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ABSTRACT

We have produced Co, Cu, and Fe nano-particles by Laser-induced solution deposition (LISD) as evidenced by TEM investigations. Sizes of the nano-particles created are in the order of 5 nm. The LISD system could generate nano-particles in quantities only in the order of a milligram. This may be mainly due to the limited photo induced reactions taking place on the surface of the solutions. We have designed experiments to use drop flow technique with LISD for nano-particle deposition on micro-reactors. Preliminary work has been done on Co and Fe thin film deposited micro-reactors. We are also investigating the catalytic properties of nano-particles of FeO and CoO prepared by ball milling and dispersed into sol-gel prepared alumina granules.

We have continued our investigation of catalytic reactions of Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe on alumina support. The metal oxides were first reduced with hydrogen and used for the conversion of CO/H_2. The surface area of the catalysts has been determined by nitrogen disorption. They are in the range of 200-300 m^2/g. Cu, Co, Fe, Co/Fe, Cu/Co and Cu/Fe showed increasing order of catalytic activity for CO/H_2 conversion. We are also studying catalytic conversion rates for CO_2/H_2 and $CO/CO_2/H_2$ mixtures using these catalysts. Our investigations of Co and Fe thin film deposited micro-reactors showed higher CO/H_2 conversion for Fe compared to Co.

We have used vibrating sample magnetometer (VSM) to study the magnetic characteristics of as prepared, reduced, post-reaction catalysts. Comparative study of the ferromagnetic component of these samples gives the reduction efficiency and the changes in metal centers during catalytic reactions. Magnetic studies of post-reaction Co and Fe micro-reactors show that more carbide formation occurs for iron compared to cobalt.

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INTRODUCTION

Nano-scale 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. Since the efficient conversion of CO/CO_2 gases to useful fuels is a major challenge facing scientific community, novel nano-particle catalysts seem to provide a promising alternative to conventional catalysts. We used laser induced solution deposition (LISD) technique[1,2] to prepare nano-particle syngas conversion catalysts contain ferromagnetic metals (Fe, Co) in order to control the particle size in a narrow size range since the nanometer scale metal clusters exhibit size dependent physical properties.[3,4] The state of the unfilled d-shells and unpaired electrons, morphology and metallic charge distribution of these catalysts are known to govern both their catalytic and magnetic behavior.[5] We examine the inter-relations between catalytic and magnetic properties of specially prepared iron and cobalt catalysts for CO/CO_2 hydrogenation to mixed alcohols. Although the catalytic behavior of several iron-based Fischer-Tropsch catalysts has been studied for hydrogenation of carbon monoxide,[6-8] relatively little work has been done with CO/CO_2 mixtures as feed stock, and very little is known about the mechanisms. A detailed analysis of catalytic character and the corresponding changes, if any, in the magnetic character of post-use catalysts could reveal the intricacies of involved mechanisms. CO/CO_2 is the abundant from coal burning. Therefore the proposed magneto-chemical character investigations of Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe on alumina support catalysts should prove valuable in exploring processes for efficient hydrogenation of CO/CO_2.

We propose to:

a) Synthesize Fe, Cu and Co nano-particles impregnated on granular Al_2O_3 supports employing two novel techniques - Laser Induced Solution Deposition (LISD) of organic/inorganic precursors and Sol-Gel technique[9,10] for the preparation of granular catalyst supports.

b) Prepare Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe nano-particles in alumina granules using sol-gel/oil-drop methods.[11,12]

c) Investigate their catalytic character (conversion efficiency and product distribution) a batch processing, bench-model slurry reactor with $CO/CO_2/H_2$ as the feedstock.

d) Investigate the magnetic and electronic structural characteristics of pre and post use nano-catalysts by i) Magnetization - VSM study, ii) SEM & EDXS study iii) Nitrogen Disorption and iv) XRD powder analysis of the catalyst composites.

EXECUTIVE SUMMARY

We have set up successfully two experimental systems a) sol-gel chemical method[9,10] for preparing γ-Al_2O_3 granular support particles and b) the laser-induced solution deposition (LISD) technique[1,2] for nano-particle catalysts containing Fe and Co on the granular support. We have prepared γ-Al_2O_3 granular support particles by sol-gel method through three steps: boehmite sol (γ-AlOOH) preparation, sol gelatinization and shaping (oil dropping), and dry and calcinations. The structures were identified by x-ray diffraction (XRD), and the surface morphology, composition and particle size were examined by scanning electron microscope (SEM) with energy depressive X-ray EDX spectrometer. The prepared γ-Al_2O_3 granular particles were uniform in composition and structure. LISD is a novel method for preparing proposed nano-particle Fe/Cu and Co/Cu catalysts. We have chosen various precursors (solutes) such as metal chlorides $CoCl_2$, $FeCl_2$, and $CuCl_2$, and metal nitrates $Co(NO_3)_2$, $Fe(NO_3)_3$, and $Co(NO_3)_2$ in the LISD solution deposition. They were dissolved in the solution of ammonia in distill water or with various mixtures of solvents of methanol, cyclohexane, tetrahydrofuran (THF) and diethylether. The granular γ-Al_2O_3 particles prepared by oil-drop sol-gel method were put at the bottom of the solution. Catalytic samples were analyzed by gas chromatography (GC) method, nitrogen disorption, DTA, SEM, XRD, and magnetization measurements using vibrating sample magnetometer (VSM).

The studies on LISD produced catalysts showed that the sizes of the nano-particles created are in the order of 5 nm. The LISD system could generate nano-particles in quantities only in the order of a milligram. This may be mainly due to the limited photo induced reactions taking place on the surface of the solutions. We have designed experiments to use drop flow technique with LISD for nano-particle deposition on micro-reactors. Preliminary work has been done on Co and Fe thin film deposited micro-reactors.

