

**CARBON COATED (CARBONOUS) CATALYST IN EBULLATED BED REACTOR
FOR PRODUCTION OF OXYGENATED CHEMICALS FROM SYNGAS/CO₂**

Support of Advanced Fuel Research Program

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FIRST ANNUAL REPORT

Project Summary

This report summarizes the work accomplished in the first year (October, 1999 to September, 2000) of the R&D project under DOE's Support of Advanced Fuel Research program, Contract No. DEFG26-99FT40681.

Majority of the work accomplished in the first year of the program are in the following areas:

Task I: a) Preparation of SOTA zinc-chromite catalyst extrudates by carbonous extrusion and carbon coating; b) Preparation of advanced K-Mn promoted ZrO₂ catalyst extrudates by carbonous extrusion and carbon coating.

Task II: Characterization of the Catalyst Extrudates prepared in Task I.

Procedures for carbonous extrusion and carbon coating of SOTA zinc-chromite and advanced K-Mn promoted ZrO₂ catalysts were developed with success. Carbon coated catalyst extrudates have reasonable surface area with high attrition resistance and appear to be suitable for use in ebullated bed operation.

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CARBON COATED CATALYST IN EBULLATED BED REACTOR FOR PRODUCTION OF OXYGENATED CHEMICALS FROM SYNGAS/CO₂

INTRODUCTION

There are a number of exothermic chemical reactions which might benefit from the temperature control and freedom from catalyst fouling provided by the ebullated bed reactor technology. A particularly promising area is production of oxygenated chemicals, such as alcohols and ethers, from synthesis gas, which can be economically produced from coal or biomass. The ebullated bed operation requires that the small-diameter (~ 1/32") catalyst particles have enough mechanical strength to avoid loss by attrition. However, all of the State Of The Art (SOTA) catalysts and advanced catalysts for the purpose are low in mechanical strength. The patented carbon-coated catalyst technology developed in our laboratory converts catalyst particles with low mechanical strength to strong catalysts suitable for ebullated bed application.

This R&D program is concerned with the modification on the mechanical strength of the SOTA and advanced catalysts so that the ebullated bed technology can be utilized to produce valuable oxygenated chemicals from syngas/CO₂ efficiently and economically.

OBJECTIVE

The objective of this R&D program is to study the technical and economic feasibility of selective production of high-value oxygenated chemicals from synthesis gas and CO₂ mixed feed in an ebullated bed reactor using carbon-coated catalyst particles.

WORK PLAN

The following tasks are to be performed in the three years program to attain the objectives of the R&D program.

Task I: Preparation of Carbon-Coated Catalysts

Task II: Characterization of Catalysts

Task III: Evaluation of Catalyst Activities

Task IV: Large Scale Production of Optimum Catalysts

Task V: Bench Scale Ebullated Bed Evaluation of the Optimum Catalyst

Task VI: Economic Assessment of the Carbon-Coated Catalyst--Ebullated Bed Technology

Task VII: Preparation of Final Report

WORK ACCOMPLISHED IN THE FIRST YEAR OF THE PROGRAM

In the first year of the program, majority of the work accomplished is for Task I and Task II including some preparation work for Task III.

Task I: Preparation of Carbon-Coated Catalyst

Two types of catalysts, (i) SOTA Cesium-promoted ZnO-Cr₂O₃ catalyst and (ii) Advanced Mn and K promoted ZrO₂ catalyst, are to be prepared by carbonous extrusion of catalyst powder followed by carbon-coating of the catalyst extrudates in this task.

In case of SOTA catalyst, both the catalyst powder prepared in our laboratory and a sample of commercial zinc-chromite catalyst powder were utilized for preparation of the carbon-coated extrudates. In case of the advanced catalyst, the catalyst powder used for carbonous extrusion was prepared in our laboratory.

Carbonous extrusion consists of mixing catalyst powder and a carbon-coating agent followed by extruding the mixture in a laboratory scale extruder to prepare small diameter (<1/32") catalyst extrudates. These extrudates are carbonized at 1000°F to 1350°F in nitrogen atmosphere followed by partial oxidation at 700 to 850°F to form porous carbon coating. In most of the cases, a second carbon-coating of the extrudates is needed to achieve desirable crush strength.

Task II: Characterization of Carbon-Coated Catalysts

Most of the catalyst extrudates were characterized by the following analyses:
Crush Strength (ASTM D4179-82), BET surface area, Carbon content.

