TITLE PAGE

Report Title: Annual Technical Report

"Preparation and Characterization of Nanostructured Granular Support Particles and Catalytic Materials"

Type of Report: Annual

Reporting Period Start Date: 09/01/2000

Reporting Period End Date: 12/31/2001

Principal Author: Zhenchen Zhong

Date Report was Issued: January 15, 2002

DOE Award Number: DE-FG26-00NT40836

Name and Address of Submitting Organization: Grambling State University

Co-PI: Upali Siriwardane, Seetala V. Naidu, and Akundi N. Murty[1]

Subcontractor: Louisiana Tech University

Industrial Collaborator: Hydrocarbon Technologies, Inc

(Performance Period: 09/01/2000 to 08/31/2003 for three years)

DISCLAIMER

ABSTRACT

We have set up successfully two experimental systems during the past time of the project. The first system is sol-gel chemical method for preparing γ-Al_2O_3, SiO_2, Cr_2O_3 granular support particles. The second system is the laser-induced solution deposition (LISD) technique for nanoparticle catalysts containing Fe/Cu, and Co/Cu on the granular support.

We have successfully deposited γ-Al_2O_3, SiO_2, Cr_2O_3 granular support particles by sol-gel method and Co and CoO nanoparticles by LISD novel fabrication technique. The characterization methods we have used include scanning electron microscope (SEM), high-resolution transmission electron microscope (HRTEM) and X-Ray diffraction (XRD). The research toward to the proposed direction is in good progress. We have given three presentations in national and local materials meetings and have submitted another two papers in another two key national meetings in nanotechnology and American Physical Annual March Meeting 2002. A couple of papers are in prepration.

TABLE OF CONTENTS

INTRODUCTION

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. 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. In the present work we plan to use laser induced solution deposition (LISD) technique 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. 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.

It is the intent of this proposal to examine the inter-relations between catalytic and magnetic properties of specially prepared iron 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, 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 as the feed stock changes from $CO/CO_2/H_2$ to alcohol 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 and iron is by far the cheapest of the three catalysts. Therefore the proposed magneto-chemical character investigations of Fe/Cu and Co/Cu bimetallic catalysts should also prove valuable in exploring processes for efficient hydrogenation of CO/CO_2.

We propose to:

a) Synthesize Fe/Cu and Co/Cu bimetallic catalysts impregnated on granular Al_2O_3, SiO_2 and Cr_2O_3 supports employing two novel techniques - Laser Induced Solution Deposition (LISD) of organic/inorganic precursors and Sol-Gel technique for the preparation of granular catalyst supports.

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

c) Investigate the magnetic and electronic structural characteristics of pre and post use nano-catalysts by i) Mossbauer study of Fe, ii) ZFNMR study of Co, iii) NQR study of Cu, iv) Magnetization study, v) SEM study and vi) XRD powder analysis of the catalyst composites.

EXECUTIVE SUMMARY

We have set up successfully two experimental systems during the past time of the project. The first system is sol-gel chemical method for preparing γ-Al_2O_3, SiO_2, Cr_2O_3 granular support particles. The second system is the laser-induced solution deposition (LISD) technique for nanoparticle catalysts containing Fe/Cu, and Co/Cu 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 EDX. The prepared γ-Al_2O_3 granular particles were uniform in composition and structure.

LISD is a novel method for preparing proposed nanoparticle 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 dielether. 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 proposed to be analyzed by chemical method, SEM, XRD, magnetization measurements, and other special characterization techniques such as Mossbauer study for Fe, zero filed nuclear magneto resonance (ZFNMR) for Co, and NQR for Cu.

In the initial experiments, we have tried to deposit nanostrucured pure Co before depositing the complex bimetallic catalysts. We have obtained nanostructured Co or Co oxide nanoparticles from the analysis of scanning electron microscope and its energy dispersive X-ray spectroscopy (EDX). Further high-resolution X-ray diffraction and transmission electron microscopy analysis need to be done to identify the exact structures. The preliminary results of Co deposition have shown promising in the proposed project although they have not shown complete success in the formation of bimetallic catalysts as we proposed. We will make further efforts in the future to get better results.

