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ABSTRACT

We have developed effective nanoparticle incorporated heterogeneous F-T catalysts starting with the synthesis of Fe, Co, Cu nanoparticles using $\text{Fe}(\text{acac})_3$, $\text{Co}(\text{acac})_2$, and $\text{Cu}(\text{acac})_2$ precursors and incorporating the nanoparticles into alumina sol-gel to yield higher alkanes production. SEM/EDX, XRD, BET, VSM and SQUID experimental techniques were used to characterize the catalysts, and GC/MS were used for catalytic product analysis.

The nanoparticle oxide method gave the highest metal loading. In case of mixed metals it seems that Co or Cu interferes and reduces Fe metal loading. The XRD pattern for nanoparticle mixed metal oxides show alloy formation between cobalt and iron, and between copper and iron in sol-gel prepared alumina granules. The alloy formation is also supported by DTA and VMS data. The magnetization studies were used to estimate the catalyst activity in pre- and post-catalysts. A lower limit of $\sim 40\%$ for the reduction efficiency was obtained due to hydrogenation at 450°C for 4 hrs. About 85% of the catalyst has become inactive after 25 hrs of catalytic reaction, probably by forming carbides of Fe and Co. The low temperature (300 K to 4.2 K) SQUID magnetometer results indicate a superparamagnetic character of metal nanoparticles with a wide size distribution of < 20 nm nanoparticles.

We have developed an efficient and economical procedure for analyzing the F-T products using low cost GC-TCD system with hydrogen as a carrier gas. Two GC columns DC 200/500 and Supelco Carboxen-1000 column were tested for the separation of higher alkanes and the non-condensable gases. The Co/Fe on alumina sol-gel catalyst showed the highest yield for methane among Fe, Co, Cu, Co/Fe, Cu/Co, Fe/Cu. The optimization of CO/H_2 ratio indicated that 1:1 ratio gave more alkanes distribution in F-T process with Co/Fe (6% each) impregnated on alumina mesoporous catalyst.

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INTRODUCTION

Heterogeneous catalysts play an essential role in converting syngas (CO/H_2 mixtures) to fuel. The Fischer–Tropsch (F-T) synthesis is used for several years to produce liquid aliphatic hydrocarbons and oxygenates by the hydrogenation of CO [1]. The significance of synthesis of higher alkanes lies in liquefying natural gas for easy transport, rocket fuel production, and fuel cell production, and thus has been the main focus of the research and development programs of corporations like Shell, Sasol, Exxon-Mobil, Syntroleum, and Rentech. Many studies have taken place to develop or improve technologies on F-T process. For this process, the development of catalysts is a key role [2]. The research of nanoparticles has been a very important topic over the past couple of years. The high surface area and rapid heat dissipation properties of nanoparticles to overcome reaction's high exothermic nature are expected to give high conversion of synthesis gas. 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 [3]. Thus the novel nano-particle catalysts seem to provide a promising alternative to conventional catalysts. The nanometer scale metal clusters are known to exhibit size dependent physical properties [4]. The state of the unfilled d-shells and unpaired electrons, morphology and metallic charge distribution of the transition metal (Fe, Co) catalysts are known to govern both their catalytic and magnetic behavior [5]. Mesoporous materials (silica or alumina) are used as the support for the FT catalysts [6], and incorporated transition metals (iron and cobalt) into the mesoporous material framework. Here, we study the structure and composition of novel Co/Fe nanoparticle syngas conversion catalyst granules prepared using sol-gel/oil-drop methods [7,8] by incorporating metal oxide nanoparticles into alumina sol-gel matrix.

One of the objectives in this report period is to develop methods to prepare effective nanoparticle incorporated heterogeneous F-T catalysts. This objective was achieved through following steps: 1) synthesize nanoparticle precursors- $\text{Fe}(\text{acac})_3$, $\text{Co}(\text{acac})_2$, and $\text{Cu}(\text{acac})_2$, 2) synthesize Fe, Co, Cu nanoparticles using chemical methods, 3) incorporating the nanoparticles into alumina sol-gel and improve metal loading, and 4) prepare the catalyst granules for syngas conversion to yield higher alkanes production.

It is important to characterize the nano-particle nature of the catalysts using Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD). The surface area of the nanoparticles can be measured using Brunauer-Emmett-Teller (BET) method. The magnetic characteristics of Co and Fe nanoparticles can be analyzed using Vibrating Sample Magnetometer (VSM) and Superconducting Quantum Interface Device (SQUID). It is also important to develop GC method conditions for separating the components produced by syngas conversions. We planned to develop an efficient and economical procedure for analyzing the products from synthesis gas reaction with Co/Fe impregnated alumina catalyst. The F-T product separation using low cost GC-TCD system with appropriate columns will be helpful. Different carrier gases hydrogen, helium, nitrogen are also needed to be tested for efficient separations.