We have prepared alumina impregnated CuO, CoO, Fe_2O_3, CuO/CoO, CuO/Fe_2O_3 and CoO/Fe_2O_3 particles using sol-gel/oil-drop method. Synthesis was carried out using both alumium tri-sec-butoxide (ALTSB) and aluminum tri-iso-propoxide (ALTIP). The efficiencies of two reagents were compared. The optimum calcination temperature was studied by differential thermal analysis (DTA). The metal oxides were reduced by hydrogen to form alumina impregnated Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe nano-particles. The surface area of the catalysts was determined by nitrogen disorption. They were in the mesoporus range of 200-400 m^2/g. Powder X-ray diffraction results show that the metal oxides are in the nano particle range and the alumina support has very low crystlallinity as expected for sol-gel type synthesis. The particle size and metal loading of catalysts were studied by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The metal loading results were used to optimize the synthesis process for obtaining consistent metal compositions.

The sol-gel prepared alumina particles, impregnated with metal oxides CuO, CoO, Fe_2O_3, CoO/Fe_2O_3, CuO/CoO and CuO/Fe_2O_3, were first reduced with hydrogen at 450°C. Then we have investigated the catalytic reactions of Cu, Co, Fe, Cu/Co, Cu/Fe

and Co/Fe on alumina for the conversion of CO in $CO/H_2/N_2$ mixtures. Slurry phase batch reactor was used. The catalytic activity and the CO conversion efficiencies were studied. Our earlier studies of Co and Fe thin film deposited on micro-reactors show higher CO conversion rate of CO/H_2 mixtures for Fe than Co.

Vibrating sample magnetometer (VSM) was employed to study the magnetic characteristics of the precursors, reduced, and post-reaction catalysts. Comparative study of the ferromagnetic component of these samples allowed us to gain insight into the reduction efficiency and the changes in metal centers during catalytic reactions. Magnetic studies of post-reaction Co and Fe micro-reactors showed that formation of carbides is higher for iron compared to cobalt.

We are also investigating the catalytic properties of nano-particles of FeO and CoO prepared by ball milling and dispersed into sol-gel prepared alumina granules.

EXPERIMENTAL

(I) Nano-fabrication of Nano-structured Co-nano-particles by LISD technique

The laser-induced solution deposition (LISD) system for depositing nano-particle catalysts is shown in Figure 1. This system uses a laser to initiate chemical reactions. The products are deposited in solution. We combined LISD method to impregnate nano-particle catalysts into the granular supports produced by sol-gel method.

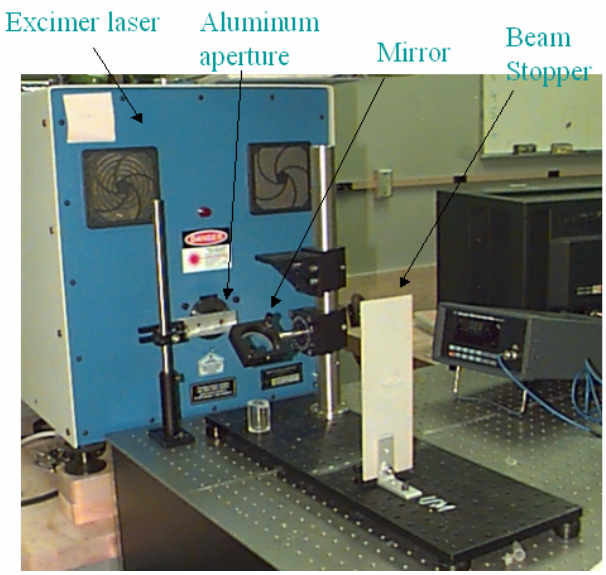


Figure 1. The laser-induced solution deposition (LISD) system

All deposition experiments were carried out in the solutions of ammonia dissolved in distilled water or solutions containing various mixtures of methanol, cyclohexane, tetrahydrofuran (THF) and diethylether. The selection of solvents is crucial for successful deposition. The principle of solvent selection was based on solubility and the solvent/solute mixture is transparent in the laser wavelength used in the experiment. The ASX-750(KrF) excimer laser from MPB Technologies Inc. Operating at wavelengths of 193, 248, 308 and 351 nm respectively. 193 nm wavelength was used. The selection of the wavelength is based on the absorption spectrum of precursor solutions. LISD experimental system in Figure 1 shows the picture 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 the schematic diagram shown in Figure 2.

The laser parameters: Pulse Frequency 40 Hz, Work Voltage 27.6 kV, Chamber Pressure 2.96—3.13 bar. Average output 1.20 W, i.e. about 300 mJ/pulse Exposure Duration 5000 pulses.

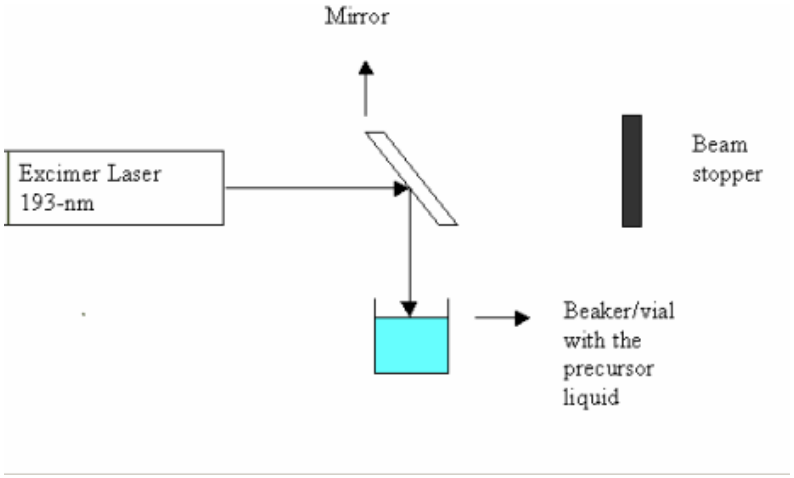


Figure 2. A schematic diagram of laser-induced deposition from solution (LISD)

