

## TITLE PAGE

**Report Title:** Annual Technical Report  
“Novel Preparation and Magneto Chemical Characterization of Nano-Particle Mixed Alcohol Catalysts”

**Type of Report:** Annual

**Reporting Period Start Date:** 09/01/2002

**Reporting Period End Date:** 08/31/2003

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**Date Report was Issued:** Feb. 23, 2004

**DOE Award Number:** DE-FG26-00NT40836

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**Subcontractor:** Louisiana Tech University

**Industrial Collaborator:** Hydrocarbon Technologies, Inc

(Performance Period: 09/01/2000 to 08/31/2004 for three years)

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## ABSTRACT

The preparation of Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe nano-particle metal loaded mesoporous 1 mm spherical granular  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, by combined sol-gel/oil-drop methods followed by calcination and hydrogenation steps, is accomplished. Parameters for calcination process were optimized using DTA. The properties of metal loaded  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> granules were compared for the preparations starting with two precursors: aluminum tri-sec-butoxide (ALTSB) and aluminum tri-iso-propoxide (ALTIP). Three sol-gel/oil-drop catalyst preparation methods; 1) Metal nitrate solutions co-entrapped-sol-gel 2) nano-particle metal oxide co-entrapped-sol-gel, and 3) Metal impregnation on preformed alumina granules, were used.

Structure and composition of metal-loaded-granules were investigated using XRD, SEM, EDX, and surface area measurements (BET method). The nano-particle nature of catalysts was confirmed using SEM and X-ray diffraction. The reduction efficiency of hydrogenation of catalysts was examined by magnetic studies using a vibrating sample magnetometer (VSM). Catalysts could be effectively calcined at 450°C and the surface area values obtained were between 200-350 m<sup>2</sup>/g, indicating the mesoporous nature of catalyst support. Parameters affecting the metal loading process were also studied, and the optimum conditions were identified and reported for reproducible synthesis of the metal loaded  $\gamma$ -alumina granular particles.

The catalyst activities of Fe, Co, and Co/Fe on alumina for the conversion of CO/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> mixtures were investigated using Gas chromatography (GC) with N<sub>2</sub> as a standard carrier gas. Both, slurry-phase-batch and gas-phase-continuous-flow, reactors were used. Magnetization studies on reduced, CO/H<sub>2</sub> post-reaction catalyst in both gas and slurry phase were performed using vibrating sample magnetometer (VSM). Magnetic studies of post-reaction Co and Fe nano-catalysts showed that the formation of carbides is higher for iron compared to cobalt. In the Fe/Co mixed catalyst, it is observed that the presence of iron enhances the cobalt oxide reduction.

Catalyst with mixed metal Fe/Co compositions at 12% nitrate solutions (prepared by sol-gel/oil-drop) showed the best conversion rates for the syngas (CO+H<sub>2</sub>). Nano-particle catalysts on sol-gel prepared mesoporous  $\gamma$ -alumina (particularly the nano-particle metal oxide co-entrapped-sol-gel) showed higher conversion rates compared to conventional catalysts prepared by co-precipitation methods.

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## INTRODUCTION

The Fischer–Tropsch synthesis is used for several years to produce liquid aliphatic hydrocarbons and oxygenates by the hydrogenation of CO<sup>1-3</sup>. In the Fischer-Tropsch (FT) process, synthesis gas, a mixture of predominantly CO and H<sub>2</sub>, obtained from either coal, peat, biomass or natural gas is converted to a multicomponent mixture of hydrocarbons. Fuels produced with the FT process are of high quality due to a very low aromaticity and absence of sulfur.

The most important aspects for FT reactor development are the high reaction heats and the large number of products (gas, liquid and waxy hydrocarbons). The favorite reactor system for the Fischer-Tropsch synthesis of high molecular weight products is the slurry bubble column reactor. Excellent heat transfer characteristics of this reactor result in isothermal conditions. Both iron and cobalt are used FT-catalysts at a temperature of 200 to 300 °C and at 10 to 60 bar pressure<sup>4,5</sup>. The sensitivity of this reaction to metal particle size, however, is not well-understood<sup>6</sup>. Mesoporous materials (silica or alumina) are used as the support for the Fischer-Tropsch synthesis catalysts<sup>7-10</sup>, and incorporated transition metals into the mesoporous material framework<sup>11</sup>. It is reported that the F-T reaction activity and the selectivity for higher hydrocarbons increases with metal centers' dispersion<sup>12,13</sup>. Nanoscale and well-dispersed fine particle catalysts offer a large number of advantages such as least diffusion resistance, easy accessibility to reactants, and large number of active sites. Thus the novel nano-particle catalysts seem to provide a promising alternative to conventional catalysts. We used sol-gel/oil-drop methods<sup>14,15</sup> to prepare nano-particle syngas conversion catalysts containing ferromagnetic metals (Fe, Co). The nanometer scale metal clusters are known to exhibit size dependent physical properties<sup>16,17</sup>. The state of the unfilled d-shells and unpaired electrons, morphology and metallic charge distribution of these catalysts are known to govern both their catalytic and magnetic behavior<sup>18</sup>. The addition of small amounts of other metals such as Al, Cu, Ti have shown to enhance the dispersion of Fe/Co catalytic centers in the support and also influence the selectivity<sup>19-22</sup>. In the present work, we examine the inter-relations between catalytic and magnetic properties of sol-gel prepared iron/copper and cobalt nano-catalysts for CO hydrogenation to mixed alcohols.

