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ABSTRACT

We have developed and streamlined the experimental systems:

a) Laser-induced solution deposition (LISD) photosynthesis, ball-milling, and chemical synthesis of Fe, Co, and Cu nanoparticle catalysts;
b) Sol-gel method for mesoporous γ-Al_2O_3, SiO_2, hybrid alumina/silica granular supports;
c) Three sol-gel/oil-drop catalyst preparation methods to incorporate metal nanoparticles into mesoporous 1 mm granular supports;
d) Low-cost GC-TCD system with hydrogen as carrier gas for the determination of wide spectrum of alkanes produced during the F-T reactions; and
e) Gas-flow reactor and microchannel reactor for fast screening of catalysts.

The LISD method could produce Co, Cu, and Fe (5 nm) nanoparticles, but in milligram quantities. We could produce nanoparticles in gram quantities using high-energy ball milling and chemical synthesis methods. Ball milling gave wide particle size distribution compared to the chemical synthesis method that gave almost uniform size (~5 nm) particles.

Metal nanoparticles Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe were loaded (2-12 wt%) uniformly into γ-Al_2O_3, SiO_2, or alumina/silica hybrid supports by combined sol-gel/oil-drop methods followed by calcination and hydrogenation steps, prior to syngas FT reaction studies. The properties of metal loaded γ-Al_2O_3 granules were compared for the two precursors: aluminum tri-sec-butoxide (ALTSB) and aluminum tri-iso-propoxide (ALTIP). The effect of sol-gel supports alumina, silica, and alumina/silica hybrid were examined on catalytic properties.

Metal loading efficiencies for pure metal catalysts increased in the order Co, Cu and Fe in agreement with solubility of metal hydroxides. In case of mixed metals, Co and Cu seams to interfere and reduce Fe metal loading when metal nitrate solutions are used. The solubility differences of metal hydroxides would not allow precise control of metal loading. We have overcome this problem by introducing a novel method of nanoparticle metal oxide co-entrapped-sol-gel that gave the highest metal loading with precise control and reproducibility, and greater mechanical strength of granules than the metal nitrate solution co-entrapping and wet impregnation methods.

Both, slurry-phase-batch and gas-phase-continuous-flow, reactors were used for syngas conversion reactions. Our investigations of Co and Fe thin film deposited micro-reactors showed higher CO/H_2 conversion for Fe compared to Co. The catalytic activity for CO/H_2 conversion was observed in the increasing order for the nanocatalysts Cu, Co, Fe, Co/Fe, Cu/Co and Cu/Fe in alumina sol-gel support, and Co/Fe showed the highest yield for methane. 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. We could estimate the activity of catalysts (involving Co, Fe) during hydrogenation and after catalytic reaction using magnetization studies.

In summary our accomplishments are:

1) Novel chemical methods for the synthesis of (5 nm) Fe, Co, Cu nanoparticles with narrow size distribution.
2) Developing a method of metal oxide nanoparticles addition to alumina/silica sol-gel to control metal loading of pure and mixed metal catalysts compositions in high yields.
3) A low-cost GC-TCD system to analyze wide spectrum of alkanes (F-T reaction products).
4) Fe/Co mixed metal alumina/silica mesoporous catalysts with higher FT activity.
5) Characterizing nanoparticle catalysts and supports for detail understanding of FT-process.

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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 [1-4]. 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 of programs at large 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 [5]. 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 [6]. Thus the novel nanoparticle catalysts seem to provide a promising alternative to conventional catalysts. The nanometer scale metal clusters are known to exhibit size dependent physical properties [7]. 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 [8]. Mesoporous materials (silica or alumina) are used as the support for the FT catalysts [9, 10], 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 [11-13] by incorporating metal oxide nanoparticles into alumina, silica or alumina/silica hybrid sol-gel matrix.

The main objectives in this project are to develop methods to prepare nanoparticles in sufficient quantities, incorporate nanoparticles onto heterogeneous mesoporous F-T catalysts, and optimize catalysts for the syngas conversion to alkanes. These objectives were achieved through following steps: 1) Synthesize nanoparticles using photochemical (LISD), chemical and ball-milling methods, 2) Prepare alumina, silica and alumina/silica hybrid sol-gels using precursors: aluminum tri-sec-butoxide (ALTSB), aluminum tri-iso-propoxide (ALTIP), and tetra-ethyl-ortho-silicate (TEOS), 3) Incorporate metals in sol-gels using three sol-gel/oil-drop catalyst preparation methods - a) metal nitrate solutions co-entrapped-sol-gel, b) nanoparticle metal oxide co-entrapped-sol-gel, and c) metal impregnation (wet impregnation) on preformed alumina/silica granules, and 4) Optimize catalytic reaction conditions for the syngas conversion.

The nanoparticles and the catalysts produced were characterized using Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) method for surface area, differential thermal analysis/thermal gravimetric analysis (DTA/TGA) for thermal properties, Vibrating Sample Magnetometer (VSM) and Superconducting Quantum Interface Device (SQUID) for magnetic characteristics. It was also important to develop GC method conditions for separating the components produced during syngas conversion. We developed an efficient and economical procedure for analyzing the products from syngas reaction with Co/Fe nanoparticle incorporated alumina/silica catalysts. Different carrier gases hydrogen, helium, nitrogen were tested for efficient separations and a low cost GC-TCD system was developed for the F-T product separation using with appropriate columns.

Various metals such as Fe, Co, and Cu were incorporated into catalysts in pure and mixed form to study the effects of pure metals and metal combinations on catalytic activity. Mixed metal catalysts are expected to show superior catalytic activity as different metals together enhanced the reaction known as synergism or promoter effect [14, 15]. We studied Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe nanoparticle metal loaded mesoporous 1 mm spherical granular γ-Al_2O_3 and SiO_2 support catalysts, by combined sol-gel/oil-drop methods followed by calcination and hydrogenation. Parameters for calcination process were optimized using DTA/TGA. Various properties of metal loaded γ-Al_2O_3, SiO_2 and hybrid Al_2O_3/SiO_2 granules were compared for the preparations starting with three precursors: aluminum tri-sec-butoxide (ALTSB), aluminum tri-iso-propoxide (ALTIP), and tetra-ethyl-ortho-silicate (TEOS).

Besides the type of catalyst and support combinations, the F-T product distribution also depends on the ratio of CO/H_2, which affects the selectivity of alkanes. Thus, we have tested different ratios of CO/H_2 and compositions of catalyst and support combinations in order to produce higher alkanes.

EXECUTIVE SUMMARY

We are able to produce Fe, Co, and Cu nanoparticles using LISD technique. However, the LISD system produced the nanoparticles only in milligram quantities, which could be due to absorption of laser radiation by solvent, thereby significantly reducing the yield of the nanoparticles. We are able to produce Fe, Co and Cu nanoparticles in larger quantities by high-energy ball milling and chemical synthesis methods. EDX analysis of ball milled particles showed contamination through chemical reactions and alloy formations with other milling materials during the ball-milling process. Further, the ball-milled particles have wide range of size distribution and needed differential centrifugation to partially separate the particles (20-50 nm). We were successful in the synthesis of nanoparticles in gram quantities with a narrower particles size (~5 nm) distribution using polyol reduction chemical method.

We have developed a reproducible procedure for the synthesis of alumina, silica, alumina/silica-hybrid nanocatalyst granules, and extended this procedure to coat thin films on silicon wafers and microreactor channels. Several experimental techniques were used to characterize the nanoparticle catalysts, supports, and reaction products. The particle size, surface, porosity, and crystal structure were characterized using Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), surface area using Brunauer-Emmett-Teller (BET) method, thermal properties using differential thermal analysis/thermal gravimetric analysis (DTA/TGA), magnetic characteristics of Co and Fe catalysts were analyzed using Vibrating Sample Magnetometer (VSM) and Superconducting Quantum Interface Device (SQUID), which gives an estimate of reduction efficiency during hydrogenation of catalysts and pure metal conversion to carbide and carbonyl complexes during catalytic reactions. We have developed GC method conditions for separating the components produced by syngas conversions.