(II) Micro-reactor Fabrication

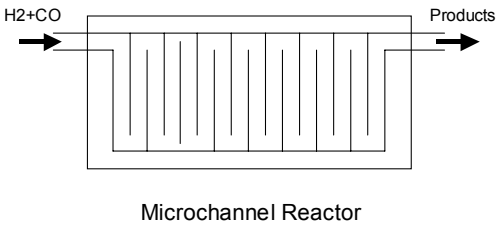


Figure 3. Schematic diagram of a micro-reactor

The Inductively Coupled Plasma (ICP) etching is to produce reactor masks along with the AutoCAD software. The masks were used to pattern wafers, which were etched by the ICP process. A picture of the patterns is found below. The micro-reactor features 5 μm micro-channels, approximately 700 in number. The micro-channels have been deposited with Fe or Co catalyst by sputtering.

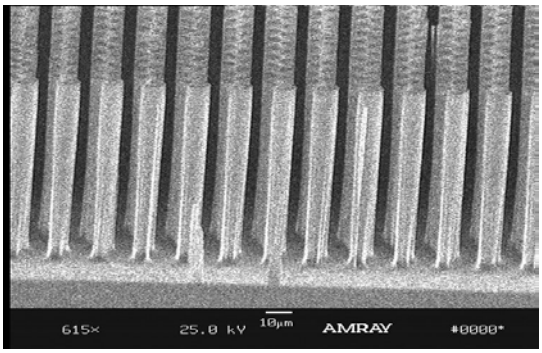


Figure 4. SEM image of micro-channels of a micro-reactor.

(III) Catalysts Preparation

Sol-gel system for the production of alumina granular supports is shown in Figure 5. The sol-gel method we used consists of three steps:

(a) Boehmite sol (γ-AlOOH) preparation;
(b) Sol gelation and shaping;
(c) Dry and calcinations.

Figure 5. The Sol-gel System

Step 1: Boehmite Sol (γ-AlOOH) Preparation

We have chosen aluminum tri-sec-butoxide (ALTSB, 97%) (52 ml) dissolved in distilled water (100 ml) as precursor and 1M HNO_3 as adjusting pH value. The chemical reactions will be:

$$Al(O\text{-}Bu)_3 + 3\ H_2O \rightarrow Al(OH)_3 + 3\ Bu\text{-}OH$$

$$Al(OH)_3 + Al(O{=}H,R) \rightarrow [Al\text{-}OH\text{-}Al] + H_2O + ROH \quad R = alkyl$$

$$Al(OH)_3 + Al\text{-}OR \rightarrow [Al\text{-}O\text{-}Al] + H_2O + ROH$$

It took about 1h to slowly and uniformly add the aluminates (52 ml) into the distilled water. Stirring the hydrolysis products and keeping the reaction temperature around 70ºC -80ºC, greatly help the heat and mass transport. When the flock deposits appeared in the solution, added gradually 1M HNO_3 into the solution (about 15ml). Because the acidity of the reaction media affects the microstructure of the final sol significantly, we added HNO_3 to adjust the PH value. Urea could be another reagent to modify the pH more finely. It took about 14 h to make the pesudo-boehmite sol (γ-AlOOH) more stable.

Step 2: Sol Gelation and Shaping. (Oil Dropping)

Following ingredients, 1M HNO_3, paraffin oil (density 0.786g/cm^2, kinematical viscosity 34.5, Fisher Scientific), 2M boehmite sol, and 10 wt % ammonia solution were used in this process. Firstly, 1M HNO_3 (around 20 ml) was added into 2M boehmite sol

and the aging temperature was kept at 75ºC for 45 min. Then the sol was carefully transferred into rubber droppers. The droplets were dropped into the hot mineral oil (<100ºC) and the gel was consolidated in the layer of 8 –10% ammonia solution. It was useful to keep the good transporting conditions in the oil and ammonia interphase by slow stirring (30 rpm). The particles were removed from the ammonia and washed by the sequence of the cooling water, hot water, alcohol, and cooling water for 2 cycles.

Step 3: Dry and Calcinations

The gel particles were dried for about 48 hours in the oven at 50ºC and calcinated in air at 450 ºC for about 4 hours using a furnace. We have used DTA, X-ray diffraction and SEM with EDX to get the calcination temperature and to identify the composition and structures.

(IV) Surface Area Measurements

We have analyzed adsorption data in these systems using the Brunauer-Emmett-Teller (BET) isotherm.[16,17] However; there are empirical methods like t-plot and α_s method, which can be used in conjunction with the BET method to compute the surface area. The difference between the BET method and the latter is that the BET method helps to determine the surface area of the monolayer as well as the multilayers formed due to the adsorption process whereas the latter methods only determine the surface area of the multilayers.

(V) Magnetic and Structural Characterization

It is important during this project to determine whether a true bimetallic catalyst is formed or whether separate Fe and Cu or Co particles are formed. Several characterization techniques will be used to answer this question. The catalysts were analyzed by magnetization studies using vibrating sample magnetometer (VSM), SEM and XRD studies of the composite.

The magnetization characters were studied using 880A Digital Measurement Systems Vibrating Sample Magnetometer (VSM). The sensitivity of the system is about 5 micro EMU with 100 averages. The system is microprocessor controlled and auto ranges full-scale measurement from 0.04 EMU-4000 EMU. In the present arrangement a maximum magnetic field of 13.5 kOe can be applied.

