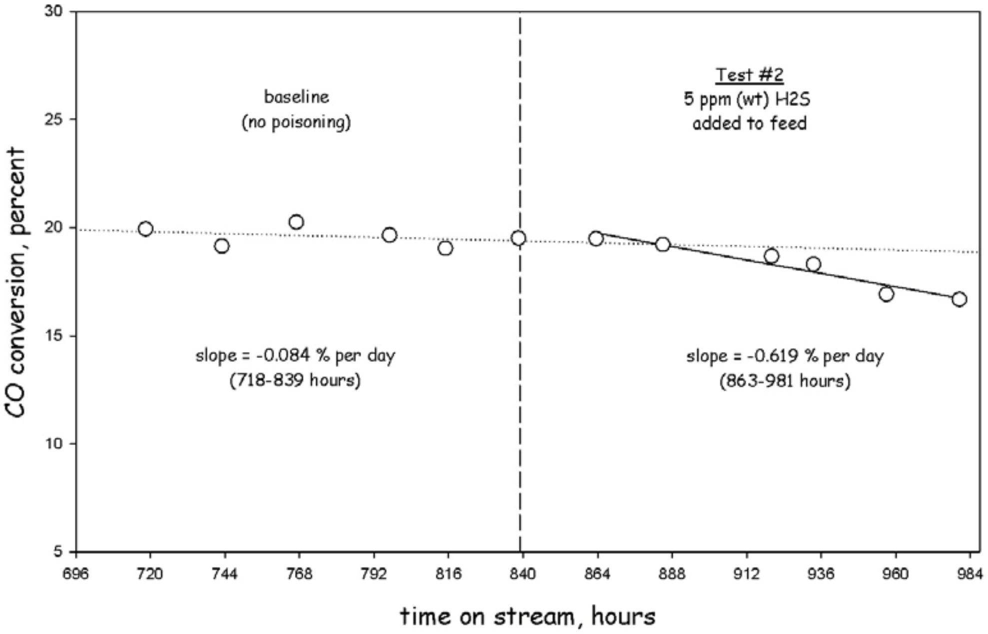


Figure 92: Reactor #20, Run #AWP049. CO conversion versus time on-stream. H_2S Test#2 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.5 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

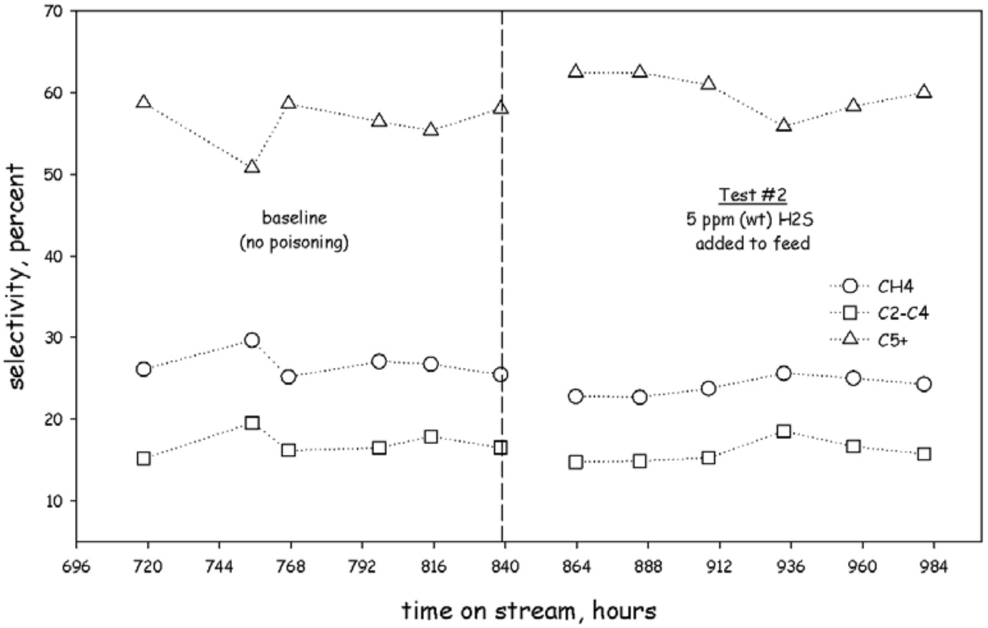


Figure 93: Reactor #20, Run #AWP049. Selectivity versus time on-stream. H_2S Test#2 using 8.4 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 1.5 slph/g, H_2/CO = 2.0, T = 220^{o}C, and P = 280 psig.

H_2S Trial #2

The second H_2S run, RAM080, was carried out using Reactor #20 during the period 13 Aug - 26 Sep, 2011. This run tested H_2S at concentrations of 257 ppb, 494 ppb, and 1.08 ppm (all by volume or mole). Instead of the 16-20 hours used in the earlier runs, the catalyst charge used for this run was reduced for 36 hours at 350^{o}C in a 25% H_2/He mixture. Starting with an SV of 6 slph/g, and the usual 220^{o}C and 280 psig, the first sample was not collected until almost 24 hours on stream. It showed a CO conversion of 35%, or about 6 slph of CO>HC, which is typical for this catalyst after one day of operation (Figure 94).

