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Shape-Selective Catalysts for Fischer-Tropsch Chemistry: Atomic Layer Deposition of Active Catalytic Metals

Activity Report: January 1, 2005 – September 30, 2005

Chemical Sciences and Engineering Division

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by
D.C. Cronauer
Chemical Sciences and Engineering Division, Argonne National Laboratory

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Summary

Argonne National Laboratory is carrying out a research program to create, prepare, and evaluate catalysts to promote Fischer-Tropsch (FT) chemistry—specifically, the reaction of hydrogen with carbon monoxide to form long-chain hydrocarbons. In addition to needing high activity, it is desirable that the catalysts have high selectivity and stability with respect to both mechanical strength and aging properties. The broad goal is to produce diesel fraction components and avoiding excess yields of both light hydrocarbons and heavy waxes. Originally the goal was to prepare shape-selective catalysts that would limit the formation of long-chain products and yet retain the active metal sites in a protected "cage." Such catalysts were prepared with silica-containing fractal cages. The activity was essentially the same as that of catalysts without the cages. We are currently awaiting follow-up experiments to determine the attrition strength of these catalysts.

A second experimental stage was undertaken to prepare and evaluate active FT catalysts formed by atomic-layer deposition [ALD] of active components on supported membranes and particulate supports. The concept was that of depositing active metals (i.e. ruthenium, iron or cobalt) upon membranes with well defined flow channels of small diameter and length such that the catalytic activity and product molecular weight distribution could be controlled. In order to rapidly evaluate the catalytic membranes, the ALD coating processes were performed in an 'exploratory mode' in which ALD procedures from the literature appropriate for coating flat surfaces were applied to the high surface area membranes. Consequently, the Fe and Ru loadings in the membranes were likely to be smaller than those expected for complete monolayer coverage. In addition, there was likely to be significant variation in the Fe and Ru loading among the membranes due to difficulties in nucleating these materials on the aluminum oxide surfaces.

The first series of experiments using coated membranes demonstrated that the technology needed further improvement. Specifically, observed catalytic FT activity was low. This low activity appeared to be due to: 1. low available surface area, 2. atomic deposition techniques that needed improvements, and 3. insufficient preconditioning of the catalyst surface prior to FT testing. Therefore, experimentation was expanded to the use of particulate silica supports having defined channels and reasonably high surface area. This later experimentation will be discussed in the next progress report. Subsequently, we plan to evaluate membranes after the ALD techniques are improved with a careful study to control and quantify the Fe and Ru loadings. The preconditioning of these surfaces will also be further developed. (A number of improvements have been made with particulate supports; they will be discussed in the subsequent report.)

In support of the above, there was an opportunity to undertake a short study of cobalt/promoter/support interaction using the Advanced Photon Source (APS) of Argonne. Five catalysts and a reference cobalt oxide were characterized during a temperature programmed EXAFS/XANES experimental study with the combined effort of Argonne and the Center for

Applied Energy Research (CAER) of the University of Kentucky. This project was completed, and it resulted in an extensive understanding of the preconditioning step of reducing Co-containing FT catalysts. A copy of the resulting manuscript has been submitted and accepted for publication0 A similar project was undertaken with iron-containing FT catalysts; the data is currently being studied.

Introduction

Fischer-Tropsch (FT) chemistry involves the reaction of hydrogen with carbon monoxide to form long-chain hydrocarbons. Even though this process was invented in Germany in 1923, there has been a continuing development of catalysts, the most common of which are based upon iron, cobalt, and ruthenium. Due to the water gas shift catalytic activity of iron, its use in FT catalysis is often directed toward a gas stream generated from the gasification of coal (namely, lower H/CO ratios.) In the case of gas to liquid (GTL) production, emphasis is typically directed toward supported cobalt catalysts. (During the initial stages of this project, DOE directed that research in this project center upon iron-containing catalysts with an emphasis on physical strength and catalyst activity.)

The available literature on these catalysts is very extensive, and it is beyond the scope of this project to prepare another literature survey. Only recent literature dealing with specific problem areas is cited when appropriate. For reference, a very comprehensive recent series of articles on the FT process has been edited by Hans Schulz and Michael Claeys[1]; the kinetics literature was reviewed by Van der Laan and Beenackers[2] ; see also C.N. Satterfield[3]. B. H. Davis has carried out an extensive study of FT catalysis under DOE contracts; reference is made to the Final Technical Report[4] of Contract No. PC90056; also note interim reports of PC94055. An effective review of past work was also cited in the patent application of C.L. Kibby.[5]

Iron is the least expensive FT catalyst. It is typically promoted with alkali (i.e., 0.5 wt% K_2O) for activity and stability. It has been proposed[3] that potassium donates electrons to the iron, weakens the CO bond, strengthens the Fe-C bond, and weakens the Fe-H bond, so the quantity of CO adsorbed increases and that of H_2 decreases. For reference, the fixed-bed reactors at SASOL (South African Synthetic Oil Limited) operate at about 220°C and 2.7 MPa using a precipitated iron catalyst heavily promoted with potassium. Their entrained-bed reactors operate at about 320°C and 2.2 MPa with a reduced fused magnetite catalyst of considerably lower potassium content.

CuO is added to the Fe catalyst to lower the reduction temperature of Fe_2O_3. This addition reduces sintering and apparently does not affect catalyst selectivity. SiO_2 and Al_2O_3 may be added for structural strength; however, excessive levels reduce catalyst activity.

Because alkalized iron catalysts demonstrate water gas activity, they are of particular interest when the feed stream has low hydrogen content (i.e., H_2/CO ratio of about 1.0 for coal or heavy oil gasification versus 2.0 for methane gasification). It has been reported[1] that the activity of iron catalysts is affected through the interaction with water. When these iron catalysts are used, water must be removed from recycle streams along with heavy hydrocarbon products. Typical ratios of recycle to fresh feed rates are about 2:1.

Numerous articles have indicated that iron catalysts are active for FT synthesis only when in the

carbide state. Van der Laan and Beenackers[3] provides a good summary of pertinent references; see also Bukur et al.[5] Numerous articles have demonstrated the importance of catalyst pre-conditioning treatment of fresh catalyst with CO to establish the active carbide surfaces; for example, see Shroff et al.[7] The procedure used by Davis[4] is as follows:

> "The catalyst was pretreated in CO; the sample was heated from 110 to 270°C during a period of about 2 (2°C/min) hours and then held at 270°C in a CO flow of 2 NL/g Fe/hr for 22 hours."