These characterization studies are of immense value in the determination of the various phases of iron and cobalt oxides, and carbides in the catalyst precursors, reduced samples and used samples. The structural information obtained will help to correlate magnetic properties to the catalytic activity and to build models to describe the mechanism of the catalytic process.

(VI) Chemical Analysis and Kinetic Studies

The following instrumental techniques and combinations of these techniques have been widely used for separation and characterization of hydrocarbons and other organic products from catalytic reactions: vacuum line, GC, MS, and GC-MS. Louisiana Tech University has all these standard facilities, and we conducted comprehensive experiments employing all the analytical tools to generate the necessary bench-mark data for complete product identification and characterization.

Batch Processing Slurry Reactor

To convert syngas (CO +H_2) to liquid fuels with a lower H_2/CO ratio closer to that produced by modern coal gasifiers, slurry-phase reactors have received much attention.[13-15] Reduced catalysts will be injected into modified 300 mL Parr-autoclave containing a solvent, which has been studied for CO_2 solubility at higher temperatures, such as silicone or mineral oil, under hydrogen pressure to avoid exposure to air. Continuous magnetic stirring will be employed to simulate slurry phase reactor conditions. A schematic diagram of the experimental setup for chemical analysis of

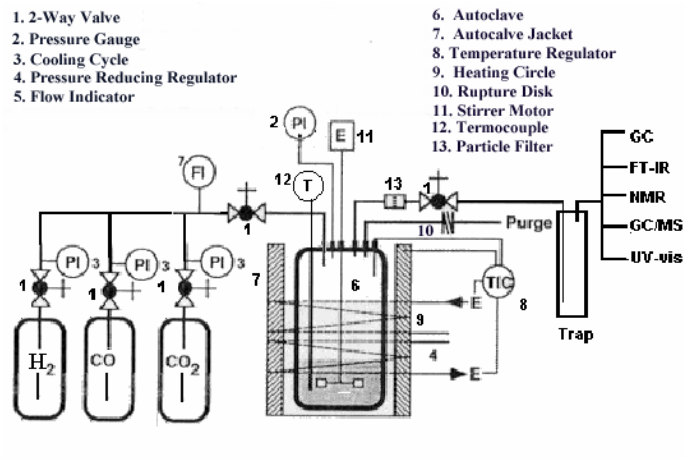


Figure 6. Schematic diagram of the experimental setup for chemical analysis

reaction products are shown in Figure 6. The reaction gases CO_2, H_2 and N_2 were introduced and heated under pressure (1 MPa) at 250^0C for about 5 hours. Runs with syngas ($CO/H_2/N_2$) or ($CO_2/H_2/N_2$) were made on standard catalysts to serve as base line data for comparison of CO and CO_2 conversion.

The schematic diagram (Figure 7) given below illustrates the integration of Parr bomb and various instruments for chemical analysis of CO/CO_2 hydrogenation products.

Figure 7. Batch Processing Slurry Reactor

GC Analysis of $CO/H_2/N_2$ Mixtures

Gases CO, and H_2 and N_2 are mixed in the gas mixing manifold and loaded into high-pressure reactor with catalyst stirred in mineral oil. Reactions are maintained at 100ºC temperature with a controller. Gases are analyzed using GC analysis system (Figure 8) for their concentrations.

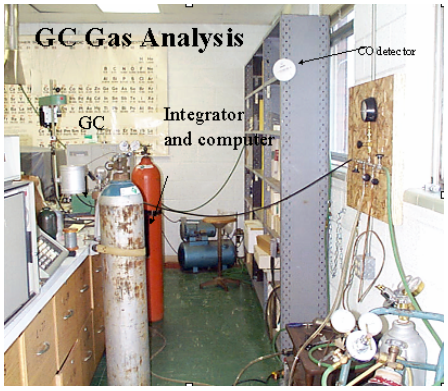


Figure 8. GC Analysis System.

Calibration of column and gas mixtures

Analysis of Gases (non-polar)
60/80 Carboxen-1000 15 ft. X 1/8 i
SS 2.1 mmID)
Oven Temperature:
35ºC-225 º C
Carrier: He
Detector: TCD

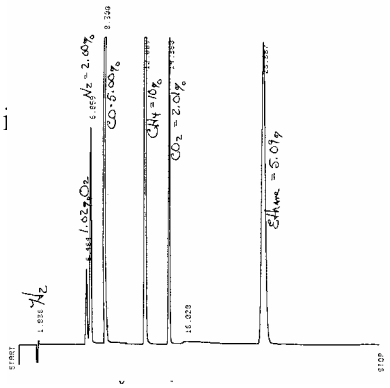


Figure 9. Calibration of gas mixtures

Calibrations of CO and CO_2

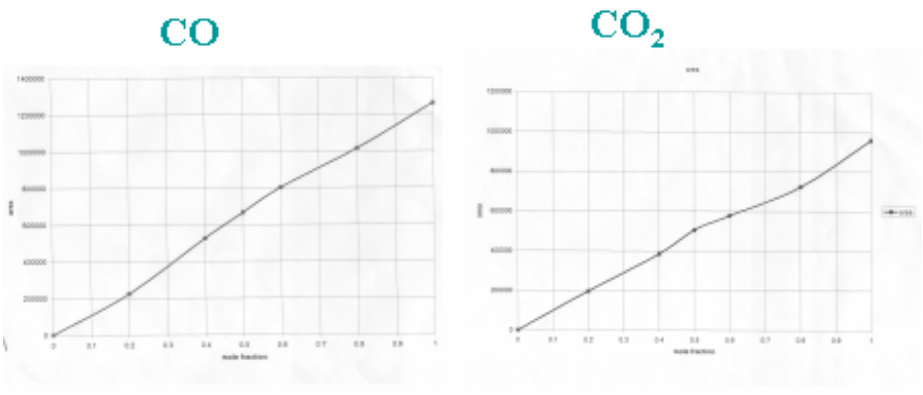


Figure 10. Calibrations Curves of CO and CO_2

RESULTS AND DISCUSSION

Nano-particles Catalysts by LISD/sol-gel techniques

In LISD experiments, we have chosen Co nitrate dissolved in ammonia (NH_3) and distill water to form complex $(Co(NH_3)_6)^{2+}$ ions. The laser energy activated the decomposition of the complex ions and transferred the Co ions into Co metal with the transfer of electrons from NH_3. Various concentrations of solutions and laser conditions have been tried. Figure 11 shows the UV-Visible Absorption Spectrum of Precursor Solutions 0.002 M $Co(NO_3)_2$ in 0.02 M ammonia**.**