After four days, the feed rate was reduced to 4 slph/g, and the CO conversion immediately began to show a flat line at about 38% conversion (4.3 slph CO>HC) for six days, and this was used as the baseline for the first test. A straight line linear regression fit indicated an average loss rate for the CO conversion of 0.024% per day during this baseline period (Figure 94).

For the first poisoning test, a gas mixture containing 19.1 ppm (vol) H_2S/H_2 was used to add 257 ppb H_2S to the syngas (Figure 95). The pure H_2 feed was reduced by the same amount so that the total feed rate and the H_2/CO ratio remained the same.

The first gas sample was taken after about 3.5 hours during this first poisoning test and it showed that the conversion had actually increased by about 5%. By the end of the first day, the conversion had returned to the baseline value and then continued to fall rapidly for the 113 hours of the test period. A total of eight samples were taken during this test, showing a steady decrease in conversion that averaged almost 3.5% per day (Figure 95) and a deleterious impact on selectivities (Figure 96).

After a two-day return to baseline conditions, the feed rate was reduced to 3 slph/g after 406 hours on stream. The reactor was held at these conditions for a week to establish a new baseline. The CO conversion fell by an average of 1.039% per day during this time (Figure 97).

The same H_2S/H_2 mixture was again added to the feed, with the amount increased to yield a concentration of 494 ppb (vol) H_2S. The twelve samples that were taken during the 194 hours of this second test (574-768 hours) showed an average loss of 1.138%, scarcely more than the rate seen during the baseline (Figure 97), although a somewhat greater impact was perhaps observed on product selectivities (Figure 98).

The H_2S concentration was again increased, this time to 1.08 ppm. This third test ran for 170 hours (768-938 hrs) and showed an even lower poisoning rate of less than 0.6% per day. As a final check, the H_2S feed was discontinued while the reactor ran for an additional five days (938-1056 hours) (Figures 97 and 98). The loss in CO conversion averaged 0.332% per day, but by this time the overall conversion was only about 14% (~1.2 slph CO>HC), so the run was terminated.

Calculations

This run had a catalyst charge of 8.6 grams, so with 228.2 x 10-6 moles of active cobalt per gram of catalyst, the starting amount of active cobalt was 1.963 x 10^{-3} moles.

Normal routine has been to take the first gas sample as soon as a sufficient number of gas turnovers in the reactor and traps have occurred to yield a sample that's representative of conditions within the reactor (typically 4-5 hours). A straight line can usually be drawn through the conversion values of the first two or three samples (all within the first day of operation) and extended back to time zero to estimate the initial conversion. But for this run, the first sample was taken at 23.5 hours, and the second sample was at 44.5 hours, missing the high conversions usually seen in the first few hours. Drawing a straight line through these two points and extrapolating it back to the first moments of the run produces a low estimate of the initial conversion of 150 mol/hr of CO>HC per mole of active cobalt.

For the other three runs of this series that were started with the same SV of 6 slph/g, the estimated initial conversions were 197, 223, and 263, with an average of 227.62, and so I've used this average value for these calculations.

At 240 hours on stream (the end of the first baseline), 4.345 standard liters (0.19385 moles) of CO was being converted to hydrocarbons per hour. Using the estimate of 227.62 moles/hr CO>HC per gram of active cobalt, then there were (0.19385 / 227.62), or 851.65 x 10^{-6} moles of active cobalt at this point, or about 43% of the starting charge. This looks reasonable, as it's common for this catalyst to lose about half of its initial activity in the first few days of the run.

A sample taken 3.5 hours after the start of the first test indicated that the CO conversion had unexpectedly increased, but even this point falls on the linear regression straight line fit of all of the samples taken during the test.

After 117 hours of H_2S addition, the CO>HC rate was 3.022 slph, or 0.13483 mol/hr. Dividing by 227.62 indicates that 592.33 x 10^{-6} moles of active cobalt remained at the end of the test. Since the baseline was essentially flat, the difference between the starting and ending values of 259.32 x 10^{-6} moles of cobalt is the amount lost due to poisoning.

The total syngas feed for this test was 1.15107 mol/hr, and the H_2S concentration was 257 ppb, so the H_2S feed was 0.29582 x 10^{-6} mol/hr. Multiplied by the 117 hours of the test, the total amount of H_2S fed was 34.6114 x 10^{-6} moles.

(259.32 x 10^{-6} moles of cobalt lost) / (34.6114 x 10^{-6} moles of H_2S) =

7.492 moles cobalt deactivated per mole of H_2S

For the two tests conducted later during this run the poisoning rate appeared to either equal or was less than the baseline loss rate, so any poisoning effect from H_2S could not be discerned.

