Catalysis Today 186 (2012) 121–127

Contents lists available at SciVerse ScienceDirect

Catalysis Today

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

FeN particles confined inside CNT for light olefin synthesis from syngas: Effects of Mn and K additives

Zhiqiang Yang[a], Xiulian Pan[a,*], Junhu Wang[b], Xinhe Bao[a,*]

[a] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China
[b] Mössbauer Effect Data Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China

ARTICLE INFO

Article history:
Received 10 July 2011
Received in revised form
14 November 2011
Accepted 27 November 2011
Available online 2 January 2012

Keywords:
CO hydrogenation
Carbon nanotubes
Confined iron nitride nanoparticles
Mn promotion
K promotion

ABSTRACT

The effects of manganese and potassium on the structural and morphological properties, phase compositions and CO adsorption behavior of the CNT-confined FeN catalyst were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), ^{57}Fe Mössbauer effect spectroscopy (MES) and CO temperature-programmed desorption (TPD). The results suggested that the presence of manganese helps retain nitrogen in cubic FeC_xN_{1-x} and facilitates CO adsorption. The selectivity to $C_2^{=}$—$C_4^{=}$ light olefins is enhanced over Mn(1.0 wt%)/FeN/CNT although the activity decreases within the loading range of 0.5–2.0 wt% for Mn. Although further promotion with K could improve the activity slightly, the selectivity to light olefins decreases. At the same time, the addition of potassium enhanced the water gas shift activity and shifted the selectivity to heavy hydrocarbons (C_{5+}), similar to the conventional reduced iron catalysts.

1. Introduction

Synthesis of light olefin such as ethylene and propylene from syngas is an attractive non-petroleum based route to obtain these basic chemicals. Recently commercial production facilities based on the methanol-to-olefin technology have been successfully installed. At the same time, direct synthesis from syngas by reducing the methanol synthesis process is also attractive. Extensive efforts have been made, mostly involving modification of Fischer–Tropsch synthesis (FTS) catalysts in order to modulate the products towards light olefins since typical FTS products follow ASF (Anderson–Schulz–Flory) distribution, which includes large amounts of saturated alkanes and long chain hydrocarbons. Among a variety of catalysts investigated, iron-based FTS catalysts appear to be more promising because of a relatively higher olefin selectivity with a lower methane selectivity [1–7]. However, the still low selectivity and yield to the desired light alkenes, and low stability of iron catalysts against oxidation under reaction conditions restricts their commercial application at an industrial scale.

In the 1950s, nitrided iron catalysts were first used for FTS by Anderson et al. at the Bureau of Mines [8]. Those epsilon iron nitride (Fe_2N) catalysts were reported to exhibit a high activity, stability and an unusual selectivity to a relatively low molecular weight product (a selectivity of 57.2 wt% to C_{1-4} hydrocarbons) with respect to the conventional reduced iron as a catalyst (47.3%) [8,9]. Yeh et al. supported iron nitride on silica, which also yielded a higher olefin selectivity, but at the same time larger proportions of higher molecular weight products than iron carbide catalyst [10]. Since then, not much work continues on iron nitride catalysts and there is only limited knowledge. We recently incorporated iron nitride (FeN) nanoparticles into the channels of carbon nanotubes (CNTs) and used them as a catalyst for light olefin synthesis from syngas [11]. Confinement inside CNTs facilitated formation of cubic iron nitride with a high N content (50 at.% N). This phase was only theoretically predicted earlier [12,13]. Such a CNT-confined iron nitride catalyst exhibited a much higher activity than the reduced iron catalyst because of its higher resistance to oxidation under reaction conditions. It was also more active than iron nitride particles dispersed on the outer walls of CNTs, likely due to a higher concentration of cubic phase iron nitride and restriction of the particle size inside CNTs. However, hydrocarbon distributions were similar in the products over these two catalysts and the selectivity to light olefins was around 35–38% with the olefin/alkane ratio around 2.6–3.0. Therefore, we explore in this study the possibility to increase the selectivity to light olefin by modifying the CNT-confined FeN catalyst with Mn and K.

Manganese and potassium oxides have been frequently used as promoters for iron catalysts to improve the light olefin selectivity [1–3,14–16], the activity and stability of Fe catalysts [15–17]. The surface basicity and the carburization of the catalyst can

---

[*] Corresponding authors. Tel.: +86 411 8468 6637; fax: +86 411 8437 9128.
E-mail addresses: panxl@dicp.ac.cn (X. Pan), xhbao@dicp.ac.cn (X. Bao).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.11.034

be improved with an appropriate amount of manganese, which resulted in an enhanced FTS activity [1,15]. The presence of manganese can also prohibit secondary hydrogenation of C_2H_4 and C_3H_6 [2], leading to a high selectivity to light olefins. But an excessive amount can retard the carburization of iron during reaction, which was considered to be essential to achieve a high activity due to enrichment of manganese on the catalyst surface [15,18–21]. The effects of potassium promotion on the catalytic behavior of iron-based FTS catalysts have also been extensively investigated [16,22–25]. An appropriate amount of potassium improved the catalytic activity, but the activity of the catalysts declined with the addition of an excess amount [16,23–25]. Formation of olefins and long chain hydrocarbons, and the carburization of surface Fe were usually facilitated while CH_4 formation was suppressed [22–25]. Following these earlier studies, we investigate the effects of manganese and potassium promoters on the structure and the catalytic performance of FeN nanoparticles confined in CNTs for light olefin synthesis from syngas.

