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Article

Nanowire accumulated $\text{Fe}_2\text{O}_3/\text{SiO}_2$ spherical catalyst for Fischer-Tropsch synthesis

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ABSTRACT

A catalyst consisting of SiO_2 nanowires and highly dispersed Fe_2O_3 (denoted NW-FS) was synthesized *in situ* by iron-assisted amine-vapor-transport treatment. NW-FS was prepared by the direct transformation of an industrial spherical $\text{Fe}_2\text{O}_3/\text{SiO}_2$ catalyst (denoted indus-FS). NW-FS was characterized by scanning electron microscopy, X-ray diffraction, transmission electron microscopy, N_2 -sorption measurements, X-ray photoelectron spectroscopy, and temperature-programmed reduction. NW-FS exhibited a high selectivity for light olefins, especially for ethene in the Fischer-Tropsch synthesis. This was because of the highly dispersed Fe_2O_3 and low diffusion resistance of its open structure. The C_2 – C_4 olefin/paraffin ratio was 3.3, which was higher than that of indus-FS at 1.9.

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1. Introduction

Loaded nanosized catalysts have received much attention because of their excellent catalytic performance [1,2]. The dispersion of the active species and the product diffusion path are important factors affecting their catalytic properties [3]. These factors are significantly affected by the properties of the support material. Several support structures have been reported, including mesoporous materials [4], zeolites [5], and carbon nanotubes or fibers [6,7]. The active species have been loaded onto these supports by wet impregnation, ion adsorption, and deposition precipitation [6–10]. However, narrow pores in these supports reportedly restrict the diffusion of reactants and products, resulting in undesired side reactions and by-products [11,12]. Designing new catalysts with highly dispersed active species and open structures is therefore of interest. We recently

reported a silicon nanowire array support that facilitated high catalytic performance. The open structure enhanced diffusion and inhibited sintering of the silver nanoparticle active material [13].

Light olefins are important raw materials in chemical industry. The rising price of petroleum has encouraged the development of petroleum-free approaches, an example of which is the methanol-to-olefin process [14–16]. The direct production of light olefins from syngas *via* the Fischer-Tropsch synthesis (FTS) is considered promising [17–21]. However, achieving sufficient selectivity for light olefins remains a challenge. This is because of the complex FTS reaction network, which includes several secondary reactions including hydrogenation, carbon-chain growth, isomerization, and hydrogenolysis [22–26]. Small active species are believed to benefit the generation of light hydrocarbon products. FTS catalysts have

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been prepared with different active species sizes, and the selectivity for short-chain products increased with decreasing size of the nano-metal active species [6–8]. High diffusivity supports should inhibit secondary hydrogenation and chain growth reactions by decreasing the re-adsorption and reaction of primary products. This should further improve the olefin selectivity [23,24].

Herein, an open-structured $\text{Fe}_2\text{O}_3/\text{SiO}_2$ catalyst consisting of a highly dispersed Fe_2O_3 on SiO_2 nanowire architecture (NW-FS) is prepared *in situ* from an industrial $\text{Fe}_2\text{O}_3/\text{SiO}_2$ catalyst (indus-FS). The method involves iron-assisted amine-vapor-transport (AVT) treatment from our previous report [27]. The initiating (catalytic) effect of the Fe_2O_3 nanoparticles [26] in indus-FS results in SiO_2 transforming into a nanowire architecture. Fe_2O_3 is highly dispersed on these nanowires. The resulting catalyst exhibits high selectivity for light olefins in FTS.

2. Experimental

2.1. Catalyst synthesis

In a typical synthesis of indus-FS, 125 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5 wt%) in 500 g of H_2O had $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25–28 wt%, w/w) added, until the pH was 7.5. Then 500 g of 40% (w/w) colloidal SiO_2 was added under vigorous stirring. The resulting mixture was subjected to spray drying. Indus-FS was obtained by calcination of the spray-dried powder at 550 °C for 4 h in a revolving furnace.