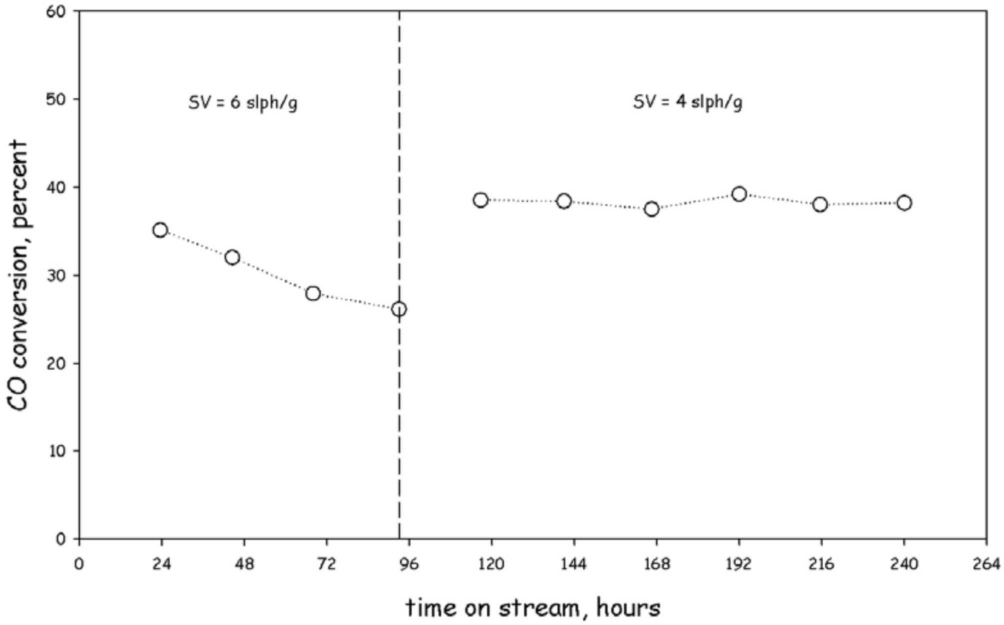


Figure 94: Reactor #20, Run #RAM080. CO conversion versus time on-stream. Startup using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 6 and 4 slph/g, H_2/CO = 2.0, T = 220^{o}C, and P = 280 psig.

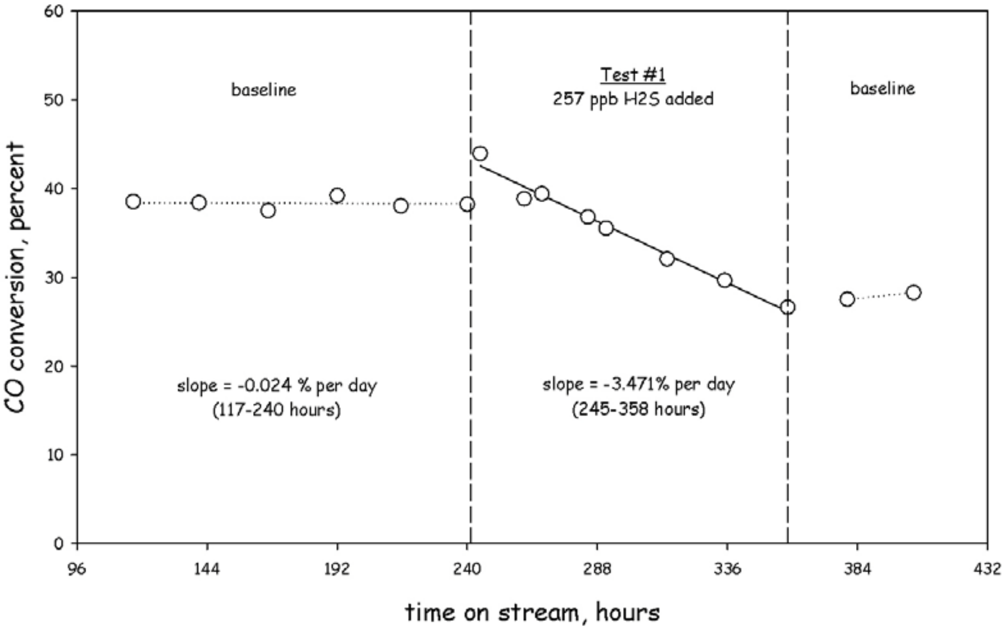


Figure 95: Reactor #20, Run #RAM080. CO conversion versus time on-stream. H_2S test#1 using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 4 slph/g, H_2/CO = 2.0, T = 220^{o}C, and P = 280 psig.

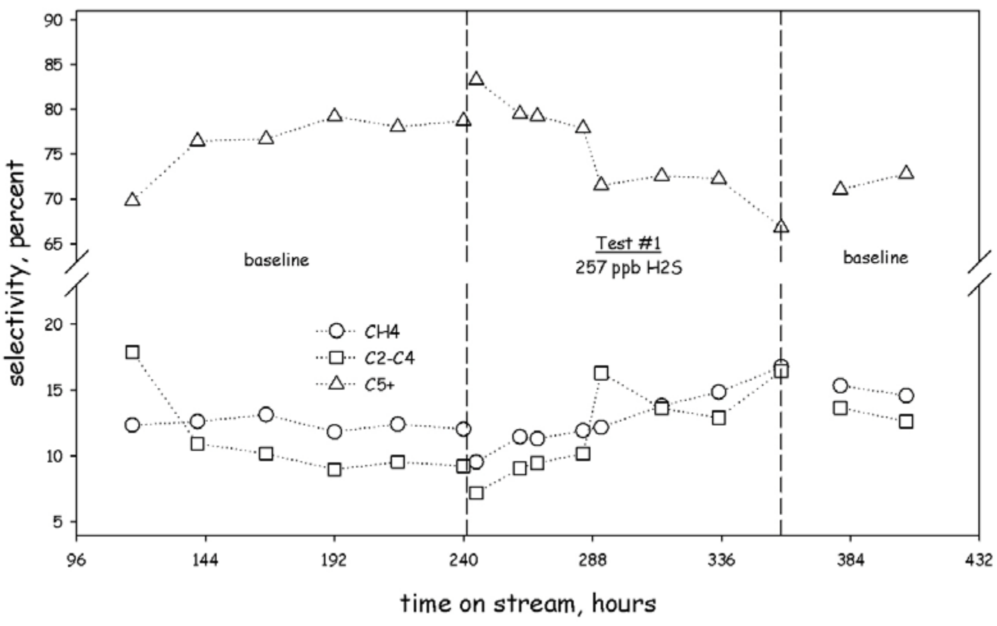


Figure 96: Reactor #20, Run #RAM080. Selectivity versus time on-stream. H_2S test#1 using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 4 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