## EXECUTIVE SUMMARY

We have prepared Fe/Co/Cu nano-catalysts on alumina support using sol-gel/oil-drop chemical methods starting with two precursors: aluminum tri-sec butoxide (ALTSB) and aluminum tri-iso-propoxide (ALTIP). After calcinations it provided uniform mesoporous (surface area in the range of 200-400 m<sup>2</sup>/g) granules. The structures were identified by x-ray diffraction (XRD), and the surface morphology, composition and particle size were examined by scanning electron microscope (SEM) with energy dispersive X-ray EDX spectrometer. The granular particles were uniform in composition and structure. The granules prepared from the two different starting precursors, have similar granular structures, but the granules prepared with ALTIP became powdery during the calcination step. These granules had weak mechanical strength. Mechanical strength of ALTIP granules can be improved by slow calcination step. The optimum calcination temperature obtained from differential thermal analysis (DTA) is about 450 °C. The DTA curves suggested a lower bond breaking for Co-O compared to Fe-O. The metal oxides were reduced by hydrogenation at 250 °C to form alumina impregnated Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe pure metal nano-particles. Powder X-ray diffraction results show that the metal oxides are in the nano

particle range and the alumina support has very low crystallinity as expected for sol-gel type synthesis. The surface area and porosity were studied by nitrogen desorption and DTA; and the magnetization measurements were done using a vibrating sample magnetometer (VSM). We have investigated the catalytic reactions of Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe on alumina for the conversion of CO in CO/H<sub>2</sub>/N<sub>2</sub> mixtures using a gas chromatography (GC) method. Slurry-phase-batch and gas-phase-continuous-flow reactors were used. The catalytic activity and the CO conversion efficiencies were studied. The conversion rates for Co/Fe catalyst were recorded at 250°C, with H<sub>2</sub> and CO in the ratio of 2:1. The catalytic activity in case of Co/Fe catalyst was found to be 79%. The activities of catalysts prepared by impregnation method were lower compared to those prepared by sol-gel method. Magnetic studies of post-reaction Co and Fe nano-catalysts showed that the formation of carbides is higher for iron compared to cobalt. In the Fe/Co mixed catalyst, it is observed that the presence of iron enhances the cobalt oxide reduction. A comparative study is made between three sol-gel/oil-drop methods of catalyst preparation: 1) Metal nitrate solutions co-entrapped-sol-gel 2) nano-particle metal oxide nano-particles co-entrapped-sol-gel, and 3) Metal impregnation on preformed alumina granules. Nano-particle catalysts on sol-gel prepared mesoporous  $\gamma$ -alumina (particularly the nano-particle metal oxide co-entrapped-sol-gel) showed higher conversion rates compared to conventional catalysts prepared by co-precipitation methods.

## EXPERIMENTAL

### 1) Catalyst preparations

Two precursors were used for the preparation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> granules using sol-gel/oil-drop method. The precursors were aluminum tri-sec butoxide 97% (ALTSB, Aldrich Chemical Company, Inc) and aluminum tri-iso-propoxide 99% (ALTIP, Aldrich Chemical Company, Inc).

#### *Preparation of Alumina-supported Catalyst Granules*

Three sol-gel/oil-drop methods of catalyst preparation used were: 1) Metal nitrate solutions co-entrapped-sol-gel 2) nano-particle metal oxide nano-particles co-entrapped-sol-gel, and 3) Metal impregnation on preformed alumina granules.

#### Metal nitrate solution co-entrapped-sol-gel method

Metal loaded alumina granules were prepared with ALTSB or ALTIP as the precursors in three steps: 1) preparation of boehmite solution, 2) preparation of metal nitrate solution, 3) gelation, and 4) shaping (oil dropping).

Step 1: ALTSB (52 ml) or ALTIP (40 g) was slowly and uniformly added for about half an hour time period to 100 ml of distilled water using a syringe in the case of ALTSB or directly in the case of ALTIP. The mixture was stirred continuously during the process and maintained at a temperature of 75-80°C. Nitric acid (1M solution, 15 ml) was added to adjust the pH when the floc deposit started to appear during the hydrolysis of ALTSB or ALTIP. The solutions were stirred for 15 minutes and then refluxed for about 12-14 hours at a temperature of 90°C to stabilize the pseudo-boehmite solution.

Step 2: The metal solution was prepared by adding a known amount of metal (copper (II), cobalt (II) and/or Iron (III)) nitrate in minimum amount of water required to dissolve the metal nitrate. The metal content of the solutions was calculated based on the weight of alumina (assuming 100% conversion of ALTSB or ALTIP to alumina) and the required metal loading (w/w). Metal solutions of different concentrations (2, 4, 6, and 12%) were prepared.

Step 3: After reflux, 20 ml of 1M HNO<sub>3</sub> solutions was added to the boehmite solution at a temperature of 75-80°C and then stirred for 45 minutes. During this time, the set-up for oil drop method was prepared as described below. The metal nitrate solution was added to the sol-gel to co-entrap metal ions inside the sol-gel matrix.