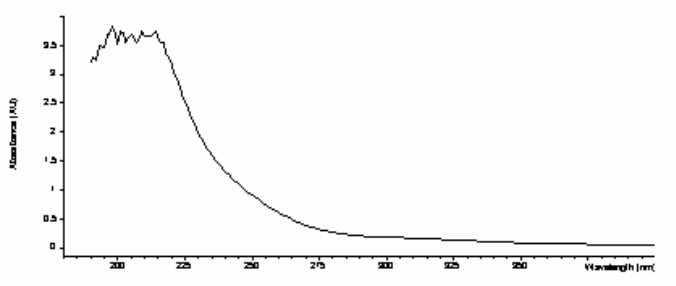


Figure 11. shows the UV-Visible Absorption Spectrum of Precursor Solutions 0.002 M $Co(NO_3)_2$ in 0.02 M ammonia**.**

Here we present a typical data for the solution with 0.1 M $Co(NO_3)_2$ + $NH_3 \bullet H_2O$ under the exposure of focused laser beam (power = 1.7 w) in the region of UV for the deposition time = 40 min. Figure 12 shows the Co (or cobalt oxide) nano-particle clusters deposited on the silicon substrate.

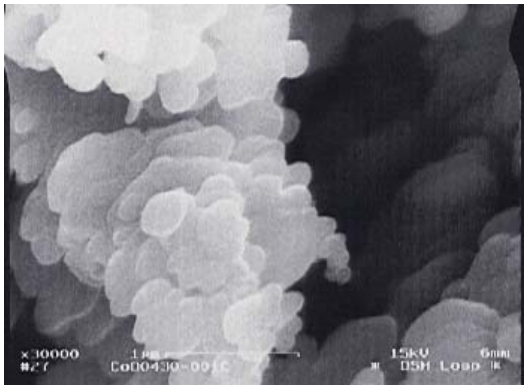


Figure 12. The SEM image of Co/CoO_X nano-particle clusters on Si substrate taken from the laser beam center area. The particle cluster size is about 100 – 500 nm in diameter (magnification of 30,000X)

The average diameter of the particle clusters is about 100 to 500 nm. We used EDX spectroscopy to show that the clusters are composed of Co metal. The EDX spectrum for one of the Co/Fe deposited surface is shown in Figure 13.

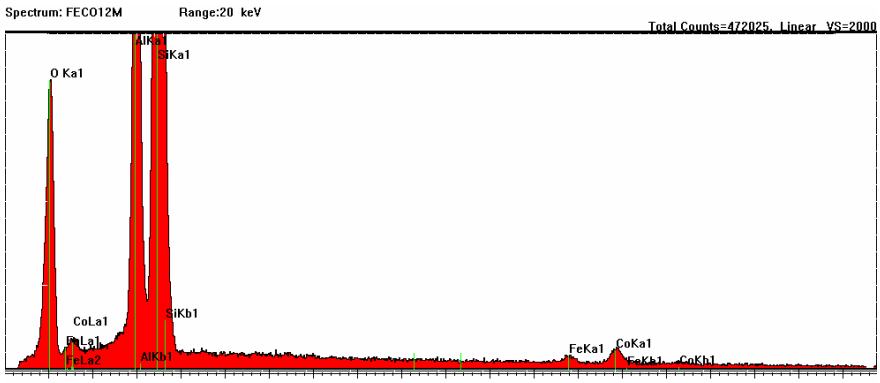


Figure 13. The EDX spectrum for LISD deposited Co/Fe nano-particle clusters on Si surface

The oxygen peak in the spectrum indicates that the oxygen contamination or the formation of cobalt oxides had occurred. The exact structures of the deposits need to be investigated by high resolution X-ray diffraction and transmission. Figure 14 shows the high-resolution TEM image of the Co/CoOx nano-particles directly taken from the solution after the deposition. The diameters of the deposited particles we measured are less than 5 nm with very narrow regime.

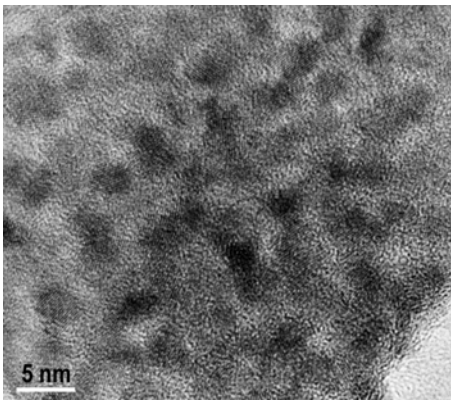


Figure 14. The high-resolution TEM image of the Co/CoOx nano-particles directly taken from the solution after the deposition.

These results demonstrate that we are able to produce nano-catalysts of the order of 5 nm using the LISD and sol-gel techniques. But unfortunately, the LISD system could generate nano-particles in quantities only in the order of a milligram. This may be mainly due to the limited photo induced reactions taking place on the surface of the solutions. We have designed experiments to use drop flow technique with LISD for nano-particle deposition on micro-reactors. Preliminary work has been done on Co and Fe thin film deposited micro-reactors.