Only a selected few of the catalyst extrudates were subjected to the following tests:
Cold-flow ebullated bed testing for attrition resistance,
Drum attrition loss testing (Adaptation of ASTM D4058), and
Pore size distribution.

For the convenience of understanding the experiments, results and discussion, Task I and Task II works are described simultaneously.

Task III: Catalyst Activity Studies

For this task of experimental runs for catalyst activity studies, only the experimental run plan and equipment preparation were initiated

1) EXPERIMENTAL

Carbon Coating Agent: Different liquid hydrocarbons utilized for preparing carbon-coated

extrudates are described as the followings.

(i) PPFA: The partially polymerized furfuryl alcohol (PPFA) used for carbonous extrusion and carbon-coating of catalysts were prepared by heating the alcohol at its boiling point from 4 to 8 hours. The apparatus for the purpose consists of a 500 c.c. flask attached to a reflux condenser and heated on a hot plate equipped with temperature controller and monitor.

The viscosity (a parameter representing degree of polymerization) of polymerized furfuryl alcohol increase with increasing polymerization time at its boiling point as shown in the following table:

Time of Polymerization (hr)	4	6	8
Viscosity (CST) @ 100°F	3.66	4.05	4.27
@122°F	2.59	2.87	2.89

(ii) MPFA: To prepare a polymer with moderate degree of polymerization (MPFA), furfuryl alcohol with 0.3 to 0.5 v% concentrated sulfuric acid was heated at 70-80°C for 5-6 minutes with constant stirring.

(iii) Coal Liquid: Liquid from a catalytic coal liquefaction PDU run---- vacuum still overhead fraction (12.5 API gravity, 500-900oF B.P. range).

(iv) Wax from Fisher-Tropsch synthesis in DOE La Porte PDU Run 1 (provided by Southwest Research Institute)

Extruder: A laboratory scale extruder from The Bonnot Company was modified into the manual mode and fitted with die for making 1/30" and 1/40"(0.7 mm diameter) extrudates.

Carbonous Extrusion and Carbon-Coating:

To prepare catalyst extrudates, finely ground catalyst powder is thoroughly mixed with 20 to 35 w% carbon-coating agent to obtain a paste suitable for extrusion. This paste is introduced in the extruder and different diameter extrudates are formed using different size die. The carbonous extrudates are subjected to carbonization and partial oxidation as described below under carbon-coating.

Carbon-Coating of Extrudates:

To apply carbon coating on catalyst extrudates, the extrudates are soaked in a carbon-coating agent for 30 minutes followed by filtering out the excess liquid, carbonization and partial

oxidation as described below.

Carbonization and Partial Oxidation:

In carbonization procedure, the carbon-coating agent in the extrudates is heated at high temperature in an inert atmosphere in order to yield a carbon-coating of the catalyst particles. Partial oxidation of the carbon-coated extrudates allow to develop pores on the carbon coating.

Apparatus for (i) carbonization of carbon-coating agent containing catalyst extrudates, and (ii) partial oxidation of the carbonized catalyst particles:

A 1" o.d. x 24" long quartz reactor system equipped with a tube-furnace, temperature controller, gas (nitrogen and air) with pressure regulators, and gas flow meters was utilized for carbonization and partial oxidation. Carbonization is conducted at 1000°F to 1350°F temperatures for 4 to 9 hours in a flow of nitrogen gas. Partial oxidation is conducted at 700°F to 900°F temperatures in a flow of a mixture of nitrogen and air containing 0.5 to 3.0 v% oxygen for 1 to 4 hours.

Preparation of Zinc-chromite (ZnO-Cr₂O₃) Catalyst Powder.

The zinc chromite catalyst powder was prepared by co-precipitation of aqueous solutions of zinc nitrate and chromium nitrate in a basic solution followed by heating the solution, filtering the slurry, washing, and calcining the powder. The aqueous solution of zinc nitrate and chromium nitrate in desired proportion is poured slowly into an aqueous solution of K₂CO₃ and KOH (pH=10) with stirring. The precipitated product was heated to 70°C and stirred for 3 hours. The product was filtered and rinsed three times with de-ionized water. The powder was dried at 100°C in a vacuum oven and analyzed to ensure that K level was <300 ppm. The powder was calcined at 325°C in air for 2 to 3 hours.

