TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSIS

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Abstract

The goal of the proposed work is the development of iron-based Fischer-Tropsch catalysts that combined high activity, selectivity and life with physical robustness for slurry phase reactors that will produce either low-alpha or high-alpha products. The catalyst that is developed will be suitable for testing at the Advanced Fuels Development Facility at LaPorte, Texas or similar sized plant. Previous work by the offeror has produced a catalyst formulation that is 1.5 times as active as the "standard-catalyst" developed by German workers for slurry phase synthesis. The proposed work will optimize the catalyst composition and pretreatment operation for this low-alpha catalyst. In parallel, work will be conducted to design a high-alpha iron catalyst that is suitable for slurry phase synthesis. Studies will be conducted to define the chemical phases present at various stages of the pretreatment and synthesis stages and to define the course of these changes. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for catalysts synthesized in this program for activity, selectivity and aging characteristics.

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1.0 Executive Summary

A series of runs were made in the CSTR system to provide a comparison of five Fe-based silica catalysts and five Fe-based alumina catalysts at 250°C and 230°C for their performance. Both series of catalysts were prepared to obtain atomic ratios of Fe to Al or Si of 4.4% and 3 wt.% Cu (relative to Fe). Each series had varying amountsof potassium (0.0 wt.% K, 2.5 wt.% K, 5.0 wt.% K, 7.5 wt.% K and 10.0 wt.% K) relative to Fe.

In general, the following trends were observed for the %CO conversion,

☞ For Both 230°C and 250°C Synthesis Temperatures

Silica Series Better Than Alumina Series

☞ For Both Alumina and Silica Series

%CO Conversions Better at 250°C than at 230°C

☞ For The Alumina Series

230°C : 2.5wt%K ≈ 5.0wt% > 7.5wt%K > 10.0wt%K

250°C : 2.5wt%K >> 5.0wt%K > 7.5wt%K >> 10.0wt%K >0.0wt%K

☞ For The Silica Series

230°C : 7.5wt%K ≥ 5.0wt% ≥ 2.5wt%K >> 10.0wt%K > 0.0wt%K

250°C : 2.5wt%K ≥ 5.0wt%K ≥ 7.5wt%K >> 10.0wt%K >0.0wt%K

2.0 Introduction

The objective of this research project is to develop the technology for the production of physically robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry phase synthesis reactor

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development. The catalysts that are developed shall be suitable for testing in the Advanced Fuels Development Facility at LaPorte, Texas, to produce either low- or high-alpha product distributions. Previous work by the offeror has produced a catalyst formulation that is 1.5 times as active as the "standard-catalyst" developed by German workers for slurry phase synthesis. The proposed work will optimize the catalyst composition and pretreatment operation for this low-alpha catalyst. In parallel, work will be conducted to design a high-alpha iron catalyst this is suitable for slurry phase synthesis. Studies will be conducted to define the chemical phases present at various stages of the pretreatment and synthesis stages and to define the course of these changes. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for catalysts synthesized in this program for activity, selectivity and aging characteristics.

The research is divided into four major topical areas: (a) catalyst preparation and characterization, (b) product characterization, (c) reactor operations, and (d) data assessment.

To accomplish the objectives of the project, these topics have been organized into the following technical tasks:

a. Task 1.0 Development of Optimum Promoter Levels for Low- and High-Alpha

Catalysts

The goal of this task is to identify and optimize procedure for the preparation of iron-based catalysts that combine high activity selectivity and life with physical

robustness. Each of the subtasks address an area of considerable uncertainty in the synthesis of catalysts.

    1.1   Determine Optimized Synthesis Procedure for High-Alpha Iron-Based Fischer-Tropsch Catalysts

- Role of precursor particle size on activity.
- Role of Cu in precipitated catalysts.
- Define attrition resistance.

    1.2   Prepare Catalysts that can be Used to Determine the Role of Promoters for Low- and High-Alpha Catalysts

- Define optimum SiO_2.
- Define optimum Al_2O_3.

    1.3   Prepare Catalysts that can be Used to Quantify the Role of K on Product Selectivity in both Low- and High-Alpha Catalysts.