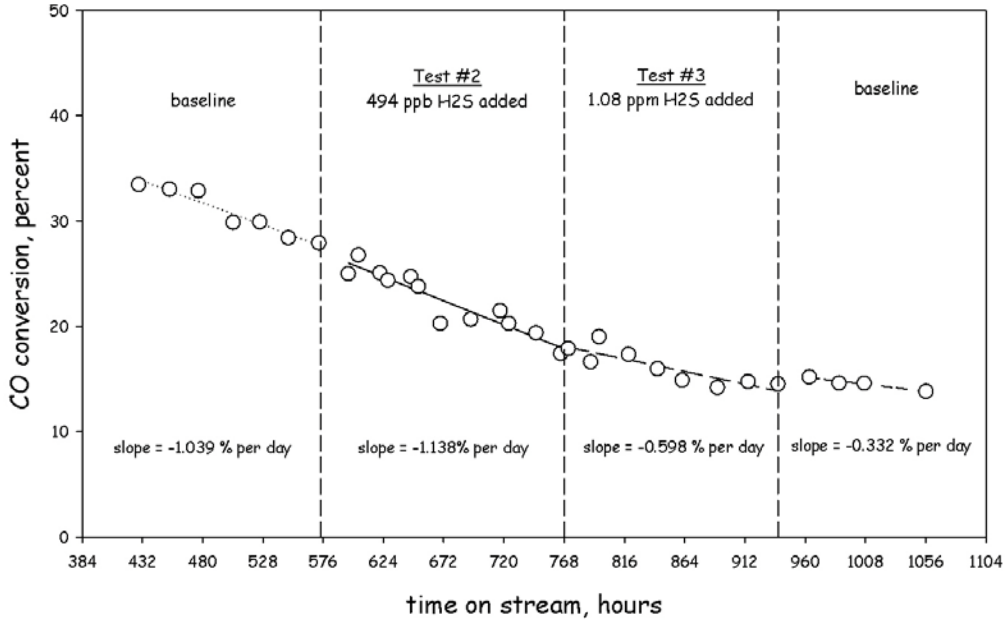


Figure 97: Reactor #20, Run #RAM080. CO conversion versus time on-stream. H_2S tests #2and 3 using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 4 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

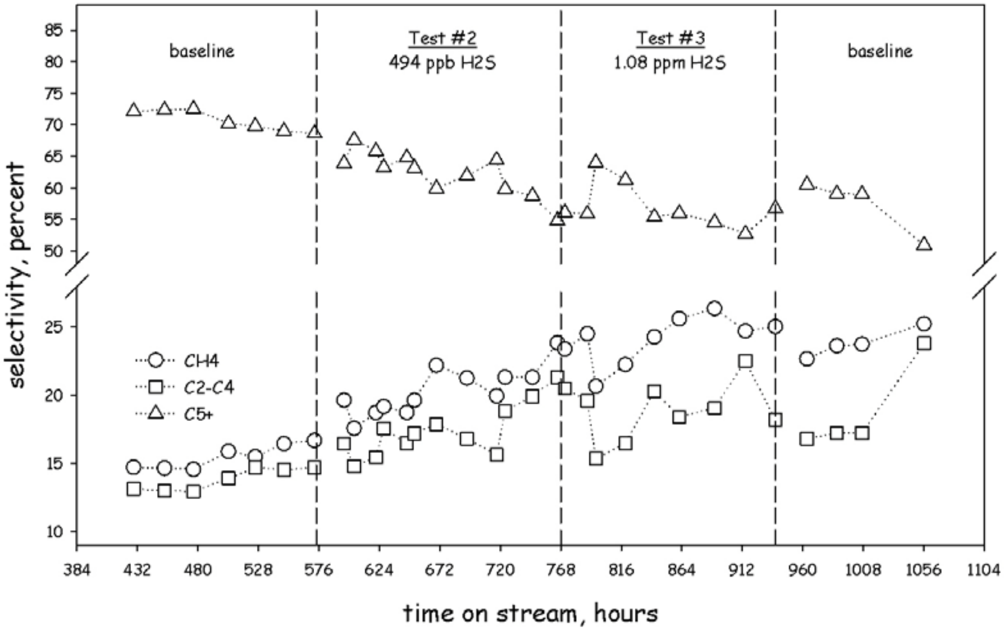


Figure 98: Reactor #20, Run #RAM080. Selectivity versus time on-stream. H_2S tests #2and 3 using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 4 slph/g, H_2/CO = 2.0, T = 220^{o}C, and P = 280 psig.