Cesium Doping of Zinc-Chromite Extrudates

Prior to impregnation with cesium compound, the zinc-chromite catalyst powder was subjected to carbonous extrusion and carbon coating procedure to prepare catalyst extrudates. The reason is that the high temperature of carbon coating procedure may deactivate the cesium component of the catalyst. Cesium doping with formate salt CsOOCH was effected by adding the catalyst extrudates in a nitrogen purged aqueous CsOOCH solution with desired concentration at 323°K. The weight ratio of catalyst to aqueous solution was 1:10. The solution was then evaporated to dryness. The target cesium concentration on the catalyst was 3 mole%.

Preparation of K and Mn promoted ZrO₂ catalyst.

Potassium and Mn promoted ZrO₂ catalyst powder was prepared by co-precipitation. Aqueous solution of ZrOCl₂, aqueous solution of Mn(NO₃)₂ and 3.5M ammonium hydroxide solution were concurrently added to a container with continuous stirring at 50°C keeping the solution pH

at 9. The precipitate was filtered and washed with deionized water. The powder was dried at 120°C in a vacuum oven for 4 hours. The powder was calcined at 600°C in air for 5 hours. K₂CO₃ (2 w% based on K₂O) was then impregnated into the powder using aqueous solution incipient impregnation procedure. The powder was dried and calcined at 600°C for 5 hours.

Cold-Flow Ebullated Bed Reactor

A laboratory scale (½" i.d. x 3 ft high glass tube) cold flow ebullated bed reactor system was set up to test the attrition resistance at room temperature of small quantity of carbonous catalyst extrudates prepared in the laboratory. Heptane was pumped as the liquid ebullating medium and air was blown at the bottom of the reactor to achieve approximately 30 to 40% bed expansion.

2) RESULTS

Carbon Coating of Catalyst Extrudates Using Partially Polymerized Furfuryl Alcohol

A Ni-Mo on gamma-alumina catalyst (HTI 6321) extrudate (1/32") was selected for first carbon coating test because of its relatively low crush strength (2.46 lb/mm). Partially polymerized furfuryl alcohol (PPFA) prepared at different duration of polymerization (4 hours, 6 hours, and 8 hours) was utilized. Crush strength, carbon content, and surface area data of the carbon coated catalyst samples are presented in the following table:

PPFA Polymerization Time, Hours (Sample #)	Carbon, w%	Crush Strength, lb/mm	BET Surface Area, m ² /gm
4 (CC4-111299)	12.6	4.2	
6 (CC6-111999)	10.8	4.4	
8 (CC8-111799)	8.6	5.2	352
4 (CC4-121599)	8.6	4.3	358
8 (CC8-121499)	7.4	4.1	364
8 (CC8-110999)	15.1	5.8	
Fresh Catalyst(HTI 6321)	0.0	2.46	224

These results show that

(i) Crush strength of the carbon coated catalyst, with 7 to 12 w% carbon content is at least 4.0 lb/mm, which is significantly higher than that of the fresh catalyst.

(ii) The surface area of the carbon coated catalyst is approximately 350 m²/gm. The fresh catalyst has a surface area of 224 m²/gm. Comparison of pore size distribution show that higher

surface area than that of the fresh catalyst is due to micro-pores formed on the carbon coating surface.

Carbon Coating Using F-T Wax

HTI 6321 catalyst (Ni-Mo on gamma-alumina) extrudates were carbon coated using F-T wax provided by South West Research Institute (Sample ID # FL-2559) and the standard procedure of soaking, carbonization and partial oxidation. The carbon content, crush strength, and surface area of the carbon coated extrudates are presented in the following table:

Sample No.	Carbon Content, w%	Crush Strength, lb/mm	BET Surface Area, m ² /gm
WC122999	5.1	4.84	
WC011300	8.3	3.06	
WC011800	8.6	4.14	220
HTI 6321	0.0	2.46	224

These results show that the carbon coating procedure using F-T wax is successful in improving crush strength of the catalyst extrudate from 2.46 lb/mm to the range of 3.1 and 4.8 lb/mm. There is no apparent loss in overall surface area.

Carbon Coating Using Coal Liquid

The HTI 6321 catalyst (Ni-Mo on gamma-alumina) extrudates were carbon coated using a liquid fraction (vacuum still overhead) from a coal liquefaction PDU run and utilizing the standard carbon coating procedure. The one-time carbon coated extrudates had 5 w% carbon content. After applying a second coating, the carbon content was 8.9 w% and the crush strength was 3.82 lb/mm. Catalyst properties are presented in the following table:

Sample No.	Carbon Content (w%)	Surface Area (m ² /gm)	Crush Strength (lb/mm)
CCN2-040400	5.0	208.9	2.58
RCN2-040400*	10.7	199.5	5.1
CCN2-041900**	8.9	212.4	3.82
HTI 6321	0.0	224	2.46

* Second coating and oxidation at 800°F for one hour.