    1.4   Complete the Optimization of the Two Best Low-Alpha, Iron-Based Fischer-Tropsch Catalysts Developed during the Previous Contract.

b. Task 2.0 Definition of Preferred Pretreatment for both Low- and High-Alpha Fischer-Tropsch Catalysts.

The goals of this task are to define the preferred treatment, to define the role of Cu and K during the pretreatment on activity and selectivity and to define the chemical and physical changes which occur during the preferred pretreatment. The subtasks address each of these goals.

    2.1   Determine the Role of Cu in the Activation of Precipitated Low- and High-Alpha, Iron-Based Fischer-Tropsch Catalysts.

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2.2   Determine the Effect of K Content on Activation Procedures and Determine if the Method of Addition has any Effect on Catalyst Activity and Life.

2.3   Determine the Physical and Chemical Changes that Occur during Catalyst Pretreatment and Use and Determine how these Changes Effect the Strength of the Catalysts.

2.4   Evaluate the Effect of Carbon Deposition during Catalyst Activation on Activity, Selectivity and Aging Characteristics.

c. Task 3.0   Catalyst Structure and Characterization.

The goal of this task is to provide basic analyses (surface area, XRD) of all catalyst prepared and to provide additional techniques as required (Mössbauer, SEM, XPS, etc.) to answer specific questions or to provide basic required characterization data for the catalysts.

d. Task 4.0   Catalyst Testing.

The goals of this task are to operate the eight CSTR reactors, measure catalyst performance, determine the stable phases that exist during synthesis at low and high conversions and to determine the rates of interconversion of iron oxide and carbide.

4.1   Verify the Quality of Data Obtained from the CSTR's.

4.2   Measure Catalyst Performance.

4.3   Determine the Stable Phases that Exist during Synthesis at Low and High CO Conversion Levels.

4.4   Obtain Data on the Rates Involved in the Interconversion of Iron Oxide and Iron Carbide.

Comparison of Alumina and Silica Based High-Alpha Catalyst at 230°C and 250°C

Once it was shown that the Polywax PW$_R$3000 was a suitable reactor solvent, five Fe-based/silica catalysts and five Fe-based/alumina catalysts were tested at both 250°C and 230°C for their conversion performance in the one liter continuously stirred tank reactors (CSTR). The ten catalysts tested at the two synthesis temperatures are referred to as the hi-alpha catalyst studies. All catalysts were activated with syngas (H$_2$/CO = 0.7) at 270°C, ambient pressure and a space velocity of 3.11 (STP) h^{-1} g-Fe for 24 h. The reactor pressure was increased to 1.3 MPa after activation and FT synthesis was started. The alumina and silica series catalysts were both co-precipitated with the iron such that atomic ratios of aluminum(silicon) relative to Fe was 0.044 or, 4.4atomic% Al(Si). All ten catalysts were impregnated with copper so that the copper was present at a 3.0wt%Cu, relative to iron. Both the silica and alumina series Fe-based catalysts had varying amounts of potassium, specifically 0.0wt%K, 2.5wt%K, 5.0wt%K, 7.5wt%K, and 10.0wt%K, relative to Fe. The following list identifies the catalyst and gives an atomic(mole) representation of the Si/Al, Cu, and K, based on 100 atoms/moles of Fe.

Silica Series:

RJO228(0.0wt%K) 100Fe:4.60Si/2.72Cu/0.00K

RJO229(2.5wt%K) 100Fe:4.60Si/2.72Cu/3.66K

RJO230(5.0wt%K) 100Fe:4.60Si/2.72Cu/7.52K

RJO231(7.5wt%K) 100Fe:4.60Si/2.72Cu/11.58K

RJO232(10.0wt%K) 100Fe:4.60Si/2.72Cu/15.87K

Alumina Series:

        RJO250(0.0wt%K) 100Fe:4.60Al/2.72Cu/0.00K

        RJO251(2.5wt%K) 100Fe:4.60Al/2.72Cu/3.66K

        RJO252(5.0wt%K) 100Fe:4.60Al/2.72Cu/7.52K

        RJO254(7.5wt%K) 100Fe:4.60Al/2.72Cu/11.58K

        RJO255(10.0wt%K) 100Fe:4.60Al/2.72Cu/15.87K

The silica series catalysts at a synthesis temperature of 250°C were tested first and Figure 1 shows the %CO conversion versus time on stream. These runs were designated as LGX254-258 and used the RJO232, RJO231, RJO230, RJO229, and RJO228 catalyst, respectively. The %CO conversion for the silica series at 230°C is presented in Figure 2 (runs LGX259-263 utilizing the RJO232-228, respectively).

