Title: First Annual Topical 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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DISCLAIMER* --

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.

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Executive Summary

At the October 16, 2008 project kickoff meeting, UK-CAER was requested to provide the four groups involved in the project with standard 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.

Initially, UK-CAER prepared and tested a 0.5%Pt promoted 25%Co/Al_2O_3 catalyst supported on Sasol 200 m^2/g γ-Al_2O_3. Although the catalyst displayed good activity and stability in a clean baseline test, it was difficult to achieve reproducible baseline tests in subsequent studies. This is likely attributed to the strong interaction of the γ-Al_2O_3 support with the cobalt species. Although the interaction results in a smaller Co metal particle size upon reduction in hydrogen, the extent of reduction is difficult to reproduce. Therefore, UK-CAER obtained and opted to use the lower surface area 150 m^2/g γ-Al_2O_3 support, where we have in the past observed greater reproducibility in catalyst performance, due to the somewhat larger but more robust cluster size that results.

Where possible, UK-CAER carried out preliminary catalyst characterization tests as necessary to achieve the project goals, 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.

UK-CAER completed baseline clean tests for Fischer-Tropsch synthesis on the cobalt and iron FT catalysts previously discussed and constructed continuously stirred tank reactors (CSTRs) for future FT poisoning investigations. Both baseline clean tests, as well as KCl and NaCl poisoning tests, were completed for the Sud-Chemie, Inc. Fe-Cr HTS catalyst. The ratios of syngas utilized for the iron and cobalt catalyst tests were completely different. Since the iron catalysts possess intrinsic water-gas shift activity, both FT and water-gas shift can be carried out in a single reactor. Thus, the H_2/CO ratio of 0.7 – 0.8 was used directly. Cobalt catalysts possess low intrinsic shift activity, thus requiring the need for the upstream Fe-Cr HTS catalyst, which received a H_2/CO ratio of 0.7 – 0.8. To mimic the adjustment in the feed ratio, the cobalt FT catalyst was supplied with a H_2/CO ratio of 2.0. The following topical report provides a summary of the preparation, characterization, and FT and WGS tests carried out to date.

Report Details –

Experimental methods:

Catalyst Preparation

0.5%Pt-25%Co/Al_2O_3: 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^{o}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^{o}C. Prior to calcination, Pt promoter was added (to ~ 0.5% by weight) by aqueous impregnation of tetraammine Pt(II) nitrate. The 200 m^2/g supported Co catalyst (GJ455) was calcined at Sud-Chemie, Inc. in February, 2009. The second batch on the 150 m^2/g support (GJ456) was calcined at Sud-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.

Fe-Si-K-Cu: 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 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 overnight following impregnation. Three separate elemental analyses (Galbraith Laboratories) were carried out on the as prepared catalyst and the amount 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 was calculated using an average of the three analyses as a basis. Further loading of K and Cu was carried out respectively using sequential incipient wetness impregnation 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 Sud-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.

Catalyst procurement:

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

Catalyst characterization:

Elemental Analysis

Inductively coupled plasma (ICP) was used to obtain weight percentages of Pt, Co, Fe, Si, K and Cu in the sample. 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 at a diameter of less than 10 m 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 element analysis. The ICP analysis was conducted at Galbraith Laboratories.

BET Surface Area and 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. 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 analysis was performed at the boiling temperature of liquid nitrogen. Prior to the measurement, the sample was slowly ramped to 433K and evacuated overnight to approximately 6.7 Pa. Pore size distributions (PSD) of a number of supports and catalysts were also quantified by the Barrett, Joyner, Halenda (BJH) desorption model, 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.

Temperature Programmed Reduction (TPR)

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.

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 $80^{o}C$. The sample was held at $80^{o}C$ 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, Cu^0 reoxidized to CuO, and that Au and Ag did not reoxidize. In the case of Cu, the assumption was made that the Cu oxidized first, prior to cobalt oxidation. While the uncorrected dispersions, which represent the combined metals when two are present, are based on the assumption of complete reduction, the corrected dispersions reported include the percentage of reduced metal as follows. A 1:1 ratio of H:Co site was assumed.

%D = (# of cobalt atoms on surface × 100%)/(total # cobalt atoms)

%D = (# of cobalt atoms on surface × 100%)/[(total # cobalt atoms)(fraction reduced)]

Fischer-Tropsch synthesis catalytic testing in the CSTR

Cobalt catalysts: The FTS experiments over cobalt catalysts were conducted in a 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 micron opening) extends below the liquid level of the reactor for withdrawing reactor wax 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 operated at 750 rpm. The reactor slurry temperature was maintained constant (±1°C) by a temperature controller.

Prior to loading into 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 then 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 up to 280 ºC at a rate of 2 ºC /min and held at 280 ºC for 24 hours.

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. 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. Conversions of CO was obtained by gas-chromatography analysis (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.

Iron catalyst: The 100Fe/ 5.1Si/ 3.0K/ 2.0Cu catalyst GJ457 was tested using similar reactor system. However, the catalyst 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 [2]. The temperature was 270^{o}C and the pressure was 175 psig.

Fe-Cr High temperature shift (HTS) Catalyst

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 is used to mimic the outlet of the coal gasification processes. The gas compositions from the Texaco gasification process are 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 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 is controlled by a three stage temperature controller, to monitor the changes in temperature throughout the fixed bed more accurately. The products are passed though a cold trap, cooled to 0^{o}C, set up to condense the liquids (mainly water, and its solutes) out from the

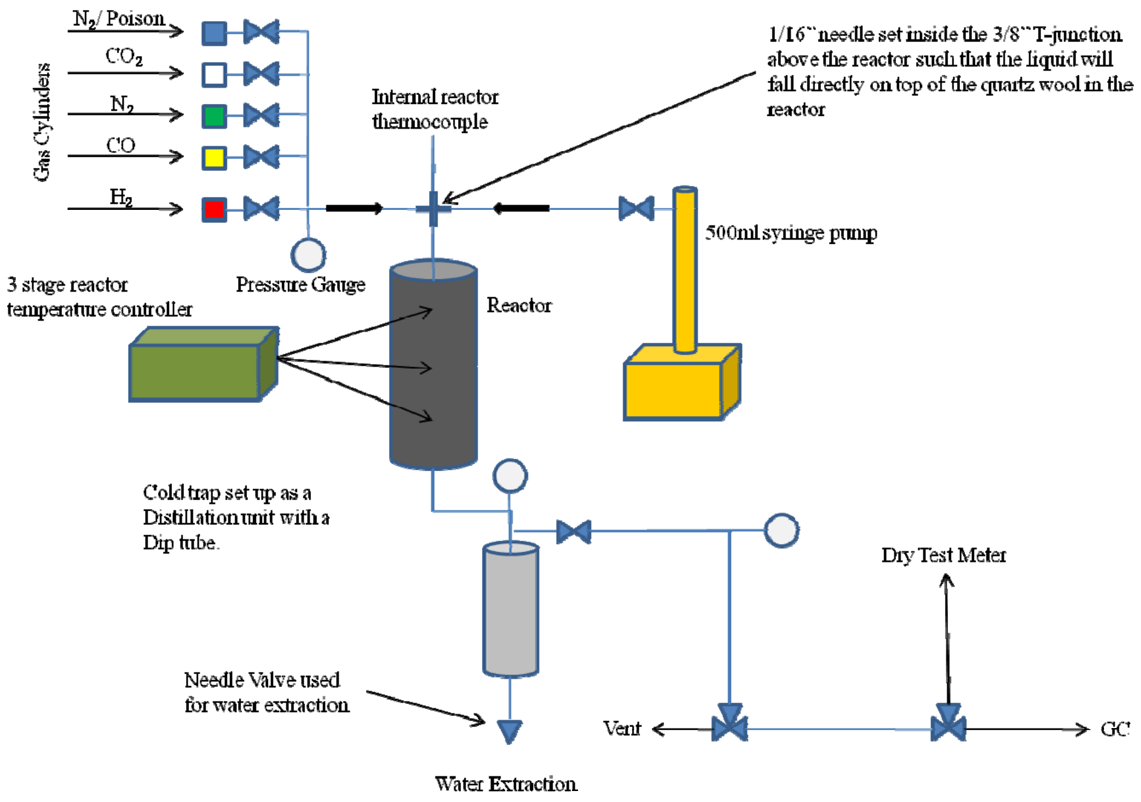


Figure 1: High-temperature shift reaction system.

gas. The liquids are extracted from the cold trap by opening a needle valve. After the gas passes thought the cold trap, an option is set up such that the gas can pass to a vent, or pass through a dry test meter for flow measurements and a GC to analyze the exiting products.