Step 4: Set up for oil drop method: An aqueous solution of 10% NH<sub>3</sub> (w/w) was prepared. The metal solution with calculated concentrations was added to the 10% ammonia solution in order to avoid the metal seepage. This ammonia solution was added to the bottom of a graduated glass cylinder and maintained at room temperature. The amount and the height of the 10% ammonia solution used in the cylinder were calculated based on the volume of alumina soft-granules formed. The mineral oil (Aldrich Chemical Company, Inc) was added to cylinder and kept at a temperature of 90-100°C, using a heating tape wrapped around the glass cylinder. A layer of approximately about 20 cm floated on top of 10% NH<sub>3</sub> solution. The ratio of heights of mineral oil to aqueous 10% NH<sub>3</sub> solution was approximately 3:1. Metal nitrate solution co-entrapped sol-gel-matrix was dropped from a syringe at a uniform pressure into the hot mineral oil layer. As a result of the surface tension, spherical wet gel particles were formed while passing through the hot oil and the surface of the granules were hardened. The uniform transporting conditions between oil and ammonia interface were maintained by stirring using a mechanical stirrer. After the granules were formed they were aged for 45 minutes in the ammonia layers to maximize metal nitrate to hydroxide conversion. They were filtered and washed with cold water and alcohol to remove any oil content and traces of ammonia present. They were dried in an oven for two days at a temperature of 50°C to remove ammonia and moisture.

#### Nano-particle metal oxide entrapped-sol-gel method

The above four-step procedure was followed with the exception of replacing metal nitrate solutions with suspensions of nano-particle metal oxides in water with appropriate metal ion concentration. Commercially (Nanophase Technologies Corporation) available nano-particle iron (III) oxide or copper (II) oxide suspensions were added to the sol-gel in the Step 3 and stirred to ensure proper mixing of metal oxide into the matrix of sol-gel. The amount of nano-particle metal oxides added was calculated based on the weight percent of  $\gamma$ - alumina as described in Step 2.

#### Metal impregnation on preformed $\gamma$ -Al<sub>2</sub>O<sub>3</sub> granules

Virgin alumina soft-granules were prepared by the sol-gel/oil-drop method as described above without adding metal catalyst component. The granules were dried in an oven for two days at a temperature of 50°C. Metal nitrate solutions of cobalt (II), iron (III) and/or copper (II) with appropriate concentration were prepared as described in Step 2 above. The dried granules were soaked in these solutions for 6 hrs to maximize metal ion impregnation into matrix of preformed granules. After the granules were impregnated they were aged for 45 minutes to maximize metal nitrate to hydroxide conversion in 10% ammonia solution with equal metal ion concentrations to avoid metal ion seeping out. They were again dried at 50°C for two days.

## *Calcination and hydrogenation of Catalyst Granules*

The calcination temperature (450°C) of the granules was selected using samples loaded onto an aluminum boat of a differential thermal analysis (Shimadzu DTA 50). The alumina catalyst granules prepared were calcined in a furnace by gradually increasing temperature to 450°C and maintaining it for 4 hrs. Catalyst granules loaded onto glass tubes for hydrogenation. The glass tubes were placed inside a tube furnace gradually heated to 400°C in a flow of hydrogen gas and maintained at 400°C for 2 hrs. Water formed was removed from catalyst granules using a vacuum suction at 400°C for 1hr. The glass tubes were sealed under vacuum for the use in further characterization.

## *Micro-channel Reactor Fabrication*

The preliminary work has been done on Co and Fe thin film deposited micro-channel reactors. A block diagram of a micro-channel reactor is described in Fig. 1.

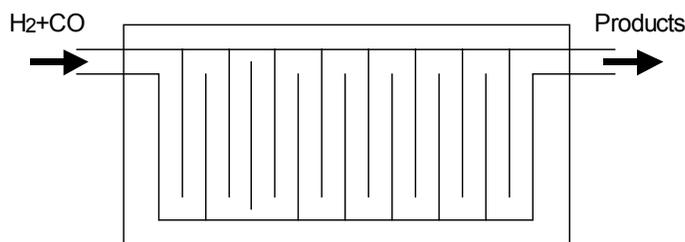


Fig. 1 Microchannel Reactor

Micro-channels of 25µm width and 100µm depth were made on a 1" x 0.5" size and 500 µm thick (100) silicon using standard photolithography, the technique used to transfer copies of a master pattern onto the surface of silicon wafer, and dry etching (inductively coupled plasma (ICP) etching). The micro-channels were coated with sol-gel encapsulated catalyst and top of the reactor was sealed by a Pyrex glass using anodic bonding technique leaving in let for syn-gas feed and outlet for products collection.

## **2) Catalytic characterization Techniques**

### *Surface Area Analyses*

The surface area and pore structure of alumina granules were analyzed by NOVA 2000 high-speed gas desorption analyzer using BET method. The data calculated were based on nitrogen desorption isotherm at liquid nitrogen temperatures and the software provided by NOVA.

### *PXRD Analyses*

The PXRD measurements were performed with a Scintag X-ray powder diffractometer using Nickel-filtered  $\text{Cu-K}\alpha$  radiation on alumina granules. The X-ray diffraction patterns were obtained for samples annealed at various temperatures to study the dynamics of crystallinity.

### *Magnetic Characterizations*

Digital measurement systems (DMS-880A) vibrating sample magnetometer (VSM) was used to study the magnetic characteristics of the calcined and hydrogenated (reduced) samples in order to study the efficiency of the hydrogenation. The system is microprocessor controlled and auto ranges full-scale measurement from 0.04-4000 emu with a sensitivity of about 5  $\mu$ emu with 100 averages. A maximum magnetic field of 13.5 kOe can be applied.