Magnetization Studies of Co and Fe Deposited 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.[18,19] Significant changes in the saturation magnetization M_S have been reported for a number of ferromagnetic catalysts due to chemisorptions of H_2 and CO. Here we studied the magnetic character of Co and Fe deposited micro-reactors after they were exposed to the syngas ($CO+H_2$).

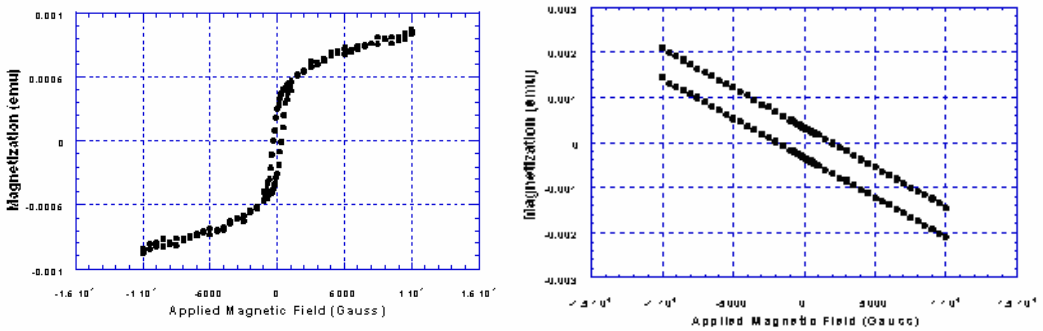


Figure 15. Magnetization results of a) Cobalt b) Iron micro-reactors after completing catalytic reactions.

The magnetization of cobalt and iron micro-reactors, respectively, with applied magnetic filed after completing catalytic reactions on these micro-reactors are shown in Figure 15a and Figure 15b. They show very little ferromagnetic character (primarily in Co micro-reactor) and a strong diamagnetic character. This is mainly because of 1) the Co or Fe deposited films are very thin thus the mass ratio between ferromagnetic metallic film and the diamagnetic silicon micro-channel substrate/Pyrex plate assembly is very small, and 2) most of Co and Fe has reacted with syngas and formed compounds (oxides and carbides) leaving very little in the metallic form. Comparing the results between the Co and Fe micro-reactors, Fe seems to interact with syngas much faster than Co and form compounds, thus almost no Fe is left in metallic form as indicated by nearly diamagnetic nature of the Fe micro-reactor (Figure 15).

Ferromagnetic nature of metallic Co in the film as shown in Figure 15a gives an estimated sigma (saturation magnetization) value of 63 emu/gr-Co. The sigma value for pure Co is 160 emu/gr-Co. This gives an estimation of only 40% Co in the pure metallic form and the rest in compound form.

We tried to correlate the magnetization results with the catalytic results on the Co and Fe deposited micro-reactors obtained from IfM. The catalytic conversion yields for Fe deposited micro-reactor are always higher than those obtained for the Co deposited micro-reactors at all temperatures. This may indicate that the required residence time for Co catalyst for reaction may be longer compared that for Fe catalyst, thus leaving more Co in metallic form compared to Fe (Fe reacts quick and starts forming compounds faster). Further systematic studies are required for firm conclusions. We are planning to sol-gel deposit the nano-catalysts on micro-channel plates to study the magnetic and catalytic properties.

Sol-Gel Preparation of Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe nano-particles in Alumina granules

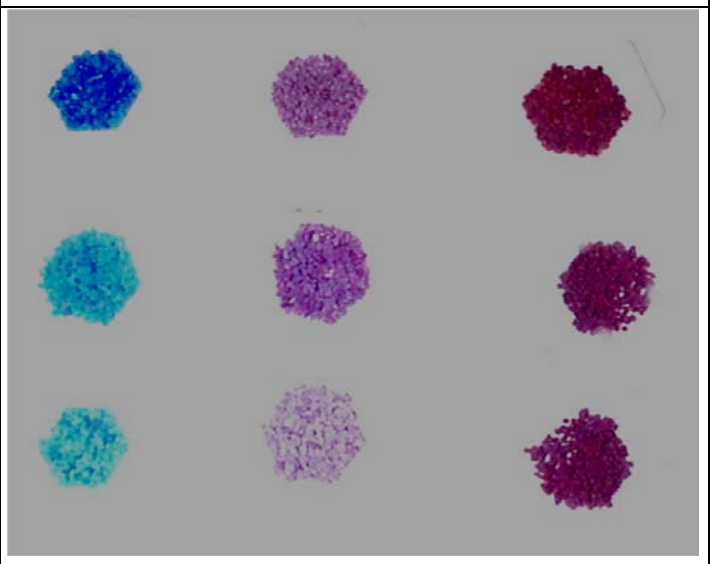
Pure metal compositions, as shown in Table 1, were incorporated into the sol-gel prepared alumina granules. Table 2 shows the pictures of the granules.

Table 1. Pure Metal Compositions

Cu (%)w/w	Co(%)w/w	Fe(%)w/w
2	2	2
4	4	4
6	6	6

% w/w are based on metal and Al_2O_3

Table 2. Pictures of Pure Metal Containing Alumina Granules

% Metal	Cu	Co	Fe
6			
4			
2			

Mixed metal compositions as shown in Table 3 were also incorporated into the sol-gel prepared alumina granules.

Table 3. Mix Metal Compositions

Total Metal	Cu/Co	Co/Fe	Cu/Fe
2%	1:1%	1:1%	1:1%
4%	2:2%	2:2%	2:2%
6%	3:3%	3:3%	3:3%

% w/w are based on metal and Al_2O_3

Figure 16. SEM picture γ-Al2O3 produced by sol-gel method.