EXPERIMENTAL

Experimental Systems

Figure 1 shows the sol-gel system for producing granular supports. Usually sol-gel method consists of three steps: (a) Boehmite sol (γ-AlOOH) preparation; (b) sol gelation and shaping; (3) Dry and calcinations. Figure 2 shows the laser-induced solution deposition (LISD) system for depositing nano-particle catalysts. This is a laser-initiated chemical processing. We combine these two methods together to impregnate nano-partile catalysts produced by the LISD technique into the granular supports produced by sol-gel method.

Fig.1 The sol-gel system

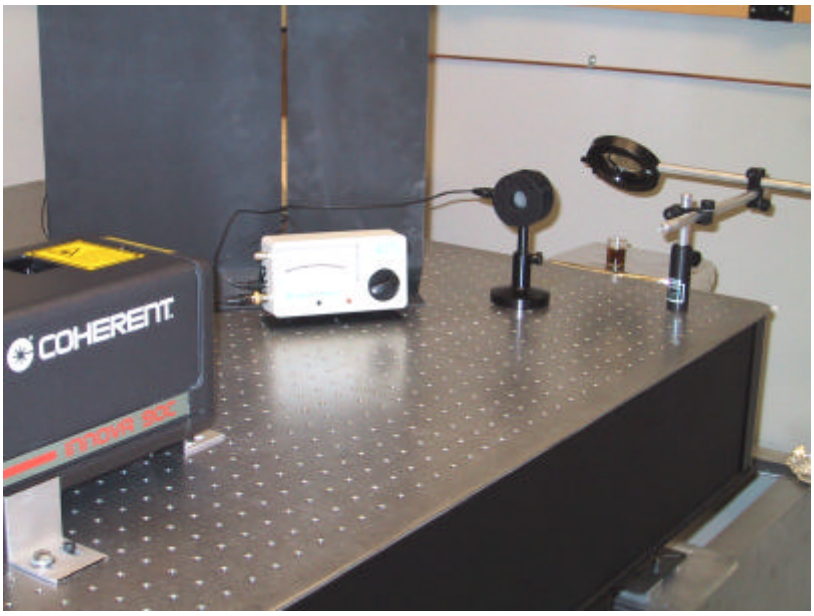

Fig.2 The laser-induced solution deposition (LISD) system

Experimental Details

(I) Sol-Gel Preparation of g-Al_2O_3 Granular Particles

Phase 1: Boehmite Sol (g-AlOOH) Preparation

We have chosen aluminum tri-sec-butoxide (ALTSB, 97%) (52 ml) dissolved in distilled water (100 ml) as precursor and 1M HNO3 as adjusting pH value. The chemical reactions will be:

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

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

$Al(OH)_3 + Al\text{-}OR \leftrightarrow [Al\text{-}O\text{-}Al] + H2O + ROH$

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 pesudoboehmite sol (γ-AlOOH) more stable.

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

1M HNO_3, paraffin oil (density 0.786g/cm2, kinematical viscosity 34.5, Fisher Scientific), 10 wt % ammonia solution, liquid soap 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 were 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 strirring (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.

Phase 3: Dry and Calcinations

The particles were dried for about 48 hours in the oven at 50ºC and calcinated in the air at 450 ºC for about 4 hours.

We have used X-ray diffraction and SEM with EDX to identify the composition and structures. It was found that the structure was γ-Al_2O_3, the composition was uniform and the shape was in granular. The granular particles were in mm scale but the porous diameter was estimated in nm or sub-micro scale.

