Fabrication of K-promoted iron/carbon nanotubes composite catalysts for the Fischer–Tropsch synthesis of lower olefins

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ABSTRACT

K-promoted iron/carbon nanotubes composite (i.e., FeK-OX) was prepared by a redox reaction between carbon nanotubes and K_2FeO_4 followed by thermal treatments on a purpose as the Fischer–Tropsch catalyst for the direct conversion of syngas to lower olefins. Its catalytic behaviors were compared with those of the other two Fe-IM and FeK-IM catalysts prepared by impregnation method followed by thermal treatments. The novel FeK-OX composite catalyst is found to exhibit higher hydrocarbon selectivity, lower olefins selectivity and chain growth probability as well as better stability. The catalyst structure-performance relationship has been established using multiple techniques including XRD, Raman, TEM and EDS elemental mapping. In addition, effects of additional potassium into the FeK-OX composite catalyst on the FTO performance were also investigated and discussed. Additional potassium promoters further endow the catalysts with higher yield of lower olefins. These results demonstrated that the introduction method of promoters and iron species plays a crucial role in the design and fabrication of highly active, selective and stable iron-based composite catalysts for the FTO reaction.

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1. Introduction

Lower olefins ($C_2^=$–$C_4^=$) are widely used as key intermediates and building blocks in the chemical industry, and they are traditionally produced by cracking of oil-derived hydrocarbons and dehydrogenation of alkanes [1–3]. A pressing necessity to address their environmental and economic challenges, however, requires the development of alternative strategies. Recently, direct conversion of coal-, biomass- and natural gas-derived syngas to lower olefins without intermediate steps, i.e., Fischer–Tropsch-to-Olefins (FTO), has gained a renewed interest as a burgeoning non-petroleum route for sustainable production of lower olefins [3–5]. This process mainly employs Ru-, Co- and Fe-based catalysts [6–10]. Relative to other FTO catalysts, Fe-based catalysts are more attractive not only for the lower cost and methanation activity at high temperature as well as higher selectivity of lower olefins, but also for the higher tolerance to the contaminants and water-gas shift (WGS) activity enabling the direct use of CO-rich syngas without purification and H_2/CO ratio adjustment [3,4].

For several decades, substantial efforts have been devoted to gaining a better understanding of the relationship between structure of Fe-based catalysts and their FTO performance [11–17]. In particular, weakly interactive supports, such as α-Al_2O_3 and carbon materials, endow iron catalysts with the favorable activation of iron species into iron carbides and thus better FTO performance [18,19]. Hierarchical structured α-Al_2O_3 in comparison to commercial α-Al_2O_3 has been developed and shown to be able to effectively disperse and immobilize iron species for the improved FTO performance [19]. Also, carbon materials with much higher specific surface area have been widely employed to support iron FTO catalysts, such as carbon nanotubes (CNTs), carbon nanofibers, graphene and activated carbon [13,18,20–27]. In addition to the selection and manipulation of supports, many different elements including K and Mn have been demonstrated as promoters to remarkably enhance the selectivity of lower olefins [3,4,6,28–36]. Recently, we have developed a novel strategy to prepare highly efficient Fe/MnK-CNTs FTO catalyst using the resultant Mn- and K-coated CNTs from a redox reaction between CNTs and $KMnO_4$ as the support, which exhibits the uniform and small-sized iron nanoparticles, well-distributed promoters, weak metal-support interaction and great defects on support [37]. As a consecutive effort, in this work, this strategy has been extended to prepare

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potassium-promoted Fe/CNTs FTO catalyst using the as-synthesized K-coated CNTs by a redox reaction between CNTs and K_2FeO_4 [38] as the support.

Herein, K-promoted iron/carbon nanotubes composite (i.e., FeK-OX) catalyst was prepared by a redox reaction between carbon nanotubes and K_2FeO_4 followed by thermal treatments for the Fischer–Tropsch synthesis of lower olefins. For comparison, the other two Fe-IM and FeK-IM catalysts prepared by impregnation method followed by thermal treatments were also tested for the FTO reaction. The calcined, reduced and/or used catalysts were characterized by multiple techniques such as XRD, Raman, TEM and EDS elemental mapping, and a plausible catalyst structure-performance relationship was established. Furthermore, effects of additional potassium into the FeK-OX composite catalyst on the FTO performance were also investigated and discussed. These results demonstrated the importance of tailor-designed CNTs for the fabrication of iron-based FTO catalysts with higher activity and selectivity as well as better stability, and this has not been reported previously.

2. Experimental

2.1. Catalyst preparation

The novel composite catalyst was synthesized by a redox reaction between potassium ferrate (K_2FeO_4) and CNTs followed by thermal treatments. Briefly, the pretreated CNTs [37] were soaked in a solution of K_2FeO_4 in aq. KOH for 30 min at 70 °C. Then, the filtrated composites were dried at 120 °C under static air for 12 h and subsequently annealed under nitrogen atmosphere at 400 °C for 2 h. The as-obtained calcined sample was denoted as FeK-OX. For comparison, unpromoted and K-promoted iron-based catalysts with the same metal loadings were prepared by traditional impregnation method. Appropriate amount of $Fe(NO_3)_3 \cdot 9H_2O$ and the mixture of $Fe(NO_3)_3 \cdot 9H_2O$ and KNO_3 dissolved in deionized water were added to the pretreated CNTs, respectively. The loadings of the two samples were the same as that of FeK-OX composite determined by ICP-AES. The samples were kept at room temperature for 24 h, and dried at 120 °C in static air for 12 h and then calcined in a flow of N_2 at 400 °C for 2 h. The as-obtained calcined samples were denoted as Fe-IM and FeK-IM, respectively. Moreover, FeK-OX samples with different contents of extra K promoter (FeK-OX-nK, n representing the nominal loading of extra K, $n = 1$, 2 or 5) were also prepared, where appropriate amount of potassium nitrate solution was further added into the FeK-OX sample. Similarly, the impregnated samples were dried at ambient temperature for 24 h, dried at 120 °C for 12 h, and calcined in a flow of pure nitrogen at 400 °C for 2 h.