Various metals such as Fe, Co, and Cu incorporated into catalysts in pure form show different catalytic activity. In the development of catalysts there is a need to study the activity of pure metals and metal combinations. Mixed metal catalysts show superior catalytic activity as different metals together could enhance the reaction known as synergism or promoter effect

[9,10]. In this project we have studied the catalytic activity of Fe, Co, Cu, Fe/Co, Fe/Cu and Co-Cu metal incorporated onto mesoporous γ -alumina catalysts. The F-T product distribution also depends on the ration of CO/H₂ and seems to have effect on the production of different alkanes. Thus, we also planned to test different ratios of CO/H₂ and study the effect on the yield of higher alkanes.

EXECUTIVE SUMMARY

One of the objectives in this report period is to develop methods to prepare effective nanoparticle incorporated heterogeneous F-T catalysts. This objective was achieved through following steps: 1) synthesize nanoparticle precursors- Fe(acac)₃, Co(acac)₂, and Cu(acac)₂, 2) synthesize Fe, Co, Cu nanoparticles using chemical methods, 3) incorporating the nanoparticles into alumina sol-gel and improve metal loading, and 4) prepare the catalyst granules for syngas conversion to yield higher alkanes production.

The nanocatalysts were characterized for size distribution and composition by TEM, SEM/EDX, for structural information by XRD, for surface area by BET, for magnetic properties by VSM and SQUID, and for catalytic product analysis by GC/MS. We have optimized the GC method conditions for separating the components produced by syngas conversions. We studied the catalytic activity of Fe, Co, Cu, Fe/Co, Fe/Cu and Co-Cu metal incorporated onto mesoporous γ -alumina catalysts. The effect of the ration of CO/H₂ on F-T product distribution in the yield of higher alkanes was examined. Metal loading efficiencies for pure metal catalysts increased in the order Co, Cu and Fe in agreement with solubility of metal hydroxides. Increasing metal ion concentration in the bottom ammonia solution increases the metal loading. In case of mixed metals it seems that Co or Cu interferes and reduces Fe metal loading. The nanoparticle oxide method is best for the metal loading because this method doesn't involve metal ion solubility equilibria.

The XRD patterns for granules prepared from metal nitrate solution method showed broader peaks for alumina and almost no peaks for metal oxides, due to poor metal loading as confirmed by EDX data. In case of metal oxide co-entrapped sol-gel prepared granules with higher metal loading, the weak peaks in XRD indicate lack of regular lattice spacing and/or smaller particle size of the metal oxides, upon heating to 450°C and 1000°C the crystallinity increased. The XRD pattern for nanoparticle mixed metal oxides show alloy formation between cobalt and iron, and between copper and iron in sol-gel prepared alumina granules. The alloy formation is also supported by DTA and VMS data.

The magnetization studies were used to estimate the catalyst activity in pre- and post-catalysts. A lower limit of ~ 40% for the reduction efficiency was obtained due to hydrogenation at 450°C for 4 hrs. More reduction of metal catalysts occurred in the method using nano-particle oxide as precursor compared to the nitrate solution sol-gel method. About 85% of the catalyst has become inactive after 25 hrs of catalytic reaction, probably by forming carbides of Fe and Co. The low temperature (300 K to 4.2 K) SQUID magnetometer results indicate a superparamagnetic character of metal nanoparticles with a wide size distribution of < 20 nm nanoparticles.

We have developed an efficient and economical procedure for analyzing the products from synthesis gas reaction with Co/Fe impregnated alumina catalyst are separated using low cost GC-TCD system with DC 200/500 column using hydrogen as a carrier gas. Two GC columns DC 200/500 and Supelco Carboxen-1000 column were tested. DC200/500 showed

remarkable separation of higher alkanes, however the non-condensable gases are not separated very well. We have compared the methane production of Fe, Co, Cu, Co/Fe, Cu/Co, Fe/Cu γ -alumina catalysts. Co/Fe alumina sol-gel catalyst showed the highest yield for methane. We have optimized the CO/ H₂ ratios to obtain conversion of synthesis gas to higher alkanes. When CO/H₂ ratio kept 1:1, we can see more alkanes distribution in F-T process with Co/Fe (6% each) impregnated on alumina mesoporous catalyst.

