Silica Xerogel Supported Cobalt Metal Fischer–Tropsch Catalysts for Syngas to Diesel Range Fuel Conversion

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Received September 19, 2003. Revised Manuscript Received June 21, 2004

Fischer–Tropsch synthesis of diesel range straight-chain hydrocarbons from CO and H2 over a cobalt nanoparticle catalyst supported by a mesoporous silica xerogel is reported. A possible advantage of sol–gel-derived catalyst supports is the tunability of their porosity to favor synthesis of diesel range hydrocarbons. The preparation of the xerogel supports, optimal loading of the supports with cobalt, the percent conversion of syngas to Fischer–Tropsch hydrocarbons, a gas chromatography–mass spectrometry analysis of the diesel range product distribution, and characterization of the catalysts are reported.

The Fischer–Tropsch (FT) synthesis of hydrocarbons from carbon monoxide and hydrogen over transition-metal catalysts is now more than 80 years old.1 It was recently reported2 that Sasol, an oil and chemicals producer in South Africa, synthesizes crude oil by the FT method for $8.00/bbl. The continuing interest in FT synthesis arises as much from the purity of FT hydrocarbons prepared from syngas as from the potentially low price of FT crude oil compared to that of the steadily diminishing world supply of petroleum.

Only a few of the many papers in the voluminous FT literature will be cited here to put the present study in context. The most frequently studied transition-metal FT catalysts are iron and cobalt, and there is growing interest in bimetallic catalysts wherein each metal possesses FT activity.3 Although cobalt is more costly than iron, supported cobalt is valued as a FT catalyst because of its stability, high activity, and low yield of oxygenated products. Focusing on cobalt-based catalysts, experimental factors3 recognized to play an important role in how well a FT catalyst performs include the operating temperature, operating pressure, particle size of the cobalt metal, oxidation state of the cobalt, number of surface defects that will become active sites, identity of the high surface area solid supporting the cobalt, pore sizes in the support material, total surface area of the support, presence of additive metals, and calcination and reduction temperatures.

Low-temperature (below 250 °C) FT synthesis is aimed at high wax production, whereas high-temperature (340 °C) FT synthesis produces alkenes, gasolines, and methane.4 There is evidence5 that one obtains a greater number of active sites as cobalt oxide is reduced to cobalt metal when cobalt is supported by alumina. Titania, silica, and zirconia are steadily less effective supports in that order. One way of producing a high surface area support for a cobalt FT catalyst is to combine a cobalt salt with a silica precursor such as tetraethoxysilane.6 The resulting liquid sol is dried to a gel that can be calcined and reduced. The “xerogel” thus produced contains dispersed nanoparticles of cobalt trapped in a silica glass of high porosity.

The catalytic activity of cobalt supported on mesoporous silica is influenced by two main factors: (1) the size of the cobalt particle, which impacts the reducibility of the cobalt,7,8 and (2) mass transport within a catalyst pore, which can alter the product distribution.8–10 When

The ability to easily alter the pore structure of a mesoporous support is provided that the cobalt particle is in the size of the pores directs the size of the resulting cobalt nanoparticles of either cobalt or cobalt oxide. The cobalt within the catalysts was characterized by XRD, SQUID magnetometry, and electron magnetic resonance (EMR). The XRD measurements indicate the presence of SiO$_2$, CoO, and Co$_0$. The ratio of Co$^2+$ to Co$^0$ increases as a function of loading. The widths of the XRD lines were used to estimate the CoO particle size at 6 nm. One catalyst, 5% Co, was examined after reaction, and Co$^0$ was detected that was not present prior to reaction. SQUID magnetometry indicated both CoO and Co$^0$ and showed the characteristic signature of a ferromagnet (Co$^0$) with an antiferromagnet (CoO) manifested in a shifted hysteresis loop. This suggests that Co$^0$ and CoO exist in a core–shell arrangement most likely with the CoO core inside a Co$^0$ shell. The presence of Co$^{2+}$ detected by EMR spectroscopy in all of the catalysts is consistent with incomplete reduction of CoO to Co$^0$.

The four xerogel supported catalysts were tested for activity in a laboratory packed-bed reactor. H$_2$ and CO were introduced in a 2:1 ratio and were mixed with helium to moderate the conversion and prevent excessive heat generation from the exothermic FT reaction. The CO conversion as a function of cobalt loading is presented in Table 1. The catalyst with the smallest cobalt impregnation onto a mesoporous support, the size of the pores directs the size of the resulting cobalt particle provided that the cobalt particle is in the mesopore and not on the surface of the support. The present sol–gel preparation is different from an impregnation method in that the cobalt is added before the support is formed; therefore, the structure of the support cannot influence the cobalt particle size. Changes in the product distribution as a function of the pore size have been attributed to restrictions on the mass transport within a catalyst particle but others have attributed the product distribution shift to changes in the product of a reaction with the pore size being a factor. The ability to easily alter the pore structure of sol–gel derived silica over an extremely wide range from dense xerogel to ultralight aerogel should allow for future investigations of the underlying mechanism provided the catalysts are active toward FT synthesis. The present work describes the catalytic behavior of silica xerogel supported catalysts.