We have compared alumina supported catalyst preparation methods: 1) Metal nitrate co-entrapped sol-gel, 2) Nanoparticle metal oxide co-entrapped sol-gel, and 3) Metal ion wet-impregnation on preformed granules. This work represents the first efforts to incorporate nanoparticle-metal-oxides into sol-gel/oil-drop method to prepare alumina granules. Fischer–Tropsch catalytic study using Fe, Co, Co/Fe, and Cu/Fe nanoparticle granular γ-Al_2O_3 and Al_2O_3

/SiO_2 to produce liquid aliphatic hydrocarbons and oxygenates. Our work clearly shows that the nanoparticle metal oxide prepared by chemical methods could be co-entrapped into sol-gel supports to give catalysts granules higher metal loading and greater mechanical strength than the metal nitrate solution co-entrapping and wet impregnation methods. The metal loading in alumina granules prepared by the three sol-gel methods is examined by EDX analysis. Metal loading increased in the following order: metal wet-impregnation on preformed granules, metal nitrate solution and nanoparticle metal oxide. In case of mixed metals, it seems that Co or Cu interferes and reduces Fe metal loading. The 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. We could overcome this problem using a novel nanoparticle metal oxide co-entrapped sol-gel method. EDX data clearly shows that nanoparticle metal oxide co-entrapped method gives more precise control and reproducible metal loading.

The absence of the iron hydroxide dehydration peak clearly indicates that during the nanoparticle iron oxide entrapped sol-gel procedure; the nanoparticle iron oxide structure is preserved without being converted to metal hydroxides. This is important because of the solubility factors involved in the metal nitrate solution co-entrapped method are circumvented and the precise control of mixed metal loading becomes feasible using metal oxides. The nanoparticle oxide method is the 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.

The XRD results on Fe, Co, Cu nanoparticles prepared by all three methods (LISD, ball-milling and chemical synthesis) showed very weak diffraction peaks, which increased as the nanoparticles were heated. Even in the case of nanoparticle metal oxide sol-gel prepared granules, which gave higher metal loading, the XRD peaks were still weak and indicated the lack of regular lattice spacing and/or smaller particle size of the metal oxides.

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. 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 and proved that hydrogen as a carrier gas showed a good response in separating the non-condensable as well as condensable gases.

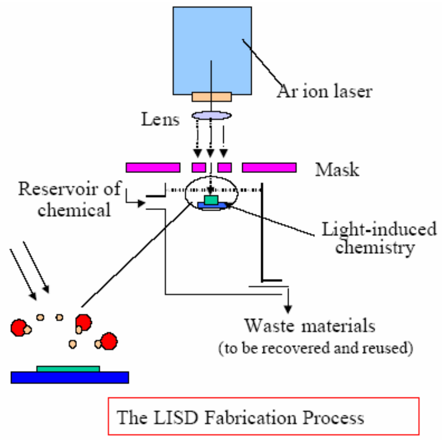
The F-T product distribution depends on the ration of the CO/H_2 and seems to have effect on the production of different alkanes. We have investigated different CO/ H_2 ratios to obtain the conversion of synthesis gas to higher alkanes. We could see more alkane distribution at CO/H_2 ratio of 1:1 in F-T process with Co /Fe (6% each) impregnated on alumina mesoporous catalyst. We have also studied the CO conversion for Fe/Co nanoparticles loaded in hybrid alumina/silica (2:1, 1:1, 3:1) mesoporous granules. We varied the alumina/silica ratio and also Fe/Co (2:1, 1:1, 1:2) ratio. Our preliminary studies indicate that the hybrid alumina/silica catalysts had higher surface area, different (smaller) pore sizes, and significantly difference in FT product distribution. Among the hybrid catalysts alumina/silica ratio of 3:1 and Fe/Co ratio of 1:1 at 6% w/w each metal loading showed significantly higher FT activity compared to alumina supported Fe/Co catalysts.

EXPERIMENTAL

Preparation of Nanoparticles

a) <u>Photochemical method (LISD)</u>

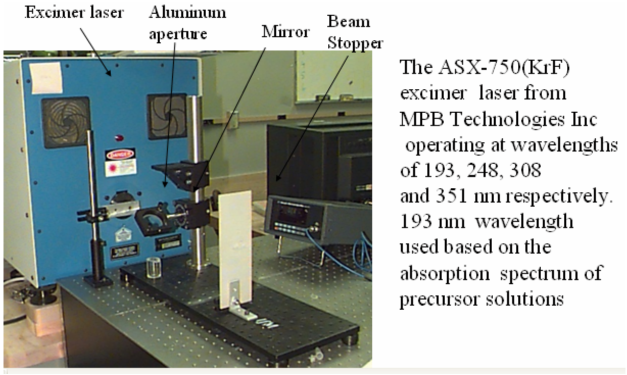
Figure 1 shows the schematic diagram of laser-induced solution deposition system (LISD) system, which was driven by an argon ion laser (I-90). The system included the necessary focusing lenses elements, mask, and chemical reactor as indicated in Figure 2. This is a laser-initiated photochemical process. Various precursors (solutes) of metal chlorides ($CoCl_2.6H_2O$, $FeCl_2$, and $CuCl_2$), and metal nitrates ($Co(NO_3)_2.6H_2O$, $Fe(NO_3)_3$. $9H_2O$, and, $Cu(NO_3)_2.2.5H_2O$, $Co(acac)_2$, $Cu(acac)_2$, $Fe(acac)_3$) were used in LISD. They were dissolved in the solution of ammonia in distill water, and various mixtures of solvents (methanol, cyclo-hexane, tetrahedron-furan (THF) and diethyl-ether). The selection of solvents is crucial for successful deposition.



<u>The laser parameters</u>:
Pulse Frequency 40 Hz
Work Voltage 27.6 kV
Chamber Pressure 2.96—3.13 bar
Average output 1.20 W (~ 300 mJ/pulse)
Exposure ~5000 pulses

Fig. 1: *A schematic diagram of laser-induced solution deposition (LISD) system*

The principle of solvent selection is that the selected solvents can dissolve solutes completely and the solvent/solute mixture is transparent in the laser wavelength used in the experiment. Following surfactants (d-sorbitol glycerol, oleyl amine and oleic acid) were also added to the solutions to prevent agglomeration of nanoparticles. The reaction mixtures containing metal nanoparticles were centrifuged at 3,100 rpm for 10-15 min to isolate the particles.



The ASX-750(KrF) excimer laser from MPB Technologies Inc operating at wavelengths of 193, 248, 308 and 351 nm respectively. 193 nm wavelength used based on the absorption spectrum of precursor solutions

Fig. 2: *A viewgraph of laser-induced solution deposition (LISD) setup.*

b) Chemical Synthesis of Fe, Co, and Cu nanoparticles: Ployol reduction method

The nanoparticles were prepared using a modification of the procedure reported by Sun et al. [6]. The synthesis procedures were carried out using airless techniques and commercially available reagents.

Fe nanoparticles

1) A solution of iron acetylacetonate, 1,2 hexadecanediol and diphenylether are place in a three necked round bottom flask and heated to 100^0 C.

2) Oleyl amine and oleic acid are added to the solution via syringe and the mixture is heated to 260^0C and refluxed for 30 min.

3) The mixture is cooled to 40 ^{0}C and ethanol 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, octane, oleylamine, and oleic acid for storage.

6) The precipitated particles are dried in oven for two days at 60^0 C before using in synthesis and analysis.

