Fischer-Tropsch Catalysts Supported on Sol-Gel Derived Silica

Departments of Chemistry and Chemical and Fuels Engineering
University of Utah
Salt Lake City, UT 84112

Introduction
Fischer-Tropsch synthesis has traditionally employed heterogeneous catalysts supported on metal oxides such as alumina, silica, or titania. The metallic catalyst is typically loaded onto the support using either an impregnation or coprecipitation technique. Neither of these methods allows for strict control over the support properties which can play a crucial role in the Fischer-Tropsch synthesis. Employing the sol-gel method to prepare amorphous silica from the polycondensation and hydrolysis of a suitable precursor, such as tetramethoxysilane, allows for control and manipulation of bulk support properties such as density, strength, pore diameter, and pore volume. The properties of the silica prepared by the sol-gel process can range from relatively dense, microporous xerogel to non-dense, mesoporous aerogel and can be controlled at all points in this continuum.

Heterogeneous catalysts prepared using sol-gel derived supports include platinum, iron, silver, gold, cobalt, and palladium. Fischer-Tropsch synthesis is typically performed utilizing either a cobalt or iron-based catalyst and the support properties greatly influence the product distribution by influencing heat and mass transport near the active metal catalyst particles. Sol-gel derived silica provides a unique opportunity for controlling the support properties and thus influencing the product distribution.

Experimental
Catalyst Preparation. The catalysts employed for Fischer-Tropsch synthesis were prepared by the sol-gel method. Water, methanol, and tetramethoxysilane (TMOS) were combined in a 16:4:1 molar ratio. An appropriate metal salt (Co(NO₃)₂, Fe(NO₃)₃, RuCl₂) was dissolved in the water to yield 5-30% by weight of the final material. The mixture was sealed in glass vials and allowed to gel and age for 14 days. The xerogels were obtained by allowing the methanol and water to evaporate under ambient conditions over a period of 14 days. The xerogels were then crushed, reduced by heating in a stream of hydrogen, and sieved for size.

Fischer-Tropsch Synthesis. The reaction between H₂ and CO was carried out in a continuous flow reactor, 6 inches by 0.25 inch in diameter. Approximately 2 g of catalyst was used for each trial and discarded after the experiment. The flow of the reactants and carrier gas were maintained with appropriate mass-flow controllers (MKS Model 1179A) and the entire reactor system, including the transfer line, was heated to ensure that no condensation of the reaction products occurred. Routine measurement of reaction products was performed with online GC monitoring and reaction product identification was performed by condensing into cold n-octane, and analyzing by off-line GC/MS.

Results and Discussion
Catalyst Characterization. One of the catalysts was examined to determine some of the porosity properties of the sol-gel derived silica and the nature of the active metal catalyst, cobalt. Table 1 lists the specific surface areas of three different xerogel catalysts: unreduced Co(NO₃)₂, metallic cobalt, and a mixture of metallic cobalt and iron.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m² / g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NO₃)₂</td>
<td>134</td>
</tr>
<tr>
<td>Co⁰</td>
<td>338</td>
</tr>
<tr>
<td>Co⁰/Fe⁰</td>
<td>245</td>
</tr>
</tbody>
</table>

Table 1. BET Surface Areas

As can be seen from Table 1, the xerogel-based catalysts possessed a significant amount of surface area. The apparent increase in surface area upon reduction of the catalyst is most likely caused by expulsion of water and methanol, produced in the sol-gel reaction, from the pores of the catalyst when the catalyst was heated in a stream of hydrogen.

During reduction with hydrogen, the catalyst noticeably changed color from red (hydrated Co(NO₃)₂) to black and became ferromagnetic. This visual indication of reduction was confirmed by XRD analysis which indicated the presence of metallic cobalt and cobalt oxide. The XRD analysis also showed that the cobalt particles were about 6 nm in diameter.