For the alumina series at 250°C, the CO conversion is given in Figure 3 (runs LGX267-271 utilizing the RJO250, RJO251, RJO252, RJO254, and RJO255 catalysts, respectively) while Figure 4 shows the %CO conversion for alumina at 230°C (runs LGX276-279 using the RJO251, RJO252, RJO254, and RJO255 catalyst, respectively, and run LGX283 using the RJO252 catalyst). Note that for the 230°C alumina series that the catalyst with 0.0wt%K was not tested and that run LGX283 is a repeat run of LGX277 (the 5.0wt%K catalyst). Also note for runs LGX276, LGX278, and LGX279, at ~run hour 183, a re-pretreatment of the catalysts with only CO gas was performed, which did not appear to help.

In general, the following trends were observed for the %CO conversion,

        ☞ For Both 230°C and 250°C Synthesis Temperatures

        Silica Series Better Than Alumina Series

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☞ For Both Alumina and Silica Series

%CO Conversions Better at 250°C than at 230°C

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☞ For The Silica Series

230°C : 7.5wt%K ≥ 5.0wt% ≥ 2.5wt%K >> 10.0wt%K > 0.0wt%K

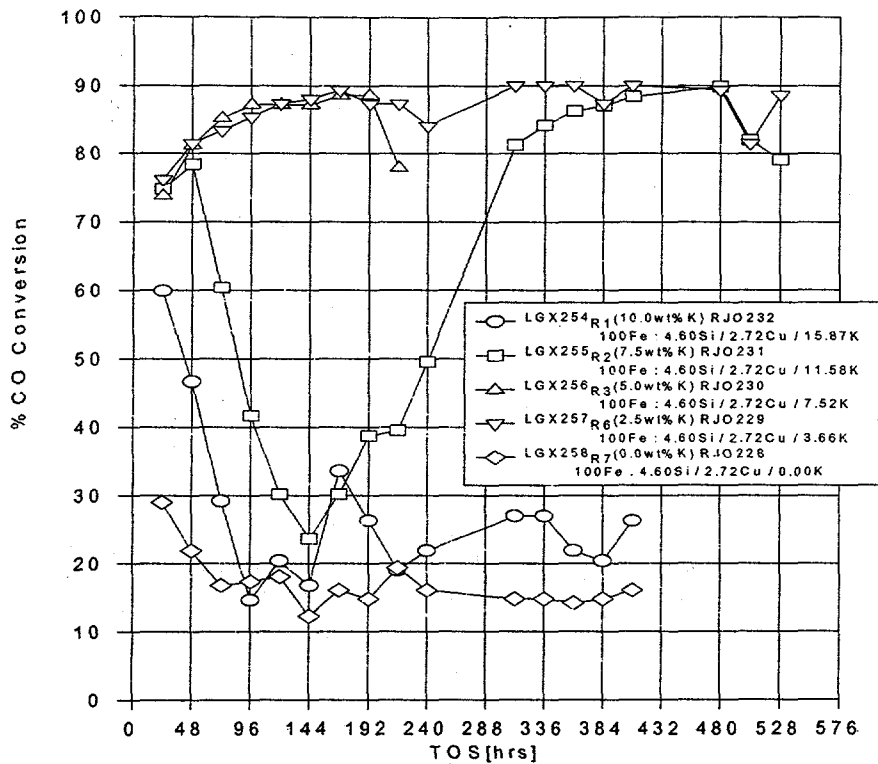250°C : 2.5wt%K ≥ 5.0wt%K ≥ 7.5wt%K >> 10.0wt%K >0.0wt%K