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

c) Nanoparticles from high energy ball-milling

High energy ball-mill, SPEX SamplePrep 8000D with two clamps was used for pulverizing CuO, Fe_2O_3, CoO, and CoO/Fe_2O_3 mixtures in the 10-gram range at room temperature, air atmosphere and 30 min milling time.

Catalyst preparation

a) Sol-gel Preparation

Alumina, silica and alumina/silica hybrid sol-gels were prepared using precursors: aluminum tri-sec-butoxide (ALTSB) (Aldrich), aluminum tri-iso-propoxide (ALTIP) (Aldrich), and tetra-ethyl-ortho-silicate (TEOS) (Aldrich).

In case of alumina sol-gel, ALTSB or ALTIP was slowly and uniformly added for about half an hour time period to distilled water using a syringe in the case of liquid ALTSB or directly in the case of solid ALTIP. The mixture was stirred continuously during the process and maintained at a temperature of 75-80°C. Nitric acid was added to adjust the pH when the flock 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. For silica sol-gel preparation, liquid tetra-ethyl-ortho-silicate (TEOS) was used as precursor under base catalysis similar to alumina sol-gel preparation. Hybrid alumina/silica sol-gel mixtures with molar ratios 3:1, 3:4 and 1:0.5, 1:5 were prepared using alumina and silica alkoxides using a combined approach described above for alumina and silica sol-gel synthesis.

b) Metal loading

Metal lading and sol-gel shaping were carried out using three sol-gel/oil-drop catalyst preparation methods:

i) *Metal nitrate solutions co-entrapped-sol-gel*

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/silica (assuming 100% conversion of ALTSB, ALTIP or TEOS to alumina/silica) and the required metal loading (w/w). Metal solutions of different concentrations (2, 4, 6, and 12%) were prepared. After reflux, HNO_3 solutions was added to the boehmite/silica solution at a temperature of ~ 80 °C and stirred for about 1 hr.

ii) *Nanoparticle metal oxide co-entrapped-sol-gel*

The above procedure was followed with the exception of replacing metal nitrate solutions with suspensions of nanoparticle metal oxides in water with appropriate metal ion concentration. Ball-milled nanoparticle iron (III) oxide, copper (II) oxide, cobalt (II) oxide, and Cobalt (II)/Iron (III) mixed metal oxide suspensions were added to the sol-gel and stirred to ensure proper mixing of metal oxide into the matrix of sol-gel. The amount of nanoparticle metal oxides to add was calculated based on the weight percent of γ- alumina/silica as described above.

iii) *Metal impregnation on preformed alumina granules*

Virgin alumina soft-granules were prepared by the sol-gel/oil-drop method as described below 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 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.

c) Sol-gels shaping and calcination

Granular Sol-gel shaping-Set up for oil drop method: An aqueous solution of ~10% NH_3 (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 ammonia solution used in the cylinder were calculated based on the volume of alumina soft-granules formed. The mineral oil (for alumina sol-gel granules) or silicone oil (for silica sol-gel granules) was added to cylinder and kept at a temperature of ~100°C, using a heating tape wrapped around the glass cylinder. A layer of approximately ~ 20 cm floated on top of the NH_3 solution. The ratio of heights of mineral oil to aqueous NH_3 solution was ~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 ~ 1 hr 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.

Set up for thin film coating method: Sol-gel matrix from step 3 is placed on a silica wafer or micro-reactor and spread thin using a glass slide. Thin sol-gel matrix was treated by heating with hot air from a blow gun for 2 min to form a harder thin gel coating on the surface, followed by covering the surface with an ammonia solution, similar to procedure in steps above for granules, washing with water, and drying at 50°C.

Calcinations of catalysts: All Granules were filtered and dried at ~ 50 °C, and calcined at ~ 450 °C for ~ 4 hrs.

Hydrogenation of catalysts: Catalysts were loaded into glass/stainless tube and/or slurry phase reactors. Hydrogen gas was passed over the catalyst while heating to 200-400 °C for 2 hrs. Catalysts were dried and water removed by vacuum suction at 200-400 °C. Again Hydrogen gas was passed over the catalyst while heated to 200°C for 2 hrs by vacuum suction for ~1hr prior to catalytic reactions.

Characterization of Catalysts

Differential Thermal and Thermal Gravimetric Analysis (DTA & TGA)

Schimadzu DTA-50 has DSC function and a wide temperature range: Room temperature to 1500°C. Schimadzu TGA-51 measures the changes in mass on the order of several micrograms. Phase transition temperatures of different crystalline forms of alumina, silica, and metals are identified in conjunction with XRD.

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

Vibrating Sample Magnetometer (VSM)

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 μemu with 100 averages. A maximum magnetic field of 13.5 kOe can be applied.

Superconducting Quantum Interface Device (SQUID)

Quantum Design MPMS-XL Superconducting Quantum Interface Device (SQUID) magnetometer 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 a resolution of 3.5 nm 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: GC 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. A block diagram of GC spectrometer setup is shown in Figure 3.

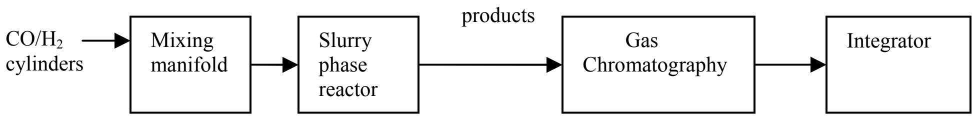


Fig. 3: *Block diagram of GC spectrometer setup.*

GC conditions: The oven temperature was initially held at 135 ^{0}C for 40 minutes and was steadily increased at a rate of 60 ^{0}C per minute till 150 ^{0}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. *GC gases used*: Carbon monoxide, hydrogen, helium, nitrogen were purchased from Red Ball Company and GC standard samples were purchased from NIST Houston, TX.

Catalytic activity: F-T catalytic activity test reactors

i) *Gas phase reactor*:

CO, H_2, and N_2, in 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 ºC. Both dynamic and batch conversions were monitored. Product mixture form 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.

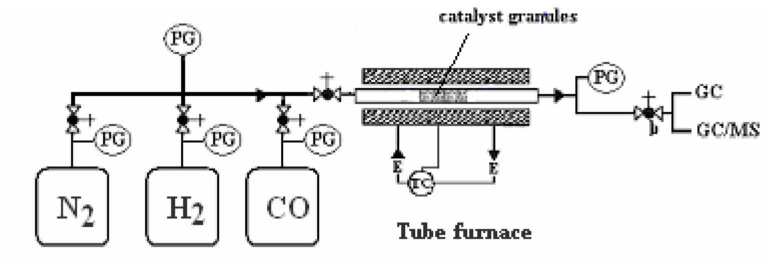


Fig. 4: *Block diagram of gas phase reactor*

ii) *Slurry Phase reactor*:

Figure 5 shows a block diagram of slurry-phase reactor. CO, H_2, and N_2, in 1:2:1 ratio are mixed in a gas mixing manifold and loaded into high-pressure reactor with catalyst stirred in silicone oil at 200 ºC and 100 psi total pressure. N_2 was used as an internal standard. Calibrations of products were carried out by internal standards and response factors for standard gas mixtures.

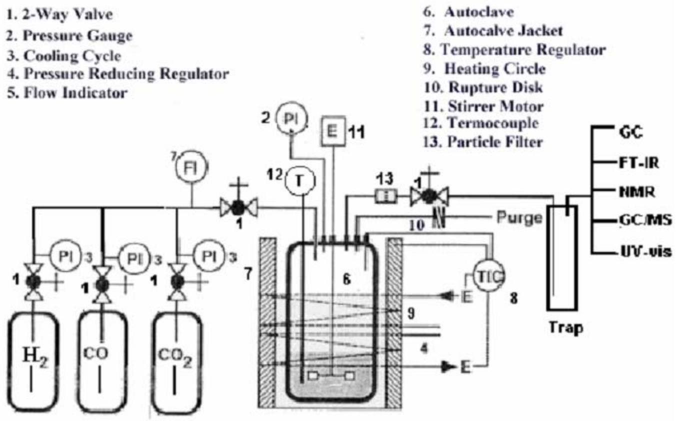


Fig. 5: *Block diagram of slurry-phase reactor*

F-T reactions were carried out in a slurry phase reactor (Parr High Pressure 1296) loaded with Co/Fe nanoparticles 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.