### *SEM-EDX Analysis*

Carl Zeiss DSM 942 SEM system was used to study the particle nature and distribution along with Kevex LPX1 SperDry Quantum Detector Energy Dispersive X-ray (EDX) system for the elemental microanalysis of the granules. The SEM has 3.5 nm resolution at 30 kV and magnification range of 4-500,000x, and produces high quality digitized images with point to point image measurement. The EDX uses a super quantum dry Si(Li) detector with a detection capability of elements : B through U with < 145 eV resolution.

## **RESULTS AND DISCUSSION**

The granules (see Fig.2) prepared from the two different starting precursors, aluminum tri-sec-butoxide (ALTSB) and aluminum tri-iso-propoxide (ALTIP), have similar granular structure<sup>23</sup>. However, metal loaded alumina granules prepared with ALTIP became powdery during the calcination step. These granules had weak mechanical strength; there by exhibiting the disadvantage of slow gas flow rates and clogging of filters during catalytic reactions. Mechanical strength of ALTIP granules can be improved by slow calcination step where granules were held at 100°C for 3 hours. The crushing strength of the granules was examined by a hydraulic press (see Table 1). The granular size and properties of catalyst particles are important in separating post catalysts in slurry phase reactors. Metal loaded alumina granules prepared using ALTIP as precursor had the advantage of low cost and ease in handling during the gel formation step compared to those prepared by precursor ALTSB under similar conditions.

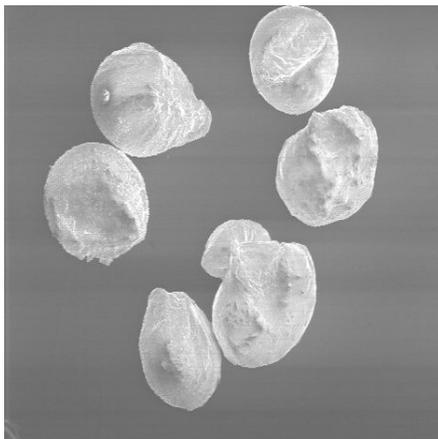


FIG. 2. SEM viewgraph of  $\gamma$ -alumina (ALTIP) granules at 50x magnification. The average granule size is  $\sim$  1 mm.

The composition of pure metals in a catalyst and their ratio to support determines the catalyst characteristics. It is important to develop repeatable synthetic procedures to make catalysts with known amount of metals incorporated inside the catalyst support. Metal loading was determined by EDX analysis, and it was observed that specific metal loading determined by EDX is reproducible for the character of the catalyst. The Nano-particle metal oxide entrapped method gives higher metal loading than metal nitrate solution co-entrapped sol-gel method.

Table 1: EDX results of metal composition in catalysts prepared by three methods.

|   | Metal nitrate solution co-entrapped | Nano-particle metal oxide entrapped | Metal impregnation on preformed granules |
|---|-------------------------------------|-------------------------------------|--|
| EDX results on Fe (12%)                 | 1.63                                | 4.22                                | 0.75                                     |
| Crushing strength of the granules (PSI) | 2,500                               | 1,500                               | 1,200                                    |

Transitions from boehmite to alumina occurred in the temperature range 375-400°C. The thermal changes above 400°C are feature less and indicating complete calcination. At temperatures 200-300°C metal hydroxides were converted to oxides. Graphs for Co, Fe, Co/Fe granules prepared by metal nitrate solution co-entrapped-sol-gel method are shown in Figures 3-7. Cobalt and iron mixed metal granules (Fig. 3 and 4) showed two broad endothermic peaks in the range 200-300°C those were attributed to dehydration of cobalt and iron, and hydroxides to metal oxide. The peaks around 217°C and 230°C were attributed to cobalt and iron, respectively, suggesting a lower bond breaking for Co-O compared to Fe-O. This is in agreement with electrostatic model of Co (II) and Fe (III) oxidation states and bond energies. The catalysts prepared by cobalt and iron metal impregnation on preformed alumina granules exhibited a different pattern from the other catalysts, having additional peaks in the range of 100-250°C. This may be due to non-uniform distribution of metal centers on these granules. A graph of pure sol-gel alumina with no metal loading was used as control (Fig.6). The nano-particle iron oxide entrapped-sol-gel method (Fig. 7) showed identical features without iron hydroxide dehydration peak. This indicates that nano-particle iron oxide entrapped-sol-gel method preserves the metal oxide in its original state in the gel.