Figure 1.   %CO Conversion vs Time on Stream for Runs LGX254-258.
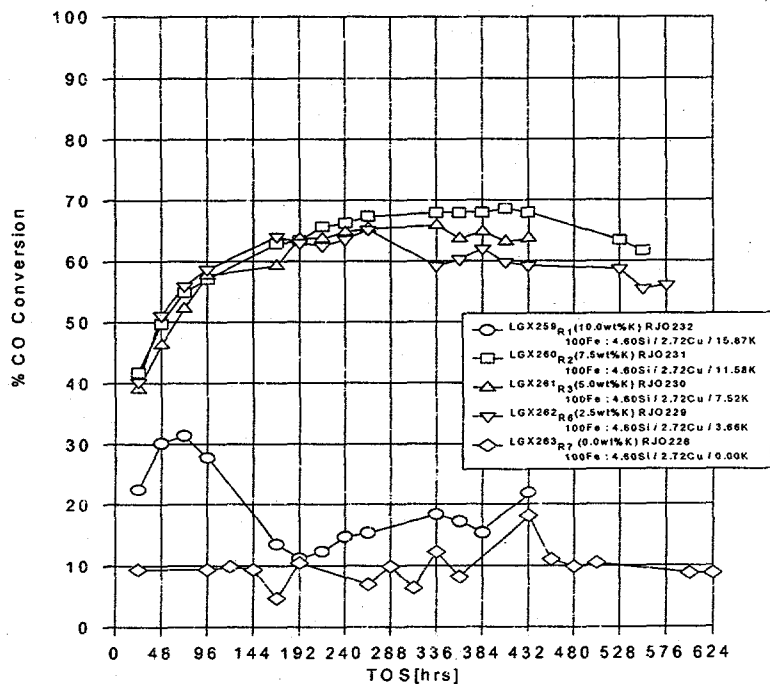

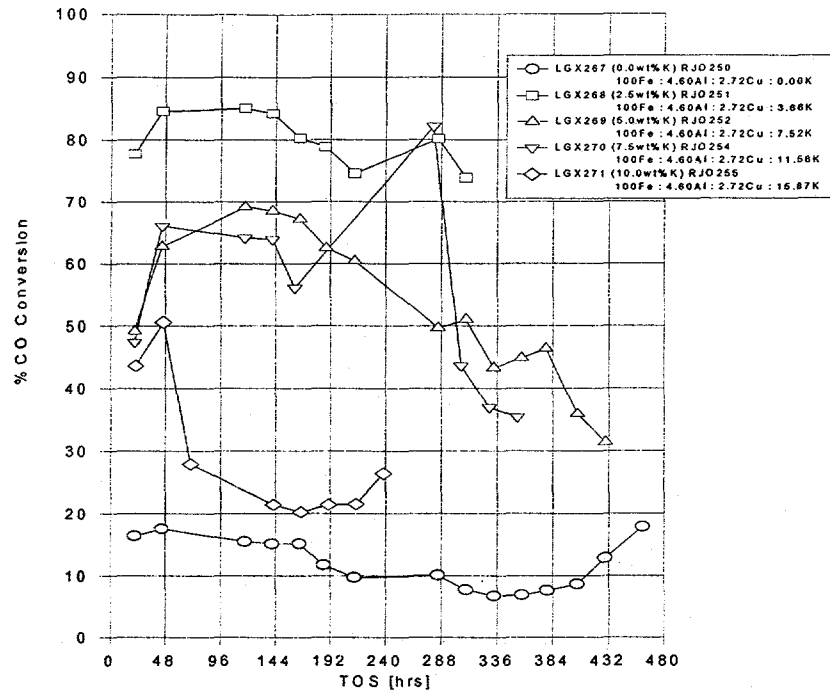Figure 2.   %CO Conversion vs Time on Stream for Runs LGX259-263.