Chromatographic study was carried out on GC using He, H_2, and N_2 carrier gases and following test mixtures.

1) Standard mixture (CO, H_2, O_2, N_2, CH_4, CO_2, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, and C_6H_6) purchased from NIST Specialty Products, TX.
2) Test gas mixture (CO, H_2, N_2, CH_4, and CO_2) 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 catalysts after 25 hr.

RESULTS AND DISCUSSION

Nanoparticle preparation

a) Photochemical (LISD) nanoparticle synthesis

In LISD experiments, we have chosen metal (M = Fe, Co, Cu) nitrates dissolved in ammonia (NH_3) and distill water to form complex $[M(NH_3)_6]^{2+}$ ions. The laser energy activated the decomposition of the complex ions and transferred electrons to the metal from NH_3, which in turn got converted to NH_4^+. Various concentrations of solutions and laser conditions were tested. Figure 6 shows a UV-Visible Absorption Spectrum of Precursor Solutions 0.002 M $Co(NO_3)_2$ in 0.02 M ammonia.

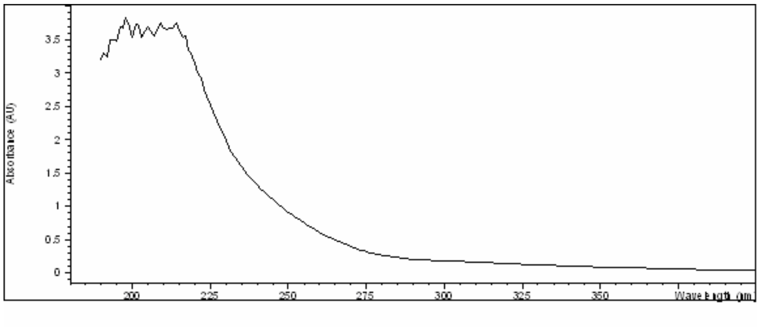


Fig. 6: *UV-Visible Absorption Spectrum of Precursor Solutions 0.002 M $Co(NO_3)_2$ in 0.02 M ammonia*

The selection of the laser

wavelength was based on absorption spectra of metal nitrate and ammonia solutions. For example, focused laser beam of 215 nm wavelength (power = 1.7 w) was selected for LISD Co nanoparticles preparation with a deposition time of ~ 40 min. TEM results on nanoparticles separated after centrifugation of LISD solutions confirmed that their sizes were in the order of 5 nm. EDX spectroscopy showed an oxygen peak, which could be oxygen contamination or the formation of metal oxides on the surface of the particles as confirmed by VSM magnetization studies [16]. However, the LISD system produced Fe, Co, and Cu nanoparticles only in milligram quantities. This could be due to absorption of laser radiation by solvent thereby significantly reducing the yield of the nanoparticles.

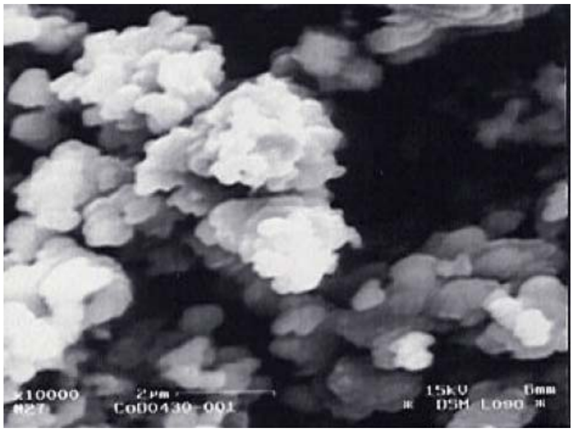


Fig.7 *SEM picture of Co nanoparticles taken from the LISD. The cluster about 200–500 nm containing 5 nm nanoparticles (magnification 10,000 X)*

Since the LISD nanoparticles were clustered as shown in Figure 7, we studied the effect of various surfactants, d-sorbitol, glycerol, oleyl amine and oleic acid, to prevent agglomeration. However, the yields of the nanoparticles were not significantly improved. These results demonstrate that we are able to produce nanoparticles of the order of 5 nm (confirmed by TEM) using the LISD techniques. Unfortunately, the LISD system could not generate nanoparticles in gram quantities required for sol-gel synthesis of F-T catalysts as we expected. Thus we decided to look for alternative ways to produce Fe, Co and Cu nanoparticles in larger quantities by ball-milling and chemical synthesis as described below.

b) Nanoparticle preparation by high-energy ball milling

It is well known that high-energy ball milling produces a wide range distribution of particles sizes (5-100 nm). The breaking up particles to sizes < 50 nm, requires higher energy. We were able to produce nanoparticle of CuO, Fe_2O_3, CoO, and CoO/Fe_2O_3 mixtures starting from micron range particles using high-energy ball-mill (SPEX SamplePrep 8000D, 10-gram range at room temperature, air atmosphere and 30 min milling time). We used centrifugation to partially separate the nanoparticles (20-50nm) according to the sizes and re-dispersed them in a solution consisting of hexane, oleylamine, oleic acid for storage. We analyzed the nanoparticles with SEM, EDX, XRD, and VSM. The magnetic studies showed Fe nanoparticles to have oxide layer and metal core estimated by saturation magnetization. EDX analysis also showed contamination of particles through chemical reactions and alloy formations with other milling materials during the ball-milling process.

c) Chemical synthesis of nanoparticles

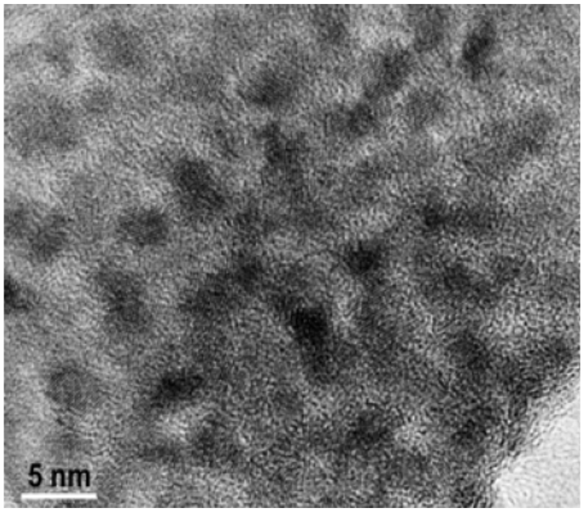


Fig. 8: *TEM image of the Co nanoparticles prepared by chemical synthesis*

Starting from organometallic precursor compounds, Fe(acac)$_3$, Co(acac)$_2$, and Cu(acac)$_2$, we have developed a procedure to synthesize Fe, Co and Cu nanoparticles. We were successful in the synthesis of nanoparticles in gram quantities with a narrower particle size (~ 5 nm) distribution. We examined the nanoparticles using TEM, SQUID, SEM/EDX, and XRD. A high-resolution TEM picture of Co nanoparticles produced from polyol reduction is shown in Figure 8.

The chemical synthesis allowed us to prepare nanoparticles in gram quantities required for sol-gel synthesis of F-T catalysts.