The strength of iron-based catalysts is of concern, particularly when used in slurry-bed catalytic reactors. Espinoza et al.[8] of SASOL states, "The main difficulty with the commercial application of the SPR (Slurry Phase Reactor) is the separation of the wax product from the catalyst. This is especially true for the relatively friable precipitated iron catalysts." D. S. Kalakkad et al.[9] studied the attrition and phase transformation of precipitated iron FT catalysts. They found that spray-dried particles (agglomerates) about 30 μm diameter easily fragmented to particles of about 1 μm size. In addition, phase transformation resulted in size reductions to about 20 μm. The recent presentation of Gormley, Deffenbaugh and Zarochark[10] also points out the difficulty of catalyst attrition with the subsequent problems of cleaning up the resulting FT wax product stream.

Interest in the first stage of this project was directed toward the formation of fractal surface structures that would provide structural strength and yet be porous for the flow of reactants and products to and from the iron-containing catalyst. Again, there is an extensive literature on the formation of fractal structures. The Symposia Proceedings of Brinker et al.,[11] the book of Brinker and Scherer,[12] the collection of manuscripts edited by Klein,[13] and the text of Zallen[14] present a good background of the subject.

The goal of the first stage of this project was to create, prepare, and evaluate catalysts to promote Fischer-Tropsch (FT) chemistry. Emphasis was placed upon iron-containing catalysts that are preferred for syngases having low ratios of H_2/CO. Emphasis was also placed upon shape-selective catalysts that had the potential to limit long-chain products and retain active metal sites in a protected "cage" to restrict their loss during use in slurry-bed reactors. The progress report covering this research stage has been issued.[15]

The goal of the current stage of this project is directed toward preparing active FT catalysts supported on porous membranes. Specifically, emphasis is being directed toward preparing thin films of catalytic metals supported on tightly controlled porous membranes. These catalytic films are being controlled down to the number of atoms of thickness and the membrane pore size. Novel catalysts have been synthesized by techniques that create composite membranes of nanopores constructed from molecular building blocks; specifically, electrochemically prepared anodic aluminum oxide materials. In addition, commercially available ceramic membranes have been coated layer by layer with alumina and active catalytic metals including ruthenium, cobalt and/or iron using an atomic layer deposition (ALD) technique. The resulting membranes have been demonstrated to have both mechanical strength and limited FT catalytic activity. Because these membranes had low effective surface areas, it was decided to expand to experimentation with preformed silica gels of high surface area to test and improve the ALD techniques. It was also determined that the preconditioning step needed improvement. After these improvements, we plan

to return to the preparation of membrane supported catalysts.

Experimentation and Results

Experimental

A continuous-flow catalytic-bed unit was modified and used for this FT study. A flow schematic for operation with a fixed bed of powdered catalyst is shown in Figure 1.

In the experiments made with a packed bed, the gaseous feed consisted of either a 1:1 or 2:1 molar blend of $H_2:CO$. The feed passed through a preheater/reactor that consisted of a 1/2-in.-O.D. (3/8-in.-I.D.) tube of 36 in. length. Gaseous flow was downward through the following zones:

1. An empty (quartz wool) zone to serve as a preheater,
2. Inert packing consisting of low-surface α-Al_2O_3 to ensure radial flow dispersion,
3. Supported catalyst that was mixed with inert filler,
4. Additional α-Al_2O_3 packing, and
5. A bottom zone made up of a low-internal-diameter tube so that the catalyst was retained in the temperature-controlled region of the tube.

The preheater/reactor had a total of six internal and two external thermocouples. The reactor temperature was controlled using the thermocouple at the center of the catalyst bed.

When experiments were made with coated membranes, the reactor tube was modified with a Swagelok VCR[R] "metal gasket face seal fitting" as shown in the Swagelok drawing below. Onto the metal seal gasket, test membranes were attached with silicon adhesive.
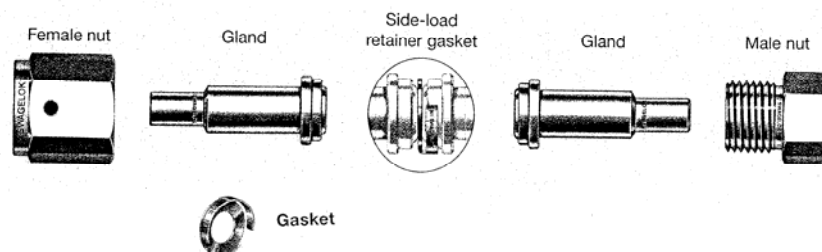
Operation was similar with the use of a membrane with the exception that the control thermocouple was located about 1 mm above the membrane. A red adhesive designated "Loctite Superflex Red High Temp RTV Silicone Adhesive Sealant" (part number 59630) has been shown to effectively hold the membrane in place on the seal ring. This adhesive remained somewhat pliable even after high temperature runs. A second adhesive designated "JB Weld Cold Weld Compound" (Part Number 8265-S) was also evaluated to hold the membranes in place, but it appeared to be more rigid, and the membranes fractured during the runs.

The FT experiments carried out with particulate catalyst were carried out at temperatures ranging from about 260°C to 300°C, pressures averaging 13.1 MPa (190 psia), H_2/CO feed molar ratios of

either 1.0 or 2.0, a gas feed rate of about 15 to 40 mL/min, and a catalyst charge of 0.1 to 0.7 g . At a gas feed rate of 40 mL/min and a catalyst charge of 0.7 g, the equivalent space velocity is about 3.4 normal liters per hour gram (NL/hr-g).

The FT experiments made with the coated membranes were carried out at similar conditions to those cited above. A reactor by-pass system was used during start-up to insure that there was no pressure surge over the membrane.

The reactor effluent was cooled in air, and then it could be passed through a wet-ice-cooled trap. There was a provision for a dry-ice trap that was not used due to plugging problems. The traps were set up for parallel operation so that periodic condensate samples could be recovered for weighing and sampling. The pressure of the off-gas was controlled, and it was subsequently metered and sampled.

The gas composition was determined using an HP 6890 Series gas chromatograph (GC) that had been modified by LINC Quantum Analytics of Foster City, CA. It had three columns: (1) a molecular sieve column (7 ft x 1/16 in. 13X 45/60) for light gas retention and separation, (2) a capillary column (50 m x 0.53 mm KCl modified Al_2O_3 PLOT) for hydrocarbon analysis by a flame ionization detector (FID), and (3) a packed column (7 ft x 1/16 in. Hayesep A 60/80) for CO_2 separation and analysis using a thermal conductivity detector (TCD).

Catalyst Preparation

A summary of all of the tested membrane catalysts is presented in Table 1, and their use in FT experiments is outlined in Table 2.

The preparation of the iron-containing particulate catalysts including those coated with fractal SiO_2 coatings have been described in the previous report.[15]   Therefore, they are not described herein.

The Fischer-Tropsch (FT) membrane catalysts were prepared by applying thin films of aluminum oxide, iron oxide and ruthenium metal onto anodic aluminum oxide (AAO) membranes using atomic layer deposition (ALD). ALD is a thin film growth technique that uses alternating exposures to reactive precursor gases. Self-limiting chemical reactions between the precursors and a solid surface ensure that each exposure produces exactly one monolayer of adsorbed species, even for surfaces with complex topographies such as the nanoporous AAO membranes.