**Fischer-Tropsch Synthesis.** Four different catalysts were employed to convert a mixture of hydrogen and carbon monoxide into higher hydrocarbons. Initial experiments were conducted using the cobalt xerogel and condensing the reaction products in cold n-octane. Figure 1 shows an offline GC/MS chromatogram of the product mixture. Hydrocarbons lower than C₆ were not observable due to their volatility and the presence of the octane. The apparent product distribution is centered around C₁₅ and the heaviest hydrocarbon observed was C₃₂. Each hydrocarbon consisted primarily of the n-alkane, but significant amounts of single unsaturated hydrocarbons were seen for the lower hydrocarbons (C₄ – C₁₅).

![Figure 1](image-url)

Figure 1. GC/MS chromatogram of Fischer-Tropsch product using 25% by weight cobalt xerogel catalyst. Reaction temperature was 225 °C and pressure was 30 psi.

Routine experiments were performed with online GC/FID detection of reaction products. Figure 2 shows a chromatogram of the reaction products using an identical catalyst as that used in Figure 1. The lowest hydrocarbons, C₁ through C₄, are not well resolved with C₅ appearing at about 7 minutes. The heaviest hydrocarbon observed with online monitoring was C₁₈ rather than C₃₂ as seen previously. Either the heavy products were not present in
high enough concentration for detection or the products were condensing somewhere in the reactor system prior to GC analysis.

Figure 2. Online chromatogram of Fischer-Tropsch product using 25% by weight cobalt xerogel catalyst. Reaction temperature was 225 °C and pressure was 30 psi.

A mixed cobalt/iron catalyst was used in the reactor and the product distribution is shown in Figure 3. The lower hydrocarbons can be seen prior to five minutes and appear to be somewhat resolved. Only a trace of heavy hydrocarbons was produced using this catalyst. Overall, the mixed cobalt/iron catalyst is much less active compared to the catalyst that contains only cobalt, although this may simply be caused by the different loadings of the cobalt.

Figure 3. Online chromatogram of Fischer-Tropsch product using 15% by weight cobalt and 15% by weight iron xerogel catalyst. Reaction temperature was 225 °C and pressure was 30 psi.

Nickel and cobalt were combined during the sol-gel preparation of another catalyst and the Fischer-Tropsch product distribution appears in Figure 4. Very small amounts of hydrocarbon products were detected using this catalyst. However, the catalyst appears to be more selective for the heaviest hydrocarbons compared with either the cobalt only or cobalt / iron catalyst.

All of the catalysts have high selectivity towards the lower hydrocarbons, C$_1$ through C$_4$, which is undesirable. It should be possible to alter the reaction conditions (temperature, pressure, reactant flow rate, residence time) to decrease the selectivity for the lower hydrocarbons and increase the selectivity for higher hydrocarbons. It is possible that these sol-gel silica supported catalysts may be more sensitive to reaction conditions than traditional catalysts. The cobalt likely resides in pores of the amorphous silica rather than simply on the outside surface of the support. This should provide for mass and heat transfer properties which are different than traditional catalysts.

Figure 4. Online chromatogram of Fischer-Tropsch product using 15% by weight cobalt and 15% by weight nickel xerogel catalyst. Reaction temperature was 225 °C and pressure was 30 psi.

Additional experiments are currently underway to more fully characterize the support properties and to prepare a series of catalysts with a range of pore sizes and volumes to determine their effects on the Fischer-Tropsch synthesis.

Conclusions
The sol-gel technique for preparing amorphous silica is capable of incorporating metal salts into the structure of the support and, after reduction, the catalysts are active for Fischer-Tropsch synthesis. The unique nature of the sol-gel chemistry should allow for strict control and manipulation of the support properties in order to tune the catalyst for a desired product distribution.

Acknowledgement. The authors would like to thank Dr. M. Seehra and Dr. A. Punnoose of West Virginia University for performing the XRD analysis and Dr. R. Cutler and Lyle Miller of Ceramatec, Inc. for performing the BET analysis. The financial support of the Consortium for Fossil Fuel Science (CFFS) is gratefully acknowledged.

References