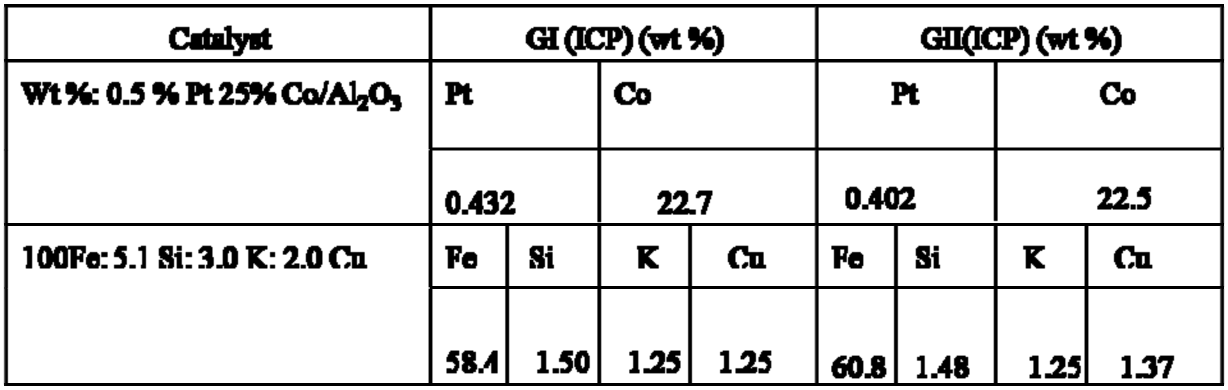
In case of liquid poisoning, the solution is pumped into the top of the reactor by a 500 ml high performance syringe pump, and mixed with the gas before reaching the catalyst. The liquid passes though 1/8” heated stainless steel tubing, before passing into a 1/16” needle with a side port hole. 1/16” needle is 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 The idea is to vaporize the water before it drips into the reactor; however, the water that is not vaporized should evenly spray and be distributed throughout the entire reactor. For poisoning studies, the poison is pre-mixed with the water and pumped into the reactor.

Results and Discussion -

A. Catalyst Characterization

***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

BET Surface Area and BJH Porosity: Below are the results for the BET surface area and BJH porosity measurements over the 200 and 150 m^2/g γ-Al_2O_3 supports and supported 0.5%Pt-25%Co catalysts labeled GJ455 and GJ456, respectively, and the Fe/Si/K/Cu catalyst, GJ457.

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)
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
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

For catalyst GJ455, the BET surface areas were 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 were 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 little above this range, little pore blockage

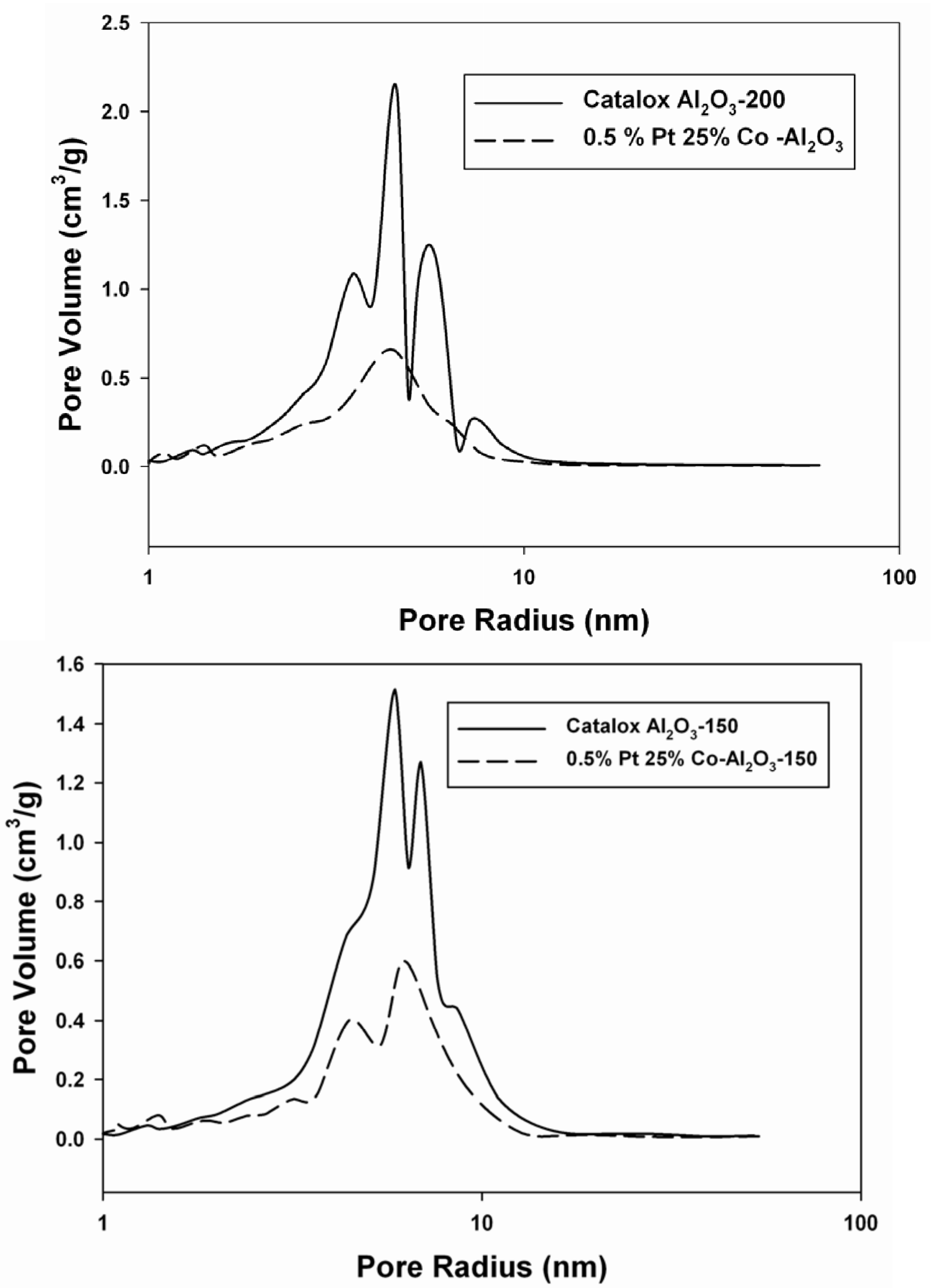


Figure 2: BJH adsorption pore size distributions for (top) γ-Al_2O_3 200 m^2/g support and 0.5%Pt-25%Co/Al_2O_3 GJ455 and (bottom) γ-Al_2O_3 150 m^2/g support and 0.5%Pt-25%Co/Al_2O_3 GJ456.