** Oxidation of RCN2-040400 at 800°F for another two hours.

These results show that carbon coating using a light coal liquid can improve crush strength of catalyst extrudates without any significant loss of the overall surface area. These results show that coal liquids can be viable products for carbon coating catalyst extrudates. Carbon coating using heavier fraction of coal liquid (such as adding pressure-filter-liquid to vacuum still overhead) is recommended to improve crush strength and add carbonous surface area to the coated catalyst.

Carbonous Extrusion of Alumina Powder

Carbonous catalyst extrudates were prepared in a laboratory scale extruder using a gamma-alumina powder thoroughly mixed with partially polymerized furfuryl alcohol (PPFA). The gamma-alumina powder, which can be used as catalyst substrate, has a surface area of 24.7 m²/gm. Properties of the carbonous catalyst extrudates are presented in the following table:

Sample No.	Carbon Content, w%	Crush Strength, lb/mm	Surface Area, m ² /gm
Al-011900	2.2	1.73	34.1
Alumina-powder	0.0	-----	24.7

The crush strength and surface area of the carbonous extrudates with low carbon content look quite encouraging for application in an ebullated bed reactor. The increase in surface area for the carbonous extrudates is due to micro-pore formation on the carbon coating surface.

Preparation of Zinc-chromite Catalyst Powder

Several batches of zinc-chromite catalyst powder with ZnO/Cr₂O₃ ratio of 3/1 were prepared using the procedure described under the experimental section. The aqueous solution of zinc nitrate and chromium nitrate was poured slowly into an aqueous solution of K₂CO₃ and KOH (pH=10) with stirring. The precipitated product was heated to 70°C and stirred for 3 hours. The product was filtered and rinsed three times with de-ionized water. The remaining product dried at 100°C in a vacuum oven and analyzed to ensure that K level is <300 ppm. The powder was calcined at 325°C in air for 2 to 3 hours.

The yield of catalyst powder was 70 to 90 w%. The BET surface area of the catalyst powder was in the range of 110 to 140 m²/gm.

Carbonous Extrusion and Carbon Coating Commercial Zinc-Chromite Catalyst Powder

Commercial zinc-chromite (ZnO/Cr₂O₃ ratio of 3/1) catalyst powder sample was ground to -200 mesh powder. The powder was mixed with partially polymerized furfuryl alcohol to prepare a paste with suitable consistency for extrusion. The paste was processed in the laboratory scale extruder described under the experimental section to prepare extrudates of 0.7 mm diameter. The extrudates were carbonized at 1100 to 1350°F for 2 hours. In certain cases where the carbonized extrudates had low crush strength, a second coating of PPFA was applied

on the extrudates followed by the carbonization and partial oxidation procedure. The carbonized extrudates were partially oxidized at 750 to 800°F for one hour. The characteristics of the catalyst extrudates are presented in the following table:

Sample	Carbon Content (Wt%)	Crush Strength (Lb/mm)	Surface Area (M ² /gm)
RCZnCr-050900		2.37	
RCZnCr-050900A		3.26	131.3
RCZnCr-051500A	3.49	1.45	76.7
RCZnCr-051500AR	4.73	3.96	73.5
RCZnCr-053100	5.42	2.12	
RCZnCr-061600		3.08	84.6

Carbonous extrusion and carbon coating of alumina powder described earlier did not present any problem. However carbonization and oxidation steps for zinc-chromite extrudates were resulting in extrudates with low crush strength (< 1 lb/mm). These problems may be due to oxidizing activity of the chromia in the catalyst powder. A second coating and milder processing conditions were applied to achieve reasonable crush strength and surface area of these catalyst extrudates.

The above results show that adjusting the carbon coating processing conditions, the 0.7 mm diameter carbon-coated extrudates had reasonable crush strength and surface area.

