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Comparison of Fe/Co/Cu metal loading in mesoporous γ-alumina prepared by three sol-gel methods

Upali Siriwardane*[a], Naidu V. Seetala[b], Naga S. Vegesna[a], Satyendra Vudarapu[a], and Karen Luurtsema[a]

[a] Department of Chemistry and Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA, 71272 USA
[b] Department of Physics, Grambling State University, Grambling, LA 71245 USA

*Address for correspondence: Upali Siriwardane, Carson Taylor 316, 600 West Arizona, Department of Chemistry, Louisiana Tech University, Ruston, LA, 71272 USA.
Phone: (318) 257-4941.
Fax: (318) 257-3823.
e-mail: upali@chem.latech.edu

Running title: Fe/Co/Cu metal loading in sol-gel alumina

Abstract

Nanoparticle Fe/Co/Cu loaded mesoporous γ-Al_2O_3 spherical (~ 1 mm diameter) catalyst granules were prepared by three sol-gel/oil-drop methods: 1) nanoparticle-metal-oxide, 2) metal-nitrate-solution, and 3) metal-ion-wet-impregnation. The granules were characterized by EDX, BET surface area, DTA/TGA, XRD, SEM, EDX and TEM. Thermal analysis of metal-oxide-method prepared granules confirmed that the metal oxide structure remain intact during calcinations while other two methods showed the conversion of metal hydroxides to metal oxides. Alumina granular surface areas are in the mesoporous range 195-315 m^2/g with an average pore diameter of 5 nm. EDX and PXRD analyses showed that the metal loading efficiency of the methods to decrease in the order: nanoparticle-metal-oxide (74%), metal-nitrate-solution (22%), and metal-ion-wet-impregnation (13%). The attrition resistance of the alumina granules also decreased in the same order. Metal loading efficiencies of pure metals using metal-nitrates-solution method correlated with increasing order of solubility (K_{sp}) of metal hydroxides: Fe, Cu and Co. In mixed metal loading, Co and Cu interfered and reduced Fe metal loading when metal-nitrate-solution method is used. This work represents the first efforts to incorporate nanoparticle metal oxide suspensions directly into alumina sol-gel/oil-drop procedure to circumvent metal ion interference. The nanoparticle-metal-oxide method developed allows higher metal loading and precise control of mixed metal (Fe/Co/Cu) compositions in alumina catalyst granules.

Author Keywords: Metal loading, sol-gel; oil-drop; nanoparticle; mesoporous; catalyst; alumina; syngas; Fisher-Tropsch.

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1. Introduction

Heterogeneous catalysts are easy to immobilize/separate than homogeneous catalysts and play an essential role in converting syngas (CO/H_2 mixtures) to fuel. The Fischer Tropsch (FT) synthesis has become the main focus of research and development programs at Shell, Sasol, Exxon-Mobil, Syntroleum, and Rentech to produce liquid aliphatic hydrocarbons and oxygenates by the hydrogenation of CO [1-4] that is essential for the gas to liquid technology (GLT).

The development of catalysts plays a key role [5] in improving FT based GLT. In this effort nanoparticulate catalysts have become very important over the past years due to their high surface area and rapid heat dissipation properties to overcome high exothermic nature of FT reactions and expected to give high conversion of synthesis gas. The nanometer scale metal clusters are known to exhibit size dependent physical properties [6]. Nanoscale and well-dispersed fine particle catalysts offer a large number of advantages such as least diffusion resistance and large number of active sites [7] compared to conventional catalysts. A zeolite with well-dispersed metal nanoparticles trapped inside the pore structure was first prepared by hydrothermal synthesis [8]. These types of mesoporous aluminosilicate supported catalysts [9, 10] showed higher activity compared to bulk metals [11, 12]. Thus the metal nanoparticle incorporated novel mesoporous catalysts seem to provide a promising alternative to conventional catalysts.

Sol-gel synthesis [13-15] has evolved as a powerful alternative to hydrothermal synthesis due to its versatility. It provides an easier control of the pore structure and chemical properties of the support, and homogenous dispersion of metal nanoparticles. It has become popular to prepare variety of mesoporous support/hosts with nanocatalyst particles incorporated into the extended pore structure. Mesoporous silica materials loaded with cobalt have been used as FT catalysts [16]. Preparations of mixed metal catalysts have become important because of their superior catalytic activity due to synergism or promoter effect [12, 17] of several metal centers.

Lin et al. [18, 19] used a combined 'sol-gel' and 'oil-drop' (metal-nitrate-solution) method to produce single metal loaded alumina granules with approximately 1 mm size, spherical shape, and higher attrition resistance [20]. The granular size and attrition resistance are essential properties for industrial catalysts to separate from the products without clogging filters. However, Lin's method gives lower metal loading due to metal ion seepage. Adding a higher metal ion concentration to the bottom ammonia solution in his procedure has complicated the metal loading by surface deposition. Thus there is a need to develop an alternative sol-gel method to increase the metal loading and reduce metal seepage. Lin's combined metal-nitrate-solution/sol-gel/oil-drop procedure has more serious complications when extended to loading mixed metal compositions due to metal ion interference resulting from solubility equilibriums and would not allow accurate control of mixed metal compositions of the alumina granules.