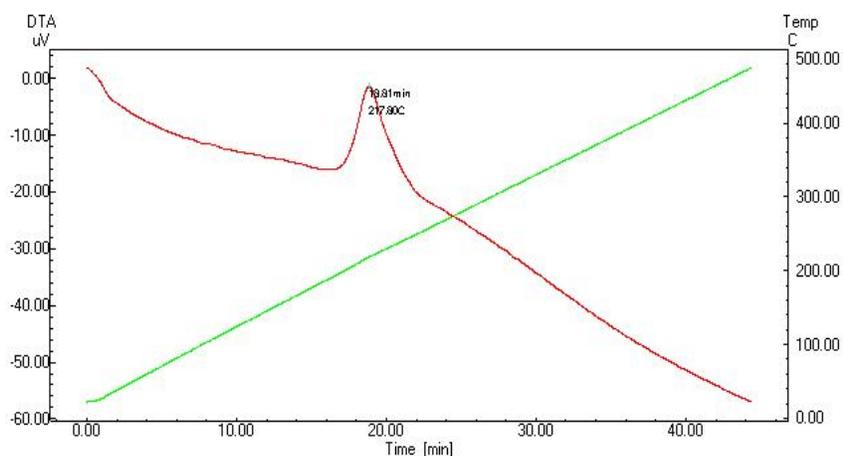


Figure 3: DTA curve for Cobalt loaded on alumina with ALTSB as precursor

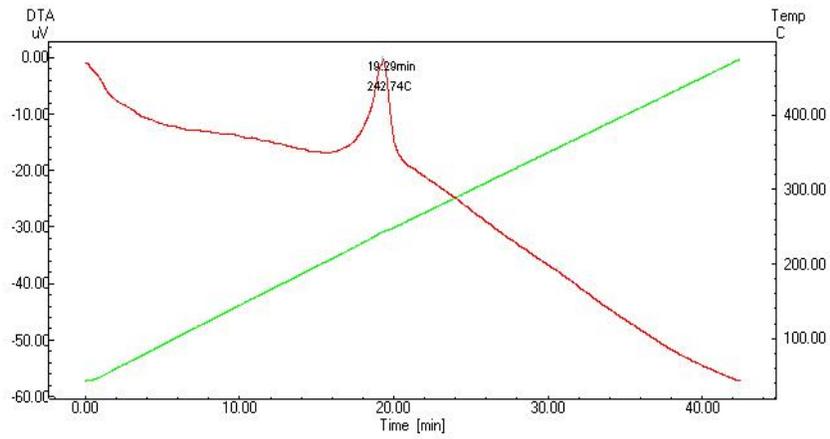


Figure 4: DTA curve for Iron loaded on alumina with ALTSB as precursor

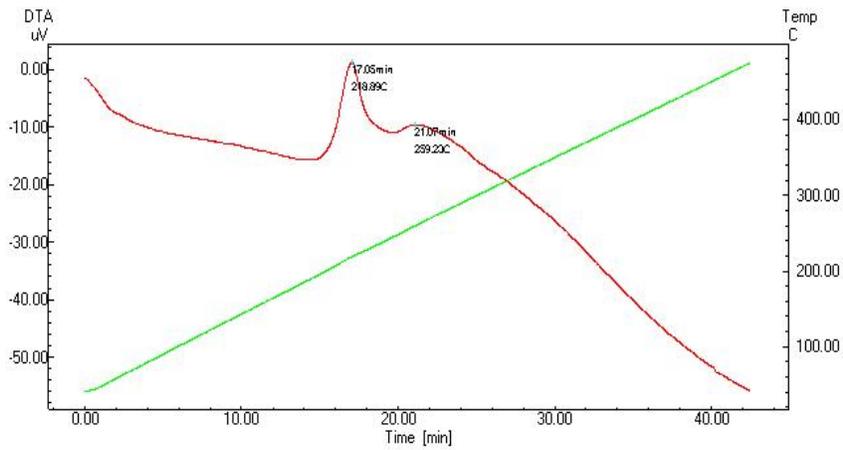


Figure 5: DTA curve for Cobalt/Iron loaded on alumina with ALTSB as precursor

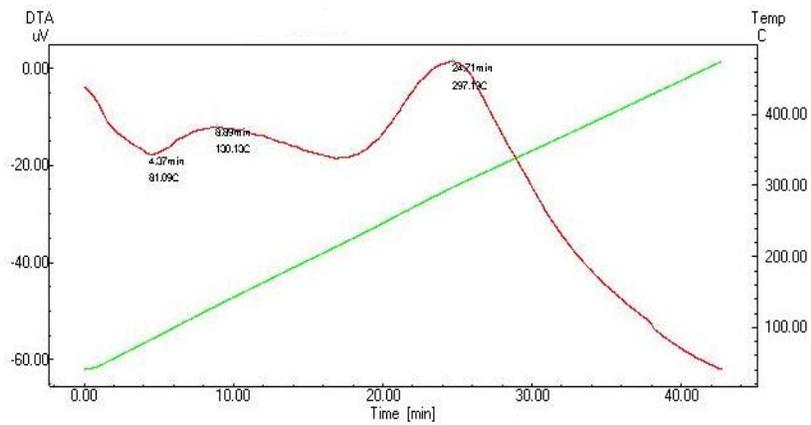


Figure 6: DTA curve for Sol-gel alumina with no metal coating

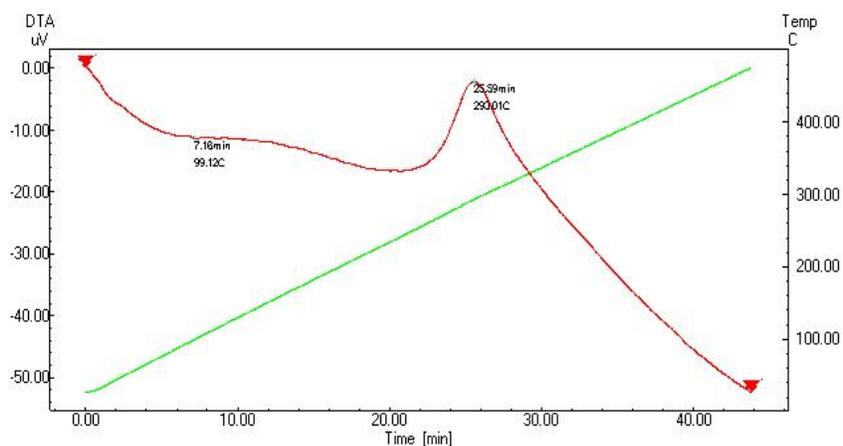


Figure 7: DTA curve for nano-particle iron oxide loaded on alumina with ALISOP as precursor

