Characterization of Alumina and Silica Sol-Gel Encapsulated Fe/Co/Ru Nanocatalysts in Microchannel Reactors for F-T Synthesis of Higher Alkanes

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We have been investigating conversion of syngas (CO: H2) to higher alkanes (Fischer-Tropsch Process) in 5 μm and 25 μm channel microreactors coated with sol-gel encapsulated Fe/Co-nanocatalysts. These nano-metal-catalysts were incorporated into the sol-gel matrix by two methods: 1) metal nitrate solutions; 2) nano-particle metal oxides. Characterization of these catalysts containing Co and Fe in alumina and silica sol-gel has been carried out by several techniques. The surface area measurements by BET method show average specific surface area of 285 m2/g for alumina and 300 m2/g for silica sol-gel encapsulated catalysts. Coating uniformity and elemental composition were examined by SEM/AFM and EDX to optimize the sol-gel preparation, deposition in the microchannels, and catalytic efficiency. Hydrogenation-reduction efficiency of the activated Fe-Co catalysts and the level of poisoning after the reaction were estimated using a vibrating sample magnetometer (VSM). The results suggest more efficient reduction in the case of the nano-particle metal oxides compared to that derived from metal nitrate solutions. Conversion of syngas to higher alkanes was monitored using a mass spectrometer. In overall, 85% of the catalyst is poisoned after 25 hrs of catalytic reaction. The surface area and the syngas conversion results indicate that silica sol-gel matrix may be a better catalyst support. For alumina sol-gel support, higher conversion of syn-gas is observed with 25 □m microreactor channels. For silica sol-gel, syngas conversion as high as 73% has been achieved by adding Ru as a promoter to the Fe/Co catalyst mixture.

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Characterization of Alumina and Silica Sol-Gel Encapsulated Fe/Co/Ru Nanocatalysts in Microchannel Reactors for F-T Synthesis of Higher Alkanes

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ABSTRACT

We have been investigating conversion of syngas (CO: H_2) to higher alkanes [Fischer-Tropsch (F-T) Process] in 5 μm and 25 μm channel microreactors coated with sol-gel encapsulated Fe/Co-nanocatalysts. These nano-metal-catalysts were incorporated into the sol-gel matrix by two methods: 1) metal nitrate solutions; 2) metal oxide nano-particles. Characterization of these catalysts containing Co and Fe in alumina and silica sol-gel has been carried out by several techniques. The BET measurements show an average specific surface area of 285 m^2/g for alumina and 300 m^2/g for silica sol-gel encapsulated catalysts. The elemental composition of sol-gel encapsulated catalyst was examined by EDX to optimize the sol-gel preparation and deposition in the microchannels. The SEM and AFM images of the reactors before and after deposition of the catalysts have been studied. Hydrogenation-reduction efficiency of the activated Fe-Co catalysts and the level of poisoning after the reaction were estimated using a vibrating sample magnetometer (VSM). The result suggests more efficient reduction in the case of the nano-particle metal oxides compared to that derived from metal nitrate solutions. In overall, 85% of the catalyst is poisoned after 25 hrs of catalytic reaction. The surface area and the syngas conversion results indicate that silica sol-gel matrix may be a better catalyst support. For alumina sol-gel support, higher conversion of syn-gas is observed with 25 μm microreactor channels. For silica sol-gel, syngas conversion as high as 73% has been achieved by adding Ru as a promoter to the Fe/Co catalyst mixture.

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INTRODUCTION

Technology for conversion of natural gas-to-liquids (GTL) is an attractive alternative for the petroleum industry [1]. Catalyst development is an important part of this technology as the properties of the catalysts and their support are critical for increasing the catalyst's activity during these conversions. This technology is based on Fischer-Tropsch (F-T) process of converting syngas (CO: H_2) to heavy hydrocarbons using a cobalt-based slurry. The influence of various support materials such as alumina [2], silica [3], titania [4] and ceria [5] on the activity of cobalt catalysts for CO conversion has been studied extensively.

Microchannel reactors or microreactors are miniature reaction systems fabricated using various micromachining techniques. The significance of the microreactor is its high surface to volume ratio created by the microchannels. This allows more active sites for the reactants to be adsorbed and get converted to more products. They are ideal systems for catalyst development as they provide unique advantages such as low consumption of reactants, greater speeds in catalyst characterization and easy integration with other devices such as sensors, valves and heaters [6]. More significantly, higher surface area of the reactor inhibits gas-phase free-radical reactions and improves heat transfer for different chemical reactions [7].