Carbonous Extrusion and Carbon-Coating of Synthesized Zinc-Chromite Catalyst Powder

The synthesized zinc-chromite catalyst powder was subjected to carbonous extrusion and carbon-coating processing using partially polymerized furfuryl alcohol (PPFA8) to prepare 0.7 mm diameter catalyst extrudates. Details are presented in the earlier section. Characteristics of the carbon-coated extrudates are presented in the following table:

Sample	Carbon Content, w%	Crush Strength, lb/mm	Surface Area, m ² /gm
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CZnCr-021800	3.1	1.1	
CZnCr-050400		2.6	
CZnCr-050900		2.2	
CZnCr-050400A*		3.4	68.2
CZnCr-061900	7.1	2.5	69.2

* CZnCr-050400A is the second carbon-coated extrudate of CZnCr-050400.

Cold-Flow Ebullated Bed Testing of Carbon-Coated Zinc-Chromite Extrudates

The laboratory scale (1/2" diameter) Cold-Flow Ebullated Bed Reactor described under the experimental section was tested to verify proper operation using HTI-6321 (Ni-Mo-Al₂O₃) 1/32" diameter catalyst extrudates. The test was successful.

Two batches of 0.7 mm diameter zinc-chromite catalyst extrudates were prepared by carbonous extrusion of synthesized zinc-chromite powder using PPFA followed by carbon coating and partial oxidation procedure. The properties of the extrudates are presented in the following table. The extrudates with low crush strength (1.46 lb/mm) were selected for cold-flow ebullated bed testing with the assumption that beside the strength criteria carbon coating will provide additional protection against attrition loss.

Sample	Carbon Content, w%	Crush Strength, lb/mm	Surface Area, m ² /gm
RCZnCr-050400	5.42	2.63	68.19
RCZnCr-051500	3.49	1.46	76.74
Zinc-Chromite Powder	0.0	-----	69.9

Heptane was pumped as the liquid ebullating medium and air was blown at the bottom of the reactor to achieve 30-35% expansion of the catalyst extrudate bed following the standard test procedure developed in our laboratory. The run was conducted for 15 days. There was no apparent reduction in size of the catalyst extrudates. The recovered and solvent-free catalyst extrudates were measured for weight and volume.

The weight and volume of the recovered catalyst extrudates were exactly the same as those of the initial feed catalyst. According to the cold-flow ebullated-bed test results, attrition loss is zero for the carbonous zinc-chromite extrudates. For commercial catalysts, the attrition loss must

be less than 5 w%.

Drum Attrition Loss Test

Since the cold-flow ebullated-bed testing of a carbon-coated zinc-chromite catalyst showed no attrition loss, a large batch of carbon-coated zinc-chromite catalyst extrudates were prepared for an accelerated severe attrition loss study called Drum Attrition Loss Test. The test method is an adaptation of ASTM D4058 method. The drum with catalyst extrudates is rotated at 60 rpm for 7.25 hours. A catalyst is good for ebullated bed reactor operation, if the attrition loss in this test is less than or equal to 5 w%. The characteristics of the catalyst extrudates are presented in the following table:

Sample	Carbon Content, W%	Surface Area, M ² /gm	Crush Strength, Lb/mm	Drum Attrition Test Loss , w%
CZnCr-061900	7.07	69.24	2.48	1.45

The carbon-coated zinc-chromite catalyst extrudates had an attrition loss of 1.45 w% in the Drum Attrition Loss test. This result indicates that even under severe conditions in an ebullated bed reactor, the attrition loss will be low.

Preparation of K and Mn Promoted ZrO₂ Catalyst Powder

The advanced catalyst of K and Mn promoted ZrO₂ was prepared by co-precipitation method as described under the Experimental section. Aqueous solution of ZrOCl₂, Mn(NO₃)₂ and 3.5M ammonium hydroxide were concurrently added with continuous stirring into a container at 50°C keeping the solution pH at ~9. The precipitate was filtered and washed with de-ionized water, and the gel was dried at 120°C in a vacuum oven for 4 hours. The dried gel was calcined at 600°C for 5 hours. Potassium carbonate (2% based on K₂O) was impregnated into the calcined powder, dried, and calcined again at 600°C for 5 hours.

BET surface area of the catalyst powder was ~300 m²/gm.

Carbonous Extrusion and Carbon Coating of K and Mn Promoted ZrO₂ Catalyst Powder

Carbonous extrusion and carbon coating of the Mn-K-promoted ZrO₂ catalyst powder using the laboratory scale extruder and the following carbonous media did not yield sufficient crush strength (<1 lb/mm) of the catalyst extrudates even after optimization of the operating conditions.