(II) Nanofabrication of Nanostructured Co-nanoparticles by LISD technique

Laser pyrolysis and photolysis are popular methods that have been used to prepare catalytic materials. LISD offers several advantages over other methods because the deposition takes place in solution. All deposition experiments are carried out in the solutions of ammonia dissolved in distilled water or containing various mixtures of methanol, cyclohexane, tetrahydrofuran (THF) and dielether. The selection of solvents is crucial for successful deposition. 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. Our preliminary results demonstrate clearly the feasibility using LISD technique making deposits of nano/micro particles and thin films of gadolinium borides. We have also succeeded in producing well-dispersed uniform nanoparticle magnetic oxides such as CrO_2 and Cr_2O_3. Selective area deposition of metallic nanoparticles and thin films from solution is known and has also been applied to the deposition of copper and other materials including complex compound materials. Compared with other techniques LISD is a unique method to fabricate nanoscale complex materials. We believe in that LISD is also a unique method to produce nanoscale and well dispersed catalyst particles because it can meet the needs of high yield, high selectivity and size controllability perfectly.

In this project we will develop LISD technique to fabricate nanoparticle catalysts: Co-Cu-Cr_2O_3, Co-Cu-Al_2O_3, Co-Cu-SiO_2 and Fe-Cu-Cr_2O_3, Fe-Cu-Al_2O_3, Fe-Cu-SiO_2 and we will characterize the obtained nano-particle catalysts using magneto chemical and surface analysis techniques. Laser power and wavelength could be selected to optimize the deposition. LISD experimental system Figure 1 shows the 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 Fig. 3.

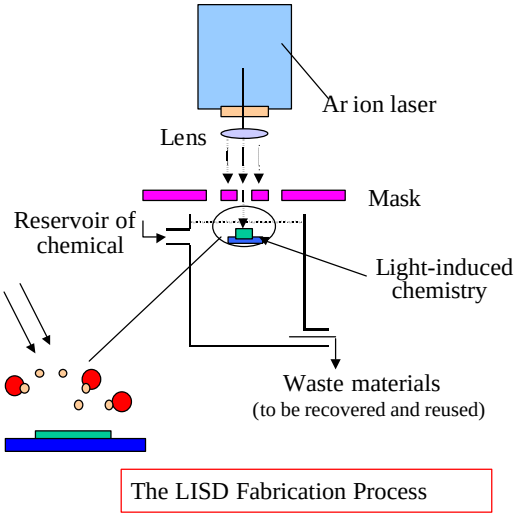

Fig. 3 A diagram of laser-induced deposition from solution (LISD)

RESULTS AND DISCUSSION

Figure 4 and Figure 5 show the image of the γ-Al_2O_3 produced by sol-gel method. In the initial experiment of LISD, 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 transferthe Co ions into Co with the transferring electrons from $(NH_3)_6$. Various concentrations of solutions and laser conditions have been tried. Here shown is 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 6 and Figure 7 show the scanning electron microscope images of deposition area. Figure 8 and Figure 9 show the Co (or cobalt oxide) nanoparticles deposited on the silicon substrate. Figure 10 and Figure 11 show the Co (or cobalt oxide) nanoparticles directly taken from the solution. The SEM results clearly indicate that Co (or cobalt oxide) nanoparticles have been deposited. The average diameter is about 100 to 500 nm. It is obvious that the particles (average diameter ~ 100 – 200 nm) directly from the solution is smaller than those deposited on the silicon substrate (average diameter ~ 300 – 500 nm). We postulated that the growth rate of the nucleated particles on the substrates is faster than that in the solutions. EDX spectroscopy shows oxygen peak, which indicates oxygen contamination or the formation of cobalt oxides as shown in Fig. 12. The exact structures of the deposits need to be investigated by high resolution X-ray diffraction and transmission

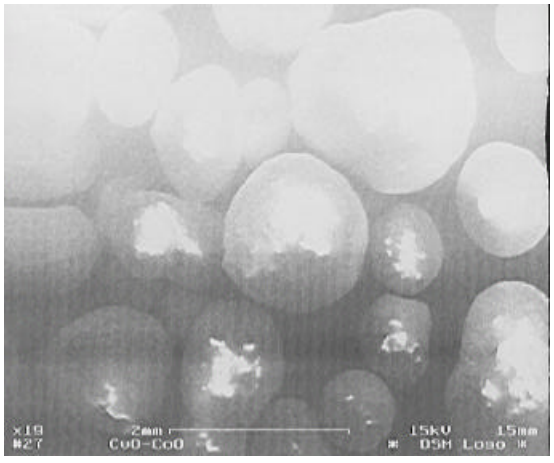

Fig. 4. γ-Al_2O_3 granular particles prepared by sol-gel method (in low magnification)