Four cobalt on silica xerogel catalysts have been synthesized using a sol–gel route beginning with tetramethoxysilane. The nominal cobalt loading was 5%, 10%, 15%, and 20%. The catalysts were characterized by N$_2$ adsorption to determine the surface area, pore volume, and average pore diameter. X-ray diffraction (XRD) measurements were conducted to investigate the oxidation state of the cobalt prior to its use as a catalyst and after reaction to evaluate changes that occurred as a result of exposure to reaction conditions. The catalysts were tested in a laboratory-scale packed-bed reactor with online monitoring of the product stream with gas chromatography–mass spectrometry and gas chromatography with thermal conductivity and flame ionization detectors. Details of the experimental procedures can be found in the Supporting Information.

Surface area and porosity properties of the four xerogel supported catalysts are listed in Table 1. As the loading of cobalt increases from 5% Co to 20% Co, the surface area decreases from 485.2 to 229.0 m$^2$/g while the average pore diameter increases from 2.21 to 4.52 nm. The decrease in the surface area is likely caused by filling in the micropores of the xerogel support with nanoparticles of either cobalt or cobalt oxide. The increase in the average pore diameter with increasing cobalt loading was an unexpected result. The cause of this phenomenon is likely the dynamic nature of the formation of the xerogel from the wet gel. The wet gel consists of small particles of amorphous silica held together with relatively weak surface interactions. As the solvent evaporates from the pores of the wet gel, stress on the surrounding particles of silica is not uniform. This differential stress results in collapse of the pores and a decrease in the bulk volume by a factor of 8. Crystals of Co(NO$_3$)$_2$ form when the solubility limit is surpassed during solvent evaporation, and the silica particles must collapse around the Co(NO$_3$)$_2$ particle. The pore that remains when Co(NO$_3$)$_2$ is reduced to Co$^0$ is related to the size of the original Co(NO$_3$)$_2$ crystal. As the concentration is increased from 5% to 20%, larger crystals result and therefore larger pores are left behind.

Transmission electron microscopy (TEM) micrographs of the 10% Co and 20% Co xerogel supported catalyst samples are shown in Figure S1 of the Supporting Information. The metallic cobalt particles are easily distinguished from the surrounding amorphous silica because of mass thickness contrast as well as lattice fringes in Co single crystals. The 10% Co sample indicates reasonably uniform particles with a diameter of approximately 7 nm. However, the limited field of observation may be giving a false impression of the uniformity of the particle size. The 20% Co sample shows cobalt particles with vastly different sizes, one spherical particle of about 15 nm diameter and one oblong particle of 25 nm x 37 nm. The size of the cobalt particles from the TEM images is consistent with the XRD data.

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amount of cobalt showed virtually no activity and the most heavily loaded catalyst showed the most activity with a CO conversion of 13.4%. This activity is considerably lower than the 84–89% conversion reported for a cobalt catalyst prepared from cobalt nitrate and supported on mesoporous silica. The incorporation of helium in the present experiments and incomplete reduction of cobalt oxide to metallic cobalt both tend to decrease FT activity.

The selectivity toward producing hydrocarbons is shown in Figure 1. As the loading of cobalt is increased, the fraction of heavier hydrocarbons increases. The C8–C10 fraction increases from 16.8% to 24.2%, the C11–C13 fraction increases from 3.8% to 12.6%, and the C14+ fraction increases from 1.8% to 4.6%. Hydrocarbons heavier than C17 were not detected with the present catalysts. In going from 10% Co to 20% Co, the total C8+ fraction increased from 22.3% to 41.4%. This C8+ fraction is similar to the 30% selectivity reported for the C10–C20 fraction. The inclusion of C8 and C9 in the present work accounts for the apparent difference. The shift in product distributions toward larger hydrocarbons may result from the different pore size of the catalysts. The present results indicate that, as the average pore size of the xerogel support increases, the product distribution shifts away from smaller hydrocarbons and toward larger hydrocarbons. The present results cannot distinguish between the mass-transport restriction theory and the changing gas adsorption theory, but the overall trend of larger pores leading to larger hydrocarbons is consistent with previous reports. Because the pore size of xerogel supports can be controlled during preparation, the FT product distribution can be directed toward the diesel fuel fraction.

Summary
A series of xerogel supported catalysts containing metallic cobalt have been prepared, characterized, and tested for FT activity. Brunauer–Emmett–Teller surface area measurements indicated that increases in the loading of cobalt lead to lower surface area, presumably because of the filling of micropores of the xerogel support. The average pore size of the support increased as a function of cobalt loading from 2.21 nm for the 5% Co catalyst to 4.52 nm for the 20% Co catalyst. TEM micrographs indicate the presence of uniform, 7-nm-diameter metallic cobalt particles in the 10% Co catalyst. However, TEM micrographs of the 20% Co catalyst indicate increased cobalt particle size heterogeneity. The lowest loading of cobalt on silica xerogel, 5% Co, showed no FT activity, while the most heavily loaded catalyst, 20% Co, converted 13.4% of the CO. The incomplete reduction of the catalyst to the Co0 state is likely responsible for the lack of optimum conversion. The selectivity toward diesel range hydrocarbon products increased as a function of increased cobalt loading and reached a maximum value of 41.4% for the C8+ fraction.

Acknowledgment. Financial support by the U.S. Department of Energy, Office of Fossil Energy, under Contract DE-FC26-02NT41954 is gratefully acknowledged.

Supporting Information Available: A detailed experimental procedure, TEM images, X-ray diffractograms, and magnetic susceptibility data are included in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

EF034059D