The main objective of this work is to develop a new sol-gel/oil-drop method to prepare heterogeneous mesoporous catalysts with increased metal loading. First, we have developed nanoparticle metal oxide suspension to achieve higher loading of pure metals, Fe, Cu and Co on to alumina granules in a controlled manner. Second, we have used mixed metal oxide nanoparticle suspensions to develop a complete new procedure to incorporate mixed metal Fe/Cu/Co compositions with higher loading and accurate control of mixed metal compositions. The advantages of the new nanoparticle-metal-oxide

method were compared to two other currently used methods: 1) metal-nitrate-solution and 2) metal-ion-wet-impregnation. The nanoparticle alumina catalysts were characterized using Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), differential thermal analysis/thermal gravimetric analysis (DTA/TGA) for thermal properties, Brunauer-Emmett-Teller (BET) method for surface area, and crushing strength for mechanical properties of the granules.

2. Experimental

2.1 Catalyst precursors and chemicals

Sol-gel/oil-drop method was used for the preparation of γ-Al_2O_3 granules starting with aluminum tri-sec butoxide (ALTSB) 97% (Aldrich) precursor. The other materials used are copper(II) nitrate (Fischer Scientific), cobalt(II) nitrate (J.T. Baker), mineral oil (Aldrich), iron(III) nitrate (Fischer Scientific), nanoparticle iron(III) oxide and copper(II) oxide (Nanophase Technologies Corporation). Nanoparticle cobalt(II) oxide was prepared by a chemical reduction of cobalt (II) acetylacetonate hydrate (Strem) in the presence of oleyl amine (Aldrich) and oleic acid (Aldrich) using a modified procedure reported by Sun et. al [7].

2.2 Preparation of alumina-supported catalyst granules

2.2.1 Metal-nitrate-solution sol-gel method

Metal loaded alumina granules were prepared with modifications to the sol-gel/oil-drop procedure reported by Wang and Lin [19]. Starting with ALTSB as the precursor, granules were prepared in four steps: 1) preparation of boehmite solution, 2) preparation of metal nitrate solution, 3) sol-gel formation, and 4) gel shaping by oil-drop method.

Step 1: ALTSB (0.20 mol, 52 mL) was added over a 30 min time period to 100 mL and the mixture was stirred at 75-80°C. Nitric acid (1M solution, 15 mL) was added until a flock deposit started to appear. The acidic solution was stirred for 15 min and refluxed for 12-14 hrs at 90°C.

Step 2: A required amount of metal (copper (II), cobalt (II) and/or Iron (III)) nitrate was dissolved in a minimum amount of water. The amount was calculated based on the weight of alumina and the desired (2, 4, 6, and 12%) metal loading (w/w) on alumina.

Step 3: A 20 mL solution of 1M HNO_3 was added to the solution (step 1) at a temperature of 75-80°C and stirred for 45 min and metal nitrate solution (step 2) was added to form a sol-gel.

Step 4:

Gel shaping/oil-drop method: A 10% ammonia solution with equal metal ion concentrations (found in the sol-gel to avoid metal ion seepage) was added to a graduated-glass cylinder. Mineral oil was added on top of this ammonia solution and the oil layer was heated to 90-100°C using a heating tape. The ratio of heights of mineral oil to aqueous 10% NH_3 solution was approximately 3:1. The alumina sol-gel formed (step 3) with the metal nitrate solutions, copper (II), cobalt (II) and/or iron (III), was dropped from a syringe at a uniform pressure into the hot mineral oil layer. The sol-gel drop granular surface was hardened during the passage through the hot oil. Mineral-oil and aqueous ammonia interface was stirred to avoid coagulation of granules. Alumina

granules in the ammonia layer were aged for 45 min, filtered, washed with cold water and alcohol, and oven dried for two days at 50°C.

2.2.2 **Nanoparticle-metal-oxide sol-gel method**

The above four steps were followed with a modification to step 3 by replacing metal nitrate solutions with metal oxide suspensions for loading nanoparticle metal oxides. Nanoparticle iron(III), cobalt(II) and copper(II) oxide suspensions were prepared by adding desired ratio of metal concentrations, oleyl amine (1 mL), oleic acid (1 mL), and water (10 mL). These suspensions were stirred/sonicated, added to alumina sol-gel and stirred. In step 4, the addition of metal nitrates to ammonia layer was omitted.

2.2.3 **Metal-solution-wet-impregnation on preformed γ-Al_2O_3 granules.**

Virgin alumina-soft-granules were prepared by the sol-gel/oil-drop method as described above without adding a metal component in Step 3. The granules were dried in an oven for two days at 50°C and calcined at 450°C. Metal nitrate solutions of cobalt(II), iron(III) and/or copper(II) with desired concentrations were prepared as described in Step 2. The calcined granules were impregnated by repeatedly soaking in the metal nitrate solution for 24 hours and removing excess water from the granules using a rotary evaporator. The impregnated granules were aged for 1 hr in a 10% ammonia solution with equal metal ion concentrations to avoid metal ion seepage, filtered, and dried at 50 °C for 2 days.