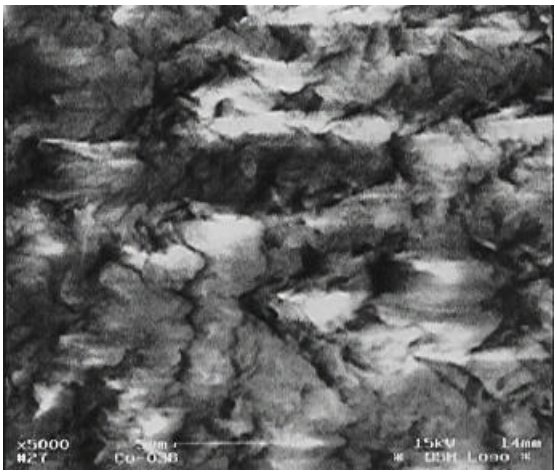

Fig. 5. γ-Al_2O_3 granular particles prepared by sol-gel method (in higher magnification)

Fig. 6 SEM image of deposition area (the "white" area) in low magnification: the center of focused laser beam and the surrounding region.

Fig. 7 SEM image of deposition area (the "white" area) in higher magnification: the center of focused laser beam and the surrounding region.

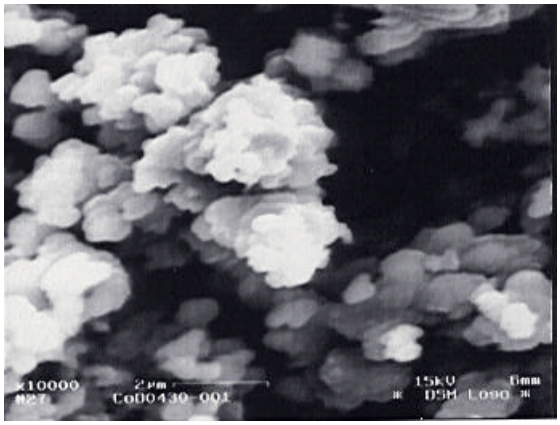

Fig.8 Co nanoparticles on Si substrate taken from the laser beam center area shown as in Fig.1. The particle size is about 200 – 500 nm in diameter (magnification 10,000 X)

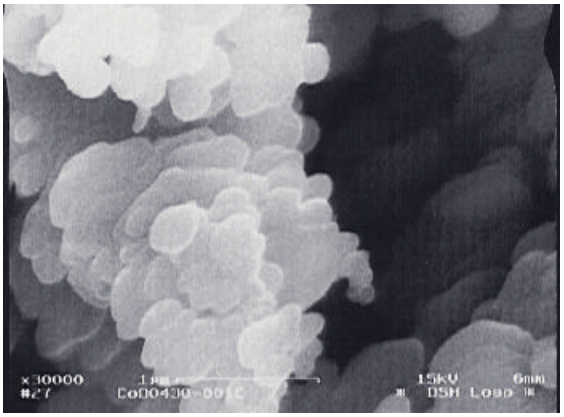

Fig.9 Co nanoparticles on Si substrate taken from the laser beam center area shown as in Fig.1. The particle size is about 200 – 500 nm in diameter (magnification 30,000 X)

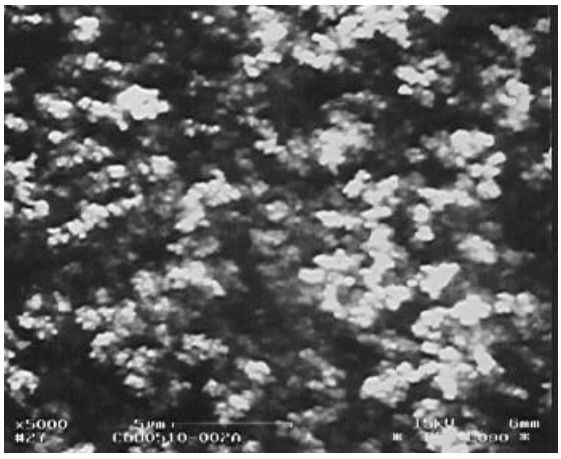

Fig. 10 Co nanoparticles directly taken from the solution after the deposition. The particle size is about 100 – 200 nm in diameter (magnification 5,000 X)