EXPERIMENTAL

Catalyst preparation

a) Nanoparticle syntheses: Fe, Co, and Cu nanoparticles from M(acac)₃ (M =Fe, Co, Cu)

i) Synthesis of Fe(acac)₃, Co(acac)₂, and Cu(acac)₂

Fe(acac)₃

- 1) 4.4156g of FeCl₃·H₂O is dissolved in 6mL H₂O.
- 2) At about 90°C, 9mL of concentrated NH₄OH is added drop wise to the Fe solution causing a dark, reddish brown filmy precipitate.
- 3) The solid is collected and washed with cold H₂O in a Buchner funnel to remove the chloride ions.
- 4) All of the synthesized iron hydroxide is transferred to an Erlenmeyer flask to which 12 mL acetylacetonate is subsequently added. This mixture is allowed to heat gently for 45 min.
- 5) The reaction mixture is allowed to cool resulting in dark, red crystals forming. They are collected and recrystallized from ethanol.
- 6) The product is stored in an oven and is allowed to dry.

Co(acac)₂:

- 1) 1.2g Of Co₂(CO₃)₃ and 10 mL acetylacetonate are placed into a 125 mL Erlenmeyer flask.
- 2) The flask is placed into a beaker of water which serves as a boiling water bath, (making sure that the boiling chips are in the beaker), the flask is clamped within the beaker for stability and the beaker is heated by using a hot plate.
- 3) After the flask is placed in the water bath and begins to boil, 15mL of H₂O₂ is added drop wise to the reaction mixture using a pipette. The adding should take 15-25 min.
- 4) Once the addition is complete, the mixture continues to heat for additional 1015 min. The flask is then removed from the water bath and is allowed to cool until the flask can be touched. The flask is then placed in an ice water bath in a beaker for 30 min.
- 5) The reaction mixture is filtered with water and with isopropyl alcohol. After drying, the material is transferred into a 250mL or 500mL Erlenmeyer flask.
- 6) 15-20mL of acetonitrile is added per gram of solid until the solid gets dissolved with as little solvent as possible. If the contents are warmed with hot tap water, it will take less solvent.
- 7) A 3-fold to 4-fold amount of water is added to the solution. The water is added slowly while swirling the flask. As the crystals begin to form, the flask is placed into an ice bath for at least 20 min.
- 8) The slurry is then filtered using a Buchner funnel while rinsing with water and briskly rinsed with 2-propanol just before drying the material.
- 9) The product is stored in an oven and is allowed to dry.

Cu(acac)₂:

- 1) 1.0g Cu(NO₃)₂ is dissolved in 40mL H₂O in a 100mL beaker.
- 2) While stirring the solution, 5mL acetylacetonate is added. The solution is stirred for 5 min.
- 3) The product is collected by using a Buchner funnel. The beaker is rinsed with water into the funnel.
- 4) The product is rinsed with a few mL of ethanol and air is pulled through the crystals for several minutes.
- 5) The product is stored in an oven and is allowed to dry.

ii) Nanoparticle synthesis: Fe, Co, and Cu

The synthetic procedures were carried out using airless procedures and commercially available reagents. A solution of cobalt acetyl acetonate (1.0 g), 1,2 hexadecanediol (2.9g), iron acetyl acetonate (0.17g) and diphenylether (117.6mL) are placed in a three necked round bottom flask and heated to 1000°C. To this solution oleyl amine (0.88mL) and oleic acid (0.88mL) are added via syringe and the mixture is heated to 260°C and kept for reflux for 30 min. The mixture is cooled to 40°C and ethanol is added a precipitate is formed. The mixture is centrifuged at 3,100 rpm for 10-15 min to isolate the particles and they are re-dispersed in a solution consisting of hexane (5mL), octane (5mL), oleylamine (0.07mL), oleic acid (0.07mL).

Cobalt nanoparticles

The nanoparticles were prepared using a modification of the procedure reported by Sun et al. [11]. The synthetic procedures were carried out using airless procedures and commercially available reagents.

- 1) A solution of cobalt acetylacetonate (1g), 1,2 hexadecanediol (2.9g) and diphenylether (117.26mL) are placed in a three necked round bottom flask and heated to 100⁰ C.
- 2) To this solution oleyl amine (0.88 mL) and oleic acid (0.88 mL) are added via syringe and the mixture is heated to 260⁰C and kept for reflux for 30 min.
- 3) The mixture is cooled to 40⁰ C and ethanol (approx 200 mL) is added, a precipitate is formed.
- 4) The resulting mixture is centrifuged at 3100 rpm for 10-15 min to isolate the particles.
- 5) The particles were dispersed in a solution consists of hexane (5mL), octane (5mL), oleylamine (0.07mL), and oleic acid (0.07mL) for storage.
- 6) The particles are dried in oven for two days at 60⁰ C before using in synthesis and analysis.