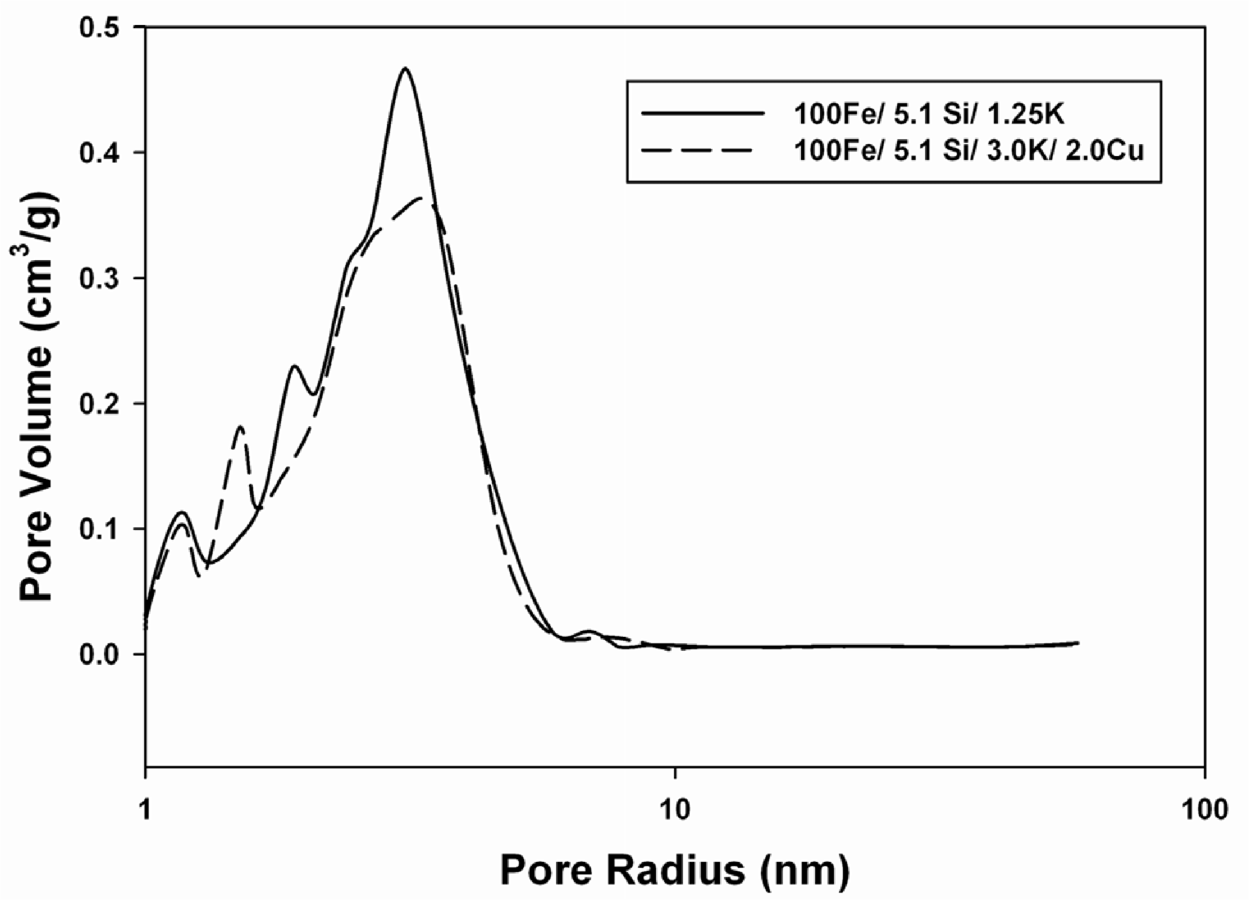


Figure 3: BJH adsorption pore size distributions for catalyst GJ457 before and after loading additional K and adding Cu.

occurred by addition of Co and Pt. 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.

Pore size distributions (PSD) are reported in Figures 2 and 3. It is evident that adding Pt and Co to γ-Al_2O_3 did not significantly impact the PSD (Figure 2). Furthermore, addition of an additional amount of K and adding Cu did not significantly alter the PSD for the Fe-based catalyst (Figure 3).

Temperature programmed reduction: 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 below in Figure 4:

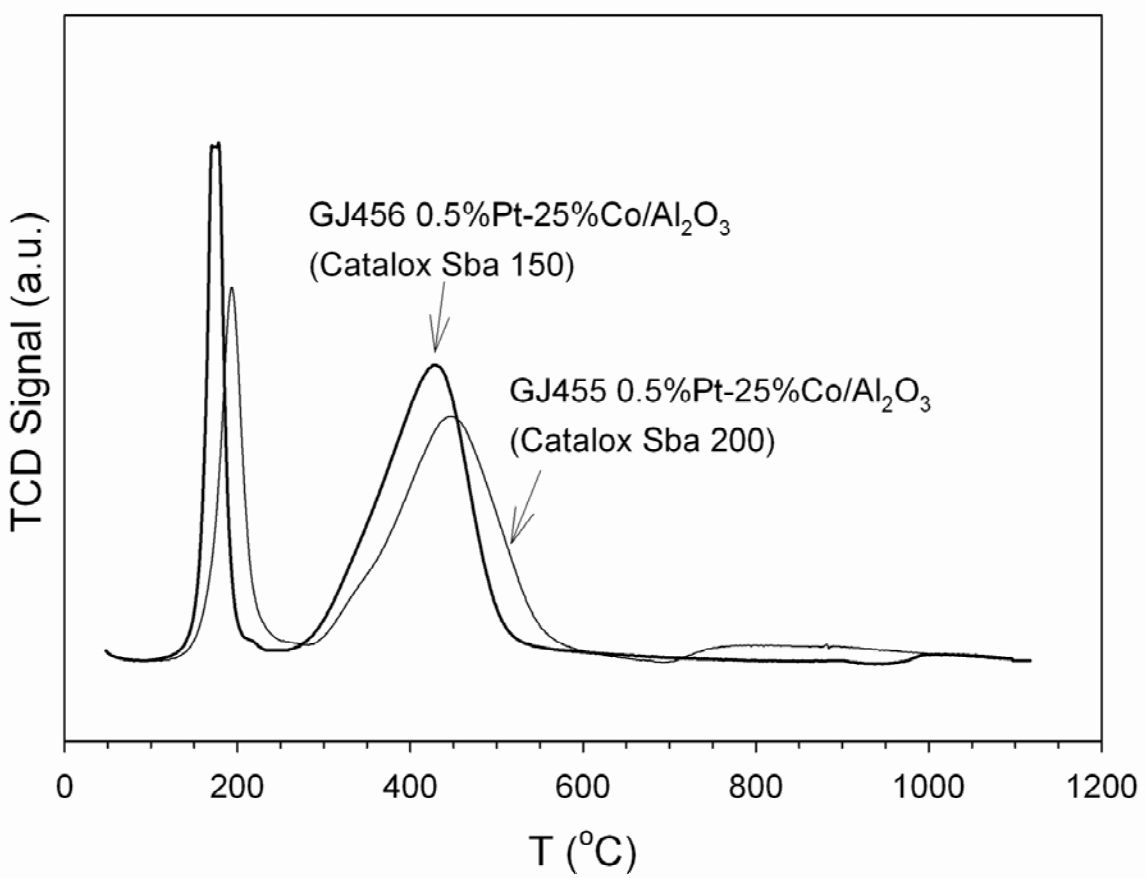


Figure 4: TPR profiles for the 0.5%Pt-25%Co/Al_2O_3 catalysts GJ455 and GJ456 supported on Catalox Sba 200 and 150, respectively.