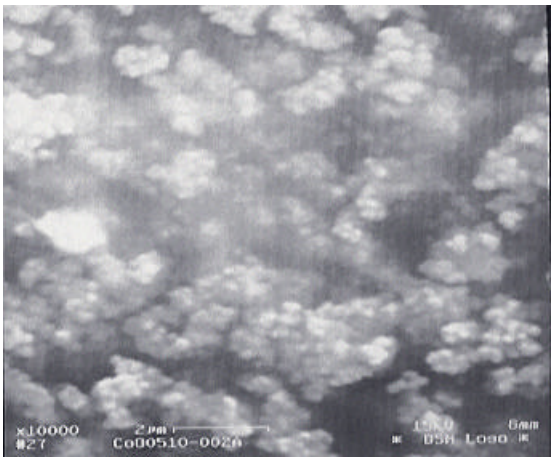

Fig. 11 Co nanoparticles directly taken from the solution after the deposition. The particle size is about 100 – 200 nm in diameter (magnification 10,000 X)

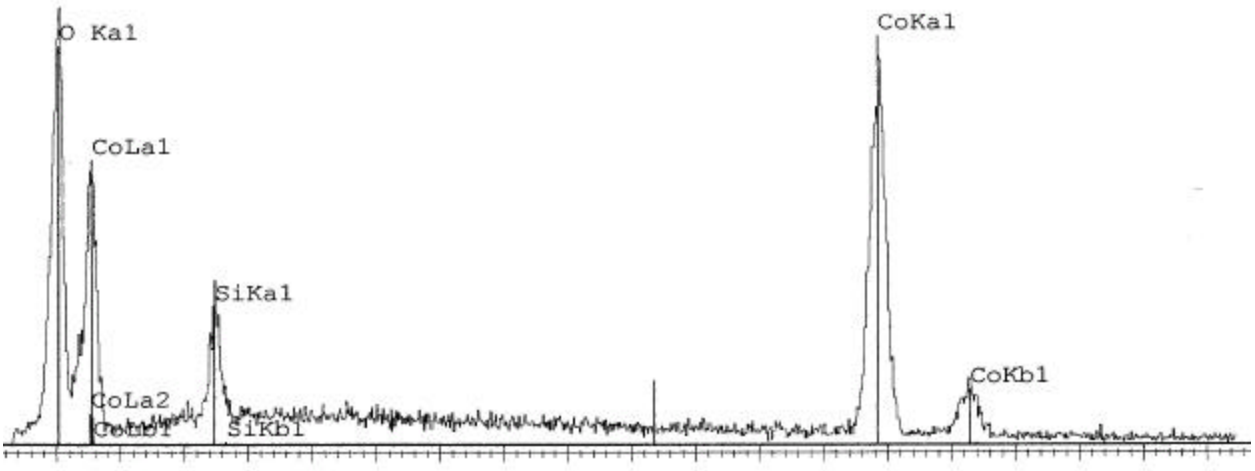

Fig. 12 The EDX composition analysis shows strong Co peaks (the O peak may indicate the contamination of oxygen and the formation of cobalt oxides)

Figure 13 shows the high-resolution TEM image of the Co/CoO_x nanoparticles 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 shows the selected – area electron diffraction pattern of the CoO_x nanoparticles directly taken from the solution after the deposition. They have shown very promising and encouraging results.

