Silica Aerogel Supported Catalysts for Fisher-Tropsch Synthesis

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Introduction

The production of hydrocarbons from Fischer-Tropsch synthesis has been known for nearly a century.[1] The reaction occurs using a heterogeneous catalyst typically composed of iron, cobalt, or ruthenium as the active catalyst supported on an inert oxide such as silica, titania, or alumina. While a vast amount of research has been conducted on modifications of the active catalyst in order to achieve improved reactivity or selectivity, the morphological properties of the oxide support have not received as much attention.

Sol-gel derived silica provides a unique method of creating and controlling texture and porosity of a silica catalyst support. The resulting silica can exist as a relatively dense, microporous xerogel[2] or it can be synthesized as a non-dense, mesoporous aerogel.[3] The three dimensional structure and porosity properties of silica aerogel[4] impart certain advantages over traditional oxide supports. Surface area can be high (>800 m^2/g), average pore size is in the mesoporous regime (2-50 nm), and the pores exist as an interconnected network. These properties lead to enhanced mass transport of reactant molecules to and product molecules away from the active metal surface. In addition, if the size of the metal particle is larger than the pore size of the support, the metal particle is effectively locked into position. This should allow for catalytic reactions to take place at high temperature without the risk of sintering the catalyst.

Experimental

Cobalt Catalyst Preparation. Aerogel supported catalysts were prepared by a modification of a published procedure.[5] A mixture of tetramethoxysilane (Aldrich, 98%) and methanol (Aldrich, spectrophotometric grade) was prepared by combining 15 mL of each reagent. The mixture was stirred until homogeneous. A solution consisting of 7.5 mL of methanol, 6 mL of water (Aldrich, HPLC grade), and 0.75 mL of 2.8% NH_4OH (Mallinckrodt, AR grade) was added to the previously prepared solution and mixed until homogeneous. Cylindrical, polyethylene forms were filled with 10 mL of the sol and gelation occurred in 10 minutes. The gels were aged in their forms for 14 days. The solid gels were removed from their forms and solvent exchanged with ethanol (Aaper, absolute), four times for four hours each, then loaded with $Co(NO_3)_2$ by soaking the gel in an ethanolic solution of $Co(NO_3)_2 \bullet 6H_2O$ of a known concentration. The concentration of $Co(NO_3)_2$ was chosen to yield a catalyst which contained either 2% or 6% by weight Co. The aerogel was formed by removing the ethanol as a supercritical fluid (T_c = 243 ^oC, P_c = 926 psi). The $Co(NO_3)_2$ loaded gels were transferred into a 42 mL autoclave and the remaining volume of the autoclave was filled with the $Co(NO_3)_2$ solution. This prevents leaching of the salt during the drying process. The autoclave was sealed and heated to 250 ^oC at 5 ^oC / min, then to 300 ^oC at 1 ^{o} C/ min. The pressure was allowed to rise to 1800 psi and maintained at this pressure by slowly venting the autoclave. The autoclave was held at 300 ^oC for 1 hour, then slowly vented to atmospheric pressure over a 1 hour period. After cooling to room temperature, the aerogels were removed from the autoclave and calcined in static air at 500 ^oC for 8 hours. The aerogel was crushed, sieved for size, and reduced in flowing hydrogen at 500 ^oC for 4 hours. The resulting aerogel supported catalyst appeared black and showed ferromagnetism indicating successful reduction to metallic cobalt.

Ruthenium Catalyst Preparation. Undoped aerogels were prepared according to the above procedure, then loaded with ruthenium by subliming an open ruthenocene, bis(2,4-dimethylpentadienyl)ruthenium,[6] into the crushed aerogel at reduced pressure.[7] The aerogel gradually took on the color of the open ruthenocene. The open ruthenocene was decomposed to an oxide by heating in flowing oxygen at 300 ^oC. The oxide was reduced to metallic ruthenium by reducing in flowing hydrogen at 500 ^oC. The resulting catalyst contained 10% Ru by weight.