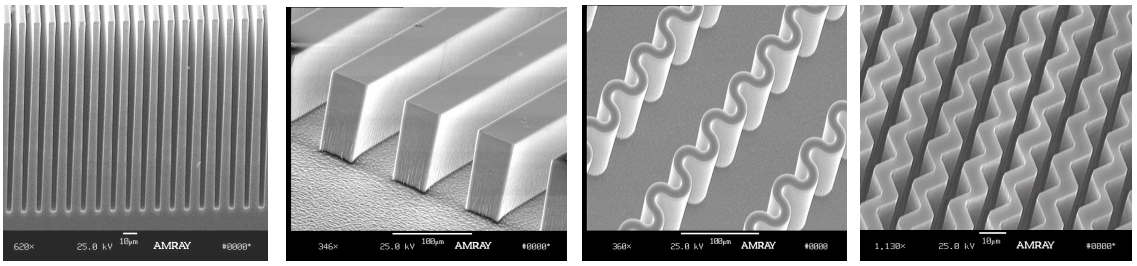
In this paper, we report the preparation and characterization of the sol-gel encapsulated iron and cobalt catalysts in microchannel reactor and its efficacy on exothermic syngas conversion to higher alkanes. We have used both alumina and silica sol-gel as catalyst supports. Nano-catalysts were prepared by two methods: 1) using metal nitrate solutions; 2) using metal oxide nanoparticles. The characterization of these catalysts by several techniques such as BET method, SEM, EDX, AFM and VSM are presented. The conversion of syngas to higher alkanes is monitored using a mass spectrometer. The effects of sol-gel and promoter on the activity of catalysts are briefly discussed.

EXPERIMENTAL

The silicon wafers were obtained from Montco silicon technologies, Inc, CA. The fabrication of the microreactors was done at the Institute for Micromanufacturing (IfM) of Louisiana Tech University. Aluminum tri-secbutoxide (97%) (Aldrich, USA), ferric nitrate (98+%) and cobalt nitrate (98+%) (Sigma-Aldrich, USA) were used as such for the preparation of sol-gel encapsulated catalysts. Iron oxide nanoparticles (Nano TeK®, Nanophase Technologies Corp., IL, USA) were used as received. CoO nanoparticles were prepared by chemical reduction of cobalt nitrates using Poly Vinyl Alcohol (99-100%) (J. T. Baker Chemical Co., NJ, USA) as the protecting agent. Ultra high purity hydrogen (Aeriform Corporation, Houston TX) and carbon monoxide (purity 99%, Aldrich Chemical Company) gases were used for syngas conversion studies. Ultra high purity helium (Aeriform Corporation, Houston, TX, USA) was used to dilute the gas exiting the reaction chamber prior to its analysis using a mass spectrometer (Stanford Research System QMS Series Gas Analyzer, CA, USA).

Microreactors

The reactor is a micro-scale device, 3.1 cm x 1.6 cm, with a reaction area of 1.3 cm x 1.2 cm and consists of feed inlet (for H_2, CO), product outlet and microchannels of width ranging from 5-50 µm and depth of 100 µm. Figure 1 shows SEM (Scanning Electron Microscopy) images of the microchannel reactors fabricated at IfM for



a) (b) (c) (d)

Figure1. Different designs of the microchannel reactors used for catalytic studies: a) 5 µm width straight channel; b) 50 µm width straight channel; c) 25 µm width wavy channel; d) 5 µm width zigzag channel reactor.

performing chemical reactions in the gas phase. The microreactors are made from a four-inch diameter, 500 µm thick, double side polished silicon wafer using two main processes: photo-lithography and Inductively Coupled Plasma (ICP) etching [7, 8]. The details of design, fabrication and packaging are reported elsewhere [9, 10].

Syngas conversion studies are currently being carried out in 5 µm zigzag and 25 µm straight channel reactors. This paper presents syngas conversion to higher alkanes in 25 µm channel reactor coated with alumina or silica sol-gel encapsulated catalysts.

Development of Catalyst

Aluminum tri-sec butoxide and tetraethylorthosilicate are used as the precursors for the preparation of alumina and silica sol-gel, respectively. The basic step involves acid hydrolysis followed by polycondensation to form a highly porous sol-gel network [11, 12]. Iron and cobalt metal catalysts were incorporated into alumina or silica sol-gel support using metal nitrates in the desired composition. The sol-gel/catalyst is deposited into the microchannels of the reactor. They were activated at 450 ^{o}C for alumina and 600 ^{o}C for silica support for 4 hrs. in an atmosphere of hydrogen to reduce the catalysts to their metallic form.