### Magnetic Studies

Fig. 8 shows the magnetic character of the catalysts obtained from VSM. The reduced catalysts show ferromagnetic nature of the Fe and Co in pure metallic form, while the post-reaction catalysts forming compounds during the reaction deactivated Fe and Co show almost paramagnetic nature. Table 2 summarizes the EDX and magnetization results of Co(12%), Fe(12%) and Fe/Co(12%) reduced and after reaction catalysts. The pure metal % has been calculated from Fe and Co compositions from EDX and saturation magnetization ( $\sigma$ ) from VSM. Co is easily reduced and does not get deactivated compared to Fe. In mixed metal composition Co has higher metal loading than Fe, which could be explained in terms of solubility of metal hydroxides formed during sol-gel preparation. Even though the Co content is higher in mixed metal catalysts compared to pure Co catalysts (see EDX results), the activation of the catalyst during reduction is very poor in mixed metal catalysts as evidenced by very low pure metal %. The interaction between Fe and Co and metal alloying could be the reason for the low activation in mixed metal catalysts. Magnetization studies of post-reaction Co and Fe nano-catalysts showed that the formation of carbides is higher Fe compared to Co.

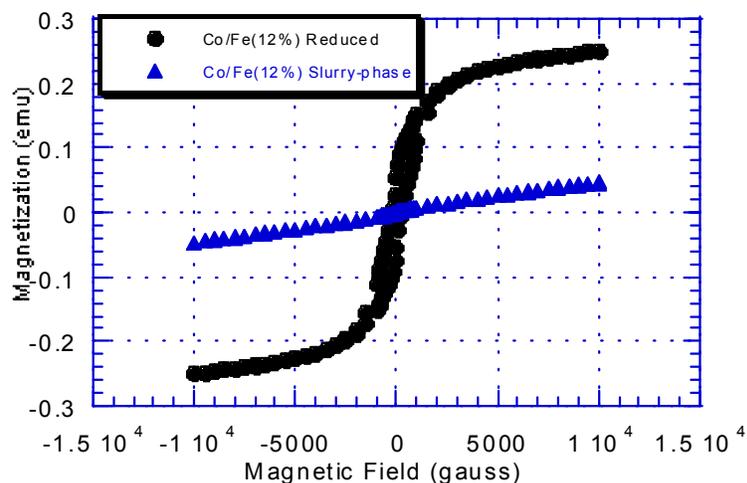


FIG. 8. Magnetization of Fe/Co (12%) catalysts: ● Reduced ▲ After slurry-phase reaction.

**Table 2. Energy Dispersive X-ray Analysis and Magnetization Results**

| <b>Sample</b>      | <b>Description</b>            | $\sigma$ (emu/g)<br>(VSM) | Fe %<br>(EDX) | Co %<br>(EDX) | Pure<br>Metal<br>% |
|--------------------|-------------------------------|---------------------------|---------------|---------------|--------------------|
| <b>Pure Co</b>     |                               |                           |               |               |                    |
| Co(12%)            | Reduced                       | 5.94                      | 0             | 3.9           | 94.35              |
| Co(12%)            | After reaction (gas-phase)    | 4.40                      | 0             | 3.9           | 69.84              |
| Co(12%)            | After reaction (slurry-phase) | 2.46                      | 0             | 3.9           | 39.05              |
| <b>Pure Fe</b>     |                               |                           |               |               |                    |
| Fe(12%)            | Reduced                       | 0.71                      | 2.1           | 0             | 15.57              |
| Fe(12%)            | After reaction (gas-phase)    | 0.05                      | 2.1           | 0             | 1.11               |
| Fe(12%)            | After reaction (slurry-phase) | 0.04                      | 2.1           | 0             | 0.81               |
| <b>Mixed Metal</b> |                               |                           |               |               |                    |
| Fe/Co(12%)         | Reduced                       | 1.81                      | 2.9           | 7.6           | 9.75               |
| Fe/Co(12%)         | After reaction (gas-phase)    | 1.56                      | 2.9           | 7.6           | 8.41               |
| Fe/Co(12%)         | After reaction (slurry-phase) | 0.05                      | 2.9           | 7.6           | 0.28               |

### *Surface Area Analysis*

Surface area values for granules were in the range of 200 – 350 m<sup>2</sup>/g. The pore structures of these granules were in the mesoporous range. Mesoporous structures contain an enormous amount of surface area relative to their volume and therefore make excellent catalysts supports.

The surface area of pure alumina granules without metal loading was 130 m<sup>2</sup>/g. Surface area values of granules prepared with ALTSB, ALISOP, nano-particle metal oxide and precipitation methods are tabulated below for 12% metal composition.

