



Preparation, surface characterization and performance of a Fischer-Tropsch catalyst of cobalt supported on silica nanosprings



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ABSTRACT

The reduction of cobalt (Co) catalyst supported on silica nanosprings for Fischer-Tropsch synthesis (FTS) has been monitored by X-ray photoelectron spectroscopy (XPS) and compared to FT catalytic activity. The cobalt is present in the starting catalyst as a Co₃O₄ spinel phase. A two-step reduction of Co₃O₄ to CoO and then to Co⁰ is observed, which is consistent with the results of H₂-temperature programmed reduction. During the reduction the two steps occur concurrently. The deconvolution of the Co 2p core level state for the catalyst reduced at 385 °C and 1.0 × 10⁻⁶ Torr of H₂ revealed signatures of Co⁰, CoO, and Co₃O₄. The reduction saturates at a Co⁰ concentration of approximately 41% after 20 h, which correlates with the activity and lifetime of the catalyst during FTS testing. Conversely, at 680 °C and 10 Torr of H₂, the catalyst is completely reduced after 10 h. The evolution of the Co d-band at the Fermi level in the valence band XPS spectrum definitively verifies the metallic phase of Co. FTS evaluation of the Co/NS catalyst reduced at 609 °C showed higher production rate (3-fold) of C₆-C₁₇ hydrocarbons than the catalyst reduced at 409 °C and is consistent with the XPS analysis.

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1. Introduction

Fischer-Tropsch synthesis (FTS) is a heterogeneous catalytic reaction for conversion of syngas (CO, H₂) into liquid hydrocarbons (fuels) and other valuable chemicals. Several metals, such as ruthenium (Ru), iron (Fe), nickel (Ni), Co, rhodium (Rh), palladium (Pd), and platinum (Pt) have been demonstrated to be effective catalysts for the FTS process. From an economic standpoint, Fe and Co catalysts are the most viable FTS catalysts. The choice of Fe or Co depends on the desired operating conditions and products of the FTS process. Generally, Co catalysts are used only at low temperatures (200–240 °C) because at high temperatures a significant amount of methane is produced [1]. Low temperature FTS yields high molecular weight linear hydrocarbons, while high temperatures (300–350 °C) produce gasoline and low molecular weight olefins. If maximizing the gasoline product fraction is desired, then it is best to use Fe catalyst at high temperature. However, if maximizing diesel product fraction is preferred, then Co catalyst is once

again the best choice [1]. FTS product selectivity depends on the reaction conditions, on the promoter, or on the nature of the support. While FTS performances of Fe based catalyst are improved by the addition of promoters, those of Co catalysts are not very sensitive to promoters. Moreover, Co catalysts lead to the formation of water and not CO₂ (a loss of carbon from the process) and their carburization is low compared to that of Fe based catalysts [2]. While Co is orders of magnitude more expensive than Fe, it is still a viable alternative to Fe because its demonstrated activity at lower synthesis pressures, reduces operating costs, thereby offsetting its higher cost [1].

Due to the cost of Co, the Co metal – which is generally accepted to be the active phase during FTS [3] – is dispersed onto a support in order to reduce catalysts costs while stabilizing and maintaining the strength of the active phase. An optimal support should be chemically inert, mechanically and thermally stable, with high specific solvent-accessible surface area, and have a balanced metal-support interaction [4,5]. This last requirement implies that the dispersed metal should not alloy with the support because with such structures the metal is difficult to reduce and therefore remains inactive in FTS. Oxides of support materials, particularly SiO₂, Al₂O₃, and TiO₂ are the most extensively investigated supports for Co catalysts [6–8]. Silica nanosprings (NS) can meet and

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exceed the above support criteria. In fact, recently, FTS catalytic performances of cobalt decorated silica nanosprings (Co/NS) were evaluated and the results compared with those of conventional silica gel supported Co catalysts [9]. Even though Co/NS catalysts had 75 times less gravimetric Co content than the sol–gel catalysts, both catalysts showed similar selectivity to C₅₊ hydrocarbons and Co/NS showed higher FTS activity. However, there was an early drop in the CO conversion for Co/NS catalysts [9]. There are many factors that can influence the CO conversion. For example, unreduced Co species are reported to give lower CO conversion rates [10]. Other causes of catalyst deactivation include coking, sintering of Co nanoparticles and poisoning.

The focus of any catalyst development is to improve key properties, which are lifetime, activity and selectivity. In order to understand low CO conversion of Co/NS catalysts during FTS, H₂-programmed temperature reduction (H₂-TPR) was carried out to assess the reducibility of the catalysts. H₂-TPR analysis revealed an incomplete reduction, which was confirmed by X-ray photoelectron spectroscopy (XPS) analysis of the spent catalysts. To improve FTS performances of the nanospring supported catalyst, it is very important to thoroughly characterize the reduced state. The goal of this work is to determine the reduction state of Fischer-Tropsch Co/NS catalysts during activation. The reduction state has been characterized using in situ X-ray photoelectron spectroscopy (XPS), H₂-TPR, and transmission electron microscopy (TEM). Furthermore, the Co/NS catalyst FTS performance has been evaluated at two different reduction temperatures.