2.3 **Calcination and hydrogenation of alumina catalyst granules**

DTA and TGA data were obtained to optimize calcination temperature. The samples were placed in aluminum boats and loaded into a Shimadzu DTA-50 Differential Thermal Analyzer (DTA) and a TGA-50/51H Thermal Gravimetric Analyzer (TGA). Calcination of alumina catalyst granules were carried out in a furnace (Thermolyne 21100) by gradually increasing the temperature to 450°C and maintaining it for 4 hrs. The calcined catalyst granules were loaded into glass tubes for hydrogenation. The glass tubes (10 mm diameter) were placed inside a tube furnace (Thermolyne 1400), gradually heated to 400°C in a flow of hydrogen gas, and maintained at 400°C for 2 hrs. The water formed was removed from the catalyst granules using intermittent vacuum suction.

2.4 **BET-Surface area/pore size analyses**

A NOVA 2000 high-speed gas desorption analyzer using Brunauer, Emmett and Teller (BET) method was used to analyze the surface area and pore structure, and to confirm the mesoporous nature of the alumina granules. The surface area and pore size calculations were based on the nitrogen desorption isotherm using Autosorob1® software provided by NOVA Inc.

2.5 **TEM/SEM-EDX Analyses**

A JEOL 2010 Scanning Transmission Electron Microscope (STEM) was used to obtain high resolution images of the catalyst granules to get the structural details.

A Carl Zeiss DSM 942 Scanning Electron Microscope (SEM) system was used to study the particle nature and distribution, and a Kevex LPX1 SperDry Quantum Detector Energy Dispersive X-ray (EDX) system was used for the elemental analysis of the granules.

2.6 **PXRD analysis**

The PXRD measurements were performed on powdered alumina granules with a Scintag X-ray powder diffractometer using Nickel-filtered Cu-K_α radiation and

DMNST® software. The X-ray diffraction patterns were obtained for samples annealed at various temperatures to study the phase composition and the dynamics of crystallinity.

3. Results and discussion

3.1 Catalyst preparations

3.1.1 Preparation methods

We have investigated the factors affecting metal loading during single-step metal-nitrate-solution sol-gel/oil-drop method. In this method a required amounts of metal (copper (II), cobalt (II) and/or Iron (III)) nitrate are dissolved in water and added to the sol-gel, shaped to granular from and dropped into the hot mineral oil layer. The granular surface is hardened during the passage through the hot oil. The next step, where granules are aged in an ammonia layer, is the most critical step for metal loading since formation of hydroxides and seeping of metal could occur. Adding metal ion to the ammonia layer should increase the metal loading by diffusing more metals ions into granules and reducing seepage. However, this step has complicated the metal loading by undesirable surface deposition of metal hydroxides. Solubility products of metal hydroxides indicate that solubility equilibriums in mixed metal hydroxide solutions should favor the precipitation of less soluble metal hydroxides while suppressing the more soluble. The combined metal-nitrate-solution sol-gel/oil-drop procedure reported by Wang and Lin [19] used with mixed metal nitrate solutions will limit/interfere metal loading and would not allow precise control of metal compositions. A second wet impregnation is required to incorporate less soluble metals. Therefore, metal-nitrate-solution sol-gel/oil-drop method is not suitable for loading mixed metal compositions.

In nanoparticle-metal-oxide sol-gel method, we used a water suspension of surfactants, and nanoparticle metal oxides (iron(III), cobalt(II) and copper(II)) to replace metal nitrate solutions. Use of metal oxides circumvents solubility factors involved in the metal hydroxide formation at the ammonia layer of the metal-nitrate-solution method. These suspensions are prepared by sonicating a mixture of nanoparticle metal oxides, water and surfactants, and then mixed with the virgin sol-gel to form a uniform sol-gel mixture. An ammonia layer without metal nitrates is used just to age and harden the alumina granules. This single-step nanoparticle-metal-oxide sol-gel/oil-drop method gives higher metal loading and accurate control of mixed metal compositions as described below in detail.

We also prepared metal loaded alumina granules using metal-solution-wet-impregnation on preformed γ-Al_2O_3 granules to compare the metal loading efficiencies with other two sol-gel/oil-drop methods: metal-oxide and metal-nitrate. The wet-impregnation method is cumbersome, complicated by the surface deposition of metal hydroxides on the surface of granules and did not control the loading of mixed metal compositions. Solubility factors still affected the metal loading and multiple wet-impregnation steps are required for mixed metal loading. Therefore, the single-step metal-oxide sol-gel/oil-drop method is preferred for mixed metal loading over metal-nitrate-solution and metal-ion-wet-impregnation sol-gel/oil-drop methods.

3.1.2 Calcination/hydrogenation

The DTA/TGA analyses are useful in studying the chemical and phase changes that take place during the calcination of alumina catalyst granules. DTA and TGA plots for iron metal loaded alumina granules prepared by the metal-nitrate-solution sol-gel

method are shown in Fig. 1a and Fig. 1e, respectively. The exothermic thermal peak observed at 210°C is attributed to the dehydration of iron hydroxides to oxides. The DTA plots inside the box in the Fig. 1 compares the DTA plots for iron loaded granules prepared by three sol-gel methods.