Fe and Cu nanoparticles: Similar procedure is followed using iron(III)acetylacetonate or copper(II) acetylacetonate in the place of cobalt(II) acetylacetonate.

iii) Preparation of catalysts granules (details found in last DOE annual report 2002-2003)

Two precursors were used for the preparation of γ -Al₂O₃ granules using sol-gel/oil-drop method: 1) aluminum tri-sec butoxide (ALTSB) 97% (Aldrich), and 2) aluminum isopropoxide (ALISOP) 99% (Aldrich). The other materials used are Copper(II) nitrate (Fischer Scientific), Cobalt(II) nitrate (J.T. Baker), Mineral oil (Aldrich), Iron(III) nitrate (Fischer Scientific), nanoparticle iron(III) oxide (Nanophase Technologies Corporation), Nanoparticle copper(II) oxide (Nanophase Technologies Corporation). Nanoparticle cobalt, iron copper were also prepared by a chemical methods using cobalt(II), iron(III), and copper(II) acetylacetonate

hydrate in the presence of oleyl amine (Aldrich) and oleic acid (Aldrich) using a modified procedure reported by S. Sun et al [11].

Obtaining Granules: Filtered and dried at 50 °C, and calcined at 450 °C.

Hydrogenation cycles: Catalysts were loaded in reactors. Hydrogen gas was passed over the catalyst while heating to 400 °C for 2 hrs. Catalysts were dried and water removed by vacuum suction at 400 °C. Again Hydrogen gas was passed over the catalyst while heated to 400°C for 2 hrs. Catalyst dried by vacuum suction at 400 °C, 1hr

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.

XRD Analyses

The XRD measurements were performed with a Scintag X-ray powder diffractometer using Nickel-filtered Cu- K_{α} 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 μ emu with 100 averages. A maximum magnetic field of 13.5 kOe can be applied.

Superconducting Quantum Interface Device (SQUID) magnetometer at GSU is used to study the low temperature magnetic properties of the nanoparticles. The SQUID can be used with maximum magnetic field of 7 Tesla in the temperature range between 1.65 K and 300 K, and it is sensitive to measure the magnetization in the order of 10^{-8} emu.

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.

GC Analysis

A HP 5890 Series II Gas Chromatograph equipped with TCD detector and columns (1. Supelco Carboxen-1000 (mesh 60/8015 ft. x 1/8 in SS 2.1 mm ID, and 2. DC 200 /500 exchangeable column of 30 feet by 1/8 inch stainless steel, 30% Dow Corning -200/500 silicon oil on Chromosorb Pink, Acid wash, 60/80 mesh) was used.

Materials used: Carbon monoxide, hydrogen, helium, nitrogen were purchased from Red Ball Company, Standard sample were purchased from NIST Houston, TX.

Fig. 1: Block diagram of GC spectrometer setup.

GC conditions:

The oven temperature was initially held at 135 °C for 40 minutes and was steadily increased at a rate of 60 °C per minute till 150 °C and maintained at that temperature for 5 minutes. The carrier gas was pressurized at 100 kpa. The detector used for this purpose is TCD.

Catalytic activity: F-T catalytic activity test reactors

i) Slurry Phase reactor:

CO, H₂ and N₂, ratios are mixed in a gas mixing manifold and loaded into high-pressure reactor with catalyst stirred in silicone oil at 200 °C and 100 psi total pressure. N₂ was used as an internal standard. Calibrations of products were carried out by internal standards and response factors for standard gas mixtures. F-T reactions were carried out in a slurry phase reactor (Parr High Pressure 1296) loaded with Co/Fe nanoparticle supported on mesoporous alumina. The gas mixture from the mixing manifold was loaded into a high-pressure reactor. The catalyst along with silicone oil was added into Teflon[®] container in the pressure reactor and maintained at a temperature and pressure.

Figure 2: Block diagram of slurry phase reactor

catalysts after 25 hr.

ii) Gas phase reactor:

CO, H₂, and N₂, (1:2:1) ratio are mixed in the gas mixing manifold and passed through a packed stainless steel column containing the catalyst maintained at 200 °C Both dynamic and batch conversion were monitored.

Chromatographic study was carried out on GC using He, H₂ and N₂ carrier gases and following test mixtures.

1) Standard mixture (CO, H₂, O₂, N₂, CH₄, CO₂, C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₂, and C₆H₆) purchased from NIST Specialty Products, TX.

2) Test gas mixture (CO, H₂, N₂, CH₄, and CO₂) obtained from Cross Oil and Refining, AR.

3) Syngas fuel mixture over Co/Fe catalysts after 12 hr

4) Syngas fuel mixture over Co/Fe

Fig. 3: Block diagram of slurry phase reactor

Product mixture from the gas-phase reactor is injected into the GC through six-port injection valve. HP 3396 Series II integrator is used to plot the peaks.