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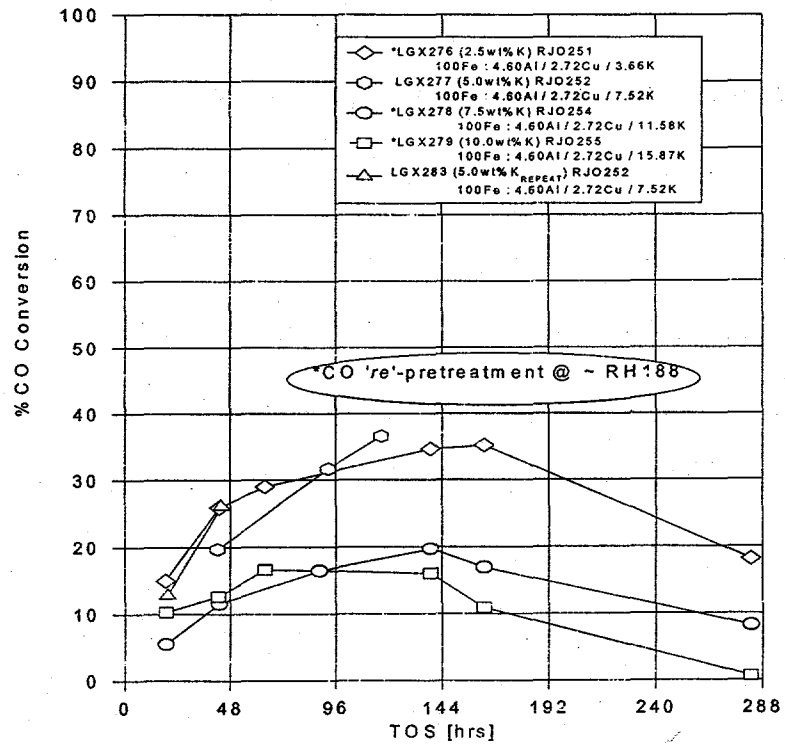Figure 3.   %CO Conversion vs Time on Stream for Runs LGX267-271.

Figure 4.   %CO Conversion vs Time on Stream for Runs LGX276-279 & LGX283.

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High-Aluminas

A series of runs was performed using catalyst that contained varying amounts of alumina as a support. The alumina, Al_2O_3, varied nominally from ~10wt% to ~53wt% for the four catalysts used in this series of runs and each catalyst had different amounts of Al, Cu, and K. The reactors had a 10.0wt% catalyst loading in the PW_R3000 polyethylene wax reactor solvent and a synthesis temperature of 270°C was used for these runs. The following list identifies the catalyst and gives an atomic(mole) representation of the Al, Cu, and K, based on 100 atoms/moles of Fe.

a. RJO274 (10.15wt%Al_2O_3 & 52.69wt%Fe), 100Fe:21.1Al/2.73Cu/11.8K

b. RJO275 (17.74wt%Al_2O_3 & 46.93wt%Fe), 100Fe:41.4Al/2.72Cu/11.6K

c. RJO276 (37.58wt%Al_2O_3 & 35.19wt%Fe), 100Fe:117Al/2.72Cu/11.6K

d. RJO277 (53.13wt%Al_2O_3 & 23.47wt%Fe), 100Fe:248Al/2.74Cu/11.6K

Figure 1 shows the %CO conversion for runs LGX284, LGX285', LGX286 and LGX287, which used catalysts RJO274, RJO275, RJO276, and RJO277, respectively.

Run LGX284 was aborted after 144 hours on stream due to the inability to withdraw liquid reactor product through the 2μ-rewax filter, which is located inside the reactor and submerged in the catalyst/wax reactor slurry at start up . It is not certain if the 2μ-rewax filter for LGX284 was blinded off from previous runs or if the tubing run from the reactor to the rewax trap (vessel for the collection of liquid reactor product) was plugged, or a combination of both. Modifications to the tubing run from the reactor to the rewax trap have been implemented to allow for a repeat of this run.

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Run LGX285' was a repeat run of LGX285, as LGX285 was aborted during the 24 hour pretreatment period due to the reactor pressure rising to ~400psig (as the pretreatment pressures are fixed at a nominal 0psig).

Although there was an inability to remove reactor product via the rewax filter for run LGX284, difficulties in catalyst/wax separation and reactor product removal was not encountered for runs LGX285'-287. In fact, there was no plugging or blinding off of the rewax filters over the course of these runs and the reactor product removed through the rewax filter was visibly free from catalyst contamination. The increased amounts of Al_2O_3 and the lower Fe content associated with these catalysts are thought to be mainly responsible for the ease of reactor product removal through the rewax filter. This, along with the fact that there were problems associated with the mass balance resulted in removal of too much reactor product via the rewax filter for runs LGX285'-287. Specifically, after the completion of these runs, the reactor contents were collected and measured and deficits of 84g 186g, and 213g from the initial catalyst/PW_R3000 wax loading of 344.0g was found for runs LGX285', LGX286, and LGX287, respectively. In effect, this results in higher percentage catalyst loadings for these runs, as well as a reduced residence time in the reactor slurry, but the effect on CO conversion is not well understood.