NH_3 addition

The effects of the addition of 1, 10, and 100 ppmw of ammonia (injected as 1 mL/hr NH_4OH) on the performance of a platinum promoted cobalt alumina Fischer-Tropsch synthesis catalyst were evaluated using a CSTR. Each concentration was tested for around 100-120 h. The effect of ammonia on CO conversion is shown in Figures 99, 100, and 102. Initially, the reaction was started with 6 slph/g catalyst; at this condition CO conversion was found to be around 25%. After 100 h on-stream the synthesis gas flow was decreased to 3 slph/g catalyst, and CO conversion was found to be around 38%. A small deactivation was observed with time at a rate of 0.5% per day. After 335 h on stream, 1 ppmw NH_4OH solution feeding to the reactor was started. In the NH_4OH test run, the catalyst displayed a similar slight deactivation (0.5% day) observed when feeding 1 ppmw NH_4OH. This indicates that there was no significant impact on CO conversion with 1 ppmw NH_4OH. After 460 h on-stream, NH_4OH pumping was stopped and a new baseline re-established during 476-645 h. During this new baseline condition, a slight decrease in CO conversion was observed with a similar deactivation rate. Introduction of 10 ppmw ammonia to the synthesis gas, a similar trend was observed. The catalyst also displayed a similar trend in the presence of 100 ppmw of ammonia. The effect of ammonia on methane selectivity and C_{5+} selectivity is shown in Figures 101 and 103. The selectivity (C_1 and C_{5+}) exhibited little change with or without addition of the ammonia to the syngas.

Calculations

Run #RAM079 was performed using Reactor #19 during the period 11 Aug – 03 Oct, 2011. This run tested NH_3 at three different concentrations by injecting 1 ml/hr of aqueous solutions of NH_4OH.

10.25g of GJ456 (sieved to 63 x 100 microns) was reduced in a flowing 25% H_2/He mixture. Note that the standard reduction scheme calls for 20-24 hours, but for this run the reduction time was extended to 36 hours. After allowing the reduced catalyst to cool in flowing H_2/He, 8.6g of the reduced catalyst was added to 300g of Polywax 3000 in R19, which had been stirring overnight at 140^{o}C under flowing N_2. After switching to 20 slph of H_2, the loaded reactor was then heated to 230^{o}C and held for 24 hours as a final reduction step before transitioning to FT synthesis.

FT synthesis conditions were reached at 14:00 on 11 August 2011. The initial feed rate of 6 slph/g was reduced to 3 slph/g at 92.5 hours (immediately after sample 004). Since the NH_3 was to be added by the injection of 1.0 ml/hr of an aqueous solution, a baseline while injecting water was desired. After demonstrating stable conversion for four days with no water injection, 1.0 ml/hr of de-ionized water was added to the reactor for a further six days (194-333 hrs) prior to the first test (Figure 99).

Stable conversion averaging 33.3% was seen for the first three days of water injection, but then the conversion increased by almost 6% for no apparent reason, showing a stable conversion averaging 39.1% for 292-332 hours. The four samples taken during this later 40 hour period were chosen as the baseline.

Note that for this particular run, 1 ppm (wt) was defined in terms of NH_4OH in the total weight of (H_2 + CO) only, while in the other tests it was defined in terms of the weight of the aqueous solution as a part of the total feed. This was due to differences in operator; the important point is that to account for how much NH_3 is being fed to the reactor.

For all three of the tests conducted during this run, the H_2 feed rate was 17.149 slph and the CO feed rate was 8.618 slph, for a syngas SV of 2.996 slph/g, and with a H_2/CO ratio of 1.993.

Assuming an ideal gas, the H_2 feed translates to (17.149 / 22.414), or 0.7651 moles/hr. With a FW of 2.016 g/mole, the H_2 feed was therefore (0.7651)(2.018), or 1.5424 g/hr. Similarly, the CO feed rate of 8.618 slph = 0.3845 mol/hr = 10.7698 g/hr, for a total of (H_2 + CO) rate of 12.3122 g/hr.

For the first test, 1 ppm (wt) of NH_4OH, or 12.3122×10^{-6} g/hr was fed to the reactor. Multiplying this by the ratio of the formula weights of NH_3 and NH_4OH (17.03 / 35.05, or 0.4860) gives an NH_3 feed rate of 5.984×10^{-6} g/hr.

And finally, converting to a mole or volume basis: $(5.984 \times 10^{-6}) / 17.03 = 0.3514 \times 10^{-6}$ moles/hr of NH_3 fed to the reactor during the first test (Figures 100 and 101).

(H_2 + CO) = (0.7651 + 0.3845) = 1.1496 mol/hr, so the NH_3 concentration in the (H_2 +CO) feed is: (0.3514×10^{-6}) / 1.1496 = 0.3056×10^{-6}, or 0.306 ppm (vol).

The concentration was increased tenfold for the second test, to 10 ppm (wt) NH_4OH in the total (H_2 + CO) feed, so the NH_3 feed rate was 3.514×10^{-6} moles/hr, and the concentration in mole or volume ratio was 3.06 ppm (Figures 102 and 103).

The concentration was increased to 100 ppm (wt) NH_4OH for the third test, so the NH_3 feed rate was 35.14×10^{-6} mol/hr, producing a mole or volume-based concentration in the (H_2 + CO) feed of 30.6 ppm (Figures 103 and 104).