Characterization of the Catalyst and its Support

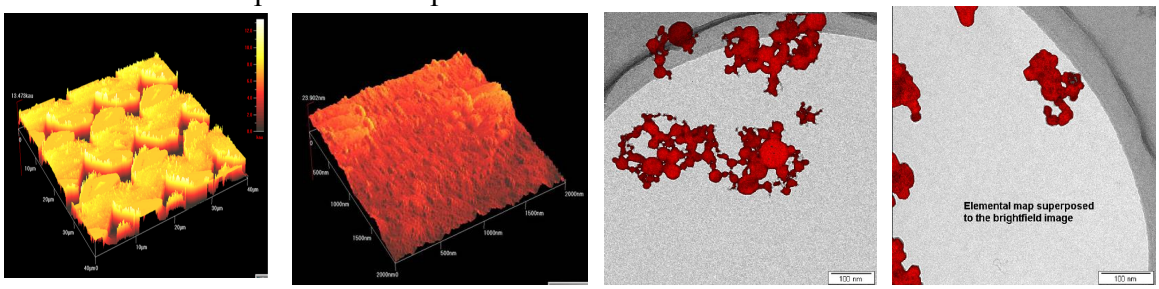
The surface area measurements for sol-gel encapsulated catalysts were performed using a Quantachrome NOVA 2000 instrument. The BET (Brunauer-Emmett-Teller) method with nitrogen as an adsorbate was used. The AFM (Atomic Force Microscopy) image was recorded using Quesant Q-scope 250 instruments. The composition of sol-gel encapsulated catalysts was analyzed using energy dispersive x-ray (EDX) attached to Carl Zeiss DSM 942 SEM. The magnetization properties of the Co/Fe encapsulated Al_2O_3 sol-gel micro-reactors are determined using 880A Digital Measurement Systems Vibrating Sample Magnetometer (VSM) before and after the reaction.

Experimental Set-up for Microreactor Studies

The experimental set-up consists of a reactor block, flow meters, pressure gauge, and a mass spectrometer. PC running LabVIEW® software is used to control and monitor the flow of feed gas and the temperature within the reactor. The effluent stream coming out of the reactor was diluted with helium prior to sampling in a mass spectrometer. The software connected to the mass spectrometer, called residual gas analyzer (RGA), collects and records the partial pressures of the outlet gases. A reference base is made by flowing CO and H_2 through the reactor without any catalyst. The partial pressures of the reactant and product gases are used to calculate conversion of CO and selectivity to higher alkanes.

RESULTS AND DISCUSSION

The AFM images of alumina sol-gel encapsulated catalysts are shown in Figures 2a and 2b. It can be inferred from Figure 2 (b) (taken on a glass slide) that the diameter of the sol-gel granules is ~ 50-100 nm. Therefore, the diameter of encapsulated metallic Fe and Co particles is expected to be less than 50 nm.



(a) (b) (c) (d)

Figure 2. AFM images of alumina sol-gel encapsulated Fe/Co catalysts (a) in the 5 µm wide zig-zag channel reactors and (b) on a glass slide. TEM images of (c) iron oxide and (d) cobalt oxide nanoparticles.

The composition of the sol-gel containing Fe and Co catalysts has been studied using an EDX spectrometer. The EDX analysis gives the details of amount of metal catalyst that has been loaded in the sol-gel coated reactor. (Table I). Although the intended metal composition of Fe and Co is 24 % (12% each), the EDX results indicate that only 4-7 % of total metal catalyst is loaded in sol-gel prepared from metal nitrate solutions. This indicates that only about 25 % of the intended metal catalysts are used for the reaction. In order to improve the metal loading, we have used commercially available nanoparticles of iron oxide and synthesized cobalt oxides as the catalyst precursors. The particle sizes of iron oxide and cobalt oxide are 10-40 nm and 15-30 nm, respectively (Figure 2 (c) & (d)). As the Table 1 indicates, the metal loading of the catalyst in the sol-gel improves significantly. This suggests that the metal oxide nanoparticles of Fe and Co are very good precursors for catalyst deposition within the microchannels compared to the metal nitrate solutions of Fe and Co.

Table1. EDX results showing the intended metal composition and the actual metal loading of iron and cobalt catalysts in alumina and silica sol-gel coated reactors.