RESULTS AND DISCUSSION

Catalyst preparation

a) Nanoparticle syntheses:

Synthesis of Fe(acac)₃, Co(acac)₂, and Cu(acac)₂

One of the objective of the research has been to synthesize of Fe(acac)₃, Co(acac)₂, and Cu(acac)₂. This report period we have devoted to creating these organometallic nanoparticle precursors compounds for the synthesis nanoparticles as a part of the project. These nanoparticles are interesting because of their increased surface area and superparamagnetic properties. We were successful in the nanoparticle synthesis and they were examined using TEM, SQUID, SEM/EDX, and XRD for characterization. These nanoparticles have been incorporated into mesoporous alumina using sol-gel/oil-drop method.

b) SEM/EDX analysis: Optimization of metal loading

There are several factors that affect the amount of metal or metal loading in the granules. It depended on the there sol-gel methods used. The efficiency of metal loading as determined by EDX analysis is given in Table 1. The EDX analysis indicates that metal loading was directly proportional to the metal ion concentration in the metal nitrate solution.

Table 1: Optimization of metal loading (w/w %) on alumina sol-gel prepared from ALTSB and metal nitrates by controlling the metal content in the bottom ammonia layer of the oil-drop method.

	Intended metal loading (w/w)%			(w/w)% metal in ammonia layer			Actual metal loading (w/w)% (EDX)			Efficiency of metal loading %		
	Co	Fe	Cu	Co	Fe	Cu	Co	Fe	Cu	Co	Fe	Cu
Co	4	-	-	4	-	-	0.91	-	-	22.8	-	-
	4	-	-	8	-	-	1.16	-	-	29.0	-	-
	2	-	-	2	-	-	0.31	-	-	15.5	-	-
Cu	-	-	4	-	-	4	-	-	1.63	-	-	40.8
	-	-	4	-	-	8	-	-	1.84	-	-	46.0
	-	-	2	-	-	2	-	-	0.54	-	-	27.1
Fe	-	4	-	-	6	-	-	3.01	-	-	75.3	-
	-	4	-	-	4	-	-	2.40	-	-	60.1	-
	-	4	-	-	0	-	-	0.92	-	-	23.0	-
Co/Fe	6	6	-	6	6	-	7.60	2.90	-	126	48.0	-
Cu/Fe	-	6	6	-	6	6	-	2.35	7.07	-	39.2	118

Metal loading efficiencies for pure metal catalysts increased in the order Co, Cu and Fe in agreement with solubility of metal hydroxides. Increasing metal ion concentration in the bottom ammonia solution increases the metal loading. In case of mixed metals it seems that Co

or Cu interferes and reduces Fe metal loading. For example higher solubility of $\text{Co}(\text{OH})_2$ increases the influx of more Co ions into granules while common ion effect of OH^- would remove Fe^{3+} ions from the bottom aqueous layer, which increases the seepage of Fe^{3+} ions from the granules. This is in agreement with solubility data [12] for Fe^{3+} , Cu^{2+} and Co^{2+} hydroxides: $\text{M}(\text{OH})_x(\text{s}) = \text{M}^{x+}(\text{aq}) + x \text{OH}^-(\text{aq})$; $K_{\text{sp}}(\text{Fe}^{3+}) = 4 \times 10^{-38} \text{ mol/L}$, $K_{\text{sp}}(\text{Cu}^{2+}) = 1.6 \times 10^{-19} \text{ mol/L}$ and $K_{\text{sp}}(\text{Co}^{2+}) = 2.5 \times 10^{-16} \text{ mol/L}$. Therefore solubility differences would not allow precise control of metal loading of mixed Co/Fe and Cu/Fe metal compositions in the granules using metal nitrate solution co-entrapped method. However, this problem could be overcome using nanoparticle metal oxide co-entrapped sol-gel method.

EDX analysis of metal loading on alumina prepared by three sol-gel methods is summarized in Table 2. Metal loading increased in the following order: metal wet-impregnation on preformed granules, metal nitrate solution and nanoparticle metal oxide.

Table 2: EDX analysis of metal loading (w/w%) on alumina prepared by three sol-gel methods.