Catalyst preparation

We have used a combined sol-gel/oil-drop methods to prepare nanoparticle metal loaded mesoporous spherical (~ 1 mm diameter) granular Fe, Co, Cu, Co/Fe, Cu/Fe-alumina and Fe, Co, Co/Fe-alumina/silica catalysts starting with aluminum tri-sec-butoxide (ALTSB), aluminum tri-isopropoxide (ALISOP), and tetra-ethyl-ortho-silicate (TEOS) as sol precursors. Objective was to study metal loading and granular characteristics for various precursors and procedures. We have compared alumina supported catalyst preparation methods: 1) Metal nitrate co-entrapped sol-gel, 2) Nanoparticle metal oxide co-entrapped sol-gel, and 3) Metal ion wet-impregnation on preformed granules. This work represents the first efforts to incorporate nanoparticle-metal-oxides into sol-gel/oil-drop method to prepare alumina/silica granules with high metal loading; and Fischer–Tropsch catalytic study using Fe, Co, Co/Fe, Cu/Fe nanoparticle granular γ-Al_2O_3 and Al_2O_3/SiO_2 to produce liquid aliphatic hydrocarbons and oxygenates.

Table 1. *Metal loading by EDX analysis and crushing strength of Fe/Al_2O_3 granules prepared by three sol-gel methods*

	Metal nitrate solution	Nanoparticle metal oxide	Metal ion wet-impregnation
EDX results on Fe/Al_2O_3 granules (12% Fe intended)	2.6%	8.9%	1.5%
Crush strength* of the granules (psi)	1500	2500	1200

* Crushing strength of granules were compared by measuring the breaking point pressure for the same amount of sample loaded on to a pellet maker using a Crystal Lab hydraulic press.

Even though all three preparation methods yielded no significant differences in alumina or alumina/silica granular characteristics such as surface area, DTA and XRD; they differed remarkably in metal loading and crushing strength as shown in Table 1 for Co/Fe alumina granules. Metal to support as well as alumina to silica ratios in the granule are important factors in determining its catalytic characteristics such as alkane distribution. Therefore, it is important to develop reproducible synthetic procedures to make mesoporous granules with desired metal loading and support characteristics. Our work clearly shows that the nanoparticle metal oxide could be co-entrapped into sol-gel supports to give catalysts granules with higher metal loading and greater mechanical strength than the metal nitrate solution co-entrapping and wet impregnation methods. EDX data clearly shows that nanoparticle metal oxide co-entrapped method gives more precise control and reproducible metal loading. We have developed a reproducible procedure for the synthesis of alumina, silica, alumina/silica hybrid nanocatalyst granules. We have extended this procedure to coat thin films on silicon wafers and microreactor channels. Figure 9 shows a block diagram of a microreactor with an in let for syngas feed and an outlet for product analysis going to GC system.

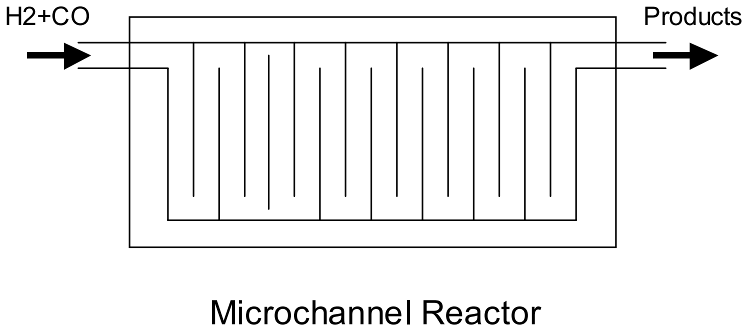


Fig. 9: *Block diagram of a microreactor with 25-100 μm channel with and 100 μm depth.*

Thermal Analysis of Catalysts

The DTA of virgin sol-gel prepared alumina (Figure 10) shows two broad peaks around 130°C and 295°C. 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. Graphs for Co, Fe, Co/Fe granules prepared by metal nitrate solution co-entrapped sol-gel are shown in the Figure 11a, b, and c, respectively. Thermal peaks observed around temperatures 200-300°C are assigned to metal hydroxides getting converted to oxides. The peaks, around 218°C and 242°C in Figure 11 are attributed to cobalt and iron, respectively, suggesting easier $Co(OH)_2$ dehydration to CoO compared to $Fe(OH)_3$. This is in agreement with electrostatic model of Co (II) and Fe (III) oxidation states and bond energies. Cobalt and iron mixed metal granules showed two broad shifted exothermic peaks at 210°C and 253°C that are attributed to dehydration of cobalt and iron-hydroxides to metal oxide, respectively. This shift in values could be attributed to Co and Fe mixed metal interactions. The

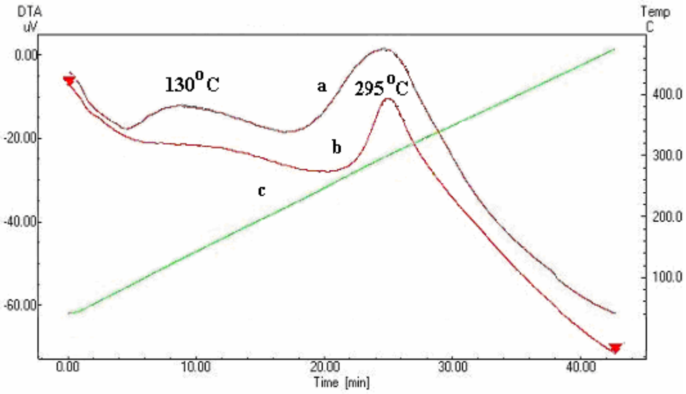


Fig. 10: *a) Sol-gel alumina without metal loading and b) Sol-gel alumina loaded with nanoparticle iron oxide, and c) Temperatures curve*

catalysts prepared by wet-impregnation of cobalt and iron metal ion on preformed alumina granules has a different DTA pattern (figure not shown) from the metal nitrate solution method having broad metal hydroxide dehydration peaks and additional peaks in the range of 100-250 °C. This maybe due to non-uniform distribution of metals on wet-impregnated granules as most of the metal deposition is on the surface.

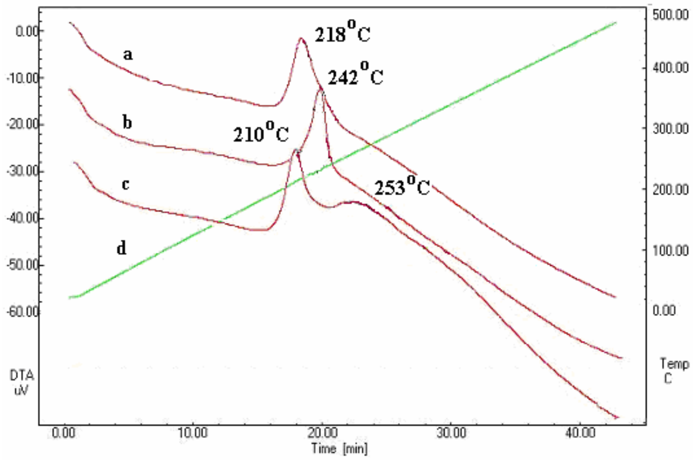


Fig. 11: *a) Cobalt b) Iron and c) Cobalt/Iron loaded on alumina using metal nitrate method (ALTSB), and d) Temperatures curve*

The DTA characteristics of metal loaded alumina prepared with nanoparticle metal oxide co-entrapped sol-gel method showed no metal hydroxide dehydration peaks, but showed identical feature as the control DTA graph of pure sol-gel alumina without metal loading as shown in Fig. 10a. The absence of iron hydroxide dehydration peak indicates that during the nanoparticle iron oxide entrapped sol-gel procedure, nanoparticle iron oxide structure is preserved without being converted to metal hydroxides. This is important as the solubility factors involved in the metal nitrate solution co-entrapped method are circumvented and the precise control of mixed metal loading becomes feasible using metal oxides.