The AAO membranes were Anodiscs (Whatman) with a diameter of 13 mm and a thickness of 60 microns. These AAO membranes have 200 nm pores that extend for the first 58 microns, and then transition to a smaller, 20 nm pore diameter for the final 2 microns of the membrane thickness. The number of pores per unit area of the 20 nm diameter pores is $10^{11} cm^{-2}$. The diameter of the AAO nanopores can be adjusted using ALD to control the contact time between the catalyst and the reactive gases.[16]

The FT catalysts were prepared using a viscous flow ALD reactor[17] at 1 Torr pressure using ultrahigh purity nitrogen carrier gas at a mass flow rate of 360 sccm. Prior to depositing the Fe_2O_3 and Ru catalysts, the diameter of the AAO membrane was first reduced from 20 nm to 10 nm using

ALD Al_2O_3. This process used 45 ALD cycles comprised of alternating exposures to trimethyl aluminum and water vapors at 350°C to deposit 5 nm of Al_2O_3[18] on all exposed surfaces of the AAO membrane including both sides of the pore walls to reduce the diameter by 10 nm. When applicable, the Fe_2O_3 catalyst layer was deposited using 30-60 alternating exposures to Iron tris (2,2,6,6-tetramethyl-3,5-heptane-dionate) and ozone at 186°C[19]. The ALD Ru was performed using 30-60 alternating exposures to Bis (cyclopentadienyl) ruthenium and oxygen at 350°C[20]. The numbers of Fe_2O_3 and Ru ALD cycles were adjusted to control the relative amounts of these two materials deposited in the AAO membranes.

Results and Discussion

I. Reference FT Experiments Using Reactors with and without Particulate Catalysts

Reference FT experiments were those made with an empty reactor, an empty reactor onto which a thin inert film of alumina was deposited using ALD techniques, a reactor filled with α-alumina particulates, iron FT catalyst supplied by CAER, and a cobalt FT catalyst supplied by CAER. The iron- and cobalt-containing catalysts were tested using the procedure described in the preceding section.

a. Empty Reactor with and without Inert Coating

Reference FT experiments were carried out using an empty reactor. There was a nominal level of CO conversion presumably due to the presence of a catalytic surface of the thermocouples and stainless steel tubes. To reduce the catalytic surface effect of the reactor, the stainless tube and associated fittings were coated with alumina using the ALD system. The results of both approaches are summarized in Figure 2 and Tables 2 through 4. As a test of the consistency of temperature effects upon reaction kinetics, the data was also plotted as ln(CO) conversion versus reciprocal temperature in Figure 3. In summary, the level of CO conversion was reduced by about one-half when the stainless steel surfaces were coated with a several Angstrom layer of alumina. The data followed typical Arrhenius correlations. The average activation energy was about 28.5 Kcal/mol.

b. α-Alumina

Initial FT experiments were undertaken using the preheater and reactor charged with only α-Al_2O_3 to ensure that there was no or only limited background catalytic activity due to the "inert" filler. Runs 85A, 85C, 87C and 85F were made at mid-bed temperatures ranging between 265° and 290°C. As shown in the previous report[15] there was only a nominal level (<0.05%) of methane generated in one of these runs and 0.02 % or less in the other runs. No other hydrocarbons or carbon dioxide were detected at levels at or above 0.01%. In summary, the α-Al_2O_3 was essentially inert at the established reaction conditions.

c. Iron-based CAER FT Catalyst

Two samples of FT catalyst were obtained from B. H. Davis of the Center of Applied Energy Research (CAER). The first consisted of a bulk spray-dried catalyst designated "RLS 4.4 Si/150 Cyclone Iron Catalyst" (RLS) and the second was freshly prepared catalyst designated "RJO 290

"100Fe/4.6Si/1.44K."

Selected CAER catalyst samples were separated by differential settling to isolate fractions of differing particle diameter as described in the previous report.[15] As-received iron-containing CAER FT catalyst was used in Runs 100 and 101, made at 268° and 284°C, respectively. With catalyst charges of about 0.70 g, 35 and 57% CO conversion levels were observed at mid-bed temperatures of 268° and 284°C, respectively. Based upon an overall carbon material balance, the selectivity of converted CO to hydrocarbons averaged 56%, with the remainder forming CO_2. Experiments with the "coarse" CAER catalyst, designated 72 CAER, were carried out at reaction temperatures between 267° and 290°C. The activity of the coarse CAER catalyst was equivalent to that of as-received CAER catalyst with the exception that nominally more CO_2 was generated (see the previous report[15]).

2. Experimentation Using Membranes

a. Reference Runs with Al_2O_3 Coating

Runs 19, 22, and 63 were made with only an Al_2O_3 coating on the SiO_2 membrane (i.e. no active metal coating). When the levels of CO conversion of these three runs were compared at similar temperatures with those of Runs 71B and D (empty reactor) and 67A and B (membrane center removed), there were no significant differences. As expected, there was no noticeable FT catalytic effect for the ALD Al_2O_3 coating. The average CO conversions were 0.44 % and 3.07 % at temperatures of about 250° and 285°C, respectively.

b. Ruthenium (only) Coated Membranes

In order to rapidly evaluate the catalytic membranes, the ALD coating processes were performed in an 'exploratory mode' in which ALD procedures from the literature appropriate for coating flat surfaces were applied to the high surface area membranes. Consequently, the Ru loadings in the membranes were likely to be smaller than those expected for complete monolayer coverage. In addition, there was likely to be significant variation in the Ru loading among the membranes due to difficulties in nucleating these materials on the aluminum oxide surfaces.

Three runs (24, 48 and 59) were carried out using Ru deposited using the ALD technique on the Al_2O_3 coated silica membranes. The observed levels of CO conversion were essentially at or below those of the Al_2O_3 support, alone, as noted in Table 4.

The estimated thickness of the Ru coating of catalyst JE289 (Run 59) was 4 Angstroms. This thickness is based upon a visual observation of a concurrently coated glass plate using a J.A. Woollam M2000 Spectroscopic Ellipsometer operating in the transmission mode. The goal was to use a minimum amount of Ru, but still to have a somewhat uniform Ru catalyst coating. This latter observation indicated that the coating was not uniform. (Subsequent experimentation has resulted in improved ALD procedures using Ru.)

It was presumed that the original thin ruthenium oxide would rapidly reduce to the active metal during the catalyst heat-up cycle. Specifically, Run 24C was heated to about 265°C in the H_2:CO

feed gas at about 200 psia in about 5 hours. Run 48 catalyst was conditioned with atmospheric H_2 while heating to 285°C in 2 hours and then being held for an additional 1 hour period prior to the run. Run 59 catalyst was conditioned with atmospheric H_2 while heating to 275°C in 2.5 hours; the run period was then started. It is apparent that additional work is necessary to establish effective preconditioning conditions.