Sol-gel Type/ Reactor	Intended Metal composition (wt %)	EDX Results	
		% Loading of Fe	% Loading of Co
Alumina sol-gel using metal nitrates	Fe12%, Co12%	2.52	3.68
Silica Sol-gel using metal nitrates	Fe12%, Co12%	2.60	2.76
Alumina sol-gel using metal oxide nanoparticles	Fe12%, Co12%	8.11	9.36

The BET surface area measurements for the sol-gel encapsulated catalysts yield an average specific surface area of 285 m^2/g for alumina and ~ 300 m^2/g for silica. This high surface area is mainly due to the high porosity of alumina and silica sol-gel observed in the AFM (Figure 2b) and SEM (not presented) images. This suggests that sol-gel is a very good support for loading the catalyst.

Conversion of CO to alkanes:

Conversion of CO to alkanes has been studied mostly in alumina sol-gel coated 25 µm channel microreactors, as the sol-gel can not penetrate well inside the 5 µm channels [9]. Figure 3 shows CO conversion in alumina sol-gel reactor to be ~ 55%. Similar studies, performed with silica sol-gel encapsulated 25 µm channel reactors in the presence of Ru-promoter, yield ~62 % conversion when the H_2: CO ratio is 3:1 (Figure 3). When this ratio is changed to 2:1, CO conversion increases to 73% [Unpublished results].

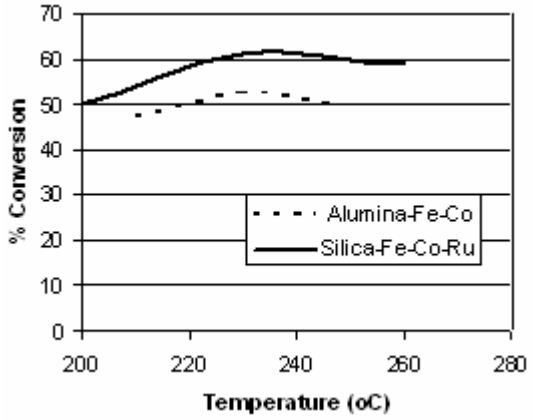


Figure 3. Conversion of syngas (H_2:CO of 3:1) in 25 µm straight channel reactors coated with alumina and silica sol-gel containing an intended 24 % Fe/Co catalysts at 1 atmosphere. The products of reaction are methane, ethane and propane (reported elsewhere) [9].

Although the conversion of CO depends on the width of the microchannels and the catalyst support, the selectivity for different alkanes does not. We could see methane, ethane and propane as the products of our reactions using a mass spectrometer. Propane has been the major product of the reaction with a selectivity up to 78%.

The stability and reusability of the catalyst have been studied using a VSM. As Fe and Co are transition elements, they have incomplete d-electron shells and unpaired

electron spins that are responsible for their specific magnetic and valuable catalytic properties. 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 [13]. To determine the nature and activity of the catalyst at different stages of preparation, magnetization studies were performed for the sol-gel encapsulated Co and Fe-catalyst coated micro-reactors after calcination, after reduction (by hydrogen) and after syn-gas ($CO+H_2$) reaction .

The catalyst in as-deposited reactor shows paramagnetic behavior mostly coming from the iron and cobalt oxides. As Fe and Co oxides are reduced to pure metals during hydrogenation, ferromagnetic behavior is observed. The saturation magnetization of the ferromagnetic component is used to estimate a lower limit of ~ 40 % for the reduction efficiency due to hydrogenation at 450^0C for 4 hrs. The ferromagnetic behavior, however, disappears in the post catalytic reaction sample. We speculate that Fe and Co are forming inactive compounds after the catalytic reactions that yields a diamagnetic curve and responsible for no or minimal catalytic activity. The magnetic data indicate that about 85% of the catalyst has become inactive after 25 hrs of catalytic reaction.

CONCLUSION

Conversion of syngas (CO: H_2) to alkanes in 25 μm channel microreactor coated with sol-gel encapsulated Fe/Co-nanocatalysts has been investigated. Characterization of these catalysts containing Co and Fe in alumina and silica sol-gel has been studied by several techniques: BET, SEM, AFM, EDX and VSM. The average specific surface area is ~285 m^2/g for alumina and 300 m^2/g for silica sol-gel encapsulated catalysts. Hydrogenation-reduction efficiency of the activated Fe-Co catalysts and the level of poisoning after the reaction are estimated using a VSM. In overall, 85% of the catalyst is poisoned after 25 hrs of catalytic reaction. The surface area analysis and the syngas conversion results indicate that silica sol-gel matrix may be a better catalyst support than alumina for these reactions.

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