- Carbonous Medium:
- 1) Partially polymerized furfuryl alcohol (PPFA)
 - 2) Wax from F-T synthesis (supplied by SWRI)
 - 3) Coal Liquid (VSOH)

It was apparent that higher degree of polymerization of the carbonous medium was necessary. PPFA with moderate degree of polymerization (MPFA) was obtained by adding 0.3 to 0.5 cc of concentrated H₂SO₄ as catalyst into 100 c.c. of furfuryl alcohol and heating at 70-80°C for 5 to 6 minutes.

Carbonous extrusion of K-Mn promoted ZrO₂ catalyst powder using MPFA and subsequent carbon coating of the extrudates using the MPFA resulted in extrudates with sufficient crush strength and reasonable surface area as presented in the following table:

Sample	Extrudate Diameter, mm	Carbon Content, w%	Crush Strength Lb/mm	Surface Area, M ² /gm
CKZrMnO _x -090800	0.7	14.35	2.2	91.9
CKZrMnO _x -091900	0.7	19.84	3.1	72.9
CKZrMnO _x -092200	0.7		2.6	60.8
CKZrMnO _x -092500	0.7		3.6	

The above results show that carbon coated K-Mn promoted ZrO₂ catalyst extrudates can be prepared with sufficient crush strength and reasonable surface area.

Preparation For An Experimental Run Under Task III (Catalyst Activity Testing)

Two large batches of carbon-coated and cesium promoted zinc chromite catalyst extrudates were prepared for the upcoming experimental run for catalyst activity testing under Task III. Commercial zinc-chromite catalyst powder was used. Carbonous extrusion and carbon coating of zinc-chromite catalyst powder was carried out using partially polymerized furfuryl alcohol under operating conditions developed earlier. The catalyst extrudates were doped with 3 w% cesium using cesium formate as the precursor. The process of cesium doping was described in the Experimental section. The properties of the 0.7 mm diameter catalyst extrudates are presented in the following table.

Sample	Carbon Content, w%	Crush Strength, lb/mm	Surface area, m ² /gm
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Tentative Run Plan for Catalyst Activity Testing

Catalyst activity testing will be conducted in a two stage Robinson-Mahoney reactor system (HTI Unit 245) consisting of two stirred 1-liter autoclave reactors with catalyst basket. A few modifications to the Unit 245 are needed for this test run. The catalyst basket in each reactor will be charged with 100 gms of carbon-coated, Cs-promoted zinc-chromite catalyst extrudates. Syngas with H₂/CO ratio of 0.75 and 5 v% CO₂ will be used as the feed gas. Decalin will be used as the liquid medium.

A 120 hours of run with two different space velocities will be conducted at 1500 psig pressure, 650-700°F temperature in the first stage and 700-790°F temperature in the second stage.

Characterization of Carbon-Coated Iron Catalyst By XPS Analysis

Per instruction from Product Manager Dr. Richard Noceti, arrangements were made with the help of Dr. Michael Nowak and Dr. Anthony Cugini for XPS analysis of carbon-coated iron powder and carbon-coated Kentucky FT-catalyst samples at NETL in-house R&D.

Four carbon-coated extrudate samples were sent to NETL (Attn: Rod Diehl/John Baltrus):

- i) Two samples (CFeb) were prepared using iron powder, and
- ii) Two samples (CFeK) were prepared using Kentucky iron catalyst.

XPS analysis results are as the followings:

- A) Major components on the surface of each sample were oxygen, carbon and iron.

- B) Fe_2O_3 and perhaps iron hydroxide on surface of CFeB samples.
- C) Fe_2O_3 on surface of CFeK samples.
- D) For CFeB samples, surface graphite with a CO species, and no iron carbide.
- E) For CFeK samples, surface graphite with no iron carbide.

In summary, carbon coating operation leads to (i) Fe_2O_3 on the surface, (ii) graphite coating on the surface, and (iii) no iron carbide on the surface.

3) CONCLUSION

The following conclusions can be reached based on the accomplishments in the first year of the R&D program:

- 1) Procedure for carbonous extrusion and carbon coating of SOTA zinc-chromite catalyst was developed with success.
- 2) Extrudates of carbon-coated SOTA catalyst have high attrition resistance. These extrudates appear to be suitable for use in ebullated bed operation.
- 3) Procedure for carbonous extrusion and carbon coating of K-Mn promoted ZrO_2 advanced catalyst was developed with success.
- 4) High crush strength of the carbon-coated K-Mn promoted ZrO_2 catalyst extrudates indicates

sufficient attrition resistance for ebullated bed operation.

5) Carbon-coated SOTA catalyst extrudates were prepared for the activity test run under Task III.