The NW-FS catalyst was prepared by the improved iron-assisted AVT treatment of indus-FS. A solution containing 3.5 g of triethylamine (98 wt%), 9.5 g of ethanediamine (98 wt%), and 2.0 g of deionized water was injected into the bottom of a polytetrafluoroethylene-lined stainless-steel autoclave. Indus-FS (1 g) was added to a basket in the upper part of the autoclave. The autoclave was sealed and heated at 200 °C for 24 h. The NW-FS catalyst formed in the amine vapor and was obtained by washing in deionized water, drying at 100 °C overnight, and calcining in air at 550 °C for 4 h.

Colloidal SiO_2 was purchased from Nalco Co. Ltd. Other reagents were purchased from Sinopharm Group Co. Ltd. and were used without further purification.

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were recorded on a Bruker D8 Advance diffractometer ($\text{Cu } K_\alpha$ radiation, 40 kV, 30 mA). Samples were scanned from 5° to 50° in 0.02° steps with a 5 s count time at each point. BET surface areas were determined by N_2 adsorption at –196 °C using a Micromeritics TriStar II 3020 instrument. The morphology of samples was examined by scanning electron microscopy (SEM, Philips XL 30). The sample was dispersed in ethanol, and a specimen stub was briefly immersed in this dispersion. The evaporation of ethanol yielded a film of sample evenly dispersed on the stub. The sample-coated stub was coated with Au by ion sputtering for 2 min. The sample components were determined by X-ray fluorescence (XRF) using a Bruker-AXS S4 explorer instrument. Transmission elec-

tron microscopy (TEM) images were recorded with a JEM-2011F microscope. Electron spin-resonance (ESR) spectra were recorded at room temperature using a Bruker EMX-8 spectrometer. X-ray photoelectron spectra (XPS) were recorded using a Shimadzu/Kratos Axis Ultra DLD spectrometer with an Al K_α excitation source. The adventitious carbonaceous C 1s line (284.6 eV) was used to calibrate binding energies. Temperature-programmed reduction (TPR) profiles of calcined catalysts were recorded using a purpose-built instrument. In TPR measurements, 20 mg of catalyst was used. A 10% H_2/Ar gas (30 cm^3/min) was introduced, and the temperature was increased to 800 °C at a rate of 10 °C/min.

2.3. FTS experiments

FTS experiments were conducted in an 8-mm internal diameter stainless-steel fixed-bed reactor. When testing the NW-FS and indus-FS catalysts, 1 g of catalyst in the reactor was reduced in a H_2 flow (50 ml/min) at 450 °C under a pressure of 0.1 MPa. Syngas was introduced into the reactor in a flow of N_2 as an internal standard. The N_2/syngas (v/v) ratio was 1/8. The weight hourly space velocity (WHSV) was controlled at 0.75 or 1.56 h^{-1} , and the H_2/CO ratio of the syngas was 1.0. The reaction temperature was 320 °C. Products were analyzed by two on-line gas chromatographs (Agilent 7890A GC) with a flame ionization detector and thermal conductivity detector using Agilent HP-1, HP-AL/M, and Haysep-D columns. The CO conversion, selectivity for hydrocarbon product x, and WHSV were calculated by:

$$\text{CO conversion} = \frac{\text{CO feed (g)} - \text{CO remaining (g)}}{\text{CO feed (g)}} \times 100\% \quad (1)$$

Selectivity for product x =

$$\frac{\text{amount of hydrocarbon x (g)}}{\text{gross amount of all hydrocarbons (g)}} \times 100\% \quad (2)$$

$$\text{WHSV} = \frac{\text{CO flow rate (g h}^{-1}\text{)}}{\text{weight of the core catalyst (g)}} \quad (3)$$

3. Results and discussion

3.1. Characterization

3.1.1. Morphology and particle size

Figure 1 shows SEM images of the indus-FS and NW-FS catalysts. Indus-FS exhibited a spherical morphology of size 10–50 μm (Fig. 1(a)). Its surface (Fig. 1(c)) was relatively smooth and contained pore-openings and small particles. After AVT treatment, NW-FS appeared to retain its original spherical morphology in the low magnification SEM image (Fig. 1(b)). However, higher magnification images revealed that the spheres gradually transformed into a nanowire architecture during AVT (Fig. 1(d) and (a)). Figure 1(f) shows numerous uniform highly dispersed Fe_2O_3 nanoparticles on the SiO_2 nanowires of NW-FS.

