



On the role of the stability of functional groups in multi-walled carbon nanotubes applied as support in iron-based high-temperature Fischer–Tropsch synthesis



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ABSTRACT

The role of the stability of surface functional groups in oxygen- and nitrogen-functionalized multi-walled carbon nanotubes (CNTs) applied as support for iron catalysts in high-temperature Fischer–Tropsch synthesis was studied in a fixed-bed U-tube reactor at 340 °C and 25 bar with a H₂:CO ratio of 1. Iron oxide nanoparticles supported on untreated oxygen-functionalized CNTs (OCNTs) and nitrogen-functionalized CNTs (NCNTs) as well as thermally treated OCNTs were synthesized by the dry impregnation method using ammonium ferric citrate as iron precursor. The properties of all catalysts were examined using X-ray diffraction, temperature-programmed reduction in H₂, X-ray photoelectron spectroscopy and temperature-programmed oxidation in O₂. The activity loss for iron nanoparticles supported on untreated OCNTs was found to originate from severe sintering and carbon encapsulation of the iron carbide nanoparticles under reaction conditions. Conversely, the sintering of the iron carbide nanoparticles on thermally treated OCNTs and untreated NCNTs during reaction was far less pronounced. The presence of more stable surface functional groups in both thermally treated OCNTs and untreated NCNTs is assumed to be responsible for the less severe sintering of the iron carbide nanoparticles during reaction. As a result, no activity loss for iron nanoparticles supported on thermally treated OCNTs and untreated NCNTs was observed, which even became gradually more active under reaction conditions.

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1. Introduction

Fischer–Tropsch synthesis (FTS) has attracted increasing attention due to its potential in producing high quality fuels and chemicals from coal, natural gas or biomass [1]. Moreover, the diminishing crude oil resources and the volatility of the crude oil price have raised the interest in FTS [2]. At present, FTS is a well established industrial process, in which synthesis gas (CO + H₂) is converted into mainly linear hydrocarbons with a broad chain-length distribution [3,4]. The most common metals used for FTS catalysts are iron, cobalt and ruthenium. Iron- and cobalt-based catalysts are used commercially at present, although ruthenium is the most active catalyst for FTS [2]. Ruthenium is excluded from industrial application due to the limited resources and its high cost. Cobalt-based catalysts are mainly used in FTS to produce long-chain hydrocarbons at low reaction temperatures (<230 °C). One of the advantages of using Co-based catalysts is its low water-gas

shift (WGS) activity, which results in less unwanted CO₂ formed in FTS compared with Fe-based catalysts. On the other hand, high reaction temperatures (>230 °C) are essential for iron-based catalysts for the production of short-chain hydrocarbons. The high WGS activity of Fe-based catalysts renders them suitable for FTS using CO-rich syngas [5].

In recent years, numerous studies have been performed focusing on catalytic activity and selectivity mostly using iron or cobalt supported on silica, alumina or titania [6–8]. In addition, carbon was also used as support and showed promising performance in FTS. An early study performed by Jones et al. [9] reported that Fe/carbon catalysts achieved higher olefin selectivity than unpromoted Fe/silica and Fe/alumina catalysts. Recently, carbon nanotubes (CNTs) have been identified as a promising support for catalysts used in FTS, because CNTs have a relatively large and freely accessible surface area and are able to improve the dispersion of the catalytically active nanoparticles [10]. The surface modification of CNTs is essential to attain high dispersion of metal particles, because CNTs are hydrophobic and inert in nature [11]. Oxygen and nitrogen functionalization are the most widely used methods for the modification of CNTs. Oxygen-containing functional groups can

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be created by treating CNTs with oxidizing agents such as nitric acid [11,12]. Nitrogen doping of CNTs can be achieved by post-treatment of oxygen-containing CNTs in flowing ammonia [13]. The generated oxygen- and nitrogen-containing functional groups are assumed to act as efficient anchoring sites for metal particles [11,14,15]. These anchoring sites immobilize the metal particles preventing them from excessive sintering upon heating [16].

Different functional groups such as carbonyl, carboxylic acid, pyrone, phenol and ether species are present on the CNT surface after nitric acid treatment. It has been reported that the nature of surface functional groups on CNTs can be altered by thermal treatments [11]. Kundu et al. [11] investigated the thermal stability of surface functional groups on oxygen-functionalized CNTs (OCNTs) after thermal treatment in ultra-high vacuum at temperatures between 300 and 720 °C for 30 min. The authors observed that the surface atomic concentration of oxygen decreased with increasing treatment temperatures. The carboxylic groups start to decompose at about 300 °C, whereas the decomposition of phenol groups occurs between 300 and 600 °C and ether decomposes at even higher temperature. Hence, it is possible to selectively remove some of the surface oxygen groups by heating OCNTs in inert atmosphere. In comparison, nitrogen groups are significantly more stable upon heating. Thermal treatment of nitrogen-functionalized CNTs (NCNTs) at 600 °C did not cause a significant loss of nitrogen except for a slight decrease of pyridinic nitrogen and a minor increase in quaternary nitrogen [13].