The SEM image of the γ-Al2O3 shown in Figure 16 which is produced by sol-gel method indicate 1 mm average size of the Al_2O_3 support granules with uniform in shape.

Catalysts Characterization

The surface areas of the catalysts were determined by nitrogen disorption. Catalysts were investigated by powder X-diffraction and results show that the metal oxides are in the nano particle range and the alumina support has very low crystlallinity as expected for sol-gel type synthesis. The particle sizes and metal loading of catalysts were studies by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The metal loading results were used to optimize the synthetic process to obtain consistent metal compositions.

Surface Area Analysis

An example of an isotherm for iron catalyst on alumina support is shown in Figure 17.

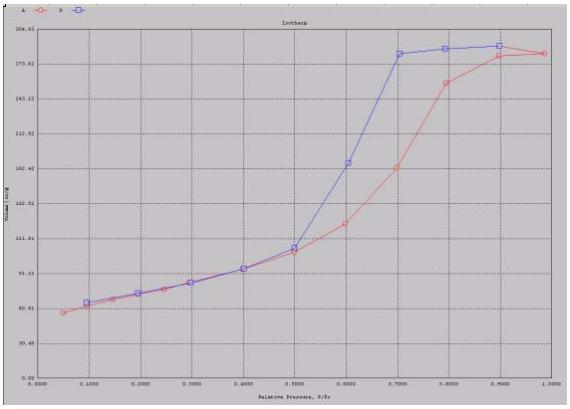


Figure 17. Isotherm of iron catalyst on alumina support

The surface areas of the catalysts were determined by nitrogen disorption. They were in the range of 250-350 m^2/g as shown in Table 4. This definitely indicates that the alumina supports we produced are mesoporous.

Table 4. Surface area of pure and mixed metal catalysts on mesoporous alumina

Metal	Composition	Surface Area
Cu(%)w/w	4	258
Co(%)w/w	4	350
Fe(%)w/w	4	310
Cu/Co(%)w/w	2:2(4)	326
Co/Fe(%)w/w	2:2(4)	351
Cu/Fe(%)w/w	2:2(4)	321
Surface area is basesd on N_2 desorption		
m2/g. Nova 3000		

Metal Loading

The Table 5 shows summarizes the % metal loading in various catalyst compositions studied by EXD analysis.

Following parameters have been found to affect the metal loading.

a) Concentration metal ions in the sol-gel is directly proportional to metal loading
b) Increasing metal ion concentration in the bottom aqueous solution increase the metal loading.
c) In Co/ Fe or Co/Cu mixtures Co interferes and reduces the Fe and Cu metal loading.
d) Specific metal loading, as determined by EDX, is reproducible.

Table 5. EDX analysis of % metal loading in pure and mixed metal catalyst on alumina.

Metal	Composition	EDX %
Cu(%)w/w	4	37
Co(%)w/w	4	20
Fe(%)w/w	4	140
Cu/Co(%)w/w	2:2(4)	11:16(27)
Co/Fe(%)w/w	2:2(4)	30:29(59)
Cu/Fe(%)w/w	2:2(4)	15:31(46)
EDX Eenergy Dispersive X-ray Analysis		

Magnetic Character

The magnetic results obtained from VSM study of various reduced catalytic composites are shown in Table 6. Detail magnetic studies on as-prepared, reduced and post-reaction catalysts are still in progress. This comparative study will provide voluble in formation on magneto-chemical character of these composites.

Table 6. Magnetic character of various reduced catalytic composites

Metal	Composition	Magnetism(reduced)
Cu(%)w/w	4	paramganetic
Co(%)w/w	4	Ferromagnetic
Fe(%)w/w	4	Ferromagnetic
Cu/Co(%)w/w	2:2(4)	Dual phase
Co/Fe(%)w/w	2:2(4)	Ferromagnetic
Cu/Fe(%)w/w	2:2(4)	Dual phase
Using Vibrating Sample Magnetometer		

Catalytic Reactions

Following reactions were monitored using GC.

$$CO + H_2 \rightarrow CH_4 + H_2O$$
$$CO2 + H_2 \rightarrow CH_4 + 2H_2O$$
$$CO + 2H_2 \rightarrow CH_3OH$$
$$2CO + 5H_2 \rightarrow C_2H_6 + 2H_2O$$

The GC chart in the Figure 18 shows a typical catalytic run.

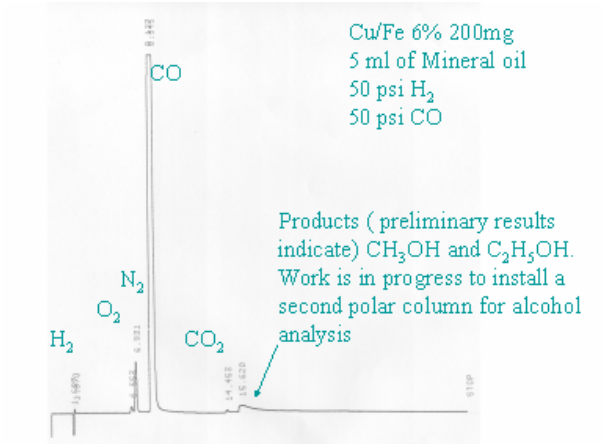


Figure 18. GC analysis of Cu/Fe 6% metal loading.

Catalytic Activity

The CO conversion shown in Table 7 is based on 100 % stating CO and N_2 as internal standard. Activities are calculated from peak area of chromatographic data. Cu, Cu/Fe, Cu/Co, Fe, Co, Co/Fe showed an increasing order of catalytic activity for CO/H_2 conversion.