The Fe_2O_3 distributions of the catalysts are shown in Fig. 2. The diameters of the nanoparticles on indus-FS were typically 3.0–4.0 nm, while most nanoparticles on NW-FS were <1.5 nm in diameter. Thus, the degree of dispersion of the Fe_2O_3 nanoparticles on NW-FS was much higher than on indus-FS.

Fig. 1. SEM images of indus-FS (a) and NW-FS (b), and high-magnification images of the surfaces of indus-FS (c) and NW-FS (d). TEM images of indus-FS (e) and NW-FS (f).

Fig. 2. Fe₂O₃ particle distributions of NW-FS (a) and indus-FS (b).

The Fe₂O₃ content of indus-FS was 13.2 wt%, as determined by XRF. After AVT treatment, NW-FS contained ~12.5 wt% of Fe₂O₃ (Table 1). The cross-sectional image of NW-FS shows that the indus-FS particles were transformed into the nanowire architecture (Fig. 3(d)). The transformation was revealed by growth time control. Figure 3 shows the time evolution of nanowire formation. We previously found that Fe species in indus-FS acted as an initiator (catalyst) for SiO₂ nanowire growth [26] and as a source of dispersed Fe species in the final catalyst.

Table 1

BET surface area (S_{BET}), pore volume (V_{pore}), and mean pore diameter (D_{pore}) of NW-FS and indus-FS.

Sample	S_{BET}^a (m ² /g)	D_{pore}^a (nm)	V_{pore}^a (cm ³ /g)	Fe ₂ O ₃ content ^b (wt%)
NW-FS	48	14.9	0.18	12.5
Indus-FS	120	5.6	0.17	13.2

^a Determined by N₂ adsorption-desorption.

^b Determined by XRF.

Fig. 3. SEM images of NW-FS after AVT treatment for 24 h (a), 16 h (b), and 8 h (c), and cross-sectional SEM image (d).

3.1.2. Catalyst structure and textural properties

Figure 4 shows the XRD patterns of indus-FS and NW-FS. A broad diffraction at ~22° was observed in both patterns, indicating that their SiO₂ components were amorphous. Their Fe species were in the form of α -Fe₂O₃ nanoparticles, as evidenced by the weak diffractions at 33.5° and 35.9° (PDF #85-0987). The intensities of the diffractions of Fe₂O₃ were lower after transformation, indicating a decrease in Fe₂O₃ particle size and/or crystallinity.

Figure 5 shows N₂-adsorption-desorption isotherms of indus-FS and NW-FS. A wide flat hysteresis loop after $p/p_0 = 0.4$ was observed in the isotherm of indus-FS, indicating mesopores with a wide size distribution. After AVT treatment, the pore volume slightly increased, but the hysteresis loop narrowed and moved to higher p/p_0 , indicating a significantly higher average pore diameter. Larger pores were likely derived from the spacings between interlaced nanowires. Such an open nanowire structure after transformation was consistent with the SEM observations and benefited diffusion-limited reactions (discussed later). The mechanical strength of NW-FS was confirmed by tablet compression. After treatment at 0.65 MPa, >80% of the NW-FS spheres (Fig. 6) retained their original shape (Fig. 1(b)). This indicates that the mechanical strength of NW-FS was sufficient for use in a fixed-bed reactor.

Fig. 4. XRD patterns of indus-FS (1) and NW-FS (2).

Fig. 5. N_2 adsorption-desorption isotherms of indus-FS (1) and NW-FS (2).

Fig. 6. SEM images of NW-FS after tablet compression at low magnification (a) and high magnification (b).