2. Experimental details

2.1. Catalyst preparation

Nanosprings (NS) were first grown on a Si wafer (p-type) using the process developed by Wang et al. [11]. Briefly, NS grow via a catalyst-assisted vapor–liquid–solid (VLS) process. The synthesis is performed in a furnace operated at atmospheric pressure. The NS process uses a thin gold film as a catalyst, which is sputtered on a substrate, then exposed to concomitant and constant flows of a proprietary silicon precursor and oxygen in a nitrogen atmosphere. To obtain Co/NS catalysts for characterization studies, Co nanoparticle decoration was performed by wet impregnation [12]. The NS-coated Si wafer was first dipped in a cobalt (III) acetylacetonate (Co(C₅H₇O₂)₃)/ethanol solution (6.95 mg mL⁻¹). After allowing the solvent to evaporate in air, the sample was baked in a preheated tube furnace at 500 °C for 15 min in a flow of Ar/H₂ (130/10 mL min⁻¹). In the last step, the sample was allowed to cool. The process was repeated twice more to achieve the desired cobalt loading. To obtain Co/NS for catalyst evaluation studies, free standing NS (50 mg) were dispersed in ethanol (10 mL) by sonication and then a Co(NO₃)₂ solution (10 mL, 4.4 mg mL⁻¹) was added drop wise (3 h, 50 °C), oven dried at 120 °C, and then calcined at 550 °C for 5 h. The process was repeated to obtain 15% (wt%) loading of Co. The Co/NS catalyst (20 mg) was reduced at either 409 or 609 °C under H₂ (30 mL min⁻¹) for 24 h in a tube furnace prior to evaluation.

2.2. Experimental techniques

2.2.1. X-ray photoelectron spectroscopy (XPS)

XPS was carried out in a custom built ultra-high vacuum (UHV) chamber with a base pressure of 1.5×10^{-10} Torr. The chamber is equipped with an Omicron EA 125 hemispherical electron energy analyzer and a dual anode X-ray source. The Mg K α emission line (1253.6 eV) was used for XPS data acquisition and the combined resolution of the X-ray/hemispherical energy analyzer was 300 meV. The sample was grounded and exposed to

a 400 eV electron beam to avoid spurious charging. The chamber is also equipped with leak valves for gas (H₂) admission. In situ heating of the sample utilized a boron nitride heater and remotely monitored with an optical pyrometer. In situ reduction consisted of timed exposures of the sample to 1.0×10^{-6} Torr of H₂ at 385 °C and XPS spectra acquired after each exposure. For the reduction at 680 °C and 10 Torr of H₂, the sample was reduced in a separate chamber for 10 h and then transferred under vacuum to the UHV chamber for XPS analysis. Note, the reduction time of 10 h was only chosen to ensure full reduction. The photoelectron binding energy was referenced to the C 1s peak (284.7 eV) of adventitious carbon. The spectra were fitted using Igor Pro v6 (WaveMetrics) software using a Shirley background and Voigt functions. The same full width at half maximum (FWHM) was used for the two Co 2p spin states with a branching ratio of 2:1 (Co 2p_{3/2}/Co 2p_{1/2}), and the spin-orbit splitting was held at 15.1 eV.

2.2.2. H₂-temperature programmed reduction (H₂-TPR)

H₂-TPR spectra of the catalysts were obtained with a Micromeritics AutoChem II 2920 Chemisorption Analyzer equipped with a thermal conductivity detector (TCD). The sample (50 mg) was loaded in a U-shape quartz reactor and first purged in a flow of He (50 mL min⁻¹) at 250 °C for 1 h to remove water, cooled to 50 °C, then a 10% H₂ in Ar (50 mL min⁻¹) was purged and heated to 800 °C. The heating rate was 10 °C min⁻¹. After water removal from the out-coming flow, H₂ consumption was measured using the TCD.

2.2.3. Transmission electron microscopy (TEM)

Morphologies of the catalysts were characterized by TEM (Jeol JEM-2010 TEM). The acceleration potential was 200 kV. Sample specimens for TEM analysis were prepared by dispersion of the catalysts in ethanol. One drop of the suspension was deposited onto a holey copper grid coated with a fine carbon film (FCF-150-Cu). Several micrographs were recorded for each sample to measure the Co particle size and determine the particle size distribution.

2.2.4. FTS catalyst evaluation

The FTS performance of Co/NS (20 mg) catalysts were evaluated in a quartz tube (10 mm ϕ \times 300 mm with a “0” quartz frit connected 180 mm from the top to support the catalyst), fixed-bed micro-reactor [9]. The reactor was heated using a small tube furnace (Supelco) and regulated with a digital temperature controller. Reactant gases (CO (30 mL min⁻¹) and H₂ (60 mL min⁻¹)) and inert gas (N₂, 10 mL min⁻¹) were introduced from the top of the reactor, and the flow rates controlled with digital mass flow controllers (GC1, Dakota Instruments). The reactor was operated at 238 °C. Products were collected every 10 h in a three-stage impinger trap placed in a liquid nitrogen bath. Condensed liquid products were analyzed by gas chromatography-mass spectrometry (GC-MS, Focus-ISQ, ThermoScientific). Separation was achieved on an RTx-5ms (30 m \times 0.25 mm) with a temperature program of 40–250 °C at 5 °C min⁻¹. 1,2,4-Trichlorobenzene was used as an internal standard. Compounds were identified by their mass spectra, library mass spectral matching (NIST 2008) and retention times of known standard n-alkanes (C₆–C₄₄).

3. Results and discussions

3.1. Characterization of the as prepared Co₃O₄/nanospring catalyst

Fig. 1(a) shows a TEM micrograph of the unreduced cobalt oxide nanoparticles on a NS, while Fig. 1(b) displays the corresponding cobalt oxide particle size distribution. A NS is formed by five to eight coherently coiled silica nanowires. The spiral structure enables

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