Schulte et al. [17] studied high-temperature FTS using OCNT- and NCNT-supported iron nanoparticles at 340 °C and 25 bar with a H₂:CO ratio of 1. They observed that the NCNT-supported iron nanoparticles with 40 wt% of iron loading were capable of achieving a high and constant degree of CO conversion under the high-temperature condition for a period of 80 h time on stream. Furthermore, the iron carbide nanoparticles found on NCNTs after reaction were smaller than on OCNTs suggesting stronger iron-nitrogen interactions. Interestingly, the CNT-supported iron nanoparticles without promoters obtained excellent olefin selectivities and moderate methanation tendency as compared to the conventional bulk iron FT catalysts. In addition, they found that iron supported on non-functionalized CNTs was nearly inactive, indicating that efficient CNT functionalization is mandatory.

The number of anchoring sites on CNT surfaces is related to the thermal stability of the supported metal particles. It has been reported that the metal particle size is one of the most important aspects that influences the catalytic activity and selectivity in FTS [8,18,19]. Park et al. [8] studied the effect of particle size on the catalytic activity and selectivity in FTS over iron oxide supported on δ -Al₂O₃. The authors observed that the turnover frequency and C₅₊ selectivity increased with increasing iron oxide particle size in the range of 2–6 nm, whereas the CH₄ and C₂–C₄ selectivities decreased correspondingly. Similar results were also obtained by Cheng et al. [18], who studied the effect of pore size in mesoporous silicas on the structure and catalytic performance of iron catalysts in high-temperature FTS. They showed that the overall catalyst reaction rate, C₂–C₄ olefin selectivity and C₅₊ selectivities increased with increasing iron carbide particle size in the range of 4–22 nm. The authors attributed the higher catalytic activity of iron catalysts containing larger iron particles to the higher degree of carbidization. Torres Galvis et al. [19] reported that the turnover frequency decreased, while C₂–C₄ olefin and C₅₊ selectivities increased with increasing iron carbide particle size up to 17 nm.

Catalyst stability is also an important issue in the design of FTS catalysts. The loss of catalytic activity for catalysts under FTS reaction conditions can be attributed to iron phase changes, deposition of inactive carbonaceous compounds, sintering of the active phase, and poisoning [20–22]. A number of studies claimed that deposition of inactive carbon species on the catalyst surface plays a significant

role in the deactivation of FT catalysts [23–26]. Torres Galvis et al. [24] studied the carbon formation on iron-based catalysts using a thermal tapered element oscillating microbalance under plug-flow conditions at 350 °C, 20 bar and a H₂:CO ratio of 1. They observed that the supported iron catalyst promoted with sodium had higher initial coking rates than the unpromoted supported iron catalyst. Therefore, the low catalytic activity of the sodium-promoted iron catalyst was ascribed to the higher extent of carbon deposition.

In this work, we studied the role of the stability of surface functional groups in CNTs applied as support for iron catalysts in high-temperature FTS. The oxygen-containing functional groups were first generated by gas-phase oxidation and then partly removed by thermal treatment of the obtained OCNTs in flowing helium. The nitrogen-containing functional groups were introduced *via* NH₃ post-treatment. The catalysts used in the FTS reaction were prepared by the dry impregnation method using ammonium ferric citrate as iron precursor. The catalytic performance of the catalysts was studied in a fixed-bed isothermal U-tube reactor. The properties of the iron catalysts before and after reaction were characterized by X-ray diffraction (XRD), temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and temperature-programmed oxidation (TPO).

2. Experimental

2.1. Catalyst preparation

Multi-walled CNTs with inner diameters of 20–50 nm and outer diameters of 70–200 nm were obtained from Applied Sciences Inc. (Ohio). As-received CNTs were subjected to nitric acid vapor treatment at 200 °C for 24 h to generate oxygen-containing functional groups [27]. In order to introduce nitrogen-containing functional groups, the OCNTs were loaded into a quartz boat and placed in the centre of a horizontal quartz reactor. The sample was treated at 400 °C for 6 h in 10% NH₃ in He with a flow rate of 25 sccm to obtain NCNTs [13]. To remove a fraction of the surface oxygen groups, the obtained OCNTs were heated to 600 °C at 10 °C min⁻¹ in helium using a flow rate of 100 sccm and treated for 1 h before cooling in the same atmosphere. The obtained OCNTs were denoted as OCNT.600. Additionally, untreated OCNTs and NCNTs were used as reference supports for comparison with the thermally treated OCNTs. The supports were loaded with iron by the dry impregnation method using sodium- and sulphur-free ammonium ferric citrate (Fluka, 14.5–16% Fe basis, purum p.a. >95.0%) as iron precursor [28]. Briefly, the supports were mixed with the aqueous solution of ammonium ferric citrate aiming at a theoretical Fe loading of 20 wt%. The mixture was dried at 50 °C overnight and subsequently, the solid product was collected and calcined at 300 °C in synthetic air (20.5% O₂ in N₂) with a flow rate of 100 sccm for 90 min. The three obtained samples were labelled as Fe/OCNT, Fe/OCNT.600 and Fe/NCNT, respectively.

2.2. Characterization

Atomic absorption spectroscopy (AAS) was used to determine the actual iron loading on the support. Powder X-ray diffraction patterns were recorded with a Panalytical MPD diffractometer using Cu K α radiation in the 2 θ range of 10–70°. Temperature-programmed reduction was performed by heating approximately 40 mg of the sample to 800 °C with a heating rate of 10 °C min⁻¹ in a gas mixture of 4.5% H₂ in Ar with a flow rate of 84.1 sccm at atmospheric pressure. X-ray photoelectron spectroscopy measurements were conducted in an ultra-high vacuum set-up utilizing a high-resolution Gammadata-Scienta SES 2002 analyzer and a monochromatic Al K α X-ray source (1486.6 eV, anode operating

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