Considering both the low levels of observed FT catalytic activity along with the anticipated catalytic activity of Ru stated in the literature, three problems may have existed as follows:

1. The amount of deposited Ru is too low,
2. The Ru deposition technique needs improvement, and/or
3. The preconditioning conditions are inadequate.

c. Ruthenium/Iron Coated Membranes

Four subsequent experiments were carried out using combinations of Ru and Fe ALD coatings on the Al_2O_3 coated silica membrane. It is again noted that these experiments were carried out in an 'exploratory mode.'

The following is a summary of the catalysts and CO conversions at reaction temperatures of about 285°C (also see Table 4):

Catalyst Designation and Composition	Run No.	% CO Conversion
JE289 – 300 short ALD cycles of Ru	59	2.44
JE121704C – 60 cycles of Ru followed by 30 cycles of Fe	57	2.81
JE121704D – 60 cycles of Ru followed by 60 cycles of Fe	55	3.66
JE121704B – 30 cycles of Ru followed by 60 cycles of Fe	44	0.87
JE012705 - 60 cycles of Fe only	50	2.13
- Average of Empty Reactor with and without Al_2O_3 coated membranes		3.07

Even if the result of Run 44 is considered an anomaly, the CO conversions of the other catalysts were low, and the techniques need to be improved. Therefore, it was decided to further develop this catalyst preparation procedure using uniform silica particulate supports of high surface area.

Interim Observations/Conclusions

The following interim observations/conclusions were drawn considering the experimentation using membranes on which active metals have been coated using Atomic Layer Deposition (ALD) techniques:

1. The flow unit that was modified for the testing of coated membranes has been used successfully at FT reaction conditions. The membranes can be held in place during the runs, and all of the gas flow is directed through the membranes.

2. The atomic layer deposition (ALD) of Ru and Fe has been carried out on Al_2O_3 coated membranes, but improvements need to be made to increase effectiveness. (Such improvements will be described in the subsequent report currently being drafted.)

The following conclusions were drawn from the experimentation undertaken using the Advanced Photon Source (APS) of Argonne National Laboratory for the preconditioning (reduction) of Co-containing FT catalysts:

1. TPR-XANES/EXAFS provided key information for verifying the nature of the chemical transformations occurring during FT cobalt-containing catalyst activation in hydrogen.

2. A two-step reduction process involving Co_3O_4 to CoO and CoO to Co^0 transformations over standard calcined catalysts was quantified over catalysts exhibiting both weak interactions (e.g., Co/SiO_2) and strong interactions (e.g., Co/Al_2O_3) with the support.

3. Cobalt loading and noble metal promoter addition (e.g., Pt) strongly affected reducibility and resulting cobalt crystallite size.

4. Increased reduction temperatures were needed to effectively reduce Co-containing catalysts deposited on strongly interacting surfaces when compared with those of unsupported Co_3O_4 or weakly supported Co catalyst.

5. The addition of the noble metal promoter greatly reduced the temperature needed to reduce the Co oxides to metal Co surfaces.

The following interim observations/conclusions were stated in the previous project report:[15]

1. Iron-based catalysts can be prepared at ANL using the techniques outlined in the CAER reports, but a high degree of mixing must be introduced to generate more uniform particle sizes. (The use of spray-drying catalyst particles should generate a more uniform distribution.)

2. The spray-dried bulk catalyst sample of CAER contains a high level of dispersed fine particles. A portion of these fines can be removed by differential settling techniques.

3. A flow unit with a fixed bed of diluted catalyst has been demonstrated for use in FT experimentation.

4. Reaction conditions have been established such that reasonable levels of CO conversion can be achieved with an active catalyst. These conditions can be used as a basis to compare catalyst samples.

5. SiO$_2$-coated iron-containing catalyst samples have been prepared using caustic precipitation techniques. A wide range of catalytic activities have been observed. As anticipated, the greatest activity was achieved with those catalysts coated with the least SiO$_2$. The activities of catalyst samples designated 135A/550 and 135A/475 were about equal to that of the CAER coarse FT catalyst from which they were prepared.

6. In the case of the 135A series, calcination at 550°C and 475°C resulted in more active catalysts than that calcined at 400°C.

7. SiO$_2$-coated catalysts were prepared using acidic precipitation techniques; HNO$_3$ and HCl were effective while H$_2$SO$_4$ was not. The greatest FT activity was achieved with the catalyst having the least SiO$_2$ (i.e., 2.2 wt%).

8. SEM study indicated that the as-received CAER catalyst recovered after differential sedimentation (132E) consisted of large (~50-70 μm) and small (~15-30 μm) spherical agglomerates along with small chips. The catalyst particles recovered from FT runs had similar appearances. SEM, even at 150K magnification, did not appear to be an effective tool to differentiate various surface treatment procedures.

9. Large spherical particles were made up of agglomerates of particles that were, in turn, also agglomerates.

10. Chips had clean, smooth surfaces that had higher Fe/Si atomic ratios than those of the rough external surfaces, even in the case of the CAER as-received sample. The chips were the result of particle crushing, and they should represent the inside catalyst material. Therefore, the Si precursor was transported to the surface during the spray drying catalyst preparation process.

11. The relative order of the surface Fe/Si atomic ratios of the catalyst samples was consistent with levels of Si used in their preparation, so the EXD approach is reasonable.

12. The EDX Fe/Si ratio analyses of the surface of catalyst particles recovered after the FT reaction were the same as those of the fresh catalyst.

13. The C/Fe atomic ratio of the surface of a recovered FT catalyst particle was high at about 6.6, while that of a smooth particle chip was only 1.0 and that of fresh catalyst averaged 0.4. Therefore, there was only a limited penetration of carbon (i.e., CO) into the FT catalyst during conditioning.

Planned Experimentation

The original goal of this program, as requested by DOE, was that this program study iron-containing FT catalysts centering upon formulating an attrition-resistant, yet catalytically active, iron-based catalyst. Experimentation has demonstrated that fractal SiO$_2$ can be coated upon FT catalysts with a minimum loss of activity. The results have been discussed with Dr. B. H. Davis of CAER and attrition tests will be done to determine if further experimentation in this area is warranted.

The second aspect was to carry out exploratory FT runs using membranes prepared with a novel technique (ALD) to deposit active catalyst on surfaces. The ALD coating processes were performed in an 'exploratory mode' in which ALD procedures from the literature appropriate for coating flat surfaces were applied to the high surface area membranes. The Fe and Ru loadings in the membranes appeared to have been smaller than expected. In addition, there was probably a significant variation in the Fe and Ru loadings due to difficulties in nucleating these materials on an aluminum oxide surface. Therefore, the experimental approach has been modified to use particulates of higher area to improve upon testing the ALD deposition technique. In addition, experimentation was also expanded to the deposition of cobalt on a silica particulate support, both with and without ALD Al_2O_3 coating.