Metals in alumina granules	Intended metal loading (w/w)%			Total metal loading efficiency by sol-gel preparation method		
				Metal nitrate	Nanoparticle metal oxide	Metal wet-impregnation
Cu	-	-	6	43.1%	71.2 %	-
Co	6	-	-	27.4%	-	23.1%
Fe	-	6	-	65.2 %	75.3%	54.2%
Co/Fe	6	6	-	49.5%	-	37.3%
Cu/Fe	-	6	6	45.1%	72.1%	-

The nanoparticle oxide method is best for the metal loading because this method doesn't involve metal ion solubility equilibria within the bottom aqueous ammonia solution layer of the oil-drop set-up. The DTA analysis confirms that nanoparticle metal oxide remains intact without being converted to soluble ions during the sol-gel/oil drop procedure.

c) XRD analysis: After calcination at 450°C, powder x-ray diffraction (XRD) peaks for sol-gel

Fig. 4: Fe_2O_3 nanoparticles heated at 450 °C and 1000 °C.

nitrate solution method showed broader peaks for alumina and almost no peaks for metal oxides, due to poor metal loading as confirmed by EDX data. This is consistent with previous work [13],

pure alumina granules prepared from ALISOP and ALTSB precursors showed (the) similar patterns. Broad peaks appeared around 38°, 49° and 67° (2θ). As the temperature increased to 1000°C, new sharper peaks corresponding to corundum appeared, as shown in Fig. 3, 4 and 5 of metal loaded alumina. XRD patterns for granules prepared from metal

where CuO peaks were observed only at higher metal loading. In case of metal oxide co-entrapped sol-gel prepared granules with higher metal loading, the weak peaks in XRD indicate lack of regular lattice spacing and/or smaller particle size of the metal oxides. Fig. 4 shows the XRD patterns for Fe₂O₃ nanoparticles without alumina heated to 450°C and 1000°C, indicating the increased crystallinity as the temperature is increased.

600°C. Our results indicate that Co_3O_4 can be formed even in Al_2O_3 in agreement with data [15], where Co_3O_4 is found in alumina even at 500 °C. These differences could be explained metal loading in alumina sol-gel as it is difficult to observe the crystalline peaks at low metal loadings.

Fig. 6: *CoO and Fe₂O₃ nanoparticle loaded alumina heated at 450°C and 1000 °C.*

The nanoparticle metal oxide pattern matched more with mixed metal cobalt-iron oxide than with either cobalt or iron oxide. This could be due to alloy formation between cobalt and iron as indicated by DTA and VMS data. We observed similar behavior for the nanoparticle copper and

Magnetization Studies of Co/Fe Encapsulated Al₂O₃ Sol-gel Micro-reactors

The pre-catalyst deposited reactor shows paramagnetic behavior mostly coming from the iron and cobalt oxides. Hydrogenation of the pre-catalyst reduces Fe and Co oxides to pure

metals, thus give ferromagnetic behavior. The ferromagnetic nature almost disappears in the post-catalysts due to formation of Fe and Co carbides or carbonyls during the reaction. The saturation magnetization of the ferromagnetic component is used to estimate the catalyst activity in pre- and post-catalysts. A lower limit of $\sim 40\%$ for the reduction efficiency was obtained due to hydrogenation at 450°C for 4 hrs. More reduction of metal catalysts occurred in the method using nano-particle oxide as precursor compared to the nitrate solution sol-gel method. About 85% of the catalyst has become inactive after 25 hrs of catalytic reaction, probably by forming carbides of Fe and Co.

SQUIS magnetization results on Co nanocatalysts in alumina sol-gel:

Fig. 7: *Magnetic hysteresis loops of Co nanoparticles at 298K and at 4.2 K.*

Superconducting Quantum Interface Device (SQUID) magnetometer at GSU is used to study the low temperature magnetic properties of Co nanoparticles in alumina sol-gel. When the Co nanoparticles are smaller than 20 nm they behave like superparamagnetic at room temperature, which does not have magnetic coercivity. At low temperatures, the super-

paramagnetic particles will transform to ferromagnetic with a magnetic coercivity. The transition temperature depends on the size of the nanoparticles, smaller size nanoparticles transform at lower temperature. Figure 7 shows the magnetic hysteresis loops at 298K and 4.2K. It is clear that the magnetic coercivity has increased by cooling the nanoparticles to 4.2K indicating the superparamagnetic to ferromagnetic transformation and the conformation of smaller size nanoparticles.

Fig. 8: *Magnetic coercivity with temperature for Co nanoparticles.*

Figure 8 shows the variations in the magnetic coercivity with temperature. Smaller size Co nanoparticles are superparamagnetic at room temperature. They are transferred to ferromagnetic at lower temperatures. The transition temperature depends on the size of the nanoparticle. The variations indicate that the Co nanoparticles have wide range size distribution, extending below 20 nm.

