

Paper 727b: Fischer-Tropsch Synthesis: Effect of Support Surface Area and Calcination Temperature on the Performance of Silica Supported Catalysts

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Abstract

The effects of calcination temperature and silica support structure on silica-supported cobalt FTS catalysts were studied. The catalysts were prepared by the incipient wetness impregnation of the cobalt precursor using various surface area silica supports. The catalysts had different drying and calcination temperatures. Deionized water was used as preparation medium. Lower surface area and calcination temperature catalysts exhibited higher activity due to lower support-cobalt phase interaction. Co/silica catalysts calcined at 573 K showed the highest CO conversion and the lowest CH₄ selectivity. Catalysts with lower surface area exhibited higher C₅₊ selectivity due to higher reducibility and dispersion. The properties of various catalysts were characterized by FTIR, XRD, BET and XPS techniques.

Introduction

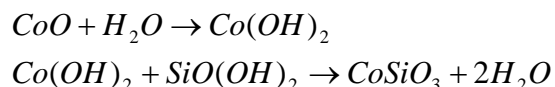
The increased global demand for clean fuels has led to increased interest in the production of clean fuels from sources other than petroleum. The use of natural gas has been attractive because of its clean burn and abundant supply. Fischer–Tropsch synthesis (FTS) is a promising way to convert coal, biomass and natural gas to clean fuels and chemicals via syngas. However, improvements in yield and selectivity of the FTS step are the key to making this process a commercially viable way to produce clean fuels from alternative sources. Cobalt-based catalysts are advantageous for the conversion of natural-gas-derived syngas because they are relatively inexpensive and have low water-gas shift activity [1]. Supported Co catalysts can be used for the synthesis of high molecular weight, paraffinic waxes which can be hydro cracked to produce clean diesel and aviation fuels.

Silica supports provide a porous framework permitting access to the active phase (Co⁰) for the reactants and free exit for the products from the catalyst particles. The high surface area silica support is able to disperse the active phase in order to increase the active surface in contact with the reactants (CO and H₂). Silica is known to have high mechanical and thermal stability in order to avoid surface area collapse during reaction or oxidative regeneration which can induce the formation of hot spots. Hot spots are one of the major problems in industrial FTS reactors. However, high reaction or calcination temperatures can result in the support sintering due to low thermal conductivity in silica. Other benefits of selecting silica as a support are that it's chemically resistant, cheap, abundant and not strategically limited.

The FTS takes place on active sites located on the surface of crystalline (Co⁰) metal formed by reduction. The chemical and texture properties of the support influence the catalytic activity and product selectivity of Co catalysts, via their modifications on the reducibility and dispersion of cobalt or the formation of well-defined phases. These oxide phases are considered desirable and easily reduced to active metallic Co⁰ particles [2]. Catalyst activity, selectivity, deactivation, and active site density has been linked to cobalt crystallite size and support interaction [1-3]. It was found that under typical FTS conditions, cobalt particles with

diameters less than 10-nm are easily oxidized in the presence of steam to cobalt oxides such as CoO. The oxides, in turn, can react irreversibly with an alumina support to form cobalt-aluminate species [4]. Carbon nanofibers have been proposed as an inert support, however, effective cobalt dispersion, uniform size/quality control as well as cost has been problematic [2]. The number of active sites is determined by the Co particle size dispersions, loading amount, and reduction degree [2, 3]. Synthesis of highly dispersed Co catalyst requires strong interaction between the support and the Co precursor, but in turn, such strong interactions generally lower reducibility of such precursors and promote the formation of undesired phases such as cobalt silicate [4]. Sun et al. [5] found that the texture, crystallite phase and acidity of silica could be influenced by the hydrothermal treatment with some solutions and hence the reducibility of supported cobalt was closely associated with the silica surface properties. On the other hand, the concentration, distribution, and nature of hydroxyl groups (silanols) on the silica surface also play an important role in the dispersion of supported metal on the silica [6]. Ming and Baker [7] reported that the catalytic performance of a cobalt–silica gel FTS catalyst was strongly affected by preparation condition such as pH value of solution containing the precursor, because the pH value of impregnation solution changed the interaction of cobalt and silica support, resulting in different dispersion and reducibility of supported cobalt.

