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Full Length Article

Efficient diesel production over the iron-based Fischer–Tropsch catalyst supported on CNTs treated by urea/NaOH

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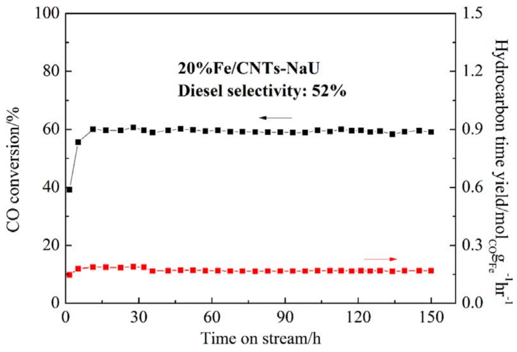
GRAPHICAL ABSTRACT



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ABSTRACT

Due to the complex control of nitrogen (N) species in functionalizing the carbon nanotubes (CNTs), the contribution of N species to catalysis is difficult to understand. In this study, we report a facile one-pot approach for the synthesis of N-doped CNTs with N present only in the pyrrolic form using a hydrothermal method and by tailoring the treatment conditions, the N content could reach 2.3 at.%. Then the N-doped CNTs are used as a support to prepare an iron-based Fischer–Tropsch synthesis (FTS) catalyst. The FTS activity and C_{5+} selectivity of N-doped CNTs supported iron catalyst increases with an increase of N content up to 2.1% but it decreases with higher pyrrolic N content. The enhanced FTS catalytic performance is attributed to increased electron conduction, electron donor effect and improved surface basicity due to the pyrrolic N incorporated into the carbon framework. Furthermore, a urea/NaOH co-treatment of CNTs is conducted and the treated CNTs is used as a support for preparing an iron catalyst. The results indicate that the synergistic modification effect of NaOH and urea effectively functionalizes the CNTs and leads to the incorporation of the pyrrolic N, to a high graphitization degree, to easy reduction, to a structural integrity and to a strong metal-support interaction of the supported iron catalyst. This results in an increased FTS activity, superior stability and remarkable diesel selectivity (52%). This synergistic effect shows the potential applications of carbon materials in the field of energy storage, carbon dioxide capture and catalysis, with appropriate functionalization.

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1. Introduction

Fischer–Tropsch synthesis (FTS) is an alternative non-oil-based route to produce super-clean transportation fuels and to build block chemicals from syngas [1–3]. Iron-based catalysts for the FTS have been widely investigated, due to their high activity and low cost [4]. Moreover, the syngas, derived from the coal or biomass with the H_2/CO ratio lower than 2:1 or CO_2-rich, can be adjusted by iron catalyst through the water-gas-shift (WGS) reaction. The physico-chemical property of the support has a great influence on the morphology, dispersion, distribution, reduction and carbonization of the supported catalyst, and consequently on the FTS reaction performance of the catalyst. However, the selective production of the desired product is a big challenge, as it is difficult to limit the chain propagation and terminate the Anderson–Schulz–Flory (ASF) distribution [5]. According to the ASF distribution, the diesel (C10-20) selectivity is limited to 39%. Moreover, by decreasing the formation of undesired by-products, the recycling of light hydrocarbon back to syngas and the hydrogenation of heavy hydrocarbons can be avoided.

For the conventional infrastructure, strong interaction between the metal and the support will cause the formation of iron phases that are difficult to be reduced, which is detrimental for the FTS performance [6]. Carbon nanotubes (CNTs) with unique properties has been intensively studied as a support. However, the inert surface and the hydrophobic properties of the CNTs are not ideal features to obtain good dispersion and anchor of the active metal [7,8]. In addition, proper interaction between the support and the active phase is required to anchor and stabilize the active site. To solve these problems, many approaches have been used to modify the carbon materials and make them more suitable as supports for these processes [9].

Indeed, the electronic structure surrounding the carbon atoms and the local charge density distribution could be systematically modulated by N atoms incorporated into the CNTs frameworks, which could lead to an enhancement of the catalytic performance [10]. The electron-donating effect of the incorporated N into the CNTs framework causes a charge transfer to the vacant d orbitals of the transition-metal, which weakens the C—O bond and increases the CO adsorption [11]. Furthermore, the intrinsic basicity of the N-doped CNTs reinforces the dissociative adsorption of CO by decreasing the C—O bond strength, which results in an improved chain growth probability and then is beneficial to the production of heavy hydrocarbons. The anchoring site of the N-doped CNTs can strongly interact with the active phase, which results in a high dispersion and thus engenders more exposed active sites [12]. At the same time, the N incorporated into the CNTs matrix can promote the electronic conductivity between the support and active phases [13]. Both *in-situ* synthesis and post-synthesis processes are used to prepare N-doped CNTs. For N-doped CNTs prepared by *in-situ* synthesis, CNTs with bamboo-like structure are often formed, which hinders the dispersion and the transfer of the active phase [14,15]. The N-doped CNTs with pyridinic N, pyrrolic N, quaternary N or N from pyridinic oxide can also be obtained with post-synthesis [7], and the CNTs prepared with these methods do not show bamboo-like structure. However, it is still difficult to properly modify the CNTs with isolated N species. Furthermore, the effect of different N species on the FTS performance is not well understood. The above difficulties are crucial issues to fully understand the mechanisms of these materials.