Reduction of Co_3O_4 clusters is proposed to occur in two steps [3], 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 all the way beyond 700^oC. Extending the TPR beyond 800^oC, there is typically a small peak for some cobalt which is sacrificed to the support as cobalt aluminate. It is clear from the figure above that both steps of the reduction process have been promoted to significantly lower temperatures, most likely via a H_2 dissociation and spillover mechanism from the Pt clusters, which nucleate the formation of Co^0 in the CoO oxide, which then grows.

The results clearly reveal 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.

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 5. However, the catalyst is typically activated in CO to carburize it [4] (not H_2).

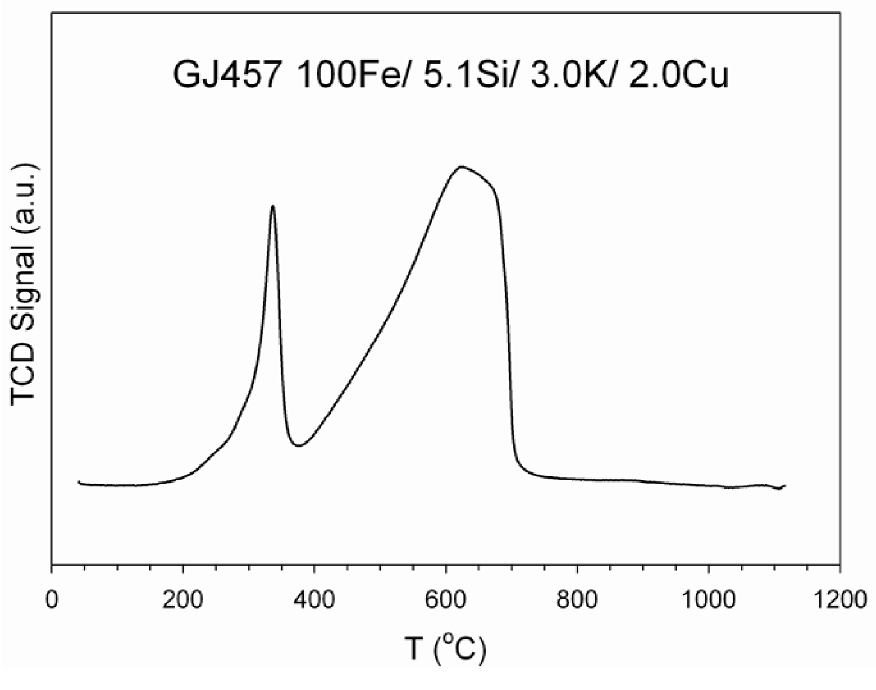


Figure 5: H_2-TPR of Fe/Si/K/Cu catalyst.

H_2 chemisorption / pulse reoxidation: Results of H_2 chemisorption / pulse reoxidation are summarized below. With the aid of the promoter, the extent of reduction increases to ~91.5%. 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 ~17.84%. Taking these two measures into account, along with geometrical arguments, the corrected average diameter was approximately 5.8 nm.

H_2 chemisorption / pulse reoxidation
Catalyst ID: GJ455
Composition: 0.5%Pt-25%Co/Al_2O_3 on Sba -200 (~200 m^2/g)
H_2 calibration: 5351.0
TPD H_2: 346.1 micromoles per g cat
O_2 calibration: 334.6
O_2 uptake: 2587.3 micromoles per g cat
Uncorrected dispersion: 16.32%
Uncorrected diameter: 6.3 nm
Extent of Reduction: 91.5%
Corrected dispersion: 17.84%
Corrected diameter: 5.8 nm

The cluster size was quite small (e.g., < 10 nm) and using the catalyst, there were difficulties in obtain 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.

B. Fischer-Tropsch Synthesis Catalytic Reaction Testing

Baseline catalyst tests (i.e., no contaminant addition) for the 0.5%Pt-25%Co/Al2O3 catalysts GJ455 (supported on Catalox Sba 200, Figure 6) and GJ456 (supported on Catalox Sba 150, Figure 7), as well as the 100Fe/ 5.1Si/ 3.0K/ 2.0Cu catalyst GJ457 (Figure 8), were completed during this quarter. Both cobalt catalysts display an initial decline in CO conversion rate during the first 100 – 150 hours onstream. This is typical for cobalt catalysts and there is a debate in the literature as to the cause. However, once the WHSV is adjusted, the catalysts were found exhibit excellent stability (Figures 5 and 6) over several hundred hours. The C_1 and C_5+ selectivities were also typical.

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.