SEM/EDX analysis

Optimization of metal loading

Table 2: *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.*

	Metal nitrate concentration in the sol-gel for Intended metal loading (w/w)%			(w/w)% metal in the bottom 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/F	6	6	-	6	6	-	7.60	2.90	-	126	48.0	-
Cu/F	-	6	6	-	6	6	-	2.35	7.07	-	39.2	118

The metal loading in the granules seems to depend on the type of sol-gel methods used. The efficiency of metal loading was determined by EDX analysis. The effect of metal content in the bottom ammonia layer of the oil-drop method on metal loading in alumina granules prepared using sol-gel and metal nitrates are shown in Table 2. The EDX analysis indicates that metal loading was directly proportional to the metal ion concentration of the metal nitrate solution as indicated by the intended metal loading (w/w%) in Table 2.

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 $Co(OH)_2$ 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 [17] for Fe^{3+}, Cu^{2+}, and Co^{2+} hydroxides: $M(OH)_x(s) = M^{x+}(aq) + x\ OH^-(aq)$; $K_{sp}(Fe^{3+}) = 4 \times 10^{-38}$ mol/L, $K_{sp}(Cu^{2+}) = 1.6 \times 10^{-19}$ mol/L and $K_{sp}(Co^{2+}) = 2.5 \times 10^{-16}$ 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 the three sol-gel methods is summarized in Table 3. Metal loading increased in the following order: metal wet-impregnation on preformed granules, metal nitrate solution, and nanoparticle metal oxide.

Table 3: *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		
	Co	Fe	Cu	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 the best for metal loading because this method does not 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.

XRD analysis

Fe, Co, Cu nanoparticles prepared by all three methods (LISD, ball-milling and chemical synthesis) showed very weak diffraction peaks, which increased as the nanoparticles were heated. Figure 12 shows the XRD patterns for the Fe_2O_3 nanoparticles as the temperature is increased to 450ºC and 1000ºC, the crystallinity of the sample was increased.

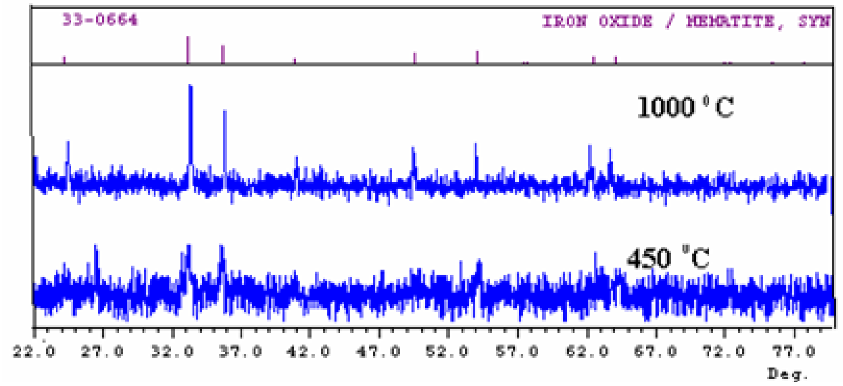


Fig. 12: *Fe_2O_3 nanoparticles heated at 450 ºC and 1000 ºC*

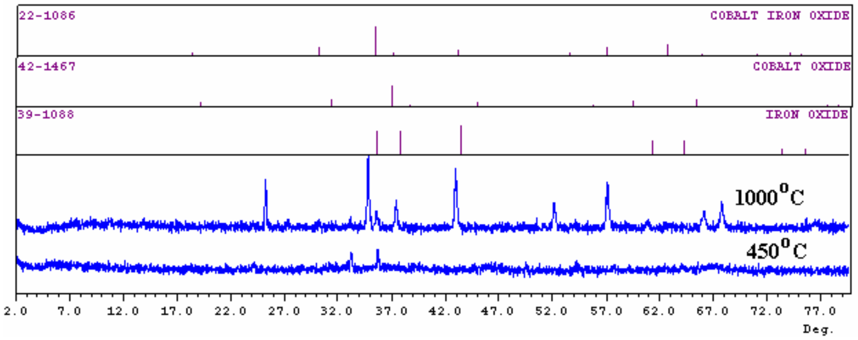


Fig. 13: *CoO and Fe_2O_3 nanoparticle loaded alumina heated at 450ºC and 1000 ºC*

All granular catalysts did not show powder x-ray diffraction (XRD) peaks before calcination. After calcination at 450°C, XRD peaks for sol-gel pure alumina granules prepared from ALISOP and ALTSB precursors showed similar patterns. Broad peaks appeared around 38º, 49º and 67º (2θ). As the temperature is increased to 1000°C, new sharper peaks corresponding to corundum appeared, as shown in Figures 13 and 14 of metal loaded alumina. 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. This is consistent with the previous work [18], where CuO peaks were observed only at higher metal loading. In case of nanoparticle metal oxide sol-gel prepared granules with higher metal loading, the still weak peaks in XRD indicate the lack of regular lattice spacing and/or smaller particle size of the metal oxides.

The XRD patterns of mixed metal Co/Fe alumina granules (heated up to 1000°C) prepared by metal-nitrate-solution and nanoparticle-metal-oxide methods are shown in Figure 13 and 14, respectively. The pattern for Fe/Co-nitrate produced granules matched only with Co_3O_4 but not with iron oxide (hematite-synthetic) as observed in Fig 14. This could be due to lower iron loading observed by EDX as a result of cobalt interference. Co_3O_4 has been observed [19] previously on wet impregnated Co/SiO_2 but not on Co/Al_2O_3 heated to 600°C. Our results indicate

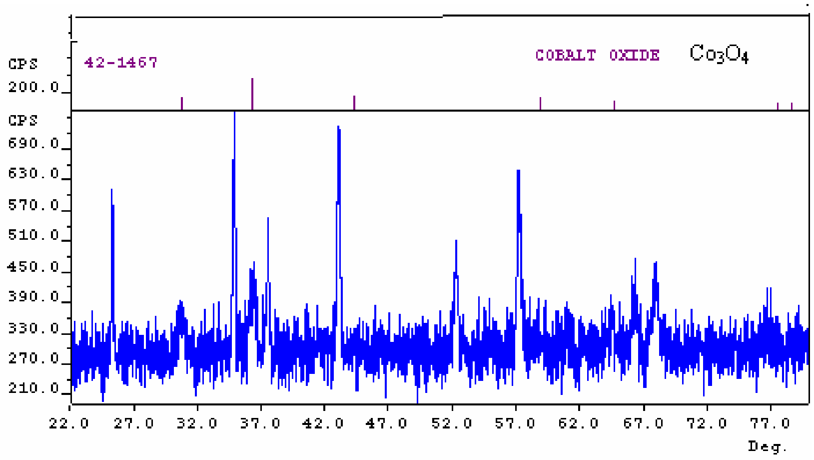


Fig. 14: *Cobalt and iron oxide loaded by nitrate solutions on alumina heated at 1000 ºC*

that Co_3O_4 can be formed even in Al_2O_3 in agreement with previous studies [20], where Co_3O_4 is found in alumina even at 500 °C. These differences could be explained by metal loading in alumina sol-gel as it is difficult to observe the crystalline peaks at low metal loadings.

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, which is also supported by DTA and VMS data. We observed similar behavior for the nanoparticle copper and iron oxide sol-gel prepared alumina granules.

Magnetization Studies of Co/Fe Encapsulated Al_2O_3 Sol-gel Micro-reactors

Most heterogeneous catalysts are comprised of transition elements, which have incomplete d-electron shell and unpaired electron spins. These features are responsible for their specific magnetic as well as their valuable catalytic properties [8, 21]. We studied [22-24] the magnetic characters of Co/Fe encapsulated Al_2O_3 sol-gel deposited 25 µm wide and 100 µm deep micro-reactors as deposited, reduced and exposed to the syngas ($CO+H_2$) using Vibrating Sample Magnetometer (VSM) in collaboration with Institute for Micromanufacturing (IfM), LaTech.

