Catalysis Today 215 (2013) 86–94

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Carbon nanotube-supported Fe–Mn nanoparticles: A model catalyst for direct conversion of syngas to lower olefins

Jing-Dong Xu, Kong-Tao Zhu, Xue-Fei Weng, Wei-Zheng Weng*, Chuan-Jing Huang, Hui-Lin Wan*

State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

ARTICLE INFO

Article history:
Received 1 November 2012
Received in revised form 15 April 2013
Accepted 23 April 2013
Available online 30 May 2013

Keywords:
Fischer–Tropsch synthesis
Monodisperse Fe–Mn nanoparticles
Carbon nanotube support
Lower olefins
Mn promotion
In situ XRD

ABSTRACT

Carbon nanotube (CNT)-supported monodisperse $Fe_{3-x}Mn_xO_4$ ($x = 0$–0.5) nanoparticles in which Mn has an intimate contact with Fe were synthesized and used as a model catalyst for investigating the promotion effect of Mn oxide on the iron-based catalysts for Fischer–Tropsch synthesis (FTS) reaction. It was found that incorporation of Mn oxide (Mn/Fe = 0.024–0.2) into a Fe_3O_4/CNT catalyst promoted the reduction of Fe_3O_4 to FeO, but retarded the further reduction of FeO to metallic Fe. Incorporation of small amount of Mn ($Mn/Fe \leq 0.01$) into the iron catalyst results in an increase in C_{5+} yield and C_2–C_4 olefin selectivity without any loss in FTS activity. However, the total selectivity of C_2–C_4 hydrocarbons is almost not affected by the addition of Mn oxide. An excess of Mn oxide in the catalysts ($Mn/Fe > 0.024$) can lead to a significant decrease in FTS activity with no further improvement in C_2–C_4 olefin selectivity. The results of temperature-dependent XRD study on the Fe_3O_4/CNT and $Fe_{2.73}Mn_{0.27}O_4$/CNT catalysts under $H_2/CO = 1$ mixture suggest that the decreasing in FTS activity on the $Fe_{3-x}Mn_xO_4$/CNT catalysts with an excess of Mn may have resulted from that the rate of carburization of metallic Fe is retarded by the Mn oxide species.

1. Introduction

Lower olefins are key building blocks for the modern chemical industry [1,2]. Traditionally, lower olefins are produced by steam cracking of naphtha or as byproducts of oil refining processes. The growth in demand and the depletion of known crude oil sources are currently driving researchers to develop alternative routes to produce chemicals. Direct conversion of coal-, biomass-, and natural gas-derived syngas (a mixture of CO and H_2) to lower olefins *via* Fischer–Tropsch synthesis (FTS) without intermediate steps is a promising route to meet the increasing demand for chemical feedstocks [3]. Increasing the selectivity of lower olefins has long been a challenging problem in FTS since typical FTS product selectivity is limited by the Anderson–Schulz–Flory distribution [4]. In recent years, many efforts have been devoted to the development of efficient FTS catalysts with high selectivity to the desired products. These efforts include the modification of supports [5–7], controlling the particle size of active metals [2,6,8,9], and using bimetallic alloys [10,11]. Another effective way to tune the selectivity of FTS is to add small amount of promoters to the catalytic materials. Manganese has been widely used as a promoter for the iron-based FTS catalysts. It was reported that the presence of manganese enhanced the selectivity of lower olefins and suppressed the formation of undesired methane [12–15]. Manganese was also found to promote the dispersion of iron and make the catalysts less prone to deactivation through carbon deposition [16]. Some authors claimed an increase in intrinsic activity for the Mn-promoted Fe catalysts [17].

Although manganese as a promoter has been extensively investigated, some inconsistencies regarding the effects of Mn oxide on the iron-based catalyst still exist. The lack of enhancement of lower olefin selectivity with Fe–Mn catalysts has been reported by some research groups [18,19], and the promotion mechanism of Mn oxide is still not completely clear. It was found that the effectiveness of Mn as a promoter in a catalyst was closely related to the location of the Mn species. The catalytic properties of a TiO_2 supported Co–Mn catalyst was not enhanced when Mn species was located on the support. Only those MnO particles not strongly interacting with the TiO_2 and locating in the proximity of the Co^0 sites led to a promotion effect [20]. This implies that the discrepancies in the promotion effect of Mn oxide may have resulted from the variety of catalyst preparation methods as well as pretreatment conditions. In addition, interpretation of the promotion effect of Mn oxide in a catalyst can be clouded if the particle size effect and the interaction between metal/promoter and support are present.