The catalysts prepared by wet-impregnation of iron metal ions onto preformed alumina granules have a slightly different DTA pattern (Fig. 1b) from those of the metal-nitrate-solution method showing broad metal hydroxide dehydration. This may be due to non-uniform distribution of metal hydroxides on the surface of wet-impregnated already calcined granules. The DTA (Fig. 1c) of granules prepared by the metal oxide method showed no metal hydroxide dehydration peaks and is almost identical to the control DTA plot of pure sol-gel alumina without metal loading as shown in Fig. 1d. The absence of

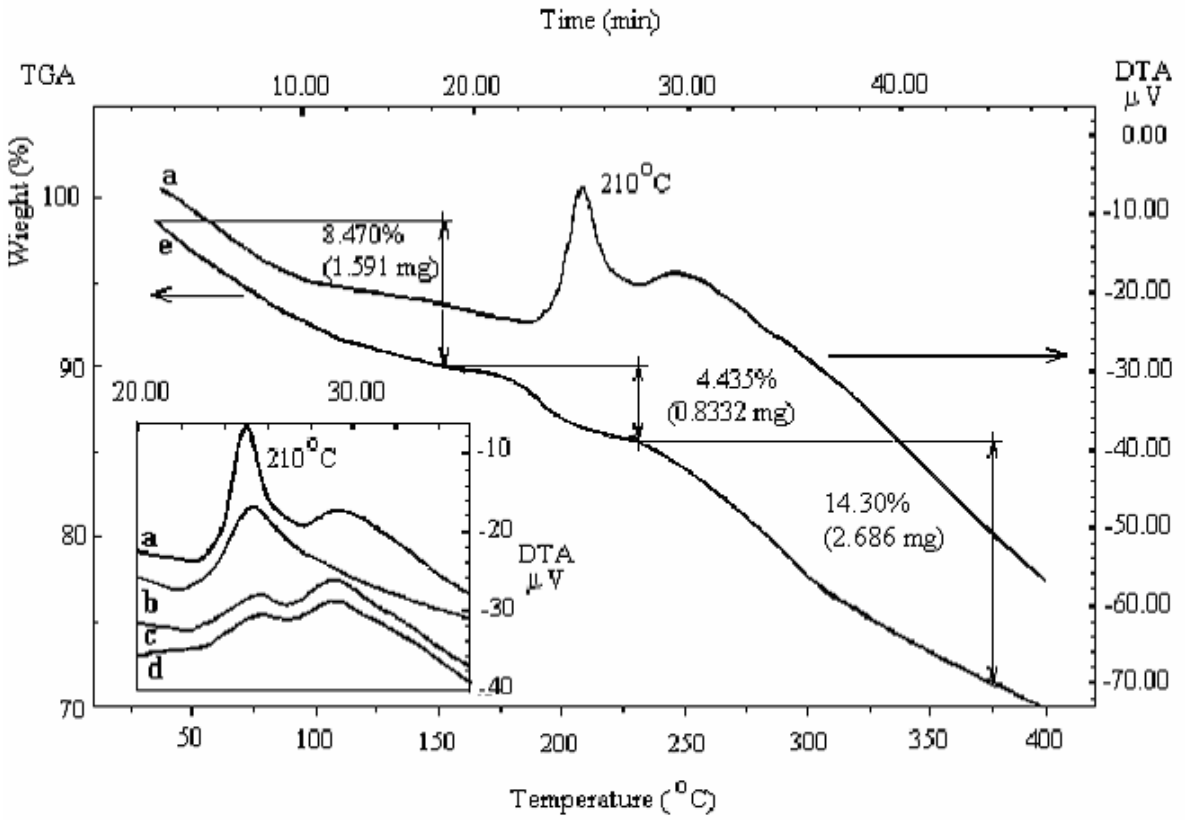

Fig. 1. a) Fe/alumina prepared by metal-nitrate method, b) Fe/ alumina prepared by wet-impregnation method c) Fe/alumina prepared by metal-oxide nanoparticle-method, d) virgin alumina prepared by sol-gel method, and e) TGA for Fe/ alumina prepared by metal-nitrate method.

the iron hydroxide dehydration peak clearly indicates that the nanoparticle iron oxide structure is preserved without being converted to metal hydroxides during the nanoparticle iron oxide sol-gel alumina granule preparation procedure. A unique contribution of our study is the precise control of the mixed metal compositions using the nanoparticle-metal-oxide sol-gel method circumventing the solubility factors involved in the metal-nitrate-solution method.

3.2 **Catalyst characterization**

3.2.1 **Structural characterization by SEM/TEM**

SEM/TEM studies of the granules produced during this work provided the evidence that our sol-gel procedure gives uniform spherical ~1 mm diameter granules, consisting of ~50 nm alumina particles with a mesoporous structure of ~5 nm pores. Fig. 2 shows average 1 mm spherical alumina granules prepared by our sol-gel/oil-drop methods. Fig. 3 shows 50 nm particles alumina in the granular structure loaded Fe_2O_3 nanoparticles. Fig. 4 shows ~5 nm pore structure of alumina support loaded with Fe_2O_3 nanoparticles. The TEM pore size of ~5 nm is in agreement with the pore diameters obtained from the nitrogen desorption described later.