2. Experimental

2.1. Catalyst preparation

Raw CNTs purchased from Chengdu Organic Chemicals (MFG code M12020702R) were first treated in concentrated HNO_3 (68 wt%) at 130 °C for 12 h. The inner and outer diameters were 4–8 nm and 10–20 nm, respectively. The catalysts were prepared following the previously reported procedure [7,11,26–28]. Briefly, aqueous solution of $Fe(NO_3)_3$ was introduced into the CNT channels by utilizing the capillary forces of CNTs aided by ultrasonication and stirring. Following controlled drying at 140 °C in air, a reported temperature-programmed-reaction (TPRe) method was adapted for the nitridation of these precursors to obtain iron nitride [11]. The sample was heated in a quartz tube reactor at 450 °C for 2 h in 50 ml/min ammonia stream. Prior to exposure to air, it was passivated in a 1% O_2/He (20 ml/min) for 12 h. The obtained sample is denoted as FeN/CNT. For preparation of Mn and K promoted FeN/CNT, a mixed aqueous solution of $Fe(NO_3)_3$, $Mn(NO_3)_2$ and KNO_3 was used as the precursor. The nominal loading of Fe in all catalysts was kept at 8.0 wt%. The resulting catalysts were denoted as K(*x* wt%)/Mn(*y* wt%)/FeN/CNT, where *x* and *y* denote the loading of K and Mn, respectively.

2.2. Catalyst characterization

X-ray diffraction (XRD) was carried out on a Rigaku D/Max 2500 diffractometer with a Cu Kα (λ = 1.541 Å) monochromatized radiation source, operated at 40 kV and 200 mA. Each sample was scanned at a rate of 5°/min, with 2θ varying from 20° to 70°.

The final compositions of the catalysts were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) on the SHIMADZU ICPS-8100. The results are listed in Table 1.

^{57}Fe Mössbauer spectra were recorded at room temperature using a Topologic 500A spectrometer with a proportional counter. ^{57}Co(Rh) moving in a constant acceleration mode was used as the radioactive source. The Doppler velocity of the spectrometer was calibrated with respect to α-Fe foil. The spectra were fitted with appropriate superpositions of Lorentzian lines using the MossWinn 3.0i computer program.

The morphology of the catalysts was characterized by transmission electron microscopy (TEM) on a FEI Tecnai G^2 microscope operated at an accelerating voltage of 120 kV. Microscopic specimens were prepared by ultrasonic dispersion of the catalysts in ethanol, and the suspensions were dropped onto a copper grid.

CO temperature programmed desorption (CO-TPD) experiments were carried out on a home-built four channel reactors equipped with an online 6-channel mass spectrometer (Omnistar GSD 301 O2 & GSS 300) as the detector. 80 mg catalyst was reduced in situ in syngas (CO/H_2 = 1:1) at 300 °C before it was exposed to a mixture of 5% CO/He, which was allowed for 30 min at room temperature. Then the catalyst was swept in a He stream for 30 min until a stable baseline had been obtained. CO desorption was performed from room temperature to 650 °C at a heating rate of 5 °C/min. In order to subtract the contribution of the oxygen functional groups of CNTs, temperature programmed desorption of CO in He was also examined from the catalysts without pre-treatment in syngas atmosphere and without pre-adsorption of CO.

2.3. Catalytic tests

CO hydrogenation was performed in a fixed bed micro reactor. A syngas mixture H_2/CO/Ar (47.5/47.5/5 vol%, purity: 99.99) was fed to the catalyst at a space velocity of 15,000 h^{-1}. Ar was used as an internal standard in order to ensure accurate mass balances.

100 mg catalyst was loaded in the reactor and was pre-treated in situ at 260 °C for 2 h in syngas stream (1 bar, 40 ml/min). Subsequently the temperature was increased to 300 °C and the pressure was increased gradually to 5 bar. The reaction was allowed for more than 24 h on stream to reach a steady state before analysis of the effluents. All gas lines after the reactor were kept at 150 °C. All products were analyzed by an online Angilent 7890A GC, which was equipped with a thermal conductivity detector (TCD), and a flame ionization detector (FID). Porapak Q and a 5 Å molecular sieves packed columns were installed to analyze H_2, Ar, CO_2, CH_4, and CO. FFAP and modified Al_2O_3 capillary columns were used for analysis of oxygenates and hydrocarbons.

3. Results and discussion

3.1. Catalytic performance of Mn, K-modified FeN/CNT catalyst

Table 2 lists the reaction results of Mn promoted FeN catalysts in syngas conversion. It can be seen that the presence of Mn additive decreases the activities with the loading in a range of 0.5–2.0%. For example, CO conversion decreases from 20.5% down to around

Table 1
Chemical composition of CNT confined K–Mn–FeN catalysts.

Catalysts	Targeted composition (wt%)			Measured composition (wt%)		
	Fe	Mn	K	Fe	Mn	K
FeN/CNT	8.0	0	0	5.46	0	0
Mn(0.5 wt%)/FeN/CNT	8.0	0.5	0	6.46	0.40	0
Mn(1.0 wt%)/FeN/CNT	8.0	1.0	0	6.44	0.77	0
Mn(2.0 wt%)/FeN/CNT	8.0	2.0	0	6.62	1.56	0
K(0.2 wt%)/Mn(1.0 wt%)/FeN/CNT	8.0	1.0	0.2	5.56	0.66	0.13
K(0.4 wt%)/Mn(1.0 wt%)/FeN/CNT	8.0	1.0	0.4	5.82	0.71	0.31
K(0.6 wt%)/Mn(1.0 wt%)/FeN/CNT	8.0	1.0	0.6	5.18	0.62	0.47
K(0.8 wt%)/Mn(1.0 wt%)/FeN/CNT	8.0	1.0	0.8	5.32	0.67	0.65