Promotional effects of multiwalled carbon nanotubes on iron catalysts for Fischer-Tropsch to olefins

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A B S T R A C T

N,O-functionalized and high-temperature-treated carbon nanotubes (N, O, HT-CNTs) were employed to investigate the promotional effects of CNT on Fe catalysts for the Fischer–Tropsch-to-olefins (FTO); particularly, the origin of active sites was explored using multiple *in/ex situ* techniques. An upward trend in initial activity, olefin selectivity, olefin/paraffin ratio, and chain growth probability is observed in the sequence of O-, N-, and HT-CNT supported catalysts. Unexpectedly, Fe/HT-CNT exhibits superb selectivity of 72.4% to C_2–C_7 olefins, closing to the Anderson–Schulz–Flory (ASF) limit. The defect-rich electron-withdrawing HT-CNT weakens the reducibility of FeO_x and the C_3H_6 adsorption on Fe, in contrast to O-, N-CNT. The defect-anchored Fe/HT-CNT promotes "Fe-C" formation and phase transformation toward $\acute{\epsilon}$-$Fe_{2.2}C/\epsilon$-Fe_2C, improving CO adsorption and activation. The above merits boost olefin selectivity on Fe/HT-CNT. However, O-CNT abounded with O groups retards the formation and deep carbonization of the active phase, indicating a gradual increase in the yield.

1. Introduction

Light olefins (ethylene, propylene, and butylene, C_2–C_4 olefins) are the cornerstone of the modern chemical industry, being raw materials for the production of dyes, plastics, drugs, rubber, lubricants and cosmetics, etc. [1–4]. Currently, those olefins are produced mainly through the steam cracking of naphtha, which primarily comes from dwindling and nonrenewable crude oil. Alternative routes for the production of those commodities are highly desired by chemical industry. Owing to low energy consumption, low cost, and high efficiency, the approach of the Fischer–Tropsch-to-olefins process (FTO) is regarded as one of the most promising platform reactions (syngas to value-added chemicals) to produce light olefins, in which the feedstock, syngas, could be obtained from coal, biomass, and shale gas [1,5]. The great challenge for this process is the development of efficient catalysts with excellent selectivity to meet the requirement for industrialization [6].

Fe-based catalysts, usually applied for Fischer–Tropsch synthesis (FTS), have also shown a high potential for FTO because of their cost -effectiveness, poison resistance, and high selectivity to olefins [5]. The governing of the Anderson–Schultz–Flory (ASF) distribution in FTS impedes the steering of the product selectivity to light olefins. Precise termination of the chain growth of hydrocarbons during CO hydrogenation by tuning the Fe surface structure has been attracting a great of effort [6]. In particular, extensive studies concerning the particle size effect [7,8] have proved that a decrease in the metal particle size of the Fe/Co FTS catalyst leads to poor olefin selectivity, a decreased probability of chain growth, and an increase in catalytic activity and CH_4 selectivity. On the other hand, the reduction of the Fe particle size could increase the number of coordinately unsaturated site (CUS) atoms and improve the dissociation of CO on Fe surfaces by reducing its Fermi level [9]. In addition, H coverage on smaller Fe particles has been found to increase significantly [9]. To achieve high selectivity to olefins, a compromise between the contributions of small and large particles to higher activity, appropriate chain growth, higher olefin/paraffin ratio, and olefin selectivity must be taken into account. Clearly, there might be an optimum range of Fe particle size around 6–10 nm for both better activity and olefin selectivity. Thus, the control of particle size is an effective way to modulate the product distribution.

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The activation energy for the diffusion of C into the Fe bulk (43.9–69.0 kJ/mol) has been found to be lower than that for the FTS reaction (89.1 ± 3.8 kJ/mol) [10]; meanwhile, the CO dissociation barrier on metallic Fe is lower than that on the Fe carbide (FeC$_x$) surface [11]. On the Fe surface, there exists an induction period for the initial reaction, in which CO dissociates easily and C atoms diffuse into the Fe surface phase by forming FeC$_x$ [10]. Theoretical study by Hu's group has demonstrated that the bond strength of C—M and O—M on Fe is too high [11,12]; however, those bonds on the FeC$_x$ surface can be alleviated remarkably, so that the activity can be enhanced rapidly. Therefore, modification of the electronic structure of Fe is crucial to achieving superior performance for FTO.

The metal–support interaction has been extensively studied for Fe-based catalysts used for CO hydrogenation, being a key issue in improving catalyst efficiency, selectivity, and stability [13–16]. Conventional oxidic supports (e.g., SiO$_2$, Al$_2$O$_3$) interact strongly with iron oxides, which leads to cumbersome activation of iron oxides [17]. The activated carbon, commonly used as a carbonaceous support, suffers from low selectivity to light olefins and a high deactivation rate [1]. Carbon nanotubes (CNTs) have triggered great attention due to their high surface area (>200 m^2/g), modifiable surface chemistry (e.g., the production of defects and functional groups), and especially appropriate metal–support interactions (e.g., the charge transfer of M−C) [17,18]. Heteroatom functionalization (e.g., N, O, B, S) is usually employed to tailor the electronic structure and chemical properties of active metals [19] (e.g., the surface acidity/basicity, the hydrophilic/hydrophobic property, and the adsorption/desorption of reactants/products), and thus affects the catalytic performance as a consequence [20].