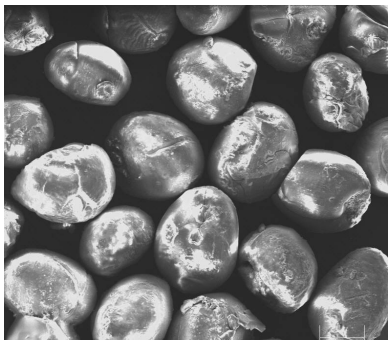

Fig. 2. SEM picture of alumina granules calcined at 450°C showing uniform 1mm average diameter.

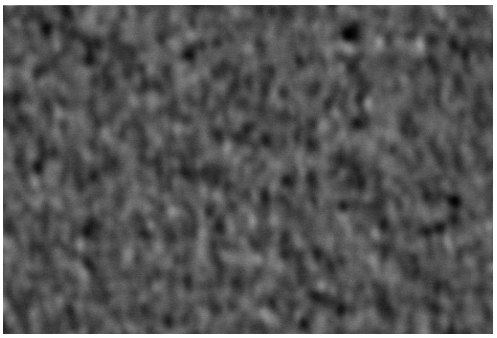

Fig. 3. SEM picture of granular alumina particles at 60,000 X showing 50 nm particles.

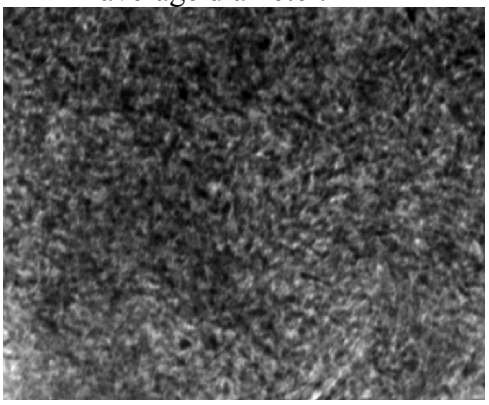

Fig. 4. TEM picture showing ~ 5 nm pore sizes of the mesoporous alumina granules.

3.2.2 **Phase characterization: PXRD**

Our PXRD studies, carried out on powders of crushed sol-gel prepared alumina granules, provided information relating to the nanoparticle nature of the metal centers, the phase characteristics of the metals and alumina support, as structural changes took place during the calcinations.

The nanoparticle nature of the alumina granules as seen by SEM/TEM study was confirmed by the lack of well defined PXRD peaks in virgin alumina granules. As the temperature was raised to 450°C, 800°C and 1000°C sharp peaks appeared indicating a change from nanoparticle/amorphous nature to increased size/crystallinity of the alumina particles as shown in Fig. 5. The sharp peaks in Fig 5c are matching with the alumina oxide (ICDD# 43-1484, synthetic corundum, the γ-alumina).

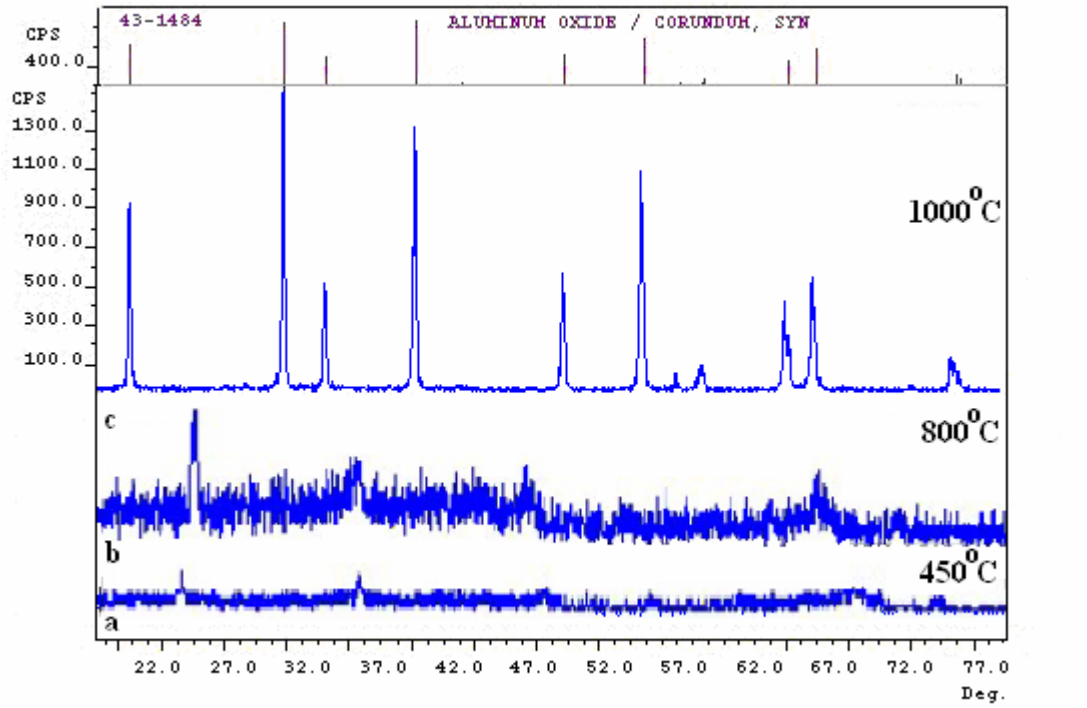

Fig. 5 PXRD patterns of virgin alumina granules heated at: a) 450ºC, b) 800ºC, and c) 1000ºC