**Table 3: Surface area of granules at 12 % metal with ALTSB as precursor**

| <b>Metal<br/>(12% concentration)</b> | <b>(ALTSB) Surface area<br/>(sq m/g)</b> | <b>(ALITIP) Surface area<br/>(sq m/g)</b> |
|--------------------------------------|--|---|
| Cu                                   | 226.7                                    | 232.4                                     |
| Co                                   | 292.6                                    | 290.4                                     |
| Fe                                   | 254.3                                    | 258.7                                     |
| Cu/Co                                | 222.0                                    | 219.8                                     |
| Cu/Fe                                | 236.9                                    | 239.4                                     |
| Co/Fe                                | 303.3                                    | 311.2                                     |

Table 4: Surface area of granules obtained from three different methods

| Metal<br>(12% concentration) | (Metal nitrate<br>solution<br>solution)<br>Surface area (sq | (Nano-particle<br>Metal Oxide)<br>Surface area (sq<br>m/g) | (Impregnation<br>on preformed<br>granules)<br>Surface area |
|------------------------------|---|--|--|
| Cu                           | 290.4   | 229.8  | 206.4  |
| Fe                           | 254.3   | 204.1  | 196.1  |
| Cu/Fe                        | 236.9   | 303.8  | 199.3  |

The surface area values of granules prepared with ALTSB and ALISOP were almost same, Co/Fe having the highest surface area and Cu/Co with least surface area in both the cases. In granules with nano-particle metal oxide, Cu/Fe had the highest surface area while Fe had lowest. The amount of metal loading was more in this case, which explained the different pattern observed in values. The surface area values of granules prepared by precipitation method were less than those prepared by sol-gel method. Granules prepared by precipitation method had less metal content, because they were deposited only on the surface of granules. The metal content in granules prepared by sol-gel method was more, because of proper mixing of metal during the process. The Co/Fe, Co, Fe granules were found to have high surface areas.

When we used the sol-gel to coat the micro-channel reactor, it is observed that the alumina sol-gel is not sticking to the walls of the micro-channel reactor. We need to improve the sol-gel deposition technique into the micro-channels with higher adhesion in order to increase the effective surface area and active catalytic reaction centers.

#### *Catalytic activity*

The CO conversions of different catalysts were performed and compared using gas chromatography (GC). A standard calibration sample (Figure 9) was used to check the identity of the compounds. Sample chromatograms for CO conversion by Co/Fe catalyst in slurry phase are sited in Figures 10 and 11.

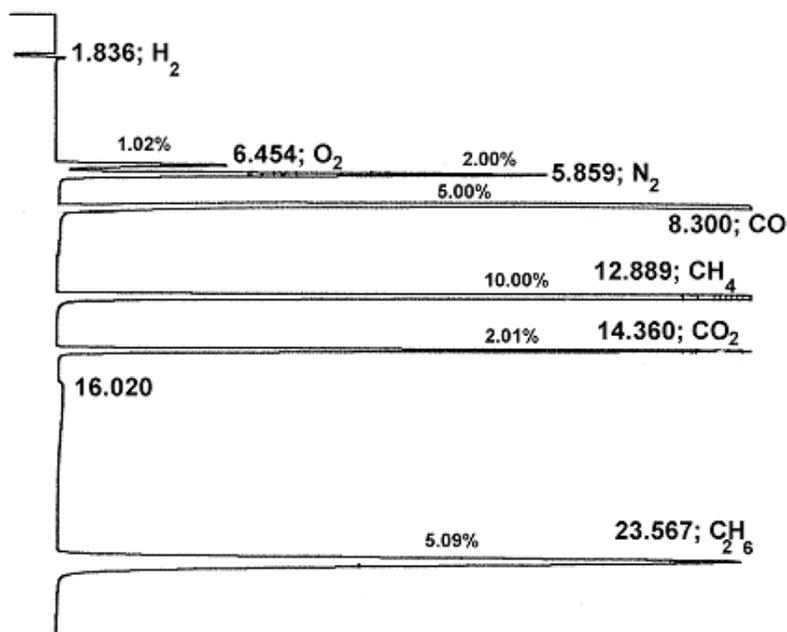


Figure 9: Chromatogram of standard sample for calibration

The conversion rates for Co/Fe catalyst was recorded at 250°C, with H<sub>2</sub> and CO in the ratio of 2:1. To make sure the conversion was complete, the catalysts were run for 20-25 hours. Catalytic activity in case of Co/Fe catalyst was found to be 79%. The catalytic activities of catalysts prepared by impregnation method had low values, compared to those prepared by sol-gel method.