Recall that the freshly reduced GJ456 catalyst has 228.2×10^{-6} moles of active cobalt on the surface per gram of catalyst, according to the hydrogen chemisorption/pulse reoxidation experiment. The total catalyst charge for this run was 8.6 grams, so there were 1.9625×10^{-3} moles of exposed cobalt at the start of the run.

Because of the volume of gas holdup in the reactor and its traps, it is not possible to measure the conversion as soon as we attain FT synthesis conditions. But using the first two samples (at 21 and 47 hours) and assuming a straight line extrapolated back to the beginning of the run yields an estimate of 0.5167 moles/hr of CO being converted to hydrocarbons during the first moments of the run.

Dividing this by the 1.9625×10^{-3} moles of active cobalt indicates that 263.3 mole/hr of CO was being converted to hydrocarbons per mole of active cobalt sites. If we assume that this value does not change during the run (and further assuming that the reactor conditions do not change), then the amount of CO>HC at any given moment during the run is directly proportional to the amount of active cobalt remaining in the reactor.

Further, we assume that the pronounced loss of conversion during the first few days of operation is due to some of the active cobalt sites either being oxidized or occluded by rewax. The conversion eventually stabilizes and we can then estimate the amount of stable, active cobalt sites.

For this run, an average of 3.348 slph of CO>HC was noted from samples 13-16 (292–332 hours) during the baseline prior to the first test. Dividing by the 22.414 std. liters / mole of an ideal gas gives a value of 0.1494 moles/hr, or only about 29% of the estimated rate for the first moments of the run.

Dividing this by the estimate of 263.3 mole/hr CO>HC per mole of cobalt indicates that there are 0.5673 x 10^{-3} moles of active cobalt in the reactor immediately prior to the first test.
In the first 50 hours (333-383 hrs) of this first test period, the CO conversion quickly falls, but then levels off at about 28.6% (with 0.1154 mol/hr CO>HC) and remains there for the remaining three days (383-459 hrs) of the test period.

(0.3514 x 10^{-6} moles/hr of NH_3 feed)(50 hrs) = 17.57 x 10^{-3} moles of NH_3 fed

(0.1154 mol/hr CO>HC

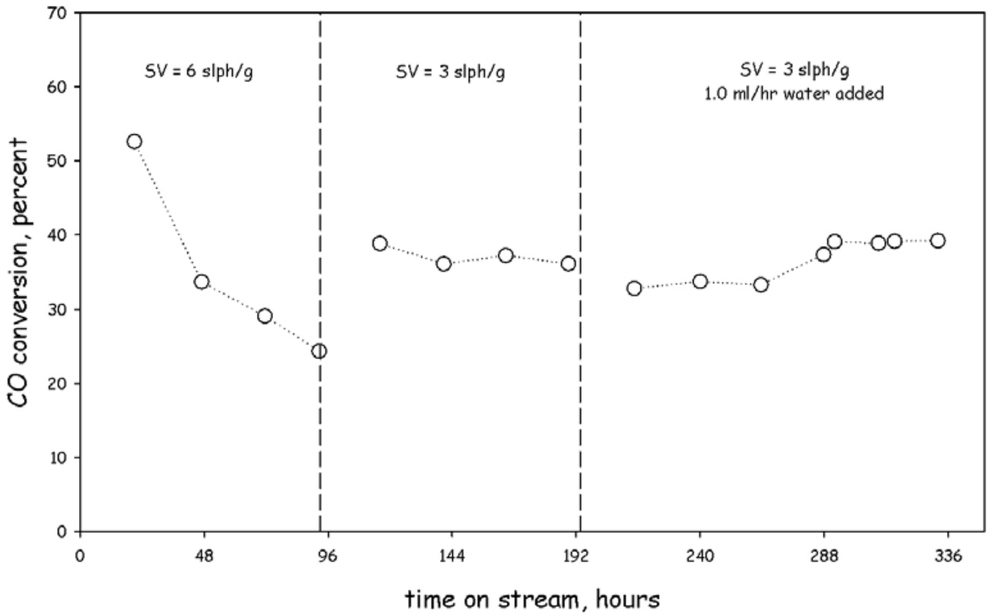


Figure 99: Reactor #19, Run #RAM079. CO conversion versus time on-stream. Startup using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 6 and 3 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