Most of the work done to date on Co/silica supported catalyst is on the Co dispersion, reduction, preparation and pore size distribution. In the present work, the Co-support interaction is studied and its effect on the formation of undesired cobalt silicate phase and in turn, its influence on the activity and performance of the catalyst. Once formed, it's difficult to reduce this phase to active metallic sites at FT reaction temperatures [8]. It's known that this phase forms due to the reaction of finely dispersed cobalt oxide and the silica support in the presence of water during reduction according to the following reaction [9]:



It has been proposed that the silica forms silanol groups on the surface following impregnation in water [8]. The active silanol group forms salicylic acid which reacts with Cobalt hydroxide to form highly amorphous inactive cobalt silicate [9]. Another aspect of this work is that the silica support was pretreated by organic solvent at room temperature before impregnation of cobalt, such as ethanol to adjust the surface properties of silica support without changing the pore structure of support. The pretreatment of the support was expected to improve the activity of catalyst due to better dispersion of the Co particles after impregnation resulting in increased surface area of the reaction and lower Cobalt oxide-support interaction in the absence of water [8, 9].

Experimental

Commercially available silica gel (Davisil grade 646, 635 and 710) were used as a support in this study. The aqueous solution of cobalt nitrate was impregnated onto the silica supports by incipient wetness method using appropriate volume of deionized water. Capillary action draws the solution into the pores (Ammonium hydroxide was added to adjust the pH). The catalyst can then be dried and calcined to drive off the volatile components within the solution, depositing the metal on the catalyst surface as oxides (CoO and Co₃O₄). The loading

of cobalt was 20 wt% for all catalysts. The particle size was kept between 0.25-0.5mm. Structural properties, drying and calcination times and temperatures are shown in Table 1.

Table 1: Silica support structural properties used in preparing the catalyst samples and their drying and calcination conditions.

Davisil Silica support	Pore vol. (cm ³ /g)	Pore Dia. (nm)	Surface area Before reaction (m ² /g)	Drying Temperature/ Time (K)/ (hr)	Calcination Temperature/ Time (K)/ (hr)
300Co-1	1.15	15	300	298/ 24	573/ 3
480Co-2	0.75	6	480	298/ 24	573/ 3
560Co-3	0.7	5	560	298/ 24	573/ 3
300Co-4	1.15	15	300	393/ 16	673/ 3
300Co-5	1.15	15	300	393/ 16	773/ 3

The catalysts were dried and calcined according to the table above. Then, the calcined samples were reduced with H₂ at 673 K for 12 hr at high space velocity (2000/hr) and 1 bar. The ramping rate was 1K/min. Co/silica catalyst ID: 300Co-1 was used as a reference.

The FTS reaction was carried out in a fixed-bed catalytic reactor tube with an inner diameter of 4mm loaded in a programmable furnace. The reduced catalyst of 1.0 g was loaded vertically in the reactor. Void fraction was calculated to be around ~15%. Gas handling was performed via programmable mass flow controllers with a static, inline mixer prior to the furnace inlet. The reaction conditions were P (total) = 0.7 MPa, T = 503 K, CO/H₂ = 1/2. Reaction gas space velocity was (1500/hr). The effluent gas from the reactor was analyzed by on-line FTIR. The analysis of hydrocarbons dissolved in a solvent after cooling in the trap was carried out with GC-FID using a special customized DB-2887 column. The reaction time was as long as 48 hr, and the activity of the catalyst was very stable.

A BIO-RAD Excalibur (FTS3000) FTIR equipped with a permanently aligned gas cell was used to analyze the continuous flow of gaseous products. The 60mm diameter gas cell provides an infrared beam path length of 2.4m and consisted of a borosilicate glass body with a KBr window and a total volume of 0.1 liter. The detector is a mercury cadmium telluride (MCT), linearized, with an effective range of analysis between 600 and 4000 cm⁻¹ wavenumbers. A Pike-Technologies diamond MIRacle single reflection horizontal attenuated total reflectance (HATR) unit designed for use in FTIR spectrometer was utilized in obtaining spectra of the fresh, calcined and reacted powder catalyst.

An X-ray diffractometer (Philips Pananalytical X'Pert) was utilized to characterize the catalyst using Cu K α radiation in a step-scan mode. It was also used to detect supported cobalt crystalline size of the catalysts. The crystalline average size was calculated by $L = K\lambda / \Delta (2\theta) \cos\theta_0$, where L is the crystalline size, K is a constant (K = 0.9–1.1), λ is the wavelength of X-ray (Cu K α = 0.154 nm), and $\Delta (2\theta)$ is the width of the peak at half height.

Results and discussion

To investigate the effects of different silica support surface area and calcination temperatures on the activity of Co/silica catalysts, FTS reaction was conducted for 48hrs in a

fixed-bed micro reactor. Table 2 shows catalyst performance parameters for all catalyst samples after reaching steady state (6hrs).

Table 2: Catalytic performance of cobalt silica-supported catalysts in FT synthesis.