3.1.3. Characterization of Fe species

The supported Fe_2O_3 was further characterized by XPS, ESR, and TPR. Figure 7 shows the XPS spectra of the Fe 2p region of NW-FS and indus-FS. The experimental data were fitted using the Voigt method, with a Lorentzian-Gaussian mixed function. For indus-FS, the Fe 2p core levels were split into $2p_{3/2}$ (712.9 eV) and $2p_{1/2}$ (725.8 eV) doublets because of spin-orbit coupling. For NW-FS, the Fe 2p core levels were split into $2p_{3/2}$ (713.2 eV) and a $2p_{1/2}$ (726.1 eV) doublet. This indicates that Fe in NW-FS largely existed as Fe(III) [28]. The Fe valency was further investigated by ESR (Fig. 8). Only one signal at $g \approx 2.0$

Fig. 7. XPS spectra of the Fe 2p region of indus-FS (1) and NW-FS (2).

Fig. 8. ESR spectra of NW-FS (1) and indus-FS (2).

Fig. 9. TPR profiles of NW-FS (1) and indus-FS (2).

was observed for both NW-FS and indus-FS, suggesting that Fe existed as Fe oxide [29]. The TPR results are shown in Fig. 9. The peak at low temperature was assigned to the reduction of Fe_2O_3 to FeO_x , and that at high temperature to the reduction of FeO_x to Fe [30]. Both catalysts exhibited similar reduction peaks, suggesting similar Fe states of Fe_2O_3 .

3.2. FTS reaction results

FTS reactions were carried out to demonstrate the advantages of highly dispersed Fe_2O_3 and the open nanowire structure of NW-FS in comparison with indus-FS. The reaction was conducted at a WHSV of 0.75 h^{-1} and similar conversions ($\sim 10\%$, by adjusting the WHSV) to compare the performance of the two catalysts (Table 2). Retaining a relative low CO conversion allowed the difference in primary reactions to be compared, and reduced the influence of water produced during FTS. Two phenomena were observed.

First, NW-FS tended to produce hydrocarbons with shorter C chains. Its selectivity for C_1 (methane) and C_2 hydrocarbons was higher than that of indus-FS, while those for products with C chains longer than C_3 were lower. No products with C chains longer than 6 were detected for NW-FS.

Second, NW-FS was well suited for generating light olefins. Its selectivity for ethylene was twice that of indus-FS, while its selectivity for ethane was less than that of the latter. NW-FS yielded olefin/paraffin ratios of C_2 (1.7) and C_2 – C_4 hydrocarbons (3.3) that were much higher than those of indus-FS (~ 0.7 and 2, respectively).

Table 2FTS conversion and product distribution for NW-FS and indus-FS catalysts (320 °C, H₂/CO = 1).

Catalyst	WHSV (h ⁻¹)	CO conversion (%)	Selectivity of hydrocarbon products (C%)									C ₂ ⁼ /C ₂ ⁰	C ₂ ⁼ -C ₄ ⁼ /C ₂ ⁰ -C ₄ ⁰
			C ₁	C ₂ ⁼	C ₂ ⁰	C ₃ ⁼	C ₃ ⁰	C ₄ ⁼	C ₄ ⁰	ΣC ₅₊	ΣC ₇₊		
NW-FS	0.75	9.2	44.6	13.1	7.9	13.3	2.4	8.5	0.4	9.8	0.0	1.7	3.3
Indus-FS	0.75	16.7	30.0	6.6	9.2	15.2	3.0	9.1	3.7	23.2	8.8	0.7	1.9
	1.56	9.9	34.1	7.3	10.0	15.6	3.0	10.5	1.7	17.8	5.2	0.7	2.3