2.2. Catalyst characterization

An inductively coupled plasma-atomic emission spectroscopy instrument (ICP-AES, Agilent 725ES, USA) was used to detect the loadings of Fe and K. X-ray diffraction (XRD, Rigaku D/Max2550VB/PC, Japan) with Cu K_α radiation ($\lambda = 1.54056$ Å) was used to characterize the crystal phases of the samples. The diffraction data of 2θ from 10º to 80º were collected at a step size of 0.02º. The reducibility of calcined catalysts was evaluated by H_2 temperature-programmed reduction (H_2-TPR) using an Autochem 2920 system (Micromeritics, USA) equipped with a thermal conductivity detector (TCD). A mixture gas of 10% H_2 in Ar was used as reductant (30 mL/min). The tests were carried out from room temperature to 800 °C at a heating rate of 10 °C/min. The surface chemistry properties of catalyst, e.g., the amounts of surface defects, were obtained from a Raman microscope (inVia Reflex, Renishaw, UK) using 514 nm laser excitation. Transmission electron
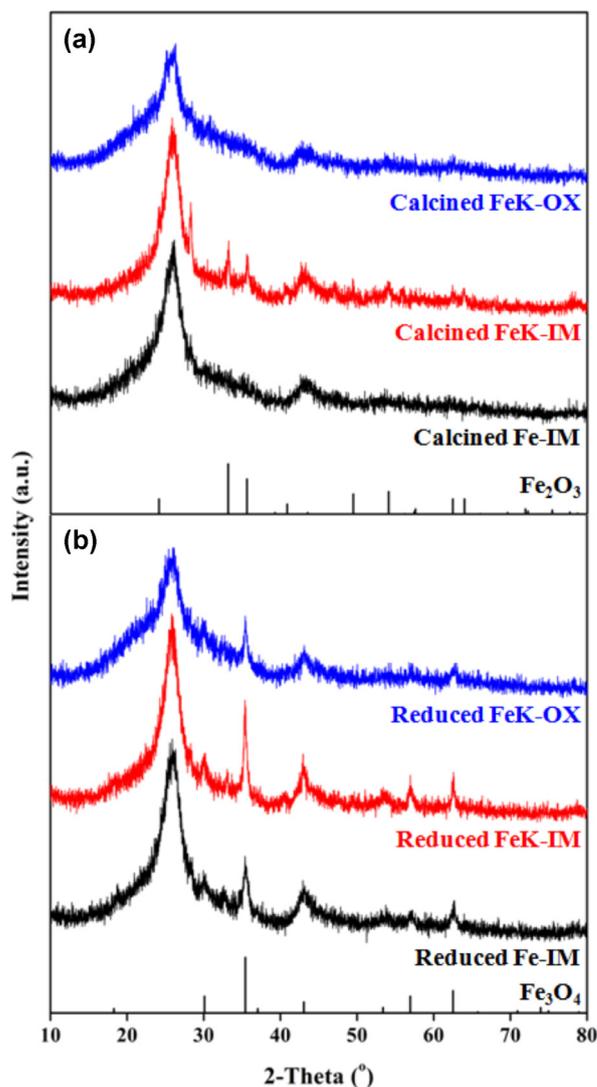

Fig. 1. XRD patterns of calcined (a) and reduced (b) samples. Standard patterns of α-Fe_2O_3 (JCPDS No. 33-0664) and Fe_3O_4 (JCPDS No. 19-0629) are also presented for comparison.

microscopy (TEM, JEOL JEM-2100, Japan) was employed to characterize the microstructures of catalysts. Elemental mappings of FeK-OX sample were carried out by an energy dispersive X-ray spectroscopy (EDS, Oxford-INCA) attached to TEM. For the characterization of reduced samples, all the calcined samples were reduced in hydrogen at 300 °C for 10 h and subsequently passivated in 0.97% O_2/Ar.

2.3. Catalytic testing

Catalytic testing was performed in a stainless steel fixed-bed reactor: ca. 0.1 g catalyst was in-situ reduced by pure hydrogen at 300 °C for 10 h at ambient pressure, the reactor was cooled to 270 °C, and then syngas (H_2/CO = 1) was introduced into the reactor. Gas chromatograph (GCA90, Echrom) was used to analyze on-line the outlet products, where a capillary column (MEGA-1) connected to a flame ionization detector was used to analyze hydrocarbons, while a packed column (Porapak Q) connected to a thermal conductivity detector to analyze CO, CO_2 and H_2. Considering the analysis complexity of other oxygenates, their quantitative analyses were not carried out in this work.

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