Subsequently, we plan to evaluate membranes after the ALD techniques are improved with a careful study to control and quantify the Fe, Co and Ru loadings. The preconditioning of these surfaces will also be further developed.

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Figure 1
Bench Scale Catalytic Unit
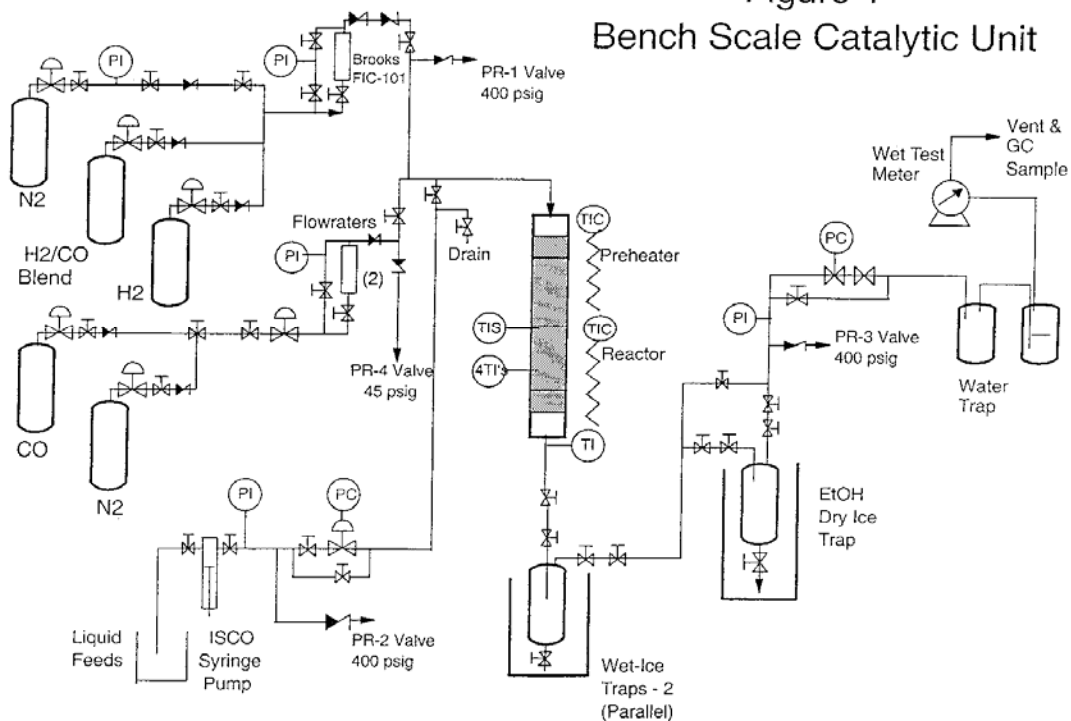
Figure 2: CO Conversion vs. Temperature in Empty & ALD Treated Reactors
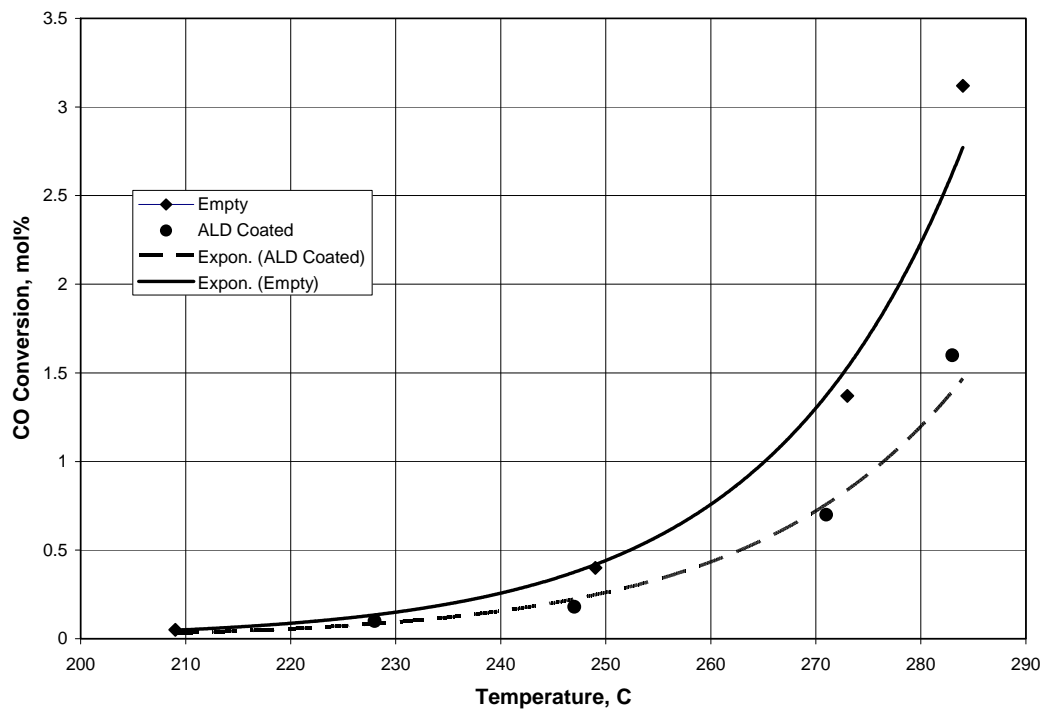
Figure 3: Arrhenius Plot of CO Conversion with Empty and ALD Treated Reactors

y = -14.16x + 25.761

y = -14.265x + 26.546

Legend:
- ◆ Empty Rx
- ■ ALD Coated RX
- — Linear (Empty Rx)
- — Linear (ALD Coated RX)