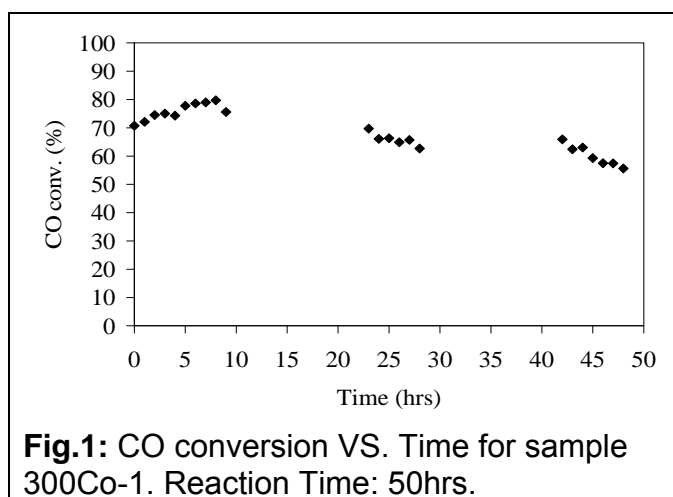
Davisil Grade, ID	STY ^a (g HC/L.hrs)	Activity ^b (hr ⁻¹)	CO conv. (%)	Selectivity (%)		
				CH ₄	CO ₂	C ₂₊
300Co-1	137	0.29	78.1	4.7	8.6	86.7
480Co-2	125	0.26	70.7	10.4	9.3	80.3
560Co-3	98	0.20	62.4	9.5	14.8	75.7
300Co-4	86	0.18	59.3	8.4	15.7	75.9
300Co-5	74	0.15	55.6	8.3	21.0	70.7

Reaction conditions: 0.7 MPa, 503 K, CO/H₂ = 1/2, gas space velocity 1500/hr
 Weight of catalyst = 1 g, Co loading = 20wt%

^a Space time yield (STY): Grams hydrocarbon product per catalyst bed including voids in Liters. * Hours operation.
^b Activity: Grams hydrocarbon product/ gram catalyst used in one hour of operation.

It can be seen from Table 2 that the 300Co-1 sample exhibited the highest CO conversion (78.1) and the lowest CH₄ and CO₂ selectivities. Furthermore, the STY and activity are the highest for this sample and drop as the surface area of the catalyst increases. The pore size of the silica support affects the rate of CH₄ production as is evident by samples 480Co-2 and 560Co-3 (6 and 5nm respectively). The small pore diameter promotes the formation of CH₄ where large pore diameters >10nm increases the probability of longer HC chain formations as is evident in sample 300Co-1. From the table, it's also noticed that the CO conversion is high (about 10% higher than reported in literature). However, it's also noticed that CO₂ selectivity is higher too (almost double the numbers reported in literature). Whereas, CH₄ selectivity is much lower than literature. This is attributed to the total pressure of the reaction. The pressure used in the sample runs is around 7 bar, where in most literature it's around 20 bar. The low reaction pressure decreases the solubility of CO and H₂ thus increasing the reaction rate to form higher amounts of CO₂. The drying and calcination temperatures had a higher impact on the catalytic activity of samples 300Co-4 and 300Co-5 where the CO conversion dropped to below 60% for these two samples in comparison to sample 646C-1 (78.1%) which has the same surface area (300m²/g). It is hypothesized that the high temperatures of calcination resulted in the sintering and agglomeration of the cobalt particles thus lowering the cobalt surface area leading to lower catalytic activity after reduction. In general, the different surface properties of the silica supports (surface area and pore diameter) had lower impact on the activity and yield of the catalyst samples in comparison with the effects of drying and calcination temperatures. Samples 300Co-1, 480Co-2 and 560Co-3 had higher CO conversion, activity and yield than samples 300Co-4 and 300Co-5 where the higher drying and calcination temperatures adversely impacted the catalytic activity.

The change in activity of Co/silica catalysts was also investigated. Fig. 1 shows the CO conversion as a function of time for the reference sample (300Co-1). The CO conversion increases initially as the catalyst reaches steady state. The conversion drops after 22 hrs, but remains stable for the rest of the run.