Optimization of GC conditions for separating and identifying F-T products

Our objectives were to provide an inexpensive single injection GC/TCD system for the analysis of F-T products. Hydrogen, carbon monoxide, carbon dioxide, nitrogen, methane, ethane, propane, butanes, pentanes, hexanes, and benzene are analyzed to assess the efficiency of the Fisher-Tropsch reaction, using two GC columns and various detecting systems. This is a time consuming procedure, requiring multiple sample injections, switching columns, and making polarity changes of the detector. For example, ASTM Method D-1946-82 requires carrier gas of 8.5% hydrogen and 91.5% helium, which is expensive.

In order to develop a convenient GC method, we used a DC 200 /500 and Supelco Carboxen -1000 GC columns, and tested their performance under various carrier gases: He, N₂ and H₂. First, the National Institute for standards and testing (NIST) standard sample is analyzed using helium as a carrier gas with DC 200/500 and Supelco Carboxen -1000 columns shown in Figure 9.

Fig. 9: Chromatogram of NIST standard sample calibration

As we can see the Carboxen column showed a good resolution of O₂, N₂, CO, CH₄, CO₂ and C₂H₆ gases but detection of higher alkanes could not be achieved. The Carboxen column detection of higher alkanes with C-number 3 or molar mass of greater than 44 amu could not be achieved.

The column stationary phase is made up of multi-layer silica gel and provides greater separation of non-condensable gases (CO, H₂, O₂, and N₂). The DC 200 /500 column could not separate non-condensable gases but desirable for all hydrocarbons CH₄, C₂H₆, C₃H₈, iso-C₄H₁₀, C₄H₁₀, iso-C₅H₁₂, C₅H₁₂, C₆H₆ using helium as a carrier gas. The low molecular weight compounds, permanent gases are not separated very well. At this stage the investigation of CO/Fe alumina catalyst syngas conversion efficiency through CO conversion and alkane formation and distribution requires changing two GC columns. An effort was made to find ways to provide CO and alkane separation in single injection. One of the choices was to use different carrier gases and see if carrier gases N₂ and H₂ carrier gases on DC-200/500 would provide better separation of non condensable gases such as H₂, O₂, N₂, CO while still being able to analyze hydrocarbons, CH₄, C₂H₆, C₃H₈, iso-C₄H₁₀, C₄H₁₀, iso-C₅H₁₂, C₅H₁₂, and C₆H₆. When switched to Nitrogen as a carrier gas for this column, it proved to bad for for the condensable gases, H₂, O₂, N₂, and CO, as well as for all hydrocarbons, CH₄, C₂H₆, C₃H₈, iso-C₄H₁₀, C₄H₁₀, iso-C₅H₁₂, C₅H₁₂, and C₆H₆ using N₂ as carrier gas. The DC 200/500 with N₂ as carrier gas is not a viable choice for non-condensable or the alkanes, C₁ through C₆, and benzene. The thermal conductivity of non-condensable as well as alkanes is very close to the thermal conductivity of N₂ gas resulting in poor TCD response. This may be due similar thermal conductivities of non-condensable and alkanes. The other choice was to use H₂ carrier gases and see if carrier gases H₂ carrier gases on DC-200/500 would provide better separation of non condensable gases such as H₂, O₂, N₂, CO while still being able to analyze hydrocarbons, CH₄,

C₂H₆, C₃H₈, iso-C₄H₁₀, C₄H₁₀, isoC₅H₁₂, C₅H₁₂, C₆H₆). This DC-200/500 column proved to an excellent choice for the condensable gases, H₂, O₂, N₂, and CO, as well as for all hydrocarbons, CH₄, C₂H₆, C₃H₈, iso-C₄H₁₀, C₄H₁₀, isoC₅H₁₂, C₅H₁₂, C₆H₆, using H₂ as carrier gas as shown in the fig below.

The DC 200/500 is an excellent column for the higher alkanes, C₁ through C₆, and benzene while using the He carrier gas. The thermal conductivity of non-condensable as well as alkanes is not close to the thermal conductivity of H₂ gas resulting in better TCD response. The low molecular weight compounds and condensable gases are also separated very well due to H₂ being carrier gas and it moves faster in the column because of its lower molecular weigh and H₂ would not respond to in the TCD leaving other gases to increase their response TCD. At this stage the investigation of CO/Fe alumina catalyst syngas conversion efficiency through CO conversion and alkane formation and distribution could be achieved with a single DC-200/500GC column using H₂ carrier gas.