Y-axis: Ln mol % CO Conversion

X-axis: Reciprical Temperature, 1/K exp 3
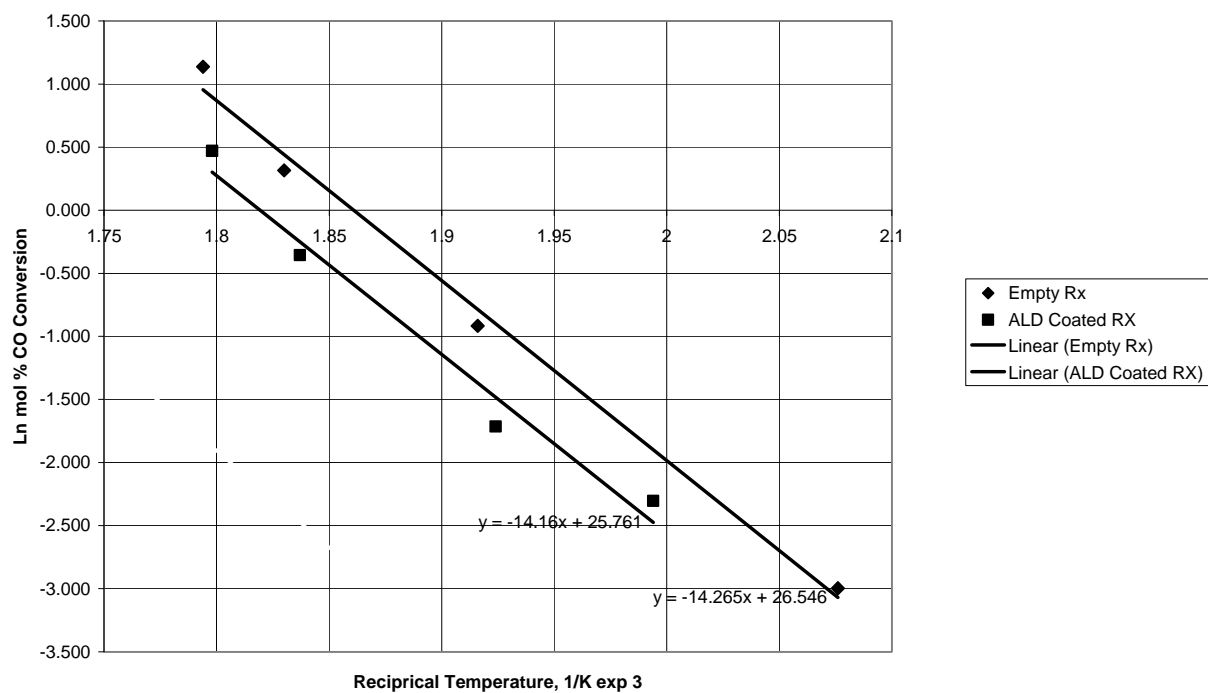
Table 1
Summary of Membrane Catalysts

Catalyst Designation	Catalyst Membrane Preparation	FT Run No.	Date of Run
Blank Test	Uncoated membrane with center broken open	67A & B	6/29/2005
JE215	50 Angstrum Al2O3 coating, but no active metal coating; gray adhesive; membrane broken.	22A & B	7/7/2004
JE216	50 Angstrum Al2O3 coating, but no active metal coating; red adhesive; membrane intact.	19A & B	7/2/2004
JE618 (Same as JE216, above)	50 Angstrum Al2O3 coating, but no active metal coating; red adhesive; membrane intact.	63A & B	5/6/2005
JE284-34C (072404)	No additional Al2O3 coating, preparation made with 330 short & long test ALD cycles with Ru.	48	2/21/2005
JE289 (072804)	40 Angstrum Al2O3 coating at 350oC, followed with 300 short ALD cycles with Ru (Note 40!)	24A & B & C	8/2/2004
JE285	50 Angstrum Al2O3 coating at 200oC, followed with 300 short ALD cycles with Ru.	59	3/27/2005
JE121704C	50 Angstrum Al2O3 coating, followed with 60 cycles of Ru and then 30 of Fe.	57	3/20/2005
JE121704D	50 Angstrum Al2O3 coating, followed with 60 cycles of Ru and then 60 of Fe.	55	3/13/2005
JE121704B	50 Angstrum Al2O3 coating, followed with 30 cycles of Ru and then 60 of Fe.	44	2/19/2005
JE012705	50 Angstrum Al2O3 coating, followed with 60 cycles of Fe, only.	50	2/2/2005

Notes: 1. The base membrane was an "Anodisc 13" of Whatman, namely a gamma Al2O3 disc of
60 um thickness (58 um having 200 um dia. holes connected to 2 um length 2 um dia. holes).
2. File -- N:/DCC_ANL/FT_FETC/Data&Results Membranes/Membrane Catalyst List ML-1.xls

Table 2

Result Summary of FT Membrane Catalytic Runs

Catalyst and Reactor Description	FT Run Number (NB 2121-)	H2/CO Rate % Rate (FIC-101)	H2/CO Rate mL/min (25C-1atm)	Added H2 Rate % Rate (FIC-102)	Added H2 Rate mL/min (25C-1atm)	Feed Gas mol% CO (Rem. H2)	Run Temperature (Degree C)	% CO Conversion CO Total	% CO Conversion C1-C6+
Empty Reactor with Swagelok VCR Gasket	71A	3.00	17.70	6.88	10.06	33.4	209	0.05	0.05
	71B	3.00	17.70	6.88	10.06	33.4	249	0.40	0.37
	71C	3.00	17.70	6.88	10.06	33.4	273	1.37	1.13
	71D	3.00	17.70	6.88	10.06	33.4	284	3.12	2.29
Empty Reactor with Swagelok VCR Gasket all coated with ALD Al2O3	74A	3.00	17.70	6.90	10.09	33.3	228	0.10	0.10
	74B	3.00	17.70	6.90	10.09	33.3	247	0.18	0.18
	74C	3.00	17.70	6.90	10.09	33.3	271	0.70	0.70
	74D	3.00	17.70	6.90	10.09	33.3	283	1.60	1.60
Blank Test using uncoated membrane with center broken open to serve as a blank	67A	3.45	20.28	1.85	24.91	23.5	246	0.52	0.52
	67B	3.45	20.28	1.85	24.91	23.5	284	3.54	3.54
JE215 (50 Angstrum Al2O3 coating, no active metal coating; gray adhesive; membrane cracked.)	22A	7.00	40.62	2.20	30.34	29.9	259	0.14	0.14
	22B	7.00	40.62	0.00	0.00	52.3	255	0.08	0.08
JE216 (50 Angstrum Al2O3 coating, no active metal coating; red adhesive; membrane intact.)	19A	6.95	40.43	0.00	0.00	52.3	255	0.10	0.10
	19B	7.00	40.62	2.07	28.64	30.7	255	0.37	0.37
JE618 (50 Angstrum Al2O3 coating, no active metal coating; red adhesive; membrane intact.)	63A	3.35	19.71	1.80	24.07	23.6	248	0.70	0.70
	63B	5.00	29.16	2.00	27.45	26.9	285	2.54	2.54
JE284(072404) (No Al2O3 coating, made with 330 short & long test ALD cycles with Ru.)	48	5.00	29.16	2.00	27.45	26.9	285	1.08	1.08
JE289 (072804) (40 Angstrum Al2O3 coating, followed with 300 short ALD cycles with Ru.)	24A	6.90	40.05	0.00	0.00	52.3	257	0.21	0.21
	24B	6.90	40.05	0.00	0.00	52.3	266	0.12	0.12
	24C	6.90	40.05	2.30	32.53	28.9	265	0.21	0.21
JE285 (50 Angstrum Al2O3 coating, followed with 300 short ALD cycles with Ru.)	59	5.00	29.16	2.00	27.45	26.9	281	2.44	2.44
JE121704C (50 Angstrum Al2O3 coating, followed with 60 cycles of Ru and then 30 of Fe.)	57	5.00	29.16	2.00	27.45	26.9	283	2.81	2.81
JE121704D (50 Angstrum Al2O3 coating, followed with 60 cycles of Ru and then 60 of Fe.)	55	5.00	29.16	2.00	27.45	26.9	286	3.66	3.66
JE121704B (50 Angstrum Al2O3 coating, followed with 30 cycles of Ru and then 60 of Fe.)	44	5.05	29.45	2.05	28.30	26.7	287	0.87	0.87
JE012705 (50 Angstrum Al2O3 coating, followed with 60 cycles of Fe, only.)	50	5.00	29.16	2.00	27.45	26.9	283	2.13	2.13