The FTS selectivity for light olefins by NW-FS was attributed to its special features, as shown in Fig. 10. A reported FTS mechanism suggested that the primary products were light olefins, which preceded the secondary reactions of hydrogenation and chain growth [19,22,31]. Two factors affecting product distribution were: (1) product diffusivity, with a high diffusivity lowering the probability of secondary reactions, therefore favoring light olefins [31]; and (2) active site size, with a smaller active species size favoring the selectivity for light hydrocarbons [6–8]. The relatively closed porous structure of indus-FS (Fig. 5) meant that primary olefins produced had longer retention times within catalyst particles. Thus, they were more likely to re-adsorb on pore walls for secondary reactions (Fig. 10(a)). The open structure of NW-FS (Fig. 10(b)) allowed primary olefins to quickly escape from the catalyst surface, lowering the probability for secondary reactions including hydrogenation and C chain growth. This was supported by the FTS results of indus-FS under different WHSV values (Table 2). Previous studies have also demonstrated an increased O/P ratio and light product selectivity with increasing WHSV [31]. NW-FS also contained uniformly and highly dispersed Fe₂O₃ (Fig. 2), which promoted the production of shorter hydrocarbon products [6–8].

The product distribution reportedly gradually decreases with increasing C chain length, with the exception of C₂ products [19,21,31]. This is because ethylene is more active in secondary reactions, so the primary ethylene product more easily grows into longer C chain products. Table 2 shows that indus-FS followed this trend, but NW-FS did not. NW-FS exhibited a higher selectivity for C₂ than C₃ because of the doubled selectivity of ethylene. This could also be explained by the facile escape of products from NW-FS, resulting in less secondary chain growth and hydrogenation. The high diffusion allowed by the open structure and small supported Fe species both contributed to the high selectivity for light olefins. These results aid the development of FTS catalysts for light olefin production

and enhance our understanding of the design of catalysts for complex reaction networks.

4. Conclusions

Fe-assisted AVT treatment was used to synthesize a spherical catalyst consisting of a SiO₂ nanowire architecture containing highly dispersed Fe₂O₃. The open structure facilitated the diffusion of products and contained uniform-sized Fe₂O₃ active species. These properties aided the high olefin/paraffin ratio and promoted the production of lighter olefin products in FTS. These results further our understanding of the design of FTS catalysts and the application of nanowire catalysts in complex reaction networks for restricting secondary reactions.

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Fig. 10. FTS processes occurring for indus-FS (a) and NW-FS (b).

Graphical Abstract

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Nanowire accumulated $\text{Fe}_2\text{O}_3/\text{SiO}_2$ spherical catalyst for Fischer-Tropsch synthesis

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A $\text{Fe}_2\text{O}_3/\text{SiO}_2$ catalyst consisting of a SiO_2 nanowire architecture containing highly dispersed Fe_2O_3 was fabricated and used in Fischer-Tropsch synthesis. The catalyst exhibited a high light hydrocarbon selectivity and large olefin/paraffin ratio because of its open support structure and small supported Fe_2O_3 nanoparticles.

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纳米线堆积的铁硅球体催化剂用于费托合成

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摘要: 以共沉淀法所制的工业铁硅球体催化剂(indus-FS)为原料, 用改进的有机胺蒸气相传输转化法, 得到了负载高分散铁的交织氧化硅纳米线球体催化剂(NW-FS), 并用于费托合成反应。在所制纳米线催化剂中, 原料催化剂中氧化硅在氧化铁诱导下成功地转变成纳米线交织微球载体, 而氧化铁组分则高度分散在氧化硅纳米线上。用扫描电镜、透射电镜、X射线衍射、低温氮吸附、X射线光电子能谱和程序升温还原等方法对所得纳米线催化剂进行了表征。在费托合成中, 纳米线铁硅催化剂由于其特殊的堆积结构所导致的低的扩散阻力和高的铁活性组分分散度, 提高了低碳烯烃尤其是乙烯的选择性。纳米线铁硅催化剂上低碳产物(C₂-C₄)的烯烷比为3.3, 高于母体工业催化剂的1.9。

关键词: 纳米线; 纳米金属催化剂; 费托合成; 煤化工; 二次反应

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1. 前言

在过去数十年里, 负载型纳米催化剂由于出色的催化性能而备受关注^[1,2]. 高分散的活性组分和较快的产物扩散速率对提升催化剂的性能非常重要^[3], 对纳米催化剂的载体提出了更高的要求. 研究者开发并应用了许