Figure 15 shows the magnetic character of the catalysts obtained from VSM. 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 gives 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 450^0C for 4 hrs. More reduction of metal catalysts occurred in the method using nanoparticle oxide as precursor compared to the nitrate solution sol-gel method. About 85% of the metal catalysts have formed carbides/carbonyls of Fe and Co after 25 hrs of catalytic reaction.

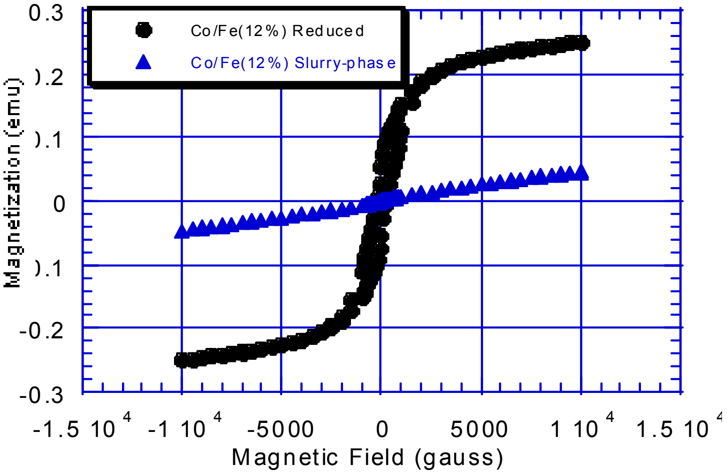


Fig. 15: *Magnetization of Fe/Co (12%) catalysts:*
● *Reduced* ▲ *After slurry-phase reaction.*

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

Superconducting Quantum Interface Device (SQUID) magnetometer 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.

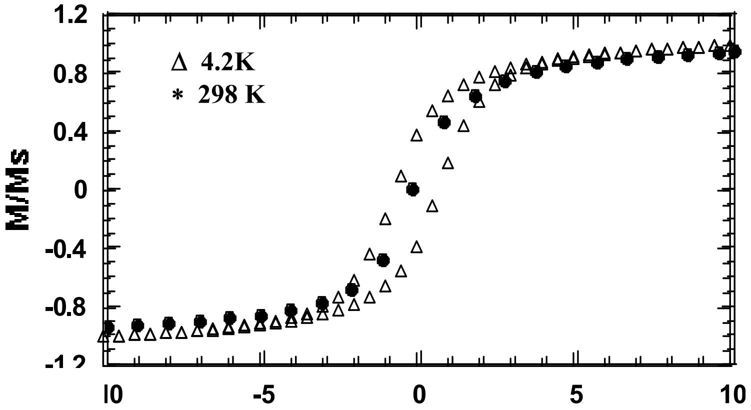


Fig. 16: *Magnetic hysteresis loops of Co nanoparticles at 298K and at 4.2 K*

Figure 16 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.

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

One of our objectives was to develop 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 F-T 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, N_2 and H_2. First, the NIST standard sample is analyzed using helium as a carrier gas with DC 200/500 and Supelco Carboxen -1000 columns shown in Figure 17. As we can see the Carboxen column showed a good resolution of O_2, N_2, CO, CH_4, CO_2, and C_2H_6 gases but detection of higher alkanes with C-number 3 or molar mass of grater 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, H_2, O_2, and N_2). The DC 200/500 column could not separate non-condensable gases but desirable for all hydrocarbons CH_4, C_2H_6, C_3H_8, isoC_4H_{10}, C_4H_{10}, isoC_5H_{12}, C_5H_{12}, and C_6H_6 using helium as a carrier gas. The low molecular weight compounds,

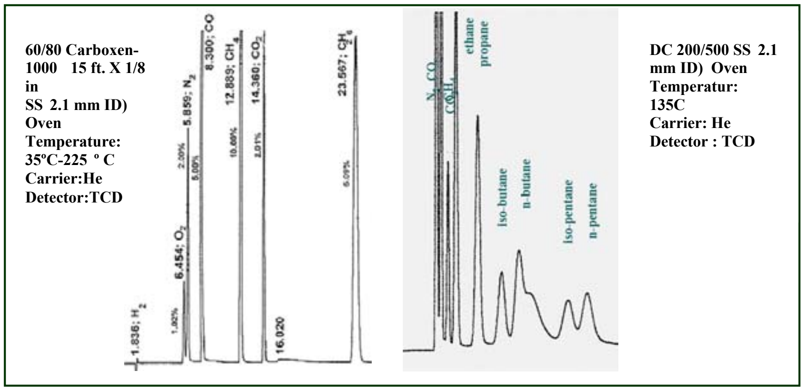


Fig. 17: *Chromatogram of NIST standard sample calibration*

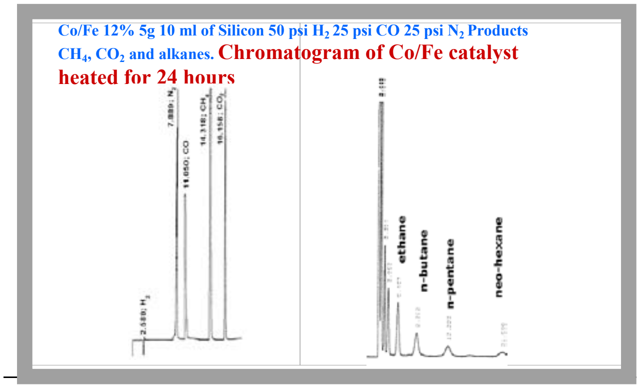
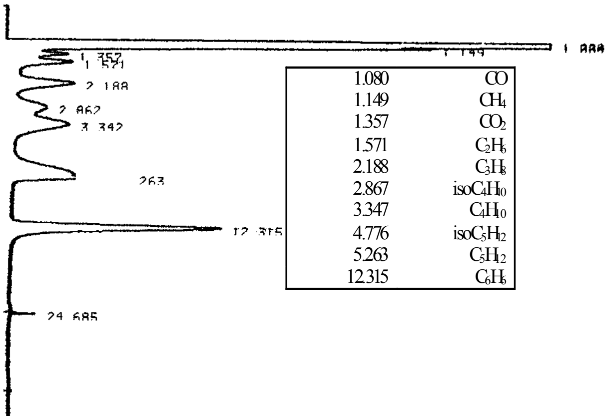


Fig. 18: *GC analysis using Carboxen-1000 and DC 200/500 columns*

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 N_2 and H_2 carrier gases on DC-200/500 would provide better separation of non-condensable gases as well as hydrocarbons. Nitrogen as a carrier gas did not work out well, since the thermal conductivity of non-condensable as well as alkanes is very close to the thermal conductivity of N_2 gas that resulted in poor TCD response. H_2 as carrier gases on DC-200/500 column proved to be an excellent choice for the separation of non-condensable gases as well as for all hydrocarbons (Fig. 18). The thermal conductivity of non-condensable as well as alkanes is not close to the thermal conductivity of H_2 gas resulting in better TCD response. The low molecular weight compounds and condensable gases are also separated very well due to H_2 being carrier gas and it moves faster in the column because of its lower molecular weigh and H_2 would not respond to in the TCD leaving other gases to increase their response TCD. We have developed an efficient and economical procedure for analyzing the products from synthesis gas reaction with Co/Fe impregnated alumina catalyst using low cost GC-TCD system with two GC columns DC 200/500 and Supelco Carboxen-1000 column using hydrogen as a carrier gas for the separation of non-condensable as well as condensable gases.