The PXRD patterns of alumina loaded with iron oxide by three different sol-gel methods (heated to 1000ºC to increase the crystallinity) are shown in Fig. 6. At 1000°C, sharper peaks corresponding to iron oxide (hematite) and to aluminum oxide (corundum) appeared, as shown in Fig. 6a, 6b, and 6c. PXRD patterns for similar alumina granules prepared by the metal-ion-wet impregnation (Fig. 6a) and metal-nitrate-solution (Fig. 6b) methods showed lower intensity peaks for iron oxide compared to metal-oxide method (Fig. 6c). Lower intensity of iron oxide peaks seen in Fig. 6a and Fig. 6b for other two methods are due to lower metal loading which was also confirmed by our EDX analyses described later. Our PXRD data is consistent with previous work [19], where copper oxide peaks were observed only metal loading grater than 5%. In Fig. 6 c, iron oxide loaded alumina granules by nanoparticle-metal-oxide method show higher metal loading compared to other two methods. Higher loading also seem to lower the crystallinity of alumina as indicated by the noise of the base line of X-ray intensities.

The PXRD 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 Fig. 7a and Fig. 7b, respectively. As observed in Fig. 7a, the pattern for Fe/Co-

nitrate produced granules matched only with Co_3O_4 but not with iron oxide (hematite-synthetic). This agrees with the lower iron loading observed by EDX analysis as a result of cobalt interference. Co_3O_4 has been observed [23] previously on wet-impregnated

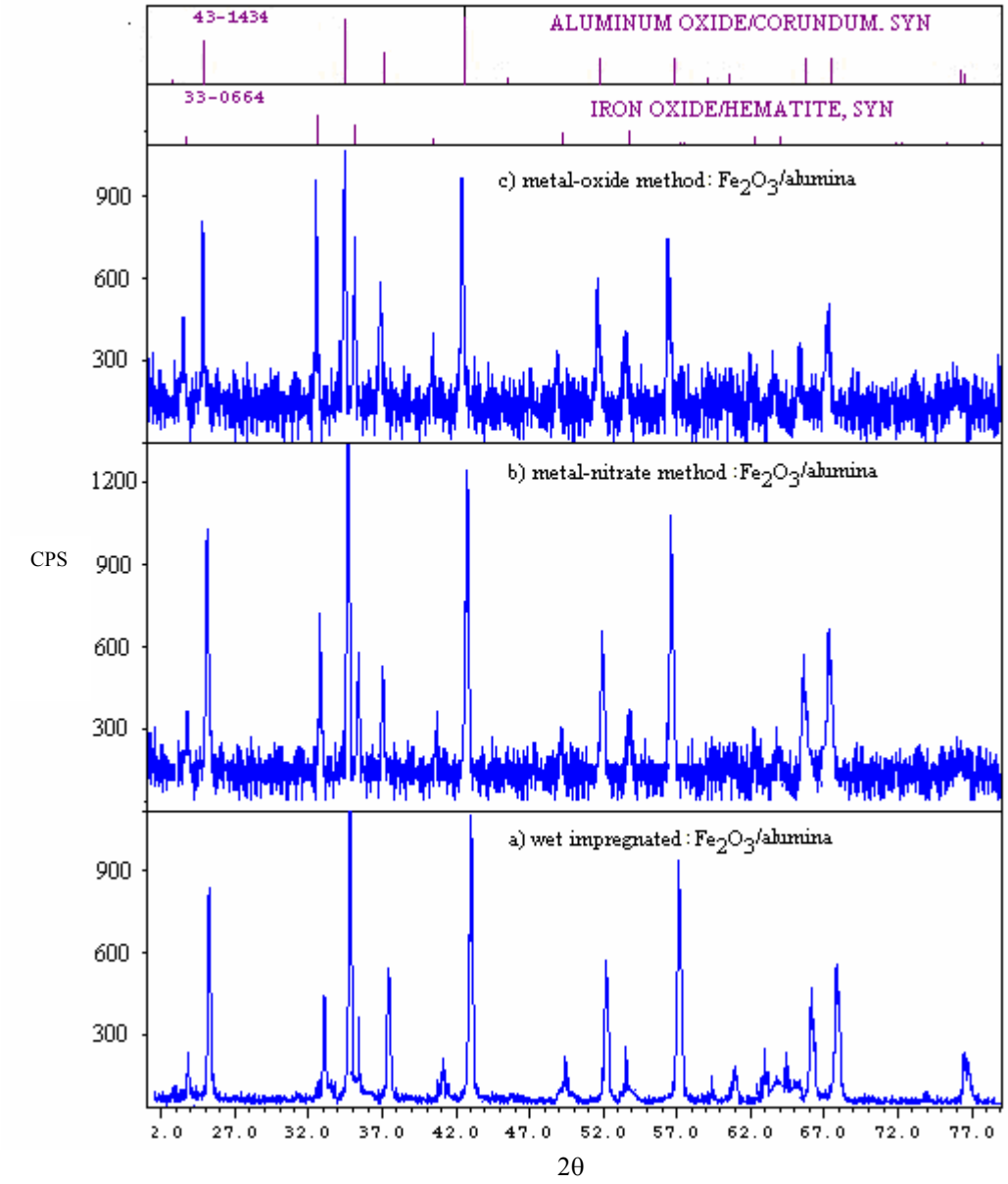

Fig 6. PXRD patterns of iron oxide loaded alumina granules heated at 1000ºC: a) Metal-ion-wet-impregnation on preformed γ-Al_2O_3 granules, b) Metal-nitrate-solution sol-gel method, and c) Nanoparticle-metal-oxide sol-gel method