多新结构催化剂载体, 如介孔材料^[4]、沸石^[5]、碳纳米管和纤维等^[6,7]. 传统上, 活性组分通常通过湿法浸渍、离子液吸附和沉降浸渍等^[6-10]等方法负载在载体上. 然而, 载体上狭窄的通道会限制反应物和产物的扩散, 并因此导致副反应^[11,12]. 因此, 设计同时具有高分散度的活性组分和敞开结构载体的新型催化剂引起人们极大的兴趣. 最

近, 我们课题组提出了一种特殊的银纳米线阵列的载体结构, 并证明其具有较好的催化性能. 由于其开放的载体结构, 载体对活性中心银纳米颗粒附近的扩散限制几乎为零, 同时也抑制了银纳米颗粒的小颗粒团聚^[13].

低碳烯烃是非常重要的化工原料. 随着原油价格日益上涨和资源逐渐枯竭, 开发低碳烯烃的非石油来源制备过程受到越来越多关注, 如甲醇制烯烃过程^[14–16]. 从合成气直接一步制备烯烃, 即费托合成被认为是更加合理的解决途径^[17–21]. 然而, 在费托合成反应中, 提高低碳烯烃的选择性仍然是一个长期困扰研究者的难题, 因为费托合成中会发生一系列的二次反应, 如加氢反应、链增长反应、异构化反应和加氢裂解反应^[22–26]. 此外, 尺寸较小的活性组分被认为有益于低碳烯烃生成. 一些研究者合成并研究了活性组分大小不同的催化剂, 并提出随着纳米金属尺寸的减小, 短链烃类的选择性会增加^[6–8]. 另外, 载体的低扩散阻力会减少二次反应, 如加氢和链增长反应, 这些可以通过减少再吸附和初级产物的二次反应来实现, 进一步提高烯烃的选择性^[23,24].

我们通过蒸气相转化方法由工业级铁硅球体催化剂(indus-FS)合成了一种敞开体系的新型球体 $\text{Fe}_2\text{O}_3/\text{SiO}_2$ 催化剂(NW-FS), Fe_2O_3 纳米颗粒高度分散在 SiO_2 纳米线载体上. 由于本体催化剂中铁纳米颗粒的诱发(或催化)作用^[27], 氧化硅材料转化为纳米线结构, 同时铁组分也高度分散在形成的纳米线上. 在催化费托合成中, 纳米线催化剂得到很高的低碳烯烃选择性.

2. 实验部分

2.1. 催化剂的合成

将 125 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5 wt%) 溶解在 500 g 水中, 加入氨水(25–28 wt%)调节pH至7.5, 然后加入500 g 硅溶胶(40 wt%), 持续剧烈搅拌. 将所得混合物投入喷雾干燥器中成球, 在旋转蒸发器中烘干, 经550 °C焙烧4 h后得到工业球体催化剂indus-FS.

接着进行有机胺蒸气相转化(AVT). 将3.5 g 三乙胺(98 wt%), 9.5 g 二乙胺(98 wt%)和2.0 g 去离子水混合, 在室温下搅拌1 h, 投入带聚四氟乙烯内衬的不锈钢反应釜底部. 然后, 将1.0 g indus-FS催化剂加入到反应釜上部悬挂的小篮中. 关上釜后, 在200 °C处理1 d, 即生成纳米线催化剂(NW-FS). 用去离子水洗涤催化剂粉体, 在100 °C干燥1 d, 最后在马弗炉中550 °C焙烧4 h.

所用试剂中, 硅溶胶购自Nalco公司, 其它原料均购自国药集团, 使用前未经进一步提纯.