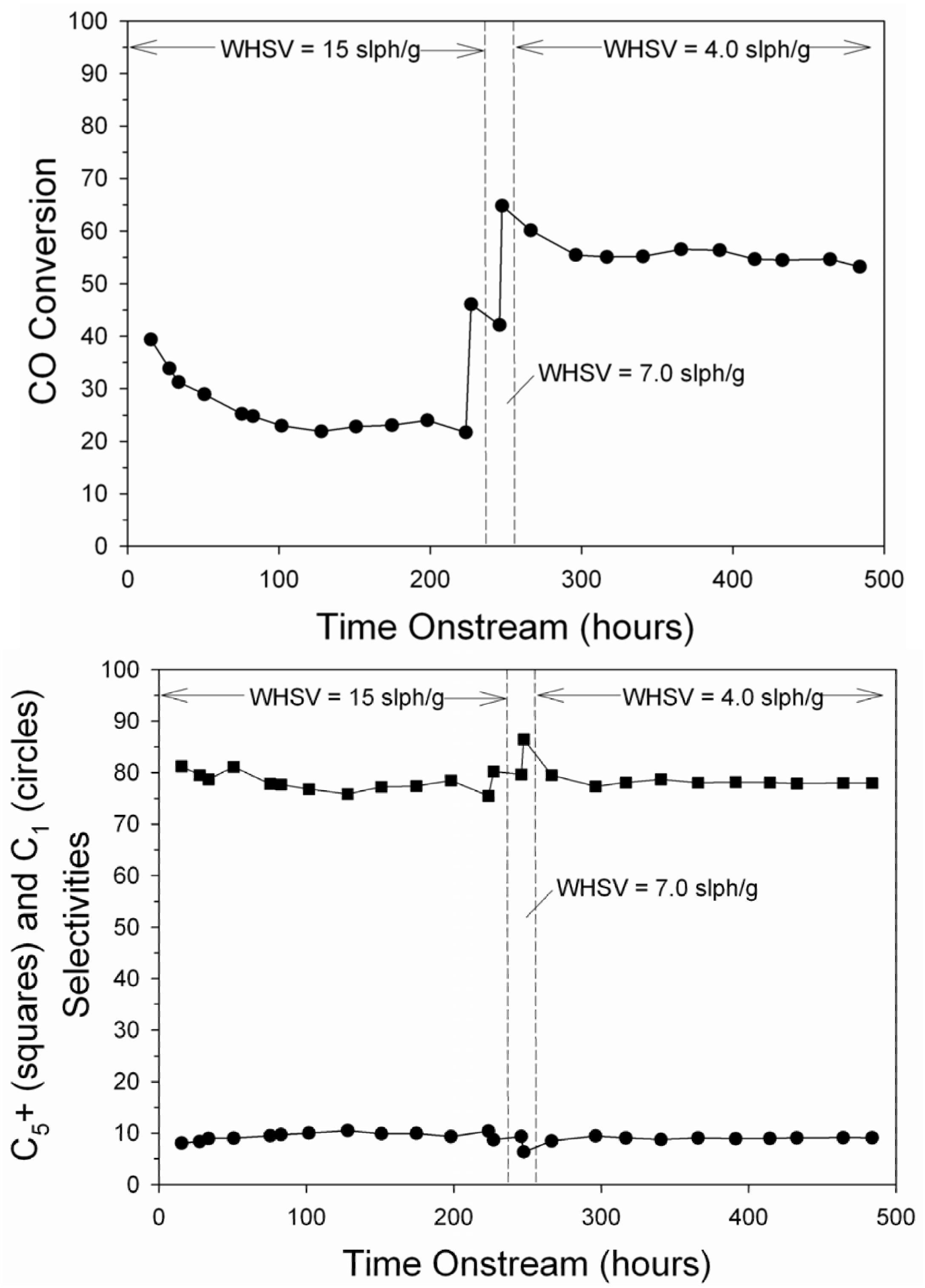


Figure 6: Change in (top) CO conversion and (bottom) HC selectivity with time on stream and space velocity over 0.5%Pt-25%Co/Al_2O_3 (GJ455, Catalox Sba 200).
Test conditions: 220 ^oC, 210 psig, H_2/CO = 1.93-1.98, SV: 15 Nl/g-cat/h (0-223h), 7 Nl/g-cat/h (223-246 h) and 4 Nl/g-cat/h (246-316 h).

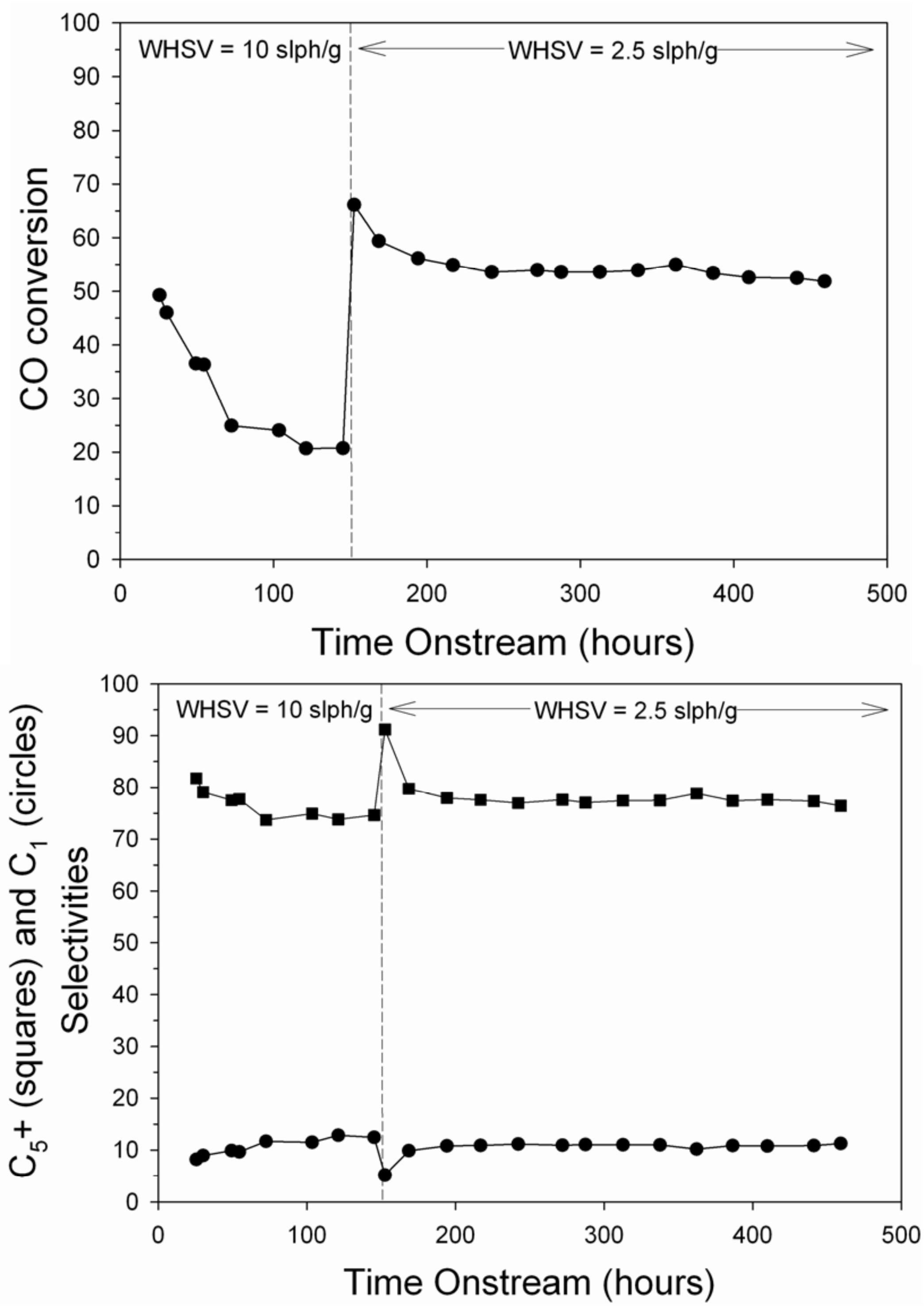


Figure 7: Change in (top) CO conversion and (bottom) HC selectivity with time on stream and space velocity over 0.5%Pt-25%Co/Al_2O_3 (GJ456, Catalox Sba 150).
Test conditions: 220 ^oC, 280 psig, $H_2/CO = 2.0$, SV: 10 Nl/g-cat/h (0-145h), 2.5 Nl/g-cat/h (145-459 h).