More recent studies have revealed that N- and O-containing functionalities are efficient sites for anchoring Fe nanoparticles (NPs) [17,21–23]. Specifically, with the assistance of N promotion by the electron-donating anchoring effect and basicity, the N-doped CNT, graphene, and mesoporous carbon as supports were found to enhance the performance of FTO [21,22,24]. Furthermore, defects play a vital role in modifying the physical properties and chemical reactivity of CNT [25]. The method of acid oxidation followed by high-temperature pretreatment has proved to be effective to create more defects on CNT [18,26].

Eschemann et al. [27] have reported that Co NPs supported on pristine CNTs shows higher initial activity for CO hydrogenation and C$_{5+}$ selectivity, but less stability than in catalysts on functionalized CNTs. On the latter, CoNPs could be strongly anchored on the support surfaces. Chew et al. [28] also found that the iron carbide NPs on the functional CNTs could be very stable during reaction. Oschatz et al. [24] found that the activity of Fe catalysts supported on N-doped mesoporous carbon and thermally treated carbon was higher than that of O-functionalized mesoporous-carbon-supported catalyst. This is due to the strong encapsulation of Fe NPs on the carbon surface, which prevents iron NPs from sintering during calcination. Up to now, the promotional effects of CNT on Fe catalysts in FTO have rarely been reported.

In this work, the Fe—C interaction is manipulated by modifying the surface chemistry of multiwalled CNTs (MWCNTs, high-temperature annealing, N- and O-functionalized). The promotional effect of the modified MWCNTs on Fe catalysts for FTO is investigated under industrially relevant conditions.

2. Materials and methods

2.1. Catalyst preparation

2.1.1. Modification of MWCNTs

Pristine close MWCNTs (p-CNTs) with a diameter of 10–15 nm (Flotube 9000, 227 m^2/g, Cnano Technology) were oxidized in a solution of 8.0 M HNO$_3$ (65 wt%, Shanghai Lingfeng Chemicals) and refluxed at 110 °C for 4 h. The obtained support was denoted as O-CNT. Here, HNO$_3$ refluxing treatment under mild conditions (8M, 110 °C for 4 h) has proven to cause little damage to the CNT structure [29]. After HNO$_3$ oxidation, the defect-rich high-temperature pretreated CNT (HT-CNT) was prepared by annealing at 850 °C under argon (Ar, 99.999%) for 2 h. N-CNT was prepared through a postdoping method, in which the pristine MWCNT was treated at 500 °C for 1 h, in an Ar flow passed through a gas-phase trap containing a saturated solution of urea (Analytical Reagent, Shanghai Lingfeng Chemicals) as N source [30].

2.1.2. Preparation of supported Fe catalysts

Fe-supported catalysts with a nominal loading of 20% were prepared by incipient wetness impregnation of modified MWCNTs (HT-CNT, N-CNT, O-CNT) with an aqueous solution containing a certain amount of ammonium iron citrate (AR, Aladdin Chemistry). The solution was added dropwise to the support with vigorous stirring until the pore volume was filled. After aging at room temperature in stagnant air for 4 h, the as-prepared precursors were dried at 100 °C for 12 h. The dried impregnates were then heated at 500 °C for 2 h at a ramping rate of 10 °C/min in an Ar flow. The as-prepared samples were denoted as Fe/HT-CNT, Fe/N-CNT, and Fe/O-CNT, respectively.

2.2. Characterization

The BET surface areas and pore volumes of MWCNTs and catalysts were measured by an ASAP-2010 system from Micromeritics at 77 K after the samples were outgassed at 190 °C and 1 mmHg for 6 h.

The zeta potentials of all MWCNTs were measured by a Malvern NPs analyzer at 25 °C. Sufficiently dilute suspensions of a given MWCNT were prepared with constant ionic strength 0.01 M. The pH of the suspensions was adjusted by small additions of 1 M HNO$_3$ or KOH solution. The point of zero charge (PZC) of the modified MWCNTs was measured by the PMT (potentiometric mass titrations) method using PHS-3C pH meter [31].

The morphology of calcined Fe/CNTs was obtained with a field-emission transmission electron microscope (TEM, FEI Tecnai G^2 F20 S-Twin) using an accelerating voltage of 200 kV. After being ground several times, the prepared samples were ultrasonically dispersed in ethanol, and then 2–3 drops of this slurry were deposited on ultrathin carbon-film-coated copper grids (Beijing Zhong-jingkeyi Technology). Prior to the measurement, the samples were dried under exposure to the infrared lamp. The average size of metal particles was determined on the basis of 250–300 particles.

Fourier transform infrared (FT-IR) spectra were measured by an FT-IR spectrometer (Perkin-Elmer, Model Spectrum 100). The sample was mixed with a KBr powder with a sample/KBr weight ratio of 1/100–1/50. The sample was then ground to 100 mesh sieves under the infrared lamp to remove adsorbed water, and afterward was pressed into a disk by applying 2.0 MPa pressure for 2 min. The semitransparent tablet was placed in the IR spectrometer for detection within the frequency range 4000–400 cm^{-1} with a spectral resolution of 4.0 cm^{-1}. Spectra were obtained in transmission mode for identification.

Raman spectrograms were collected using a confocal Raman spectroscopy (LabRAM HR, Horiba J.Y., France) equipped with a visible 514.5 nm Ar$^+$ laser and a high-grade Leica microscope (long working distance objective 50×). Single-crystal silicon was used for position correction. The confocal pore size was set to 300 μm for all tests. The attenuator was utilized to avoid signal overflow and sample oxidation. The intensity of irradiation of the samples was attenuated by a factor of 10, and no damage to the samples