Fischer–Tropsch synthesis: Iron catalysts supported on N-doped carbon spheres prepared by chemical vapor deposition and hydrothermal approaches

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ABSTRACT

Conventional carbon supports are generally treated in acid or base solutions to produce functionalized groups on the carbon surface in order to anchor active metal or metal oxide species. The use of nitrogen-doped carbon materials as supports can avoid this environmentally unfriendly step because the N atoms in the carbon materials can act as the anchoring sites. In this study, we have synthesized three different nitrogen-doped carbon sphere (NCS) supports by two different strategies: chemical vapor deposition (CVD), in either a horizontal or a vertical furnace, or using a hydrothermal approach. The three different NCSs were found to have different physical and chemical properties as revealed by TGA, XPS, Raman spectroscopy, and electron spectroscopy studies. NCSs prepared by CVD in a vertical furnace (NCS$_{ver}$) gave the smallest diameter and highest surface area materials. The NCS$_{ver}$ material presented the most defected sites and the highest N content. The NCSs prepared by the hydrothermal method (NCS$_{hyd}$) gave the largest diameter, the lowest surface area and the least amount of defect sites and the materials with the lowest N content. The NCS$_{hor}$ prepared by CVD in the horizontal furnace exhibited defect sites and an N content between the amounts measured for the NCS$_{ver}$ and NCS$_{hyd}$ materials. The surface N types, determined by XPS, varied with the synthesis strategy used. Iron species were successfully deposited on the three NCSs without a functionalization step. The Fischer–Tropsch synthesis (FTS) performances of the three Fe/NCS catalysts were found to correlate with the Fe particle size which was influenced by the different N contents, the N type, and the defect sites. It is suggested that pyrollic and pyridinic N atoms play a key role in binding the Fe atoms and that quaternary N atoms play a minor role. The Fe/NCS$_{ver}$ contained well-dispersed Fe oxide particles on CSs that had the highest N content (made of pyrollic/pyridinic N atoms) and this led to the highest FT activity. The Fe/NCS$_{hor}$ catalyst showed the lowest FT activity due to the presence of the largest Fe oxide particle sizes (50% quaternary N atoms).

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1. Introduction

Fischer–Tropsch synthesis (FTS) is an efficient route to catalytically produce liquid fuels and chemicals from syngas (CO and H$_2$) derived from coal, natural gas, or biomass [1,2]. Carbon is a promising support in FTS because the interaction between active metals and carbon is small, compared to the strong support interaction and even the formation of mixed compounds between metals and the typical oxide supports, Al$_2$O$_3$, SiO$_2$, and TiO$_2$. Furthermore, carbon supports exhibit good hydrothermal stability [3] and the surface properties of carbons can be easily tailored according to the requirements of the formed product. Currently, there is a great

interest in FTS catalysts supported on novel carbon materials such as diamond [4], carbon nanofibers (CNFs) [5,6], multi-walled carbon nanotubes (MWCNTs) [7–10], and mesoporous carbon [11,12]. This is due to the impressive mechanical properties of these carbon materials, high accessibility of the active phase and the absence of micro-porosity, thus eliminating intraparticle mass transfer in the reaction medium.

Typically, these novel carbon materials, prepared by chemical vapor deposition (CVD) must be treated in acid and/or base solutions before anchoring a metal or metal oxide particle [7,13–15]. The aim of these treatments is to introduce functionalized groups and make the carbon surface hydrophilic as well as to remove the catalyst used in the CVD process. The treatment processes can be environmentally unfriendly. An alternative to the use of these processes is to introduce N atoms into the carbon structures

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because the N sites are chemically active and allow for anchoring of the catalyst particle. Therefore, no functionalization process is needed. Indeed, nitrogen-doped carbon materials have recently been prepared [16–20] and used as supports in catalysis [21,22]. For example, in the hydrogenation of cinnamaldehyde, nitrogen-doped CNTs significantly increased the Pd metal dispersion and activity, compared to the N-free CNTs. Furthermore, nitrogen incorporation strongly improved the selectivity toward C=C bond hydrogenation [21]. Another recent study reported that Ru nanoparticles on nitrogen-doped CNFs are small due to a strong interaction between the precursor and the nitrogen groups [23]. This Ru catalyst supported on N-doped CNFs has exhibited higher NH_3 decomposition activity than a catalyst deposited on N-free CNFs. Furthermore, the catalyst with the highest amount of nitrogen retarded the oxygenation of Ru metal upon exposure to air.

Another novel carbon material, carbon spheres (CSs), which is prepared without a catalyst, is composed of random curling graphitic flakes with sp^2 hybridization [24,25]. Due to their inert surface and nonporous nature when prepared by CVD procedures, CSs can be regarded as model catalyst supports to investigate the effect of different reaction parameters (metal particle size, promoters, and deactivation) in FTS. In this respect, we have recently prepared model iron and cobalt catalysts supported on carbon spheres to investigate the effect of the preparation method, iron precursor, and promoters on FTS performance [24,26]. There is a good match of FT activity and selectivity results when the data were compared with studies on non-carbon supports. Furthermore, our preliminary studies showed that a Co precursor can be attached onto the surface of nitrogen-doped carbon spheres (NCS) without functionalization by strong acid treatments and the cobalt oxide can be autoreduced by the NCS [27]. The autoreduced catalyst showed a better FTS performance in comparison with a catalyst reduced in H_2.