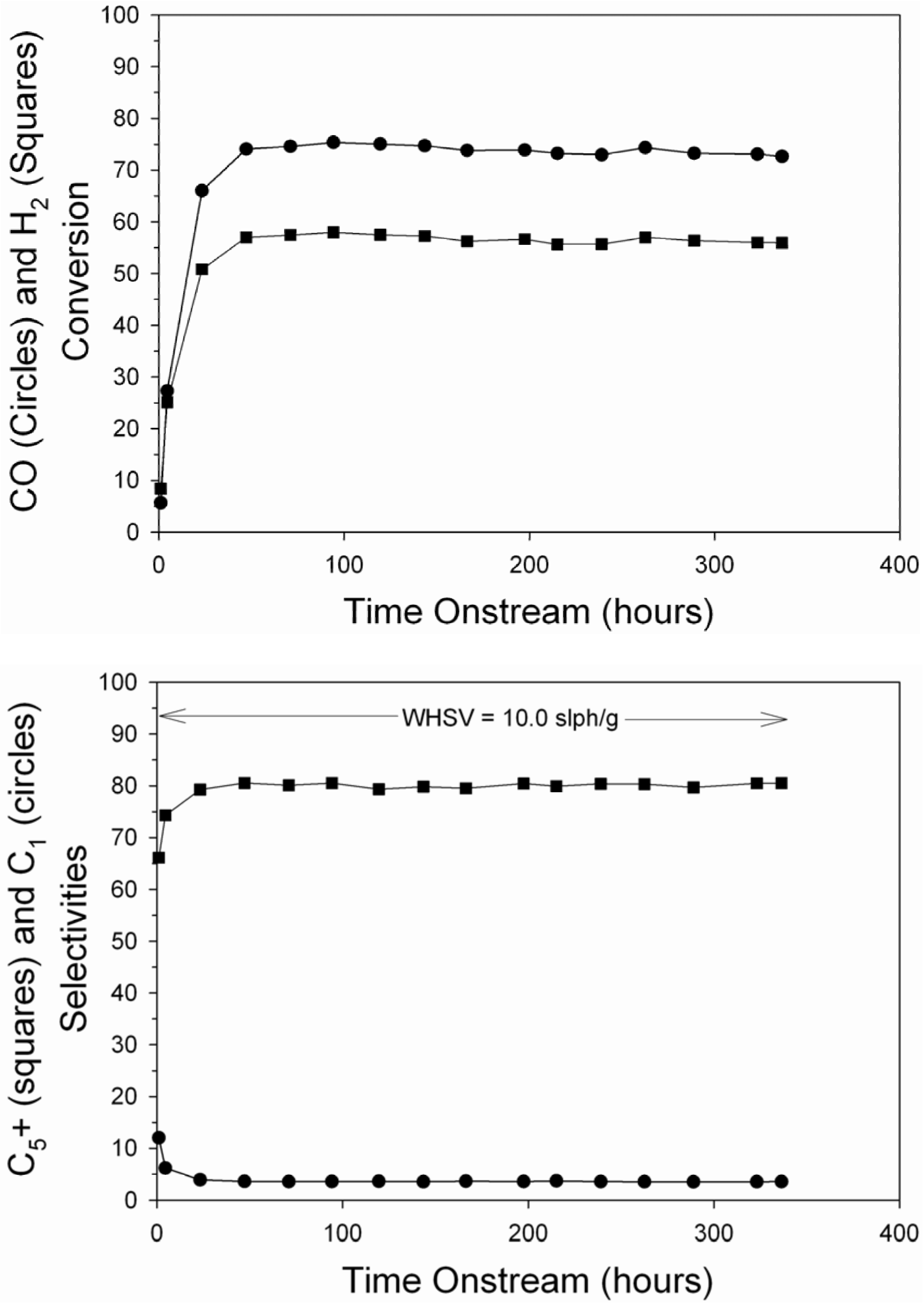


Figure 8: Change in (top) CO and H_2 conversion and (bottom) HC selectivity with time on stream over 100Fe/ 5.1Si/ 3.0K/ 2.0Cu (GJ457).
Test conditions: 270 ^{o}C, 175 psig, H_2/CO = 0.77, SV: 10 Nl/g-cat.

C. High Temperature shift study of Fe-Cr catalyst

Before starting with the stability studies (clean and poisoned) on the HTS commercial catalyst in WGS reaction, UK-CAER studied the effect of Gas Hourly Space velocity (GHSV) on WGS activity (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). The steam to dry gas ratio of unity (1:1) was used for WGS activity tests.
- Catalyst particle sizes were between 355-600 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 studied 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 MFCs and (ii) the catalyst bed length (catalyst weight) where a reliable controlled temperature can be achieved. The results of space velocity tests are shown in Figure 9. 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 is no significant effect from equilibrium on CO conversion and the conversion is high enough for the poisoning studies so that clear deactivation patterns may, if present, be observed.

A clean stability test of the Fe-Cr catalyst for 21 days under HTS conditions was carried out, and the results are displayed in Figure 10. The catalyst wass stable during the period of testing and the CO conversion was about 78 mol%. This result serves as the basis for the poisoning stability studies.

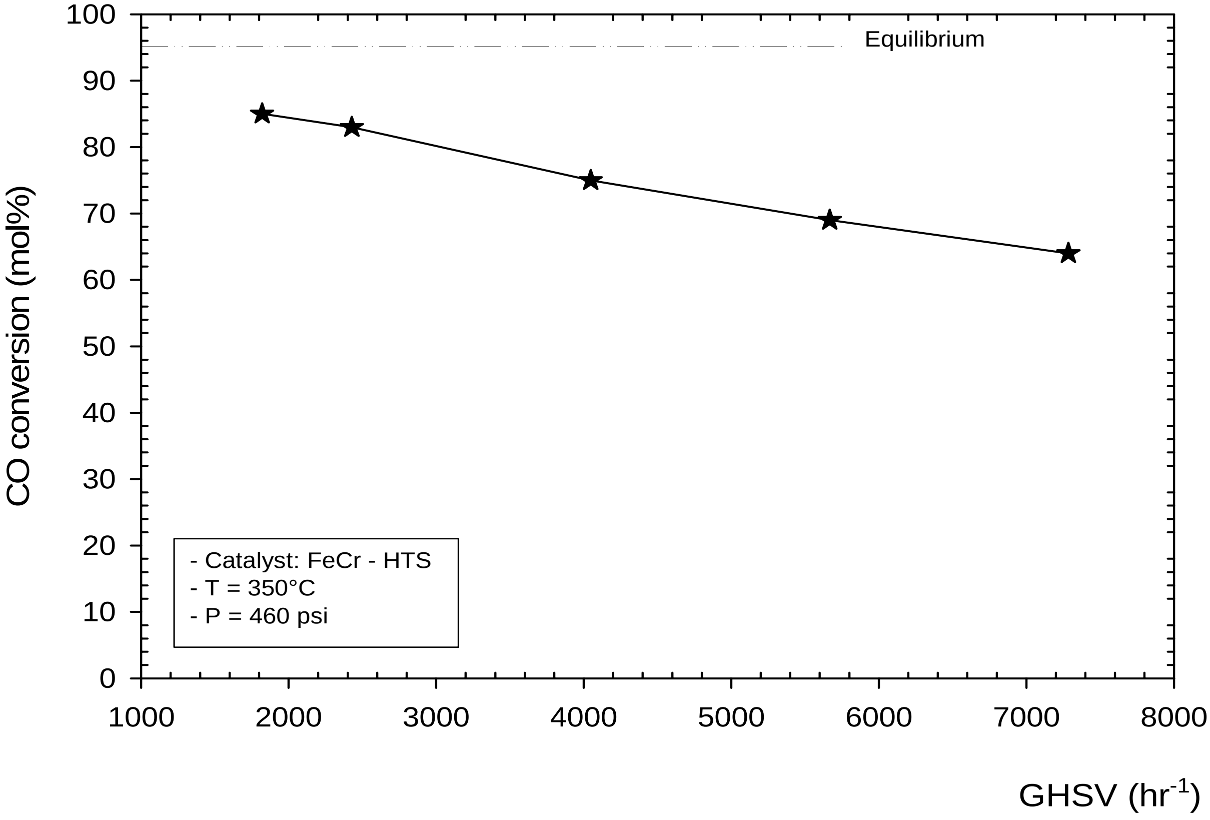


Figure 9: Effect of GHSV on WGS activity (CO conversion) over FeCr – HTS catalyst.