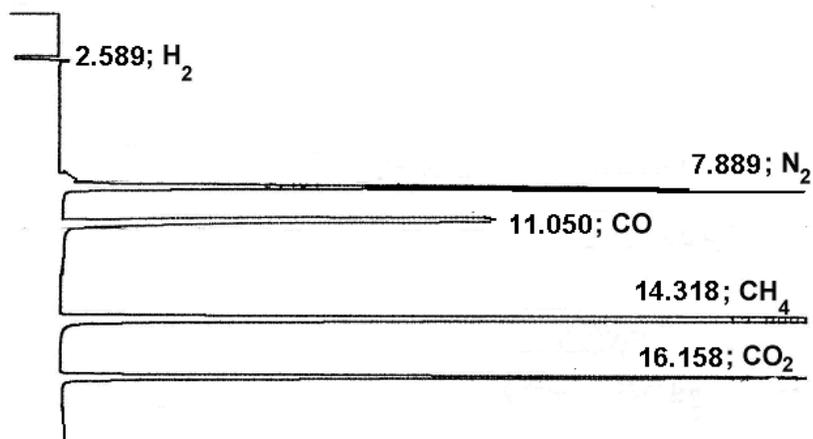


Figure 10: Chromatogram of Co/Fe catalyst heated for half an hour

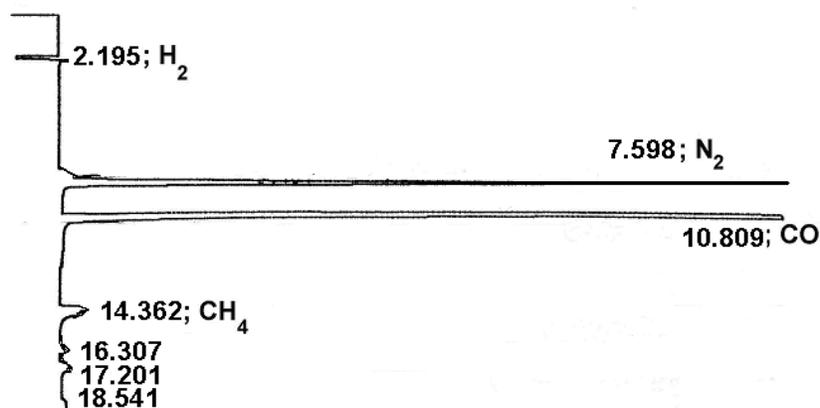


Figure 11: Chromatogram of Co/Fe catalyst heated for 25 hours

Granules with Co, Fe and Co/Fe were also prepared by conventional alumina support/precipitation method (impregnation method) to compare with granules prepared by gel-sol/metal ion solution mixing method and by nano-particle metal oxide entrapped sol-gel method. The comparison in Table 5 clearly shows that Nano-particle metal oxide catalysts on sol-gel prepared mesoporous  $\gamma$ -alumina showed higher conversion rates compared to conventional catalysts prepared by impregnation methods. Catalyst with mixed metal Fe/Co compositions showed the best conversion rates for the syngas (CO+H<sub>2</sub>).

Table 5: CO conversion data for catalysts prepared by sol-gel method using metal nitrates and nano-particle metal oxides were compared with the conventional impregnation method.

| Metal | Metal Nitrate | Nano-particle Metal Oxide | Metal Impregnation |
|-------|---------------|---------------------------|--------------------|
| Cu    | 39%           | 43%                       | -                  |
| Co    | 55%           | -                         | 44%                |
| Fe    | 48%           | 52%                       | 42%                |
| Cu/Co | 43%           | -                         | -                  |
| Co/Fe | 79%           | -                         | 60%                |
| Cu/Fe | 41%           | 47%                       | -                  |

## CONCLUSIONS

We accomplished the preparation of Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe nano-particle metal loaded mesoporous 1 mm spherical granular  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts using combined sol-gel/oil-drop methods. The properties of metal loaded  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> granules were compared for the preparations starting with two precursors: aluminum tri-sec-butoxide (ALTSB) and aluminum tri-iso-propoxide (ALTIP). Three sol-gel/oil-drop catalyst preparation methods; 1) Metal nitrate solutions co-entrapped-sol-gel 2) nano-particle metal oxide co-entrapped-sol-gel, and 3) Metal impregnation on preformed alumina granules, were used.

The nano-particle nature of catalysts was confirmed using SEM and X-ray diffraction. The reduction efficiency of hydrogenation of catalysts was examined by magnetic studies using a

vibrating sample magnetometer (VSM). Catalysts could be effectively calcined at 450°C and the surface area values obtained were between 200-350 m<sup>2</sup>/g, indicating the mesoporous nature of catalyst support. The catalyst activities were investigated using Gas chromatography (GC). Both, slurry-phase-batch and gas-phase-continuous-flow, reactors were used. The conversion rates for Co/Fe catalyst were recorded at 250°C, with H<sub>2</sub> and CO in the ratio of 2:1. The catalytic activity in case of Co/Fe catalyst was found to be 79%. The activities of catalysts prepared by impregnation method were lower compared to those prepared by sol-gel method. Magnetic studies of post-reaction Co and Fe nano-catalysts showed that the formation of carbides is higher for iron compared to cobalt. In the Fe/Co mixed catalyst, it is observed that the presence of iron enhances the cobalt oxide reduction.

Catalyst with mixed metal Fe/Co compositions at 12% nitrate solutions (prepared by sol-gel/oil-drop) showed the best conversion rates for the syngas (CO+H<sub>2</sub>). Nano-particle catalysts on sol-gel prepared mesoporous  $\gamma$ -alumina (particularly the nano-particle metal oxide co-entrapped-sol-gel) showed higher conversion rates compared to conventional catalysts prepared by co-precipitation methods.

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## **FUTURE WORK**

We plan to investigate:

- Syn-gas conversion by installing a second column to GC to analyze polar compounds such as alcohols.
- Alkane distribution and its dependence on CO/H<sub>2</sub> ratio need to be investigated.
- The Catalytic properties of nano-particles of FeO and CoO prepared by reflux method and dispersed on to sol-gel prepared alumina granules.
- CO/H<sub>2</sub> conversion of a micro-reactor with a metal impregnated thin film prepared by sol-gel coating.
- GC analysis of CO<sub>2</sub>/H<sub>2</sub> and CO/CO<sub>2</sub>/H<sub>2</sub> mixture conversions.
- The conversion rates for the sol-gel granular catalysts by replacing alumina by silica.

### **Acknowledgments**

Thanks for the support from Department of Energy (Grant Number: **DE-FG26-00NT40836**)