To further explore the use of CSs in FT catalysts, we have prepared CSs with different N contents to probe the effect of N doping on Fe FT catalyst behavior. The NCSs have been prepared by both chemical vapor deposition and hydrothermal methods. Fe catalysts were synthesized using the as-prepared NCSs, without a functionalization process. The effect of the chemical and physical properties of the different NCS supports on the FTS performance of the Fe/NCSs was investigated.

2. Experimental

2.1. Preparation of N-doped carbon spheres (NCSs) by chemical vapor deposition (CVD) and hydrothermal synthesis methods

2.1.1. N-doped CSs prepared by chemical vapor deposition in a vertical furnace (NCS$_{ver}$)

N-doped carbon spheres were prepared in a *vertically* aligned tubular quartz reactor (NCS$_{ver}$) [28]. Briefly, the reactor was placed in a vertical furnace and a round bottomed flask (500 mL) was connected to the reactor to collect the synthesized material. The furnace was heated to 900 °C at 10 °C/min under flowing Ar. Once the desired temperature was reached, Ar (300 mL/min) and C_2H_2 (200 mL/min) gases were simultaneously bubbled through a CH_3CN solution (kept at 80 °C) and the mixture passed through the reactor for 30 min. Then, the C_2H_2 gas flow was cut off and the Ar was passed through the furnace until it had cooled down to room temperature (40 mL/min). Approximately 1.5 g of NCS$_{ver}$ was obtained.

2.1.2. N-doped CSs prepared by chemical vapor deposition in a horizontal furnace (NCS$_{hor}$)

N-doped carbon spheres were prepared by chemical vapor deposition in a *horizontally* aligned quartz tubular reactor (NCS$_{hor}$)

[29]. The experiment was carried out at atmospheric pressure in a quartz tube with a 1.9 cm internal diameter and 51 cm length. The tube was placed horizontally in a furnace. The furnace temperature was raised to 950 °C at a heating rate of 10 °C/min under a flow of N_2 (60 mL/min). When the furnace temperature reached 950 °C, the N_2 was switched to acetylene at a flow rate of 100 mL/min. Acetylene gas was first bubbled through a warm CH_3CN solution (kept at 80 °C) before entering the reactor. The carbonization reaction was performed for 2 h before shutting off the acetylene and re-commencing the nitrogen gas flow. Then, the system was cooled to room temperature in a flow of N_2 and the NCS$_{hor}$ were collected (yield = 2.0 g).

2.1.3. N-doped CSs prepared by a hydrothermal approach in an autoclave (NCS$_{hyd}$)

N-doped carbon spheres were synthesized by a hydrothermal method (NCS$_{hyd}$) using a 1 M solution of a mixture of 90% sucrose and 10% urea. The aqueous mixture was placed in a Teflon cup with a total volume of 58 mL and then placed into a stainless steel autoclave which was heated to 190 °C. The reaction was allowed to proceed for 4 h once the temperature reached 190 °C. Then, the autoclave was cooled down to room temperature and the suspension was separated by centrifugation using water and ethanol at 5000 rpm for 10 min. The product NCS$_{hyd}$ was then dried in an oven at 70 °C overnight and approximately 3.0 g of product was collected.

2.2. Fe/NCS catalyst preparation

Fe catalysts (5 wt.% Fe loading) supported on the three N-doped carbon spheres were prepared by a deposition precipitation method (DPU) using urea as precipitating agent. Briefly, $Fe(NO_3)_2 \cdot 6H_2O$ (3.605 g) and urea (0.805 g; 1.5 moles urea per mole of iron) were dissolved in de-ionized water (18 mL) and added to 10 g of NCS support at room temperature. Then, the temperature was increased to 90 °C and held at 90 °C (2 h) to allow for the hydrolysis of the urea. The sample was then dried under vacuum at 90 °C overnight.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) patterns for the catalysts were recorded with a Siemens D2 diffractometer using Cu Kα radiation and a Ni filter. The scan range was 20–90° with 0.02° steps. N_2 physisorption was performed on a Micromeritics ASAP-2000 Tristar analyzer. Prior to analysis, the sample (0.2 g) was degassed in N_2 at 120 °C for 12 h using a sample degas system (Micromeritics flow Prep 060). A Perkin–Elmer STA6000 TG/DTA Thermogravimetric analyzer was used to measure weight changes in samples heated in N_2 and air at a heating rate of 10 °C/min. The sample mass used was varied between 3 and 10 mg. The nitrogen content in the NCSs was determined by CHN elemental analysis using a Carlo Erba NA1500 analyzer. Scanning electron microscopy (SEM) was performed on a Hitachi S-5200. A FEI Tecnai G^2 Spirit was used for transmission electron microscopy studies. All samples were ultrasonically suspended in ethanol and a drop of the suspension was transferred to a copper grid and allowed to dry before analysis. Raman spectroscopy measurements were carried out using a micro-Raman attachment of a Jobin-Yvon T64000 Raman spectrometer. The spot size on the sample was ~1.5 μm in diameter and the excitation wavelength was 514.5 nm from an Ar ion laser. A grating with 600 grooves/mm was used to disperse the spectrum onto a charge-coupled detector (CCD). X-ray photoelectron spectroscopy (XPS) measurements were performed in a Physical Electronics Quantum2000 with a monochromatized Al K source (1486 eV). Narrow spectra were collected with a pass energy of 30 eV. All