---

* Corresponding authors. Fax: +86 592 2185192.
E-mail addresses: wzweng@xmu.edu.cn (W.-Z. Weng), hlwan@xmu.edu.cn (H.-L. Wan).

0920-5861/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cattod.2013.04.018

Recently, a new approach for preparing supported metal catalyst through the assembling metal oxide nanoparticles synthesized from thermal decomposition of metal organic precursors was reported in the literature [21,22]. This technique enables the control of metal particles with narrow size distribution on the support regardless of metal loadings. This method can also be readily extended to the synthesis of supported Fe–Mn catalyst with uniform particle size which can be used as a model catalyst to investigate the promotion effect of Mn oxide on the iron-based catalyst.

In this paper, monodisperse Fe–Mn binary nanoparticles with tunable Mn/Fe ratio were prepared by high-temperature reduction/decomposition of iron(III) acetylacetonate and manganese(II) acetylacetonate in the presence of benzyl ether and oleylamine [23]. The Fe–Mn nanoparticles were then supported on carbon nanotube (CNT) to yield the model catalysts for FTS. CNT was chosen because it is a carrier material with limited interaction toward Fe and Mn. With these catalysts, the promotion effect of Mn oxide on the iron-based catalysts can be studied in the absence of other unnecessary disruptive factors such as metal particle sizes, co-existence of different metal crystallite phases as well as the interaction between metal/promoter and support.

2. Experimental

2.1. Chemicals

Iron(III) acetylacetonate ($Fe(acac)_3$, 99.9%), manganese(II) acetylacetonate ($Mn(acac)_2$), oleylamine (70%), benzyl ether (99%) were purchased from Sigma–Aldrich. Iron(III) nitrate ($Fe(NO_3)_3$, 98.5%), manganese(II) nitrate ($Mn(NO_3)_2$, 50% solution), absolute ethanol and hexane were purchased from Sinopharm Chemical Reagent.

2.2. Synthesis of $Fe_{3-x}Mn_xO_4$ nanoparticles

The method for the synthesis of $Fe_{3-x}Mn_xO_4$ nanoparticles reported here is a modified version of thermal decomposition of $Fe(acac)_3$ reported by Sun et al. [23]. In this work, oleylamine was chosen as the only surfactant since it can act as an alternative reducing agent as well as a stabilizer. This provides us with a much simplified and economic synthesis protocol to prepare monodisperse nanoparticles. The similar procedures can be readily extended to the synthesis of size- and composition-controlled $Fe_{3-x}Mn_xO_4$ nanoparticles.

Monodisperse $Fe_{3-x}Mn_xO_4$ nanoparticles with different Mn/Fe molar ratios were synthesized by high temperature decomposition of a mixture of $Fe(acac)_3$ and $Mn(acac)_2$ in benzyl ether solution in the presence of oleylamine. Different Mn/Fe ratios were achieved by varying the relative amounts of $Mn(acac)_2$ and $Fe(acac)_3$ precursors. The synthesized samples are denoted as $Fe_{3-x}Mn_xO_4$, where $x = 0–0.5$. In a typical procedure for the synthesis of $Fe_{2.5}Mn_{0.5}O_4$ nanoparticles, $Fe(acac)_3$ (1.81 mmol), $Mn(acac)_2$ (0.362 mmol), oleylamine (10.0 mL), and benzyl ether (10.0 mL) were mixed and magnetically stirred under a flow of N_2. The solution was heated over 30 min to 473 K and kept for 120 min. Under the protection of N_2, the mixture was then quickly heated to 573 K and refluxed for 60 min. The resulting mixture was then cooled to room temperature, and an excess amount of ethanol was added to yield a black precipitate, which was then separated by centrifuging. The black precipitate was redispersed in hexane and precipitated with ethanol and centrifuged to remove the solvent. Finally, the nanoparticle product was dried by evacuation at room temperature.