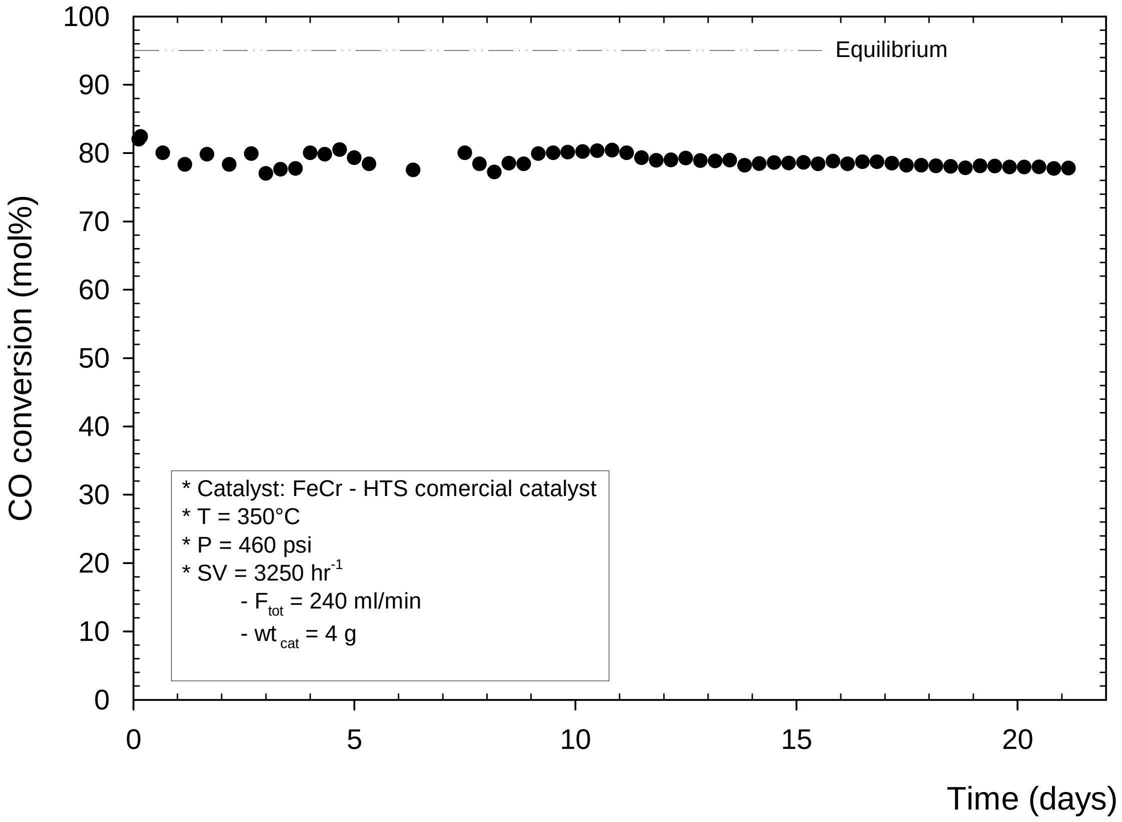


Figure 10: WGS activity (CO conversion) with time on stream over the Fe-Cr HTS commercial WGS catalyst.

D. WGS reaction: Sensitivity of HTS Sud-Chemie catalyst to co-fed KCl and NaCl.

As noted in the previous section, the Sud-Chemie high temperature shift (HTS) catalyst was demonstrated to be stable for the water-gas shift (WGS) reaction during 21 days of time on stream (TOS) testing in a fixed bed reactor. The activity was constant at about 80% CO conversion under the following testing conditions: 350ºC, 460 psi, 3250 hr^{-1} space velocity, with unity steam/dry gas ratio. The dry gas compositions were 46.5%CO, 34.9%H and 18.6%N_2. In this section we report the effect of co-feeding KCl and NaCl on the activity and stability of HTS catalyst during WGS. 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, we did not add glass wool at the top of the catalyst bed in order to reduce the chance of losing some of the poisons by adsorption on the glass wool.

Figure 11 displays the activity and stability of the HTS catalyst for the WGS reaction as a function of TOS under different KCl poison 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 tested KCl concentrations. Moreover, a slight increase in CO conversion was observed. This increase in 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. [5].

In a separate study, we have tested the role of K^+ in enhancing the WGS activity of iron-silica based catalyst by comparing the activity of K^+ promoted and unprompted iron-silica catalyst for the WGS reaction (results not shown here) and indeed found that K^+ increases the WGS activity of iron based catalysts.

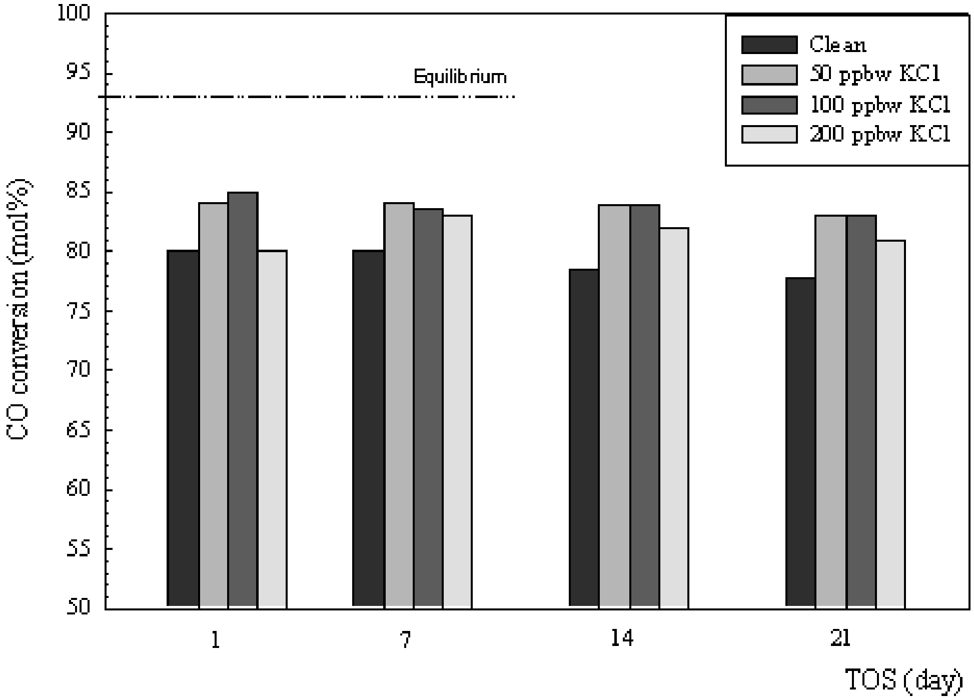


Figure 11: KCl concentration effect on the activity and stability of HTS – Sud-Chemie WGS catalyst in WGS reaction vs. TOS. Tests conditions are 350ºC, 460 psi, 3250 hr^{-1}, 240 ml/min (steam/dry gas ratio of 1), catalyst weight of 4 g.

At the highest KCl concentrations tested in this study (i.e., 200 ppbw), the concentration of Cl^- is about 95 ppbw in the gas feed mixture. The catalyst showed excellent stability against this chlorine concentration as shown in Figure 11. To verify if all the K^+ and Cl^- fed into the reactor was adsorbed on the catalyst, the water recovered from the cold trap was analyzed at different reaction times for the 200 ppbw KCl experiment and the results are summarized in Table 4. By comparing the concentration of K^+ and Cl^- in the feed with the ones collected from the cold trap at different reaction times, the results are consistent with the conclusion that most of the K^+ and Cl^- indeed adsorbed on the catalyst, suggesting that the Sud-Chemie HTS-WGS catalyst exhibits excellent stability against KCl in the tested range of concentrations. However, it is not clear at this point if the K^+ and Cl^- ions adsorbed only on the top layer of the catalyst bed or uniformly throughout the whole bed. In attempting to answer this question, we are currently repeating the 200 ppbw KCl experiment, however, by splitting the weight of catalyst into 4 separate beds separated by thin layers of glass wool. After that, the concentrations of K^+ and Cl^- will be checked in each bed to determine the distribution through the catalyst bed.

Table 4: K^+ and Cl^- in the recovered water from the WGS reaction – 200 ppbw KCl experiment.

Sample #	Time (day)	Cl^- (ppm)	K^+ (ppm)
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).

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 12. 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 showed that Na^+ did not enhance the activity of the catalyst as K^+ did since the catalyst showed an activity comparable with the clean test. Samples from the recovered water collected in the cold trap and samples from the spent catalyst (samples from different bed locations) were submitted for Na^+ and Cl^- quantification.