Catalyst Testing. All aerogel supported catalysts were evaluated in a laboratory-scale, packed bed reactor. 240 mg of the catalyst was loaded into a ¼ inch OD, stainless steel tubular reactor and held in place with quartz wool. H_2 and CO were introduced into the 265 ^oC reactor by means of mass-flow controllers. The carbon monoxide was passed through a trap containing PbO_2/Al_2O_3 (Engelhard, E-315) to remove any $Fe(CO)_5$ impurity before entering the reactor. The pressure inside the reactor was maintained at 100 psi with a back-pressure regulator. Hydrocarbon products larger than C_6 were analyzed by means of online GC/MS. Reactants and hydrocarbon products smaller than C_7 were analyzed by an online GC equipped with both TCD and FID detectors. Argon was employed as an internal standard in all measurements.

Results and Discussion

A transmission electron micrograph of the reduced 2% Co catalyst appears in Fig. 1. The aerogel support appears as semi-transparent background and the metallic cobalt appear as well-dispersed particles within the support. The cobalt particle size appears remarkably uniform at approximately 50 nm.

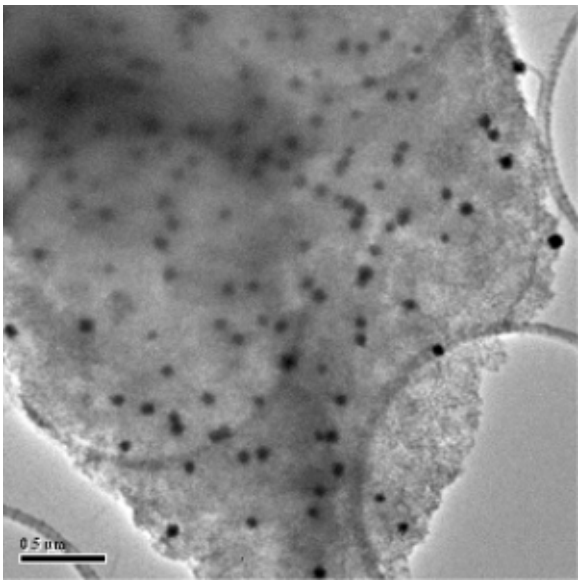

Figure 1. Transmission electron micrograph of the 2% Co catalyst supported on silica aerogel. The particles of metallic cobalt are observed as black dots surrounded by the amorphous aerogel structure.

All the catalysts tested were active towards the Fischer-Tropsch synthesis and product distributions that resulted are shown in Fig. 2. The 10% Ru catalyst was the most active at nearly 50% CO conversion and was selective towards hydrocarbons between C_8 and C_{12}. The cobalt catalysts were less active than the ruthenium catalyst with CO conversions of about 5% for the 2% Co and 22% for the 6% Co catalyst. While these product yields are not exceptionally high compared with traditional catalysts, the amount of actual metal loaded into the reactor is quite small. For the 2% Co catalyst, only 4.8 mg Co is present in the reactor.