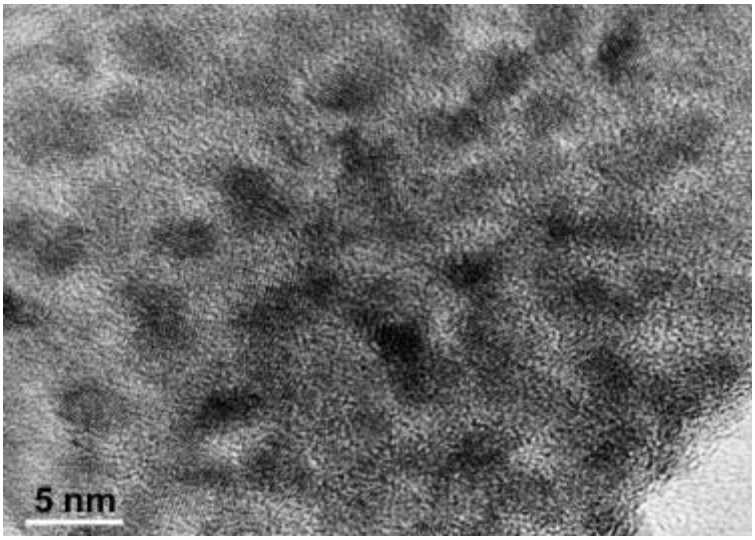

Figure 13. The high-resolution TEM image of the Co/CoO_x nanoparticles directly taken from the solution after the deposition (the diameter of the deposited particles are less than 5 nm).

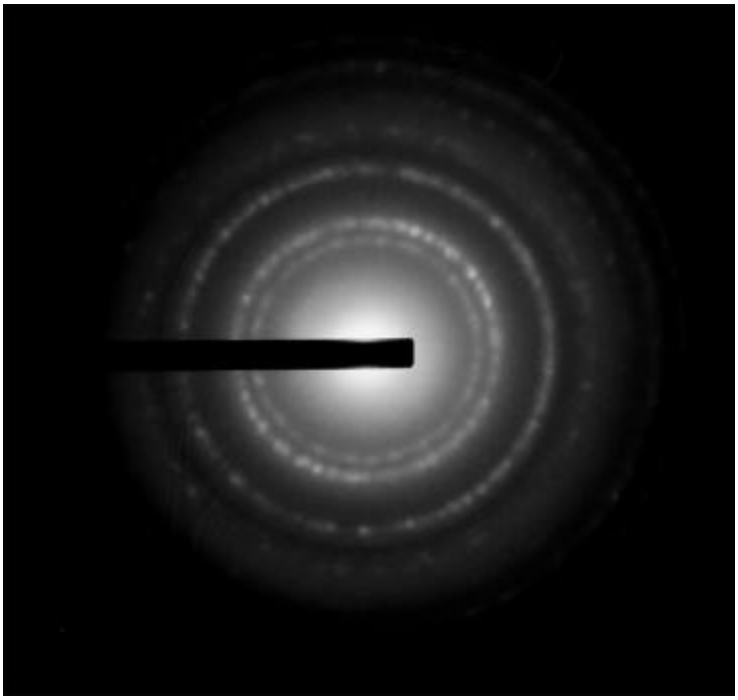

Figure 14. The selected - area electron diffraction pattern of the CoO_x nanoparticles directly taken from the solution after the deposition.

In general for the section of results, we can say that we have done pretty much for the first year. We have found that the two methods: sol-gel chemical method and laser-induced solution deposition technique we proposed were really working. We have produced the support materials such as γ-Al_2O_3 and we have synthesized Co and CoO nanoparticles. These results were expected by us because we have done various deposition of other materials by using these two methods prior to this project. The primary results will have impact on future work in three aspects. First of all, the promising results have increased students' confidence and assure them that they will finally get much more results (it is very important!). Secondly, the primary results have provided us data and materials to present in key national conferences in which we can communicate with other researchers to exchange or gain more ideas (if without primary results, sometimes it is difficult even though maybe we still can participate some meetings). Finally the single element deposition is the basis of the alloy deposition. Actually we have tried such kind of approach to eventually fulfill our proposed projects and will even possibly get better and more results than we proposed and expected.