Notes: 1. File: DCC N:/DCC_ANL/FT_FETC/Data&Results/Membrane run_outline.xls

Table 3

Result Summary: F-T Experimental Series with Open Tube and Ceramic Membranes
Runs 2121-19, 22, 63, 67, and 71

Catalyst Evaluated		Run No.	Mid-Bed Temp, C	H2	CO	CO2	C1	C2	C2=	C3	C3=	C4	All C4=	C5's	C6+	SUM C1+
Empty Reactor Tube Test	Gas Analyses, %	71A	**209**	63.81	36.18	0.000	0.004	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.007
	Conversion, %					0.05	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.05
	Selectivity, %						0.00	19.69	5.18	4.15	4.66	3.11	2.07	2.07	0.00	59.07	100.00
	Gas Analyses, %	71B	**249**	64.44	35.48	0.008	0.050	0.006	0.009	0.002	0.005	0.001	0.003	0.001	0.002	0.079
	Conversion, %					0.40	0.02	0.14	0.03	0.05	0.02	0.04	0.01	0.04	0.02	0.03	0.37
	Selectivity, %						5.67	35.60	8.23	13.19	4.04	10.64	1.99	9.65	4.61	6.38	100.00
	Gas Analyses, %	71C	**273**	64.22	35.44	0.086	0.169	0.026	0.024	0.006	0.014	0.002	0.005	0.005	0.004	0.256
	Conversion, %					1.37	0.24	0.47	0.15	0.13	0.05	0.11	0.02	0.06	0.07	0.07	1.13
	Selectivity, %						17.42	34.28	10.62	9.64	3.77	8.33	1.70	4.38	4.76	5.11	100.00
	Gas Analyses, %	71D	**284**	63.81	35.38	0.303	0.341	0.055	0.038	0.013	0.004	0.020	0.021	0.009	0.008	0.510
	Conversion, %					3.12	0.83	0.93	0.30	0.21	0.11	0.03	0.22	0.22	0.13	0.13	2.29
	Selectivity, %						26.57	29.92	9.63	6.67	3.50	1.08	7.09	7.19	4.03	4.32	100.00
Blank Test	Gas Analyses, %	67A	**246**	79.10	20.84	0.00	0.04	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.062
Blank Test using uncoated membrane	Conversion, %					0.52	0.00	0.19	0.04	0.05	0.02	0.03	0.04	0.02	0.02	0.11	0.52
with center broken open; red adhesive.	Selectivity, %						0.00	37.16	8.38	9.65	3.55	5.74	7.29	4.37	3.64	20.22	100.00
	Gas Analyses, %	67B	**284**	78.53	20.95	0.00	0.38	0.06	0.02	0.01	0.00	0.02	0.01	0.00	0.01	0.520
	Conversion, %					3.54	0.00	1.77	0.51	0.20	0.20	0.03	0.41	0.18	0.10	0.14	3.54
	Selectivity, %						0.00	49.98	14.35	5.69	5.65	0.78	11.70	4.99	2.79	4.06	100.00
JE216 (50 A Al2O3 coating, no active	Gas Analyses, %	19A	**255**	52.78	47.20	0.00	0.002	0.016	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.020
metal coating; red adhesive)	Conversion, %					0.10	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.10
	Selectivity, %						0.00	3.53	71.08	1.32	0.66	1.99	0.88	2.65	3.31	14.57	100.00
H2/CO Feed ratio change	Gas Analyses, %	19B	**255**	73.90	26.07	0.00	0.001	0.017	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.029
	Conversion, %					0.37	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.37
	Selectivity, %						0.00	1.23	35.25	0.41	0.31	0.00	0.00	0.82	0.51	61.48	100.00
JE215 (50 A Al2O3 coating, no active	Gas Analyses, %	22A	**259**	74.94	25.04	0.00	0.002	0.016	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.020
metal coating; gray adhesive;	Conversion, %					0.14	0.00	0.01	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.14
membrane was cracked.	Selectivity, %						0.00	5.88	94.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00
H2/CO Feed ratio change	Gas Analyses, %	22B	**255**	50.71	49.27	0.00	0.002	0.016	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.020
	Conversion, %					0.08	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.08
	Selectivity, %						0.00	5.29	80.10	3.02	0.76	2.27	0.00	1.01	0.00	7.56	100.00
JE618 (50 A Al2O3 coating, no active	Gas Analyses, %	63A	**248**	81.73	18.19	0.00	0.040	0.020	0.006	0.001	0.000	0.002	0.004	0.000	0.001	0.075
metal coating; red adhesive.)	Conversion, %					0.70	0.00	0.22	0.22	0.06	0.02	0.00	0.05	0.08	0.01	0.04	0.70
	Selectivity, %						0.00	31.51	31.83	8.89	3.28	0.00	6.86	11.23	0.78	5.62	100.00
	Gas Analyses, %	63B	**285**	76.02	23.59	0.00	0.268	0.048	0.023	0.010	0.000	0.023	0.006	0.008	0.003	0.389
	Conversion, %					2.54	0.00	1.11	0.39	0.19	0.13	0.00	0.38	0.10	0.17	0.07	2.54
	Selectivity, %						0.00	43.61	15.58	7.53	5.08	0.00	15.12	3.84	6.60	2.64	100.00

Notes: 1. Gas analyses is reported as mol % normalized to N2 and O2 free
2. Conversion reported as mol % of the feed carbon in CO converted to the various components.
3. Selectivity is reported as the % of the reacted carbon in feed CO that was converted to the various components.
4. File -- N:/DCC_ANL/FT_FETC/Data&Results Membranes/RS-1M (Runs 19 22 63 67 71).xls

Table 4

Result Summary: Fischer-Tropsch Experimental Series with Coated Ceramic Membranes
Runs 2121-24, 44, 48, 50, 55, 57 and 59