The hydrothermal method is widely used for material synthesis, fabrication and functionalization [16]. Besides, the inclusion of pyrrolic N into the CNTs framework always occurs at low temperature [17]. Based on this, it is reasonable to assume that the incorporation of pyrrolic N into CNTs can be achieved through a one-pot hydrothermal method. Simultaneously, the preparation of different N contents should also be possible.

Besides commonly used acid treatment of CNTs, the alkali modification of carbon material has also been reported recently [18]. Results show that an increased FTS catalytic performance is achieved with an iron catalyst supported on alkali-treated CNTs [19]. But, a gradual decline in FTS activity is observed for the iron catalyst supported on the CNTs treated by alkali solution. Furthermore, an alkali and urea mixture is often used to pretreat the fiber of cellulose, to destroy the intra- and inter-molecular hydrogen bonding at low temperature and to solvate the cellulose chain [20]. Considering this, we try to combine alkali and urea treatment for the CNTs modification and discuss their influences on the structure and property of CNTs, which has not been reported.

Here, commercial CNTs with a well-defined structure, high crystallinity and highly ordered sp^2-carbon network was used as the reference. A one-step hydrothermal method to dope the CNTs with N atom using urea was reported. Only pyrrolic N was introduced into the CNTs matrix, and in a concentration range that depends on the treatment condition. These modified CNTs were used as support for Fe-based catalysts. The physicochemical properties of such catalysts were studied and their FTS catalytic performances were assessed. The correlation between the pyrrolic N content and FTS catalytic performance was also established. In addition, the urea/NaOH mixed treatment for CNTs was studied and its synergistic effect on the catalytic performance of the supported iron catalyst was discussed in detail.

2. Experimental

2.1. Catalyst preparation

The pristine CNTs (multi-wall CNTs) sample was supplied from the Chengdu Organic Chemical Co. of Chinese Academy of Sciences. Iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), nitric acid (HNO_3, 65 wt%), urea ($CO(NH_2)_2$) and sodium hydroxide (NaOH) were purchased from Tianjin Kermel Co., LTD of China. All the reagents used were analytical grade without any further purification.

Prior to the experiment, the virgin CNTs were pretreated in concentrated nitric acid (65 wt%) at 122 °C (azeotropic point) for 6 h to remove the amorphous carbon and to create functional groups [21]. After being cooled down to room temperature, the CNTs were filtered and subsequently washed with deionized water several times until a neutral pH value was reached, and then dried at 110 °C for 12 h for further use.

The urea and alkali modification of CNTs were performed using a hydrothermal method. In a typical urea treatment, the acid treated CNTs (2.5 g) were added to an urea aqueous solution (50 mL in deionized water, 7.5 M) at ambient temperature. The mixture was placed in a Teflon cup and then transferred into the stainless steel autoclave, which was then heated at different temperatures (110, 190 and 220 °C) for 10 h. Then the autoclave was cooled down to room temperature and the resulting sample was filtered and washed with de-ionized water until a neutral pH value was reached, followed by drying at 110 °C for 12 h. The treated samples were labeled as CNTs-110, CNTs-190 and CNTs-220, respectively. To investigate the effect of peroxidation on the subsequent N-doping of CNTs, the pristine CNTs (no acid treatment) treated by urea at 110 °C was also prepared and named as CNTs-U. In addition, the CNTs-190-15 sample was prepared with the same method as mentioned above except that the urea concentration was 15 M instead of 7.5 M.

For the urea and alkali co-treated sample, 2.5 g acid treated CNTs were immersed into 50 mL aqueous solution (50 mL de-ionized water, 7.5 M urea and 7.5 M NaOH) and then the mixture was heated in a sealed Teflon-lined stainless steel autoclave at 190 °C for 10 h. The subsequent procedures, including filtration and drying, were the same as that of CNTs-110. The resulting sample was labelled as CNTs-NaU. In addition, the reference sample CNTs-Na was prepared with the same method with CNTs-NaU by using NaOH (7.5 M) as solvent instead of a mixture of urea (7.5 M) and NaOH (7.5 M).

Regarding the preparation of the catalysts, 20 wt% Fe loading was adopted with an incipient wetness impregnation method. The catalysts