Optimization of CO/ H_2 ratio

The CO/H_2 ratio in the F-T reaction mixtures is an important factor in determining the catalytic characteristics such as alkane distribution. We investigated various ratios of CO/H_2 needed to optimize the yields of higher alkanes. We found that pure metals, Fe, Co, and Cu incorporated into mesoporous γ-alumina catalysts showed different F-T catalytic activity in the increasing order: Cu, Fe, Co. We have also 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 [14, 15].



1.080	CO
1.149	CH_4
1.357	CO_2
1.571	C_2H_6
2.188	C_3H_8
2.867	isoC_4H_{10}
3.347	C_4H_{10}
4.776	isoC_5H_{12}
5.263	C_5H_{12}
12.315	C_6H_6

Fig. 19: *CG with hydrogen as a carrier gas*

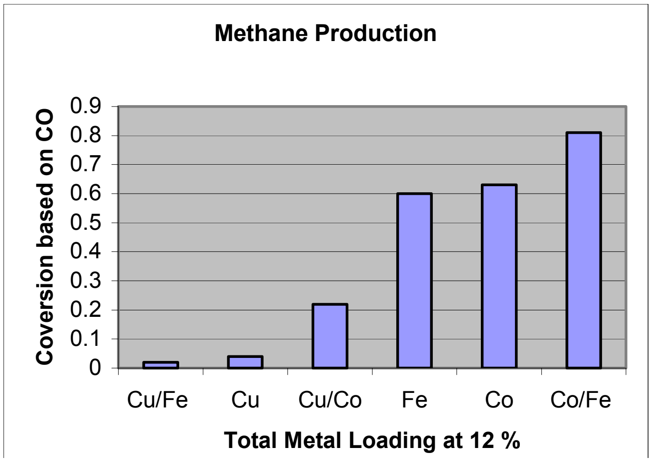


Fig. 20: *Methane production for different catalysts.*

We have used syngas gas mixtures (CO, H_2, N_2) and He or H_2 carrier gas over Fe, Co, Cu, Co/Fe, Cu/Co, Fe/Cu γ-alumina catalysts over a period of 25 hr. The gases CO and H_2, were mixed in the ratio of 1:2 in the gas mixing manifold described in the experimental section. Figure 19 shows the products form a syngas gas mixture containing (CO, H_2, N_2) and H_2 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 20.

The F-T product distribution also depends on the ration of the CO/H_2 and seems to have effect on the production of different alkanes. We have investigated different CO/ H_2 ratios to obtain conversion of synthesis gas to higher alkanes and the results are shown below in Figure 21. As we can see when CO/H_2 ratio kept 1:1, we can see more alkane distribution in F-T process with Co /Fe (6% each) impregnated on alumina mesoporous catalyst.

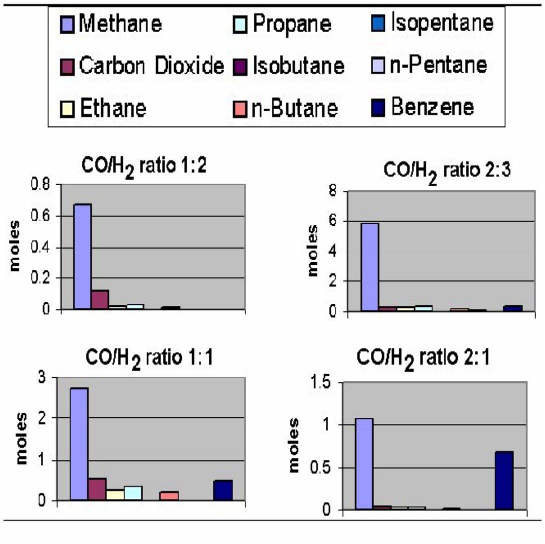


Fig. 21: *Nanoparticle Co/Fe alumina catalysts in a slurry phase. Effect of CO/H_2 ratio for higher alkanes*

The effect of catalyst support on the FT activity

We prepared Fe/Co nanoparticles loaded in hybrid alumina/silica (2:1, 1:1, 3:1) mesoporous granules. We varied the alumina/silica and also Fe/Co (2:1, 1:1, 1:2) ratios. We have characterized these granules using BET, XRD, and SEM/EDX and compared with alumina-supported catalysts described previously. Our preliminary studies indicate that the hybrid alumina/silica catalysts had higher surface area and different (smaller) pore sizes. They also show a significantly different FT product distribution. Among the hybrid catalysts alumina/silica ratio of 3:1 and Fe/Co ratio of 1:1 at 6% w/w each metal loading showed significantly higher FT activity compared to alumina supported Fe/Co catalysts.

CONCLUSIONS

We are able to produce Fe, Co, and Cu nanoparticles using LISD technique in milligram quantities. We could produce Fe, Co and Cu nanoparticles in larger (gram) quantities by high-energy ball milling and chemical synthesis. The nanoparticles produced by high-energy ball milling showed wide size distribution and contamination through chemical reactions and alloy with other milling materials. We have succeeded in chemically synthesizing Co, Fe, and Cu nanoparticles with narrow size distribution (~ 5 nm). The Fe, Co, Cu nanoparticles prepared by all three methods (LISD, ball-milling and chemical synthesis) showed very weak diffraction peaks, which increased as the nanoparticles were heated. The weak peaks in XRD indicate the lack of regular lattice spacing and/or smaller particle size of the metal oxides. 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 VMS data.

We accomplished the preparation of Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe nanoparticle metal loaded mesoporous 1 mm spherical granular γ-Al_20_3, SiO2, and alumina/silica hybrid catalysts using combined sol-gel/oil-drop methods. The properties of metal loaded γ-Al_2O_3 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. This work represents the first efforts to incorporate nanoparticle-metal-oxides into sol-gel/oil-drop method to prepare alumina/silica granules for F–T catalysts to produce liquid aliphatic hydrocarbons. The nanoparticle metal oxide co-entrapped sol-gel method gave higher metal loading, greater mechanical strength, reproducibility and precise control over the metal nitrate solution co-entrapping and wet impregnation methods. We have developed a reproducible procedure for the synthesis of alumina, silica, and alumina/silica hybrid nanocatalysts granules. During the nanoparticle oxide entrapped sol-gel procedure, the nanoparticle metal oxide structure is preserved without being converted to metal hydroxides, which circumvented the solubility factors involved in the metal nitrate solution co-entrapped method and the precise control of mixed metal loading was feasible. We have extended this procedure to coat thin films on silicon wafers and microreactor channels.

Catalysts could be effectively calcined at 450°C and the surface area was between 200-350 m^2/g, indicating the mesoporous nature of catalyst support. The reduction efficiency of hydrogenation of catalysts was examined by magnetic studies. The catalyst activities were investigated in both, slurry-phase-batch and gas-phase-continuous-flow reactors using Gas chromatography (GC). We have developed an efficient and low cost GC-TCD system for analyzing the products from synthesis gas reaction with Co/Fe/Cu impregnated alumina/silica catalysts using two GC columns DC 200/500 and Supelco Carboxen-1000 column with H_2 as carrier gas to separate wide range of alkanes as well as the non-condensable gases.

The F-T product distribution depended on the ration of the CO/H_2 and had effect on the production of different alkanes. More higher-alkane distribution was observed at CO/H_2 ratio of 1:1 in F-T process with Co/Fe (6% each) impregnated on alumina mesoporous catalyst. 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 nanocatalysts 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. The magnetization studies showed ~ 40% reduction due to hydrogenation at 450°C for 4 hrs and ~85% of the catalyst has formed metal carbides or carbonyls 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.

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. The hybrid alumina/silica catalysts had higher surface area and different (smaller) pore sizes. They also showed a significantly different FT product distribution. Among the hybrid catalysts alumina/silica ratio of 3:1 and Fe/Co ratio of 1:1 at 6% w/w each metal loading showed significantly higher FT activity compared to alumina supported Fe/Co catalysts.

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