Catalyst Evaluated		Run No.	Mid-Bed Temp, C	H2	CO	CO2	C1	C2	C2=	C3	C3=	C4	All C4=	C5's	C6+	SUM C1+
JE072404 (284) (10 Angstrum Al2O3 coating, followed with 330 short & long test ALD cycles with Ru.)	Gas Analyses, %	48	**285**	74.58	25.24	0.00	0.13	0.02	0.02	0.00	0.01	0.00	0.01	0.00	0.00	0.181
	Conversion, %					1.08	0.00	0.49	0.13	0.13	0.05	0.09	0.02	0.09	0.08	0.01	1.08
	Selectivity, %						0.00	45.40	11.75	11.60	4.24	8.70	1.89	8.27	7.07	1.09	100.00
JE072804 (50 Angstrum Al2O3 coating, followed with 300 short ALD cycles with Ru.)	Gas Analyses, %	24A	**257**	52.99	46.98	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.031
	Conversion, %					0.21	0.00	0.01	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.21
	Selectivity, %						0.00	2.92	33.23	1.61	0.30	1.21	0.40	0.81	1.51	58.01	100.00
	Gas Analyses, %	24B	**266**	54.11	45.87	0.000	0.006	0.018	0.002	0.000	0.001	0.000	0.001	0.000	0.000	0.027
	Conversion, %					0.12	0.00	0.01	0.08	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.12
	Selectivity, %						0.00	10.59	66.16	6.05	1.13	5.67	0.76	5.29	0.95	3.40	100.00
	Gas Analyses, %	24C	**265**	76.19	23.79	0.000	0.007	0.017	0.001	0.000	0.001	0.000	0.001	0.000	0.000	0.027
	Conversion, %					0.21	0.00	0.03	0.14	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.21
	Selectivity, %						0.00	13.14	66.27	5.10	1.18	4.12	0.78	4.71	0.00	4.71	100.00
JE289 (50 Angstrum Al2O3 coating, followed with 300 short ALD cycles with Ru.)	Gas Analyses, %	59	**281**	77.55	22.10	0.000	0.231	0.053	0.020	0.010	0.019	0.005	0.009	0.005	0.002	0.020
	Conversion, %					2.44	0.00	1.02	0.47	0.17	0.13	0.26	0.08	0.17	0.10	0.05	2.44
	Selectivity, %						0.00	41.70	19.15	7.15	5.26	10.46	3.25	6.79	4.07	2.17	100.00
JE121704C (50 Angstrum Al2O3 coating, followed with 60 cycles of Ru and then 30 of Fe.)	Gas Analyses, %	57	**283**	77.74	21.88	0.000	0.236	0.055	0.019	0.010	0.028	0.005	0.010	0.007	0.007	0.377
	Conversion, %					2.81	0.00	1.05	0.49	0.17	0.14	0.37	0.08	0.17	0.16	0.18	2.81
	Selectivity, %						0.00	37.25	17.42	6.13	4.84	13.13	2.97	6.20	5.61	6.45	100.00
JE121704D (50 Angstrum Al2O3 coating, followed with 60 cycles of Ru and then 60 of Fe.)	Gas Analyses, %	55	**286**	77.87	21.71	0.000	0.259	0.059	0.018	0.012	0.022	0.005	0.008	0.007	0.038	0.426
	Conversion, %					3.66	0.00	1.15	0.52	0.16	0.16	0.30	0.09	0.13	0.15	1.00	3.66
	Selectivity, %						0.00	31.38	14.23	4.42	4.30	8.12	2.43	3.69	4.07	27.38	100.00
JE121704B (50 Angstrum Al2O3 coating, followed with 30 cycles of Ru and then 60 of Fe.)	Gas Analyses, %	44	**287**	74.86	25.00	0.000	0.098	0.013	0.014	0.003	0.008	0.001	0.004	0.001	0.001	0.143
	Conversion, %					0.87	0.00	0.39	0.10	0.11	0.04	0.10	0.01	0.07	0.03	0.03	0.87
	Selectivity, %						0.00	44.41	11.55	12.64	4.36	11.05	1.45	7.82	3.18	3.55	100.00
JE012705 (50 Angstrum Al2O3 coating, followed with 60 cycles of Fe, only.)	Gas Analyses, %	50	**283**	73.90	25.78	0.000	0.219	0.036	0.019	0.009	0.003	0.015	0.003	0.003	0.019	0.325
	Conversion, %					2.13	0.00	0.83	0.27	0.15	0.10	0.03	0.23	0.04	0.05	0.43	2.13
	Selectivity, %						0.00	38.93	12.86	6.84	4.76	1.44	10.90	2.07	2.23	19.98	100.00
Empty Reactor Tube Test using an ALD Al2O3 Coating	Gas Analyses, %	74A	**228**	70.48	29.50	0.000	0.007	0.001	0.002	0.000	0.002	0.000	0.000	0.000	0.002	0.013
	Conversion, %					0.10	0.00	0.02	0.00	0.01	0.00	0.02	0.00	0.00	0.00	0.03	0.10
	Selectivity, %						0.00	23.65	4.73	11.49	3.04	15.20	1.35	2.70	3.38	34.46	100.00
	Gas Analyses, %	74B	**247**	70.04	29.93	0.000	0.018	0.002	0.005	0.001	0.004	0.000	0.001	0.000	0.000	0.031
	Conversion, %					0.18	0.00	0.06	0.01	0.03	0.01	0.04	0.00	0.01	0.00	0.01	0.18
	Selectivity, %						0.00	34.79	7.60	17.11	3.99	22.24	2.28	7.60	0.95	3.42	100.00
	Gas Analyses, %	74C	**271**	69.90	29.98	0.000	0.069	0.010	0.014	0.003	0.014	0.001	0.005	0.002	0.002	0.119
	Conversion, %					0.70	0.00	0.23	0.06	0.09	0.03	0.13	0.01	0.06	0.04	0.05	0.70
	Selectivity, %						0.00	32.47	9.14	12.91	3.68	19.09	1.89	8.67	5.66	6.50	100.00
	Gas Analyses, %	74D	**283**	69.22	30.50	0.000	0.167	0.027	0.026	0.006	0.032	0.003	0.011	0.006	0.005	0.282
	Conversion, %					1.60	0.00	0.54	0.17	0.17	0.06	0.31	0.03	0.14	0.09	0.09	1.60
	Selectivity, %						0.00	33.70	10.90	10.65	3.81	19.13	2.10	8.72	5.55	5.45	100.00

Notes: 1. Gas analyses is reported as mol % normalized to N2 and O2 free
2. Conversion reported as mol % of the feed carbon in CO converted to the various components.
3. Selectivity is reported as the % of the reacted carbon in feed CO that was converted to the various components.
4. File -- N:/DCC_ANL/FT_FETC/Data&Results Membranes/RS-2 (Runs 24 44 48 50 55 57 59).xls