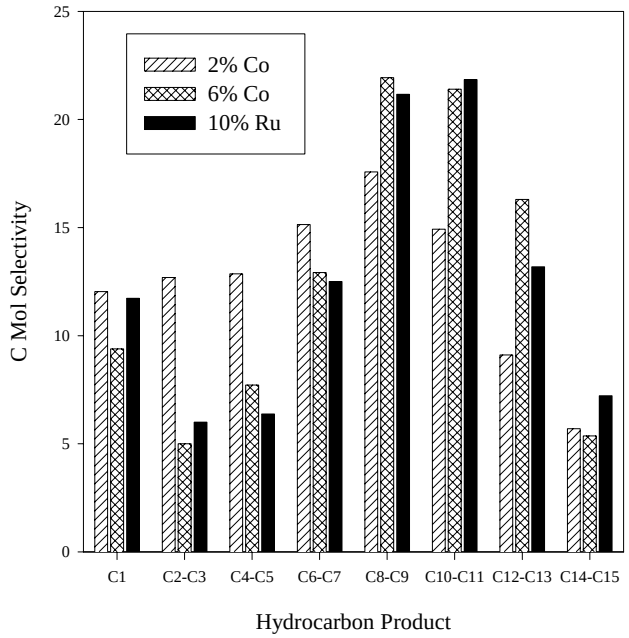

Figure 2. Hydrocarbon product distribution from 3 aerogel supported catalysts. Reaction conditions: 265 ^{o}C, 100 psi, H_2 at 36 sccm, CO at 18 sccm. The hydrocarbons have been grouped in pairs, except for methane, for the sake of clarity.

All three catalysts showed selectivity for hydrocarbons between C_8 and C_{12}. The ruthenium catalyst was particularly selective for this fraction with greater than 50% C mol selectivity for this hydrocarbon range. It has been speculated that increases in mass transport within the catalyst will tend to favor larger hydrocarbon products.[8,9] The nature of the aerogel support leads to high mass transport which in turn leads to higher selectivity towards larger hydrocarbons.

One surprising result was the percentage of olefins produced for the larger hydrocarbons. Fig. 3 shows the fraction of each carbon number which was detected as the 1-olefin. The high production of olefins is probably a direct result of the high mass transport within a catalyst particle. It has been theorized[10] that desorption of the growing hydrocarbon chain from the surface of the catalyst particle yields an olefinic species which then undergoes hydrogenation to yield the saturated hydrocarbon. With high mass transport in the catalyst, the olefinic species can easily diffuse away from the surface of the metal and not undergo hydrogenation. The olefin is then seen in the product stream.

Conclusions

Catalysts containing cobalt or ruthenium supported on silica aerogel have been synthesized and tested for activity towards the Fischer-Tropsch synthesis. After preparation and reduction, TEM indicates that the cobalt exists as discrete particles (diameter ~50 nm) suspended within the silica aerogel matrix. The catalysts are particularly selective towards hydrocarbons in the C_8 to C_{12} range with greater than 50% C mol selectivity for this fraction. The mesoporous nature of the aerogel, as well as the interconnected pore network, lead to high mass transport of H_2 and CO to the metal surface and facilitate diffusion of desorbed products away from the surface. This mass transport effect is suggested by the large fraction of each hydrocarbon which exists as the 1-olefin and the selectivity towards larger hydrocarbons.

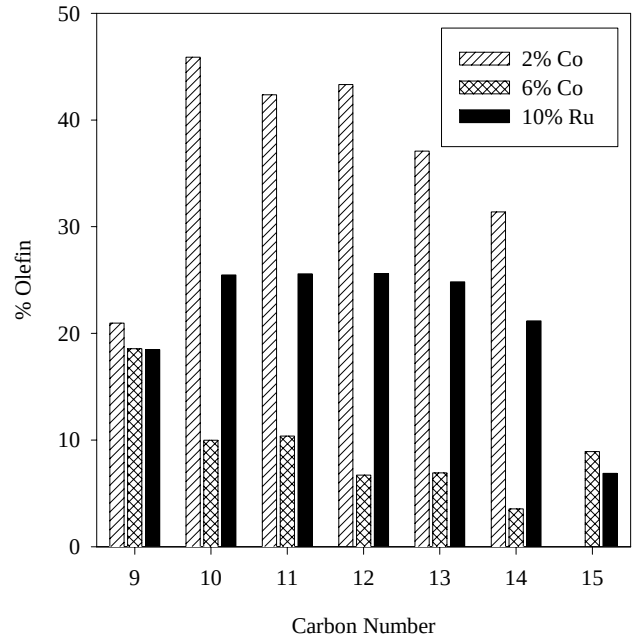

Figure 3. Fraction of each carbon number product which was detected as the olefin. Reaction conditions: 265 ^{o}C, 100 psi, H_2 at 36 sccm, CO at 18 sccm.

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