Co/SiO_2 but not on Co/Al_2O_3 heated to 600°C. Our results indicate that Co_3O_4 can be formed even in Al_2O_3 in agreement with other work [24], where Co_3O_4 is found in alumina even at 500°C. These discrepancies could be explained by the difficulties in observing the crystalline peaks at lower metal loading.

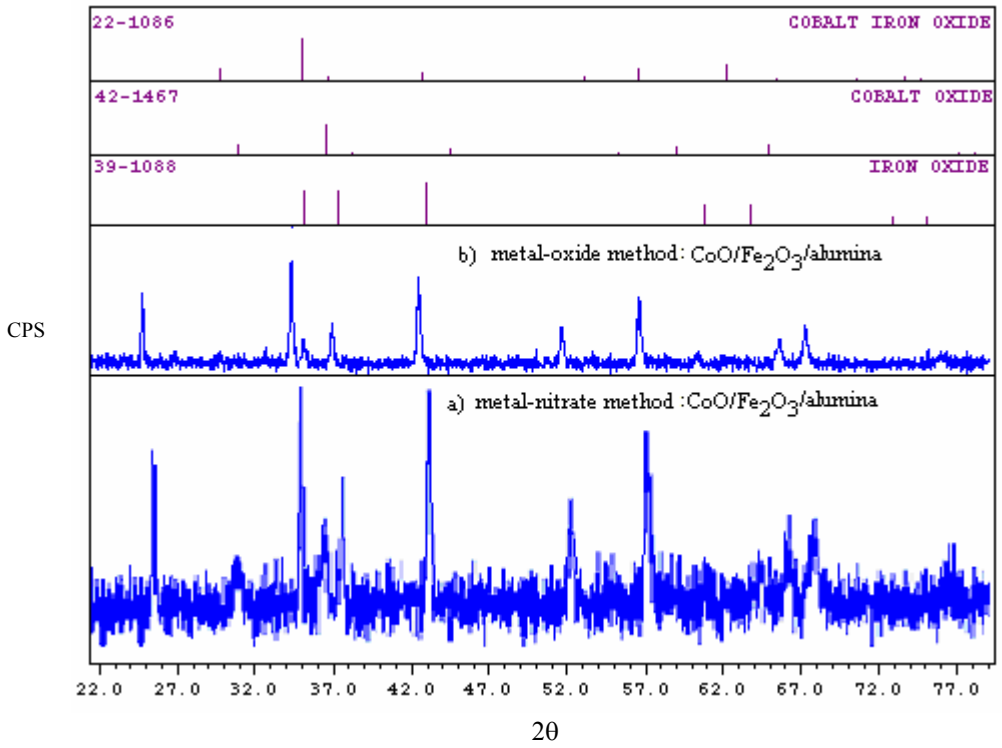

Fig 7. Cobalt and iron oxide loaded on alumina and heated at 1000ºC: a) Using metal-nitrate-solution method, and b) Using nanoparticle-metal-oxide method.

The nanoparticle metal oxide pattern (Fig. 7b) matched more with mixed metal cobalt/iron oxide (ICDD # 22-1086) than with either cobalt or iron oxide. This could be due to alloy formation between cobalt and iron that is also indicated by sifting of Co and Fe hydroxide dehydration peaks in DTA data. We observed similar PXRD and DTA behavior for nanoparticle copper and iron oxide loaded on to alumina granules.

3.2.3 **BET surface area and pore sizes**

Surface area were measured using BET method with nitrogen desorption and the results are presented in Table 1 for pure Cu, Fe, and mixed Cu/Fe metal compositions at 12% intended metal loading on alumina granules prepared by three sol-gel methods. All alumina granules had surface area in the range of 195–315 m^2/g indicating the mesoporous nature [25, 26]. The pore diameter of the alumina was calculated using BJH model and found to have an average value of ~5 nm. The mesoporous structures contain an enormous amount of surface area relative to their volume and therefore make excellent catalyst supports especially when nanoparticle catalyst metal centers are dispersed on them.

Table 1. Surface area of granules prepared by three sol-gel/oil-drop methods.

Metals loaded (12% intended) alumina sol-gel granules	Surface Area (m^2/g)		
	Nanoparticle-metal-oxide	Metal-nitrate-solution	Metal-ion-wet-impregnation
Cu	290.8(2)	226.7(3)	201.4(2)
Fe	311.1(4)	254.3(3)	196.1(2)
Cu/Fe	303.8(4)	236.9(3)	199.3(2)

Among the three methods, the nanoparticle-metal-oxide method gave the highest surface area. This may be due to higher metal loading (as observed by EDX analyses described below) for nanoparticle-metal-oxide method compared to other two methods. The granules prepared by the wet-impregnation method had the least surface area probably due to surface deposition clogging the pores. The variations in the values of surface area in different metal compositions, Cu, Fe, and Cu/Fe within each method also correlate with metal loading observed by EDX analyses.