CONCLUSIONS

As a conclusion, we can say that we have shown strongly that laser-induced solution deposition (LISD) is a novel and unique method for fabricating nanoscale particulate materials such as the nano-catalysts and the sol-gel chemical method is a good technique for producing support materials for the nanoparticle catalysts. We have set up the two experimental systems successfully and effectively. We have succeeded in synthesizing nanostructured pure Co or Co oxide nanoparticles. We have studied the micro-/nano-structure and the composition of the deposited nanopartilces by SEM, EDX, high-resolution TEM and XRD. The suspended nanopartilces in the solution are less than 5 nanometers and the distribution of the nanoparticles are in very narrow regime, which is unique and useful for the catalytic properties and other functional (chemical or physical) properties. The particles deposited on the silicon substrates are much larger, which is in the region of 100 to 500 nanometers in diameter.

REFERENCES

1. R. Subramanniaan, P. E. Denney, J. Singh and M. Ottoni, *J. Mater. Sci.*, **33**, 3471-3477 (1998).
2. T. A. Dobbins, D. Poondi and J. Singh, *J. Mater. Synth. & Processing*, **7(5),** 261-271 (1999).
3. D. Poondi, J. Singh, *J. Mater. Sci*., **35**, 2467-2476 (2000).
4. D. Poondi, T. Dobbins and J.Singh, *J. Mater. Sci.*, **36**, 6237-6243 (2000).
5. Mats Bomann, Arun Narayan, Chriiistofer Ferguson and Lars Landstorm, in the 2nd Louisiana Conference on Microfabrication and Materials Science, Baton Rouge, LA, August 20-22, 2001.
6. Z. C. Zhong, P. A. Dowben and D. J. Sellmyer, *Materials Letters*, **37**, 320 (1998).
7. P. A. Dowben, Z.C. Zhong and D. J. Sellmyer, US Patent 6,025,038 (issue date: 02/15/2000).
8. P. A. Dowben, Z.C. Zhong and D. J. Sellmyer, US Patent 6,077,617 (issue date: 06/20/2000).
9. Z. C. Zhong, R. H. Chen and P. A. Dowben, *Appl. Surf. Sci*., in press (2001).

FUTURE WORK

a) Nanofabrication of Nanoparticle Catalysts by Improved Experimental Conditions

Based on our preliminary success of fabrication Co nanoparticles, we will further fabricate Fe and Cu nanoparticles using similar approaches. We will choose Co-series (Co-Cu-Al_2O_3, Co-Cu-SiO_2, Co-Cu-Cr_2O_3) and Fe-series (Fe-Cu-Al_2O_3, Fe-Cu-SiO_2, Fe-Cu-Cr_2O_3) as our priority in this proposed project. Different compositions and ratios will be selected to decide best catalysts. Supportive particles of Al_2O_3, SiO_2 and Cr_2O_3 as suspension will be made by Sol-Gel method as stated above.

$Co(NO_3)_2$, $Cu(NO_3)_2$, $Fe(NO_3)_3$, $CoCl_2$, $FeCl_2$, and $CuCl_2$ will be chosen as precursors (solutes). Other precursors such as organometallic compounds will be also tried. Except for the solution of ammonia (NH_3) dissolved in distill water, various mixtures of solvents of methanol, cyclohexane, tetrahydrofuran (THF) and dielether will be tried. The granular Al_2O_3, SiO_2 and Cr_2O_3 prepared by oil drop Sol-gel method will be put at the bottom of the reaction solution in that the nanoparticle catalysts will be impinged into the porous granular support. Different ratios of the solute compounds will be tried and optimized finally.

Based our previous results and experiences, we will start the LISD technique using visible and UV radiation (I-90 Argon Ion Laser with wavelengths and powers 333-364 nm and 50 –500 mw in UV and 488-515 nm and 5 – 7 W in visible region). More sophisticated optical system and specially designed chemical reactors will be used in the future. We should be able to get uniform nanoscale particles through controlling nucleation and growth by proper selection of solutes, solvents and laser parameters.