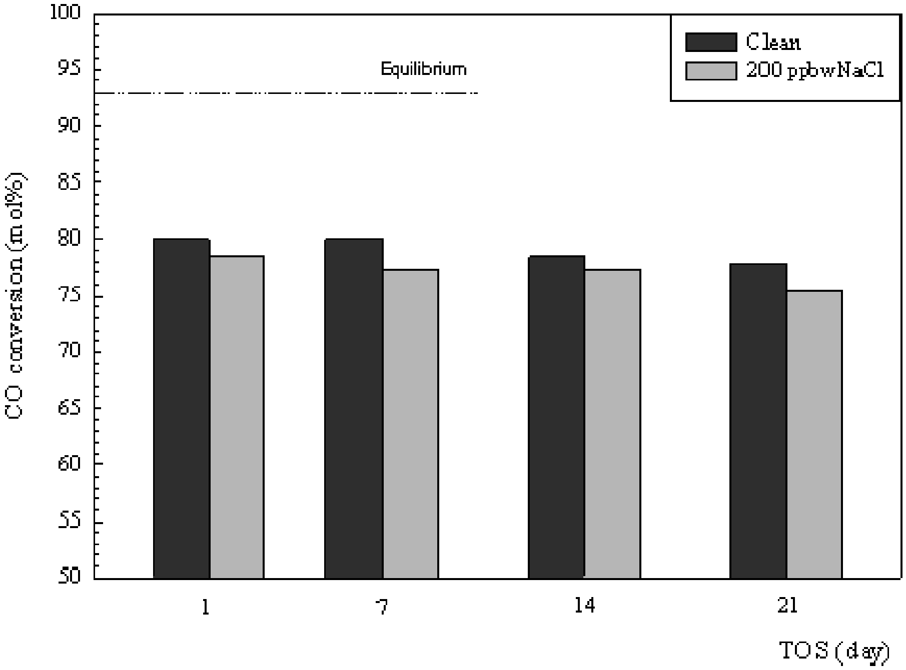


Figure 12: NaCl concentration effect on the activity and stability of HTS – Sud-Chemie WGS catalyst versus TOS. Testing conditions: 350ºC, 460 psi, 3250 hr^{-1}, 240 ml/min (steam/dry gas ratio of 1), catalyst weight of 4 g.

E. Startup of KCl and NaCl poisoning studies over FT catalysts

Poisoning reactors underwent startup studies during this annual reporting period. A run on the high alpha Fe-based Fischer-Tropsch synthesis (FT) catalyst was attempted for KCl poisoning studies. However, two problems were noted during the run. First, the CO conversion rate was moderately lower (~20%) relative to the baseline clean test reported in the previous quarter. Further, at ~100 hours of TOS, a leak developed in the inert nitrogen gas mass flow controller and the run had to be shut down. The run is provided in Figure 13, with a comparison to the baseline clean test.

Conclusions

UK-CAER completed preparation of large batches (i.e., > 2 kg) of 0.5%Pt-25%Co/γ-Al_2O_3 catalysts supported on both Catalox Sba 150 and Catalox Sba 200 supports. Furthermore, the preparation of a large batch of 100Fe/ 5.1Si/ 3.0K/ 2.0Cu high alpha iron catalyst was completed. The catalysts were shipped to Group Contacts involved in the overall DOE project. UK-CAER also completed baseline testing of the cobalt and iron Fischer-Tropsch synthesis catalysts using CSTR reactors and the selected catalysts exhibited stabilities suitable for continuing poisoning studies. The high temperature water-gas shift reactor system was completed, and UK-CAER completed both baseline and KCl/NaCl testing of the Fe-Cr Sud-Chemie HTS catalyst. The Sud-Chemie, Inc. Fe-Cr HTS catalyst exhibited good resistance to the KCl and NaCl poisons over the concentration range tested for a 21 day period. UK-CAER has overcome startup issues and is currently initiating KCl/NaCl poisoning studies over Fe and Co-based Fischer-Tropsch synthesis catalysts.

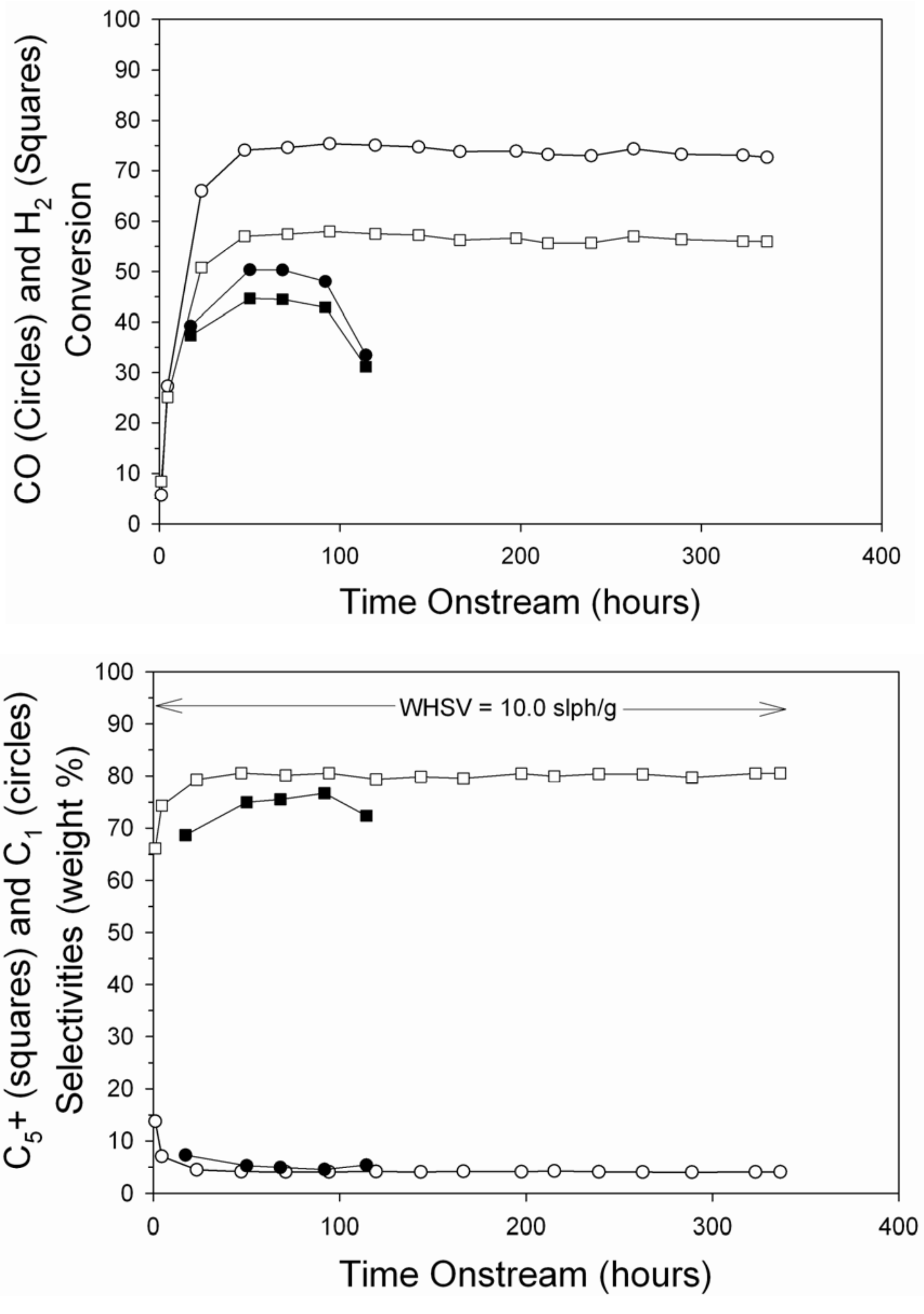


Figure 13: Change in CO and H_2 conversion and (bottom) HC selectivity (weight %) with time on stream over 100Fe/ 5.1Si/ 3.0K/ 2.0Cu (GJ457). Test conditions: 270 ^oC, 175 psig, H_2/CO = 0.77, SV: 10 Nl/g-cat.

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