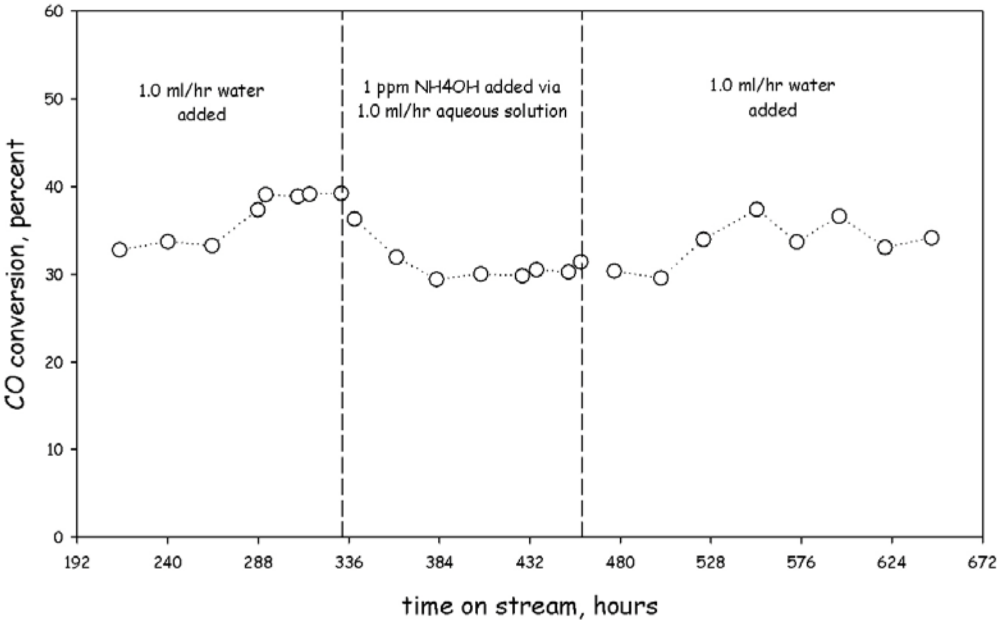


Figure 100: Reactor #19, Run #RAM079. CO conversion versus time on-stream. NH_4OH test#1 using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 3 slph/g, H_2/CO = 2.0, T = 220°C, and P = 280 psig.

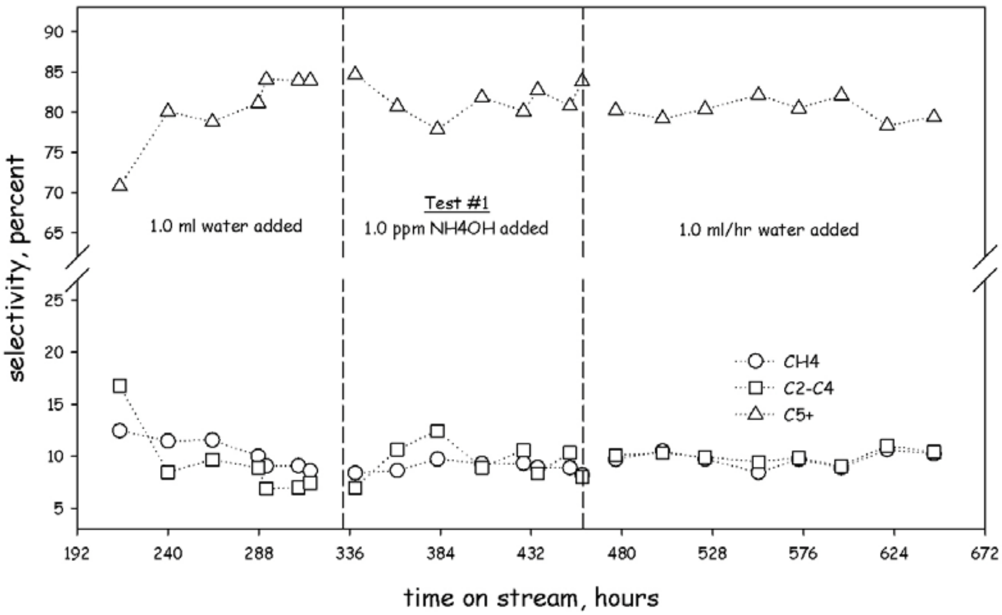


Figure 101: Reactor #19, Run #RAM079. Selectivity versus time on-stream. NH_4OH test#1 using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 3 slph/g, $H_2/CO = 2.0$, T = 220°C, and P = 280 psig.

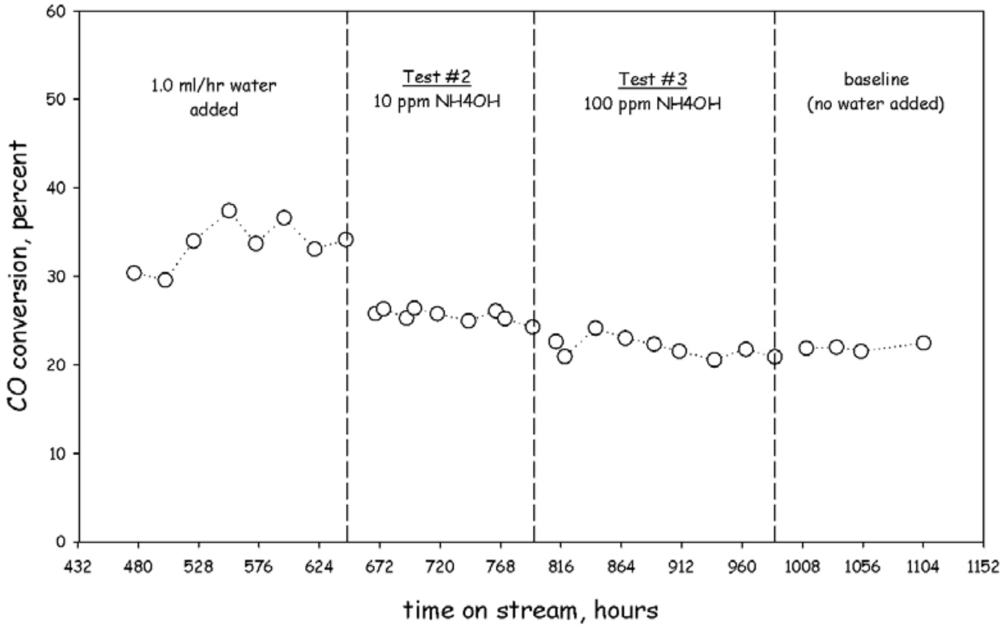


Figure 102: Reactor #19, Run #RAM079. CO conversion versus time on-stream. NH_4OH tests#2 and 3 using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 3 slph/g, $H_2/CO = 2.0$, T = 220°C, and P = 280 psig.