In this way, optimal nucleation and growth conditions for nanoparticle fabrication can be realized. For a particular material deposition in a special solution consisting of carefully selected solvents and solutes, we will study the dependence of LISD deposition on laser power and wavelength. It is expected that a certain power and wavelength is most suitable for a given material deposition, which has been proved by our previous results. We expect that efficient nano-particle catalysts with high quality will be finally produced by using the combined methods of LISD and Sol-Gel.

b) 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 K promoted bimetallic catalysts will be analyzed by Mossbauer study of iron, ZFNMR of Co, NQR of Cu and Magnetization, SEM and XRD studies of the composite. These characterization studies will be of immense value in the determination of the various phases of iron, iron oxides, iron 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.

c) 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, HPLC, MS, GC-MS, FT-IR, and FT-NMR. Louisiana Tech University has all these standard facilities, and we plan to conduct two (2) comprehensive experiments employing all the analytical tools to generate the necessary bench-mark data for complete product identification and characterization. As shown in the research plan scheme, the reference data will be generated using a representative catalyst with $CO/CO_2/H_2$ as feed stock.

d) Batch Processing Slurry Reactor

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 phenanthrene or pyrene, under hydrogen pressure to avoid exposure to air. Continuous magnetic stirring will be employed to simulate slurry phase reactor conditions. The reaction gases CO_2 and H_2 will be introduced and heated under pressure (1 MPa) at 250^0C for about 5 hours. Runs with syngas (CO/H_2) will be made on three representative catalysts to serve as base line data for comparison of $CO/CO_2/H_2$ performance. The schematic diagram (Fig.13) given below illustrates the integration of Parr bomb and various instruments for chemical analysis of CO/CO_2 hydrogenation products.

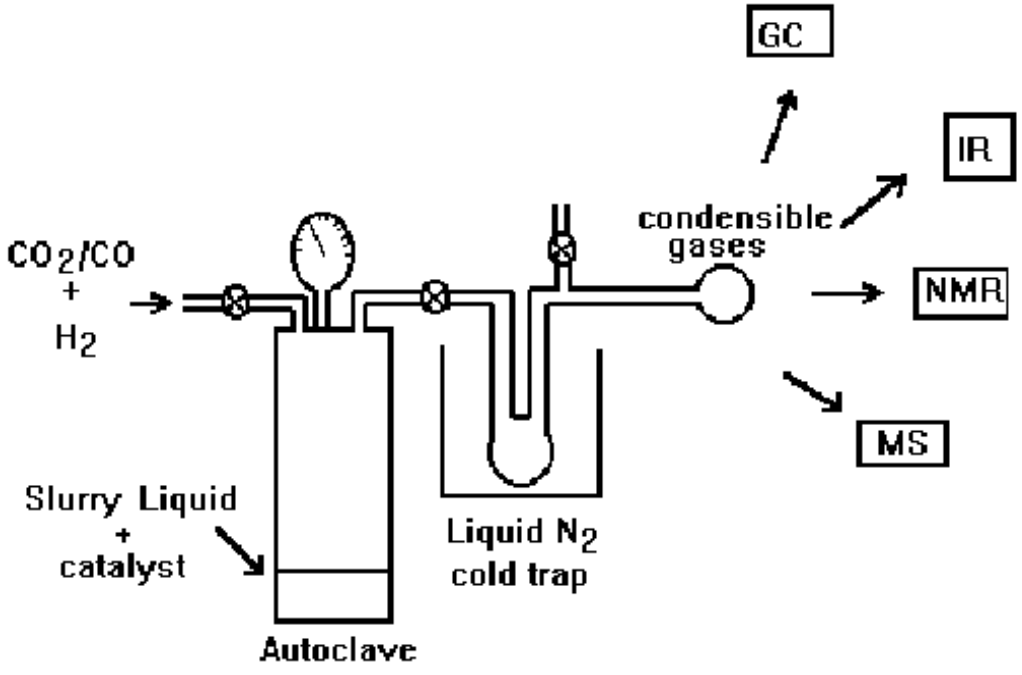

Fig. 15 Batch Processing Slurry Reactor