The previously mentioned problems present some difficulty in attempting to compare this series of runs, but with respect to the data for %CO conversion over time, the best results were obtained using the RJO276 catalyst (run LGX286) as CO conversions were maintained at levels of 70-80%. The CO conversion for runs LGX287(RJO277) and LGX285(RJO275) were comparable to one another for run

hours 100-336, but both had CO conversions of 40% at run hour 336 while for run
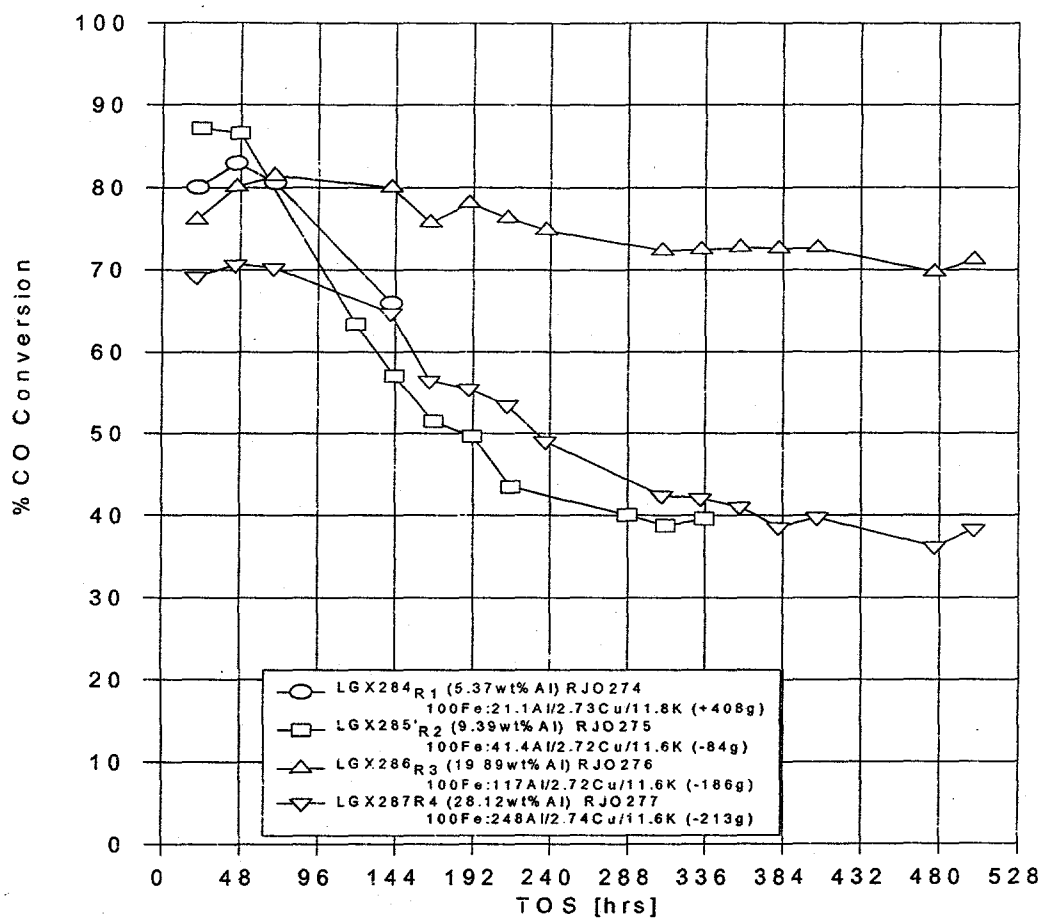
LGX286, the CO conversion was at +70%.

Figure 1.   %CO Conversion vs Time on Stream for Runs LGX284-287.