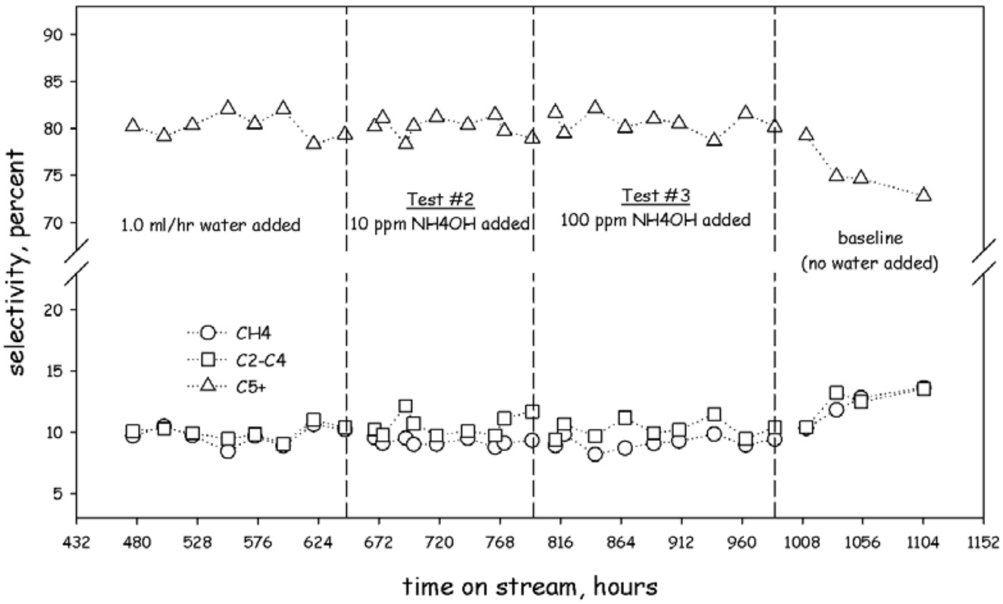


Figure 103: Reactor #19, Run #RAM079. Selectivity versus time on-stream. NH_4OH tests#2 and 3 using 8.6 g of catalyst GJ456 (0.5%Pt-25%Co/Al_2O_3) at SV = 3 slph/g, H_2/CO = 2.0, T = 220^oC, and P = 280 psig.

Conclusions

With the Sud-Chemie, Inc. high temperature shift Fe-Cr catalyst, little deactivation was observed with up to 200 ppb KCl, NaCl, up to 100 ppb $KHCO_3$, up to 1 ppm H_2S, and up to 5 ppm NH_3. With a combination of NH_3 and H_2S, little deactivation was observed with up to 0.6 ppm NH_3 in combination with up to 6 ppm H_2S. The only run in which measurable deactivation was observed was with 100 ppb $NaHCO_3$.

The impacts of each poison during Fischer-Tropsch synthesis testing are summarized in Tables 10 and 11. Note that the degree of poisoning depends on the level of poison added. Generally speaking, we did not observe significant impacts on CO conversion rates at low levels of added alkali halides, alkali bicarbonates, or ammonia for either catalyst (i.e., iron or cobalt). Acid halides were found to impact the iron based catalyst to a measurable degree and the impact was greater at higher concentration levels, while H_2S exhibited a major impact on both iron and cobalt FT catalysts at ppm levels, but had varying impacts at lower levels.

Table 10: Summary of the sensitivity of CAER high alpha Fe (100Fe/5.1SiO$_2$/2Cu/3K) to various poisons$^{(a)}$

Poison	Level of poison	Impact		
	ppmw	Low	Moderate	High
NaCl	0.1- 100	Y		
KCl	0.1-20	Y		
NaHCO$_3$	0.1-40	Y		
KHCO$_3$	0.1-40	Y		
HCl	0.1-0.75	Y		
	0.75-1.5		Y	
	20-40			Y
HBr	0.1-0.6	Y		
	0.6-5.0		Y	
	20-40			Y
HF	0.1	Y		
	20			Y
NH$_3$	0.1-200	Y		
	800			Y
H$_2$S$^{(b)}$	0.3	Y		
	1.0			Y
HCN$^{(b)}$	1.0	Y		

(a) Reaction conditions: 260-270 ^{o}C, 175 psig, H$_2$/CO = 0.67-0.77, 10 Nl/g-cat/h

(b) in ppmv

Table 11: Summary of the sensitivity of CAER cobalt catalyst (0.5%Pt-25%Co/Al_2O_3) to various poisons.

Run #	poisoning agent	maximum concentration tested (wt)	poisoning effect
AWP031	KCl	500 ppm	slight
AWP036	NaCl	50 ppm	slight
AWP042	$KHCO_3$	1000 ppm	none
AWP044	$NaHCO_3$	1000 ppm	slight
AWP046 AWP051	HCl	10 ppm 500 ppm	slight
AWP050	HBr	20 ppm	none
AWP049 RAM080	H_2S	5.4 ppm 2.9 ppm	major
RAM079	NH_4OH	100 ppm	slight

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