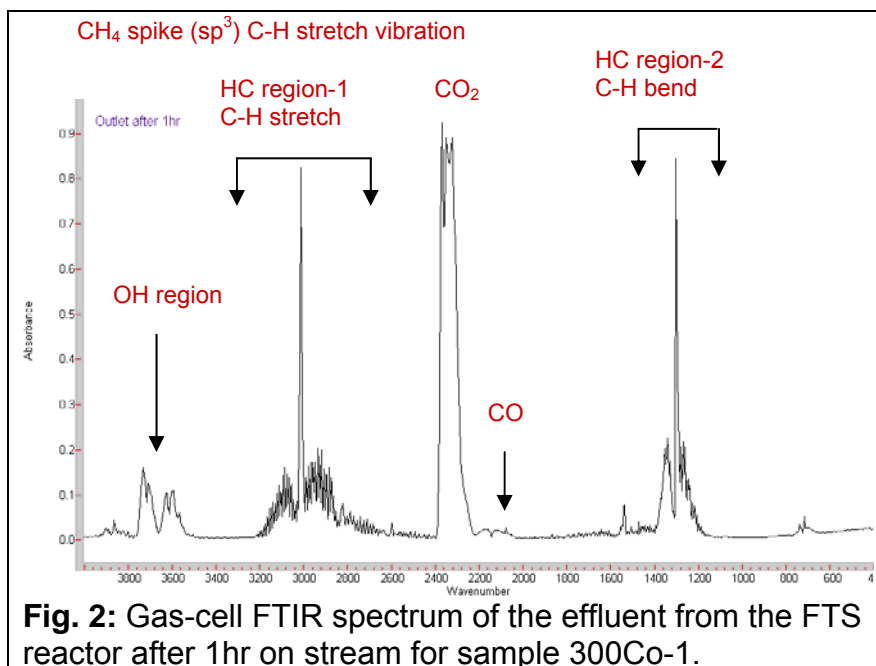


BET was used to study the loss of surface area as a result of catalyst sintering or Co particle agglomeration, high temperature calcinations as well as the filling of the support pores with Co particles. This is countered by the formation of high surface area amorphous Cobalt silicate as is evident by the FTIR-ATR results. In some of the samples prepared, ethanol was used instead of water as a medium during preparation to study its effect on the formation of cobalt silicate. The BET surface area analysis showed that the catalyst undergoes a reduction in surface area due to silica migration as a result of hot spot formation and sintering as well as Co oxide reformation. Sintering which occurs when the catalyst active phase (Co^0) particles agglomerate forming larger clusters thus decreasing the overall active surface reaction area. This happens when the exothermic heat of the reaction is trapped in the catalyst bed overtime. In industrial reactors, cooling jackets or diluents particles are added to minimize this phenomenon. The calcination temperature for sample 300Co-5 is higher than sample 300Co-1. At 573K, silica migration starts to occur (loss of surface area). However, the surface area doesn't drop significantly after 48 hrs of FT reaction since reaction temperature is only 503K, not high enough for silica migration to occur and also due to the formation of high surface area cobalt silicate, an amorphous undesired phase characterized by its high surface area which counters the effects of surface area loss due to sintering.

X-ray photoelectron spectroscopy (XPS) was used to verify the existence of cobalt oxide after calcination and before reduction to metallic Co under hydrogen flow. The spectra also indicated the formation of the undesired cobalt silicate phase. The XPS high resolution of Co 2p orbital shows how the fresh catalyst sample two main Co 2p peaks are shifted to higher binding energy than the two oxide references, which means higher Co oxidation state. This is due to cobalt silicate formation during the preparation/calcination stage. The after reaction spectra show similar binding energy as the fresh catalyst which means cobalt silicate still existed among other oxides in the system. However, the intensity was much lower indicating less species concentration.

A sample spectrum of the gaseous effluent from the reactor after 1hr on stream analyzed in the FTIR gas cell is presented in Fig. 2. The spectrum shows the stretching vibration of (-OH) group indicating water formation due to water gas shift (WGS) and the (-C-H) group from the formation of any paraffinic gaseous product including the hybrid sp^3 stretch (methane). However, since the spectrum is a representative of gaseous products, it's expected

that only C₁-C₄ gaseous products to coexist. For liquid product analysis, a GC equipped with a PLOT or specialty column is used to separate and analyze the liquid formed. The high intensity of the CO₂ band is associated with the start-up of the reaction and is common since this spectrum was collected after only 1hr on stream.



Usually it takes about 6hrs for the reaction to reach steady state. The spectrum also indicates that CO was almost completely converted and consumed in the reaction. This explains the high CO conversion data obtained and subsequently the high selectivity to HC products.

Conclusions

From this work, it was found that the activity and STY of the catalyst samples studied decrease as the surface area of the catalyst increases (300>480>560). This is also true for CO conversion where it decreases as catalyst surface area increases. When catalysts with same surface area were used it was noticed that the CO conversion decreases as drying and calcination temperatures increase from 573 to 673 and 773K. The same trend was noticed for activity and STY. This leads to the conclusion that the optimum surface area for FTS should be between 300-400m²/g and that the calcination temperature should be kept low preferably around 573K. The different surface properties of silica supports affect the product distribution. Catalyst supports with small pore diameter increased the formation of CH₄.

References

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