Fig. 10: GC analysis using Carboxen-1000 and DC 200/500 columns

with DC 200/500 column using hydrogen as a carrier gas. Two GC columns DC 200/500 and Supelco Carboxen-1000 column were tested. DC200/500 showed remarkable separation of higher alkanes, however the non-condensable gases are not separated very well. Carboxen column showed an excellent response for non-condensable gases, however detection of higher alkanes could not be accomplished. Different carrier gases hydrogen, helium, nitrogen were tested for the purpose. We proved hydrogen as a carrier gas showed a good response in separating the non-condensable as well as condensable gases. We also tested the optimum ratio of CO/ H₂ for which it showed an increase in the yield of higher alkanes.

Pure metals, Fe, Co, and Cu incorporated into mesoporous g-alumina catalysts in their pure form showed different catalytic activity in the increasing order: Cu, Fe, Co. We have investigated the effect of different bimetallic combinations and compared them to pure metal catalysts. Fe/Co mixed metal catalysts showed higher catalytic activity as different metals together could enhance the reaction known as synergism or promoter effect [9,10]. We have used syngas gas mixtures (CO, H₂, N₂) and He or H₂ carrier

The products of synthesis gas reaction are also analysed by Carboxen-1000 and DC 200/500 columns and the results are shown in the following chromatogram in the Figure 10. As we can see the carboxen column analyzed non-condensable gases and methane while DC 200/500 column analyzed higher alkanes and some of the non-condensable gases.

We have developed an efficient and economical procedure for analyzing the products from synthesis gas reaction with Co/Fe impregnated alumina catalyst are separated using low cost GC-TCD system

Fig. 11: CG with hydrogen as a carrier gas

gas over Fe, Co, Cu, Co/Fe, Cu/Co, Fe/Cu γ -alumina catalysts over a period of 25 hr. The gases CO and H₂, were mixed in the ratio of 1:2 in the gas mixing manifold described in the experimental section. Figure 11. shows the products form a syngas gas mixture containing (CO, H₂, N₂) and H₂ carrier gas over Co/Fe alumina catalyst after 25 hr. We have compared the methane production of Fe, Co, Cu, Co/Fe, Cu/Co, Fe/Cu γ -alumina catalysts as shown in Figure 12.

Fig. 12: Methane production for different catalysts.

Optimization of CO/ H₂ ratio:

The F-T product distribution also depends on the ration of the CO/H₂ and seems to have effect on the production of different alkanes. We have investigated different CO/ H₂ ratios to obtain conversion of synthesis gas to higher alkanes and the results are shown below in Figure 13. As we can see when CO/H₂ ratio kept 1:1, we can see more alkane distribution in F-T process with Co /Fe (6% each) impregnated on alumina mesoporous catalyst.

Fig. 13: Nanoparticle Co/Fe alumina catalysts in a slurry phase Effect of CO/H₂ ratio for higher alkanes.

CONCLUSIONS

We have developed heterogeneous F-T catalysts with Fe/Co/Cu nanoparticles in γ -alumina sol-gel granules for higher alkanes production. Fe, Co, Cu nanoparticles were synthesized using $\text{Fe}(\text{acac})_3$, $\text{Co}(\text{acac})_2$, and $\text{Cu}(\text{acac})_2$ precursors and incorporated into alumina sol-gel granules using sol-gel/oil-drop methods. SEM/EDX, XRD, BET, VSM and SQUID experimental techniques were used to characterize the catalysts, and GC/MS were used for catalytic product analysis.

The nanoparticle oxide method gave the highest metal loading. In mixed metals Co or Cu interfered and reduced Fe metal loading. The XRD patterns indicate alloy formation between Co and Fe, and between Cu and Fe, which is also supported by DTA and VSM data. The magnetization studies showed ~40% reduction due to hydrogenation at 450°C for 4 hrs and ~85% of the catalyst has become inactive after 25 hrs of catalytic reaction. The low temperature (300 K to 4.2 K) SQUID magnetometer results indicate a superparamagnetic character of metal nanoparticles with a wide size distribution of < 20 nm nanoparticles.

A low cost GC-TCD system is developed for analyzing the F-T products with hydrogen as a carrier gas using two GC columns DC 200/500 and Supelco Carboxen-1000 column, which gave good separation of higher alkanes and the non-condensable gases. The Co/Fe on alumina sol-gel catalyst showed the highest yield for methane among Fe, Co, Cu, Co/Fe, Cu/Co, Fe/Cu. The optimization of CO/ H_2 ratio indicated that 1:1 ratio gave more alkanes distribution in F-T process with Co/Fe (6% each) impregnated on alumina mesoporous catalyst.

FUTURE WORK

We plan to investigate:

- Preparation of Fe/Co/Cu nanoparticle incorporated alumina/silica hybrid catalysts.
- Compare the syngas conversion rates between the alumina/silica hybrid catalysts and alumina catalysts with pure metal and mixed metal nanoparticles.
- Optimize the catalytic systems for higher alkanes production.

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