Table 7. CO conversion data for sol-gel prepared nano-catalysts

Metal	Composition	Activity
Cu(%)w/w	4	0%
Co(%)w/w	4	55%
Fe(%)w/w	4	50%
Cu/Co(%)w/w	2:2(4)	43%
Co/Fe(%)w/w	2:2(4)	79%
Cu/Fe(%)w/w	2:2(4)	39%

Activity basesd on CO conversition

CONCLUSIONS

As a conclusion, we have set up the two experimental systems (LISD and Sol-gel) successfully. We have succeeded in synthesizing Co nano-particles and studied the micro-/nano-structure and the composition of the deposited nano-particles by SEM, EDX, and high resolution TEM. The suspended nano-particles in the solution are about 5 nm and the distribution of the nano-particles are in very narrow regime, which is unique and useful for the catalytic properties and other functional (chemical or physical) properties. Though the LISD system could generate nano-particles, the quantities are only in the order of a milligram. This may be mainly due to the limited photo induced reactions taking place on the surface of the solutions.

We have successfully characterized pure and mixed metal/alumina composites using SEM, EDX, VSM, surface area analysis and high solution TEM. We have used metal loading results to optimize catalytic preparation methods.

We have successfully mixed CO or CO_2 and H_2 gases in a gas mixing manifold and loaded into reactors using N_2 as the internal standard. We have developed methodology for screening catalytic activates of various metal/alumina composites using slurry phase reactor and used GC for the product analysis and activity calculations.

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FUTURE WORK

We plan to design experiments to use a drop flow method combined with LISD to deposit nano-particles on micro reactors and study CO/H_2 conversions in micro scale.

We will develop methodology for screening promising catalytic using gas phase flow reactors connected to GC for the product analysis. We plan to install a second column to GC to analyze polar compounds such as alcohols to measure thir quantities.

We will then use slurry phase reactors to to obtain kinetic data of promising catalysts. We will also provide necessary compositional data of successful catalysts using EDX and surface analysis. From this knowledge, we will develop mythology for large-scale preparation successful nano-particle catalysts.

Using our mythologies developed for sol-gel synthesis, we will optimise procedures to obtain uniform nano-particles. Using GC, MS and other sophisticated characterization methods, we will rationally design an active, stable cobalt and iron FT catalyst at the nano-scale. Doing so, we will develop methodology for the successful design of active, stable, regenerable, and attrition-resistant, supported, Co and Fe nano-catalysts. This methodology should be applicable to development of similar supported nano-catalysts.

The preliminary work has been done on Co and Fe thin film deposited micro-reactors. We will deposit sol-gel prepared catalysts on micro reactors and investigate feasibility of using micro reactors in catalyst screening. The CO/H_2 conversion of a micro-reactor with a metal impregnated thin film prepared by sol-gel coating will be studied and compared with Co and Fe sputter coated reactor using GC/MS analysis of products of CO_2/H_2 and $CO/CO_2/H_2$ mithures.

We plan to investigate catalytic properties of nano-particles of FeO and CoO prepared by ball milling and dispersed on to sol-gel prepared alumina granules. We will compare the CO/H_2 conversion of sol-gel prepared nano-catalyst and ball milled nano-particle catalyst dispersed on alumina.

PUBLICATIONS AND PRESENTATIONS

1. "Preparation and Characterization of Nano-structured Particulate Catalytic Materials", Baiyun Tong, Upali Siriwardane, Seetala, V. Naidu, Akundi N. Murty, and Zhenchen Zhong. Materials Research Society (MRS) Annual Fall Meeting (2001), November 25 - December 1, 2001, Boston, MA.

2. "Annual Report on the Research of Nanostructured Catalytic Materials", Z. C. Zhong Semi-Annual Review Meeting for NSF-EPSCoR, January 25, 2002, New Orleans, LA.

3. "Magnetic Oxides prepared by LISD and LCVD", Z. C. Zhong, R. H. Cheng, and P. A. Dowbe, Materials Research Society (MRS) Annual Fall Meeting (2001), November 25-Decemer 1, 2001, Boston, MA.

4. "Nanofabrication and Nanostructured Matrials by a novel Laser Chemical Processing", Z. C. Zhong, 2002 APS Annual March Meeting, Indianapolis, IN, March 17-22, 2002.

5. "Magnetization Studies of Cobalt and Iron Deposited Micro-reactors for syngas conversion catalysts", Joann Jones, Keatha Holmes, A.N. Murty, M.F. Ware and S.V. Naidu, Phillip Young Symposium, Grambling, Aprl. 2002

6. "Novel Preparation and Characterization of Nano-structured Catalytic Materials", Zhenchen Zhong, Seetala V. Naidu, Akundi N. Murty, and Upali Siriwardane, Zhengchun Liu and Pallavi Annumwla , DOE-University coal research conference, Pittsburg, PA. June 4-6, 2002.

7. "Magneto-Chemical Character Studies of Alumina Impregnated Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe Catalysts for Syngas Conversion", Ramkiran Goduguchinta, Sireesha Vudatha, Buddy G. Barnett, Srivani Naga Vegesna, Edwin Everett, Sheba Anderson, Ron Besser and Upali Siriwardane, Louisiana Conference on Commercial Applications of Microsystems, Materials and Nanotechnologies, Ruston, Oct. 21-22, 2002.

8. "Synthesis, Chracterization, and Optimization of Alumina Impregnated Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe Catalysts for CO Hydrogenation", Srivani Naga Vegesna, Ramkiran Goduguchinta, Edwin Everett, Karen Luurtsema, Laura Holeman, Andrew Emge and Upali Siriwardane, Louisiana Conference on Commercial Applications of Microsystems, Materials and Nanotechnologies, Ruston, Oct. 21-22, 2002.

STUDENTS WORKED ON THE PROJECT

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