2.3. Synthesis of $Fe_{3-x}Mn_xO_4$/CNT model catalysts

Catalysts preparation included the assembly of $Fe_{3-x}Mn_xO_4$ nanoparticles on CNT and thermal treatment. CNT with outer diameters of 20–60 nm and inner diameters of 3–5 nm were prepared by the methods described in the literature [24]. Raw CNT was then treated with concentrated nitric acid (68 wt%) at 383 K for 12 h in an oil bath. The treated CNT was separated by filtration, washed with distilled water until neutral pH was reached, and dried at 393 K for 12 h. BET surface area of the CNT is 155 m^2/g. To synthesis $Fe_{3-x}Mn_xO_4$/CNT catalyst, the treated CNT (1.0 g) was dispersed in 100 mL of hexane to form a CNT-hexane suspension with the help of ultrasonication. 100 mL of hexane suspension containing 100 mg of $Fe_{3-x}Mn_xO_4$ nanoparticles was then added dropwise into the CNT-hexane suspension under ultrasonication. After stirring for 24 h, the hexane was removed by evacuation at room temperature. The solid sample was heated to 673 K at a rate of 2 K/min under N_2 (30 mL/min) and calcined for 5 h. The catalysts were denoted as $Fe_{3-x}Mn_xO_4$/CNT. The metal loading (Fe, Mn) in all catalysts was 6 wt%.

The CNT supported Fe_3O_4 and $Fe_{2.5}Mn_{0.5}O_4$ catalysts were also prepared by incipient wetness impregnation method for *in situ* XRD investigation. The CNT was impregnated with appropriate amounts of aqueous solution of $Fe(NO_3)_3$ or $Fe(NO_3)_3$ and $Mn(NO_3)_2$ mixture. After keeping at room temperature for 24 h, the samples were dried at 383 K for 12 h, and calcined under N_2 at 673 K for 5 h. Fe loading on both catalysts is 10 wt%. The catalysts are denoted as Fe_3O_4/CNT-IWI and $Fe_{2.5}Mn_{0.5}O_4$/CNT-IWI.

2.4. Catalyst characterization

The microstructure of $Fe_{3-x}Mn_xO_4$ nanoparticles and $Fe_{3-x}Mn_xO_4$/CNT catalysts was examined *ex situ* by a FEI Tecnai F30 transmission electron microscopy (TEM) operated at an accelerating voltage of 300 kV. The sample for TEM measurement was prepared by depositing a drop of $Fe_{3-x}Mn_xO_4$/hexane or $Fe_{3-x}Mn_xO_4$/CNT/ethanol suspension on a carbon-film-coated copper grid. Scanning transmission electron microscopic (STEM) images were recorded with a high-angle annular dark field (HAADF) detector. Energy dispersive X-ray spectroscopy (EDS) was recorded with an EDAX system attached to the Tecnai F30 microscope.

X-ray powder diffraction (XRD) analysis was carried out by a Panalytical X'pert PRO diffractometer scanning 2θ from 20 to 80°. Cu-Kα radiation ($\lambda = 1.5406$ Å) obtained at 40 kV and 30 mA was used as the X-ray source. Average size of $Fe_{3-x}Mn_xO_4$ nanoparticles was calculated by the Scherrer's equation using the Fe_3O_4 (311) XRD peak at $2\theta = 35.5°$. The *in situ* XRD experiment was carried out on the same instrument with an Anton Paar XRK-900 reaction chamber. In the *in situ* XRD experiment, diffraction pattern of the catalyst was recorded within a 2θ range of 20–50°, because the most intense diffraction peaks of the relevant phases, *i.e.* CNT, Fe, FeO, Fe_3O_4 and Fe_xC_y, fall in this range. The scanning rate was 3°/min. In each *in situ* XRD experiment, the sample was heated in a flow of pure H_2 (50 mL/min) up to 873 K at a rate of 10 K/min. During this process, the XRD patterns were collected at the prespecified temperatures. The phase transformations of the catalysts during FTS reaction were also studied by *in situ* XRD. Before the measurement, the catalyst was reduced with H_2 (50 mL/min) at 673 K for 5 h. After cooling to 573 K, the reduced catalyst was switched to a flow of syngas ($H_2/CO = 1/1$, v/v, 30 mL/min) at atmospheric pressure. The temperature of the catalyst was then raised to the prespecified temperatures under syngas flow, and the XRD data was collected after the catalyst was treated with syngas at each specified temperature point for about 1 h.