3.2.4 **Mechanical strength**

Even though all three preparation methods showed slight differences in granular characteristics such as BET surface area, DTA, and PXRD, they differed remarkably in metal loading and crushing strengths as shown in Table 4. The data indicate that the nanoparticle-metal-oxide method produces granules with higher metal loading and greater mechanical strength than the metal-nitrate-solution and wet-impregnation methods. EDX data clearly shows that the nanoparticle-metal-oxide method gives more accurate control of mixed metal compositions and reproducible metal loading.

Table 4. Metal loading efficiency (EDX analysis) and crushing strength of Fe/Al_2O_3 granules prepared by three sol-gel methods.

	Nanoparticle-metal-oxide	Metal-nitrate-solution	Metal-ion-wet-impregnation
Metal loading efficiency (EDX) of Fe/Al_2O_3 granules	74%	22%	12.5%
Crush strength* of the granules (psi)	2500	1500	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.

3.3 **Metal loading**

3.3.1. **Metal interference on mixed metal loading in solution method**

There are several factors that affect the metal loading to granules. It definitely depends on the sol-gel method used. The efficiency of metal loading based on EDX analyses are given in Table 2. The EDX analysis indicates that metal loading is directly proportional to the metal ion concentration in the metal nitrate solution added. Single metal loading efficiencies increased in the order of Co, Cu and Fe which is in agreement with the solubility of metal hydroxides. Increasing the metal ion concentration in the

ammonia layer also increases the metal loading. However, in case of mixed metals, as shown in the Table 2, Co or Cu interfered and reduced Fe metal loading. The higher solubility of $Co(OH)_2$ increases the influx of more Co^{2+} ions into granules while the common ion effect of OH^- would reduce Fe^{3+} ions in the ammonia layer. This increases the seepage of Fe^{3+} ions from the granules. This correlates with the solubility data [21] for Fe^{3+}, Cu^{2+}, and Co^{2+} hydroxides: $K_{sp}(Fe^{3+}) = 4 \times 10^{-38}$ 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, the solubility differences of metal hydroxides would not allow accurate control of Co/Fe and Cu/Fe metal compositions in the granules using the metal-nitrate-solution method. This problem is overcome using the nanoparticle-metal-oxide sol-gel method.

Table 2. Mixed metal loading (w/w%) in alumina sol-gel granules prepared by metal-nitrate-solution method.

Metals Loaded	Intended metal loading (w/w%)			Actual metal loading (w/w%) (EDX)			Efficiency of metal loading (%)		
	Co	Fe	Cu	Co	Fe	Cu	Co	Fe	Cu
Co/Fe	6	6	-	7.6(9)	2.9(6)	-	126	48	-
Cu/Fe	-	6	6	-	2.3(5)	7.1(8)	-	39	118

3.3.2. **Comparison of metal loading for three sol-gel methods**

EDX analysis of metal loading in alumina granules prepared by three sol-gel methods is summarized in Table 3. Metal loading increased in the following order: metal wet-impregnation, metal-nitrate solution, and nanoparticle-metal-oxide.

Table 3. EDX analysis of metal loading (w/w%) in alumina prepared by three sol-gel methods.

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

The nanoparticle-metal-oxide method proves to be the best for metal loading because this method does not involve metal ion solubility equilibriums which plays an important role in metal loading at the bottom layer of aqueous ammonia used in oil-drop technique. The DTA analyses described above also confirms that nanoparticle metal oxides remain intact without being converted to soluble ions during the nanoparticle-metal-oxides sol-gel/oil drop method.

4. Conclusion

The preparation of Fe/Co/Cu nanoparticle metal loaded mesoporous spherical (~ 1 mm diameter) γ-Al_2O_3 catalyst granules were accomplished using three sol-gel/oil-drop methods: 1) nanoparticle-metal-oxide, 2) metal-nitrate-solution, and 3) metal-ion-wet-impregnation on granules. The nano-metal catalyst loaded on alumina could be effectively calcined at 450°C. BET surface area measurements confirm the mesoporous nature of all alumina catalysts prepared. The PXRD and DTA indicate a Co-Fe alloy formation in mixed Fe/Co catalysts. The PXRD and EDX analyses confirm that nanoparticle-metal-oxide sol-gel method gives the highest and most reproducible metal loading compared to metal-nitrate-solution and metal-ion-wet-impregnation methods. In preparing mixed metal Co/Fe and Cu/Fe catalysts, the metal ion interference observed in metal nitrate-solution-method was overcome using nanoparticle-metal-oxide sol-gel method to allow accurate control of mixed metal compositions in alumina granules.

We have used nanoparticle metal oxide method to deposit Co/Fe/alumina thin film layer on silicon microchannel reactors to study [27] the formation of higher alkenes from syngas. A FT catalytic study using Fe, Co, Co/Fe, or Cu/Fe nanoparticle/alumina granular catalysts prepared by three sol-gel/oil-drop methods to produce liquid aliphatic hydrocarbons and oxygenates will be reported [28] in subsequent paper.

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