2.2. 催化剂的表征

X射线多晶衍射法(XRD)在Bruker D8多晶衍射仪上进行($\text{Cu K}\alpha$ 射线, 测试电压40 kV, 测试电流30 mA). 两个样品均从 $2\theta = 5^\circ$ – 50° , 步长 0.02° , 每步停留5 s. BET表面积通过低温氮吸附测定, 实验在Micromeritics的TriStar II 3020氮吸附测试仪上于–196 °C进行. 样品的形貌通过扫描电镜(SEM, Philips XL 30)表征, 先将样品溶解在乙醇中, 超声分散, 然后将乙醇蒸发, 烘干, 待样品冷却后进行2 min电子喷射对样品进行喷金. 样品的元素含量采用X射线荧光衍射(XRF)在Bruker-AXS S4探测仪上分析. 透射电镜(TEM)图像在JEM-2011F仪器上得到. 电子顺磁共振谱(ESR)在室温下由Bruker EMX-9光谱仪测试. X射线光电子能谱(XPS)在Shimadzu/Kratos Axis Ultra DLD能谱仪上测试, 使用 $\text{Cu K}\alpha$ 射线作为激发能量源, 以C 1s作为能量校正谱(设定为284.6 eV). 程序升温还原(TPR)使用自制的升温脱附仪, 在还原过程中, 检测的样品量为20 mg, 使用10% H_2/Ar 混合气($30 \text{ cm}^3/\text{min}$), 从室温升至800 °C, 升温速率 $10^\circ\text{C}/\text{min}$.

2.3. 费托合成反应

费托反应在固定床反应管($\Phi 8 \text{ mm}$)中进行. 将1 g 催化剂装入反应器, 用 H_2 在450 °C和0.1 MPa下还原(氢气流速50 ml/min). 纳米线催化剂和工业铁硅催化剂的投料量相同. 将合成气导入反应器, 氮气比例为1/8, 空速为0.75或 1.56 h^{-1} , 氢碳比为1.0, 反应温度为320 °C. 产物由两台在线气相色谱分析仪(安捷伦7890A GC)、火焰离子化检测器(FID)、热导检测器(TCD)和安捷伦HP-1, HP-AL/M, Hayesep-D色谱柱综合进行分析. CO转化率、产物选择性和质量空速(WHSV)由以下公式计算:

$$\text{CO conversion} = (\text{CO feed (g)} - \text{CO remaining (g)}) / (\text{CO feed (g)} \times 100\%) \quad (1)$$

$$\text{Selectivity of product x} = \text{Amount of hydrocarbon x (g)} / (\text{gross amount of all hydrocarbons (g)} \times 100\%) \quad (2)$$

$$\text{WHSV} = \text{CO flow rate (g h}^{-1}\text{)} / \text{weight of the core catalyst (g)} \quad (3)$$

3. 结果与讨论

3.1. 表征结果

3.1.1. 形貌与尺寸

图1为本体催化剂(indus-FS)和纳米线催化剂(NW-FS)的SEM照片. Indus-FS是球体, 尺寸大致在10–50 μm (图1(a)), 它的表面(图1(c))相对平整, 并且存在一些孔道和小颗粒. 在有机胺蒸气相转化后, 样品仍继续保持着

球体形貌(图1(b)). 然而, 在高分辨SEM照片中可以看到, 在有机胺作用下, 这些球体转化为纳米线结构(图1(d)和(a)). 从图1(f)可清晰看出大量规整和高分散的 Fe_2O_3 纳米颗粒分布在氧化硅纳米线表面. 图2为两个催化剂上氧化铁颗粒的粒径分布. 可见indus-FS上颗粒直径为3.0–4.0 nm, 而NW-FS上大都小于1.5 nm, 说明纳米线催化剂上铁的分散度远高于本体催化剂.

XRF结果表明, 本体催化剂的氧化铁含量为13.2%, 而纳米线催化剂为12.5%(表1), 下降并不明显, 说明经过有机胺转化后Fe基本没有流失. NW-FS的截面图(图3(d))说明整个工业催化剂都被转化为纳米线结构的催化剂. 图3还示出了不同时间转化的样品照片. 我们前期发现, indus-FS中的铁物种是 SiO_2 纳米线生长^[26]的促进剂, 也是最终催化剂中铁物种的来源.

3.1.2. 催化剂结构与织构性质

图4为indus-FS和NW-FS样品的XRD图. 由图可见, 各样品在 $2\theta = 22^\circ$ 处均有一个包峰, 说明体系中的 SiO_2 是无定形的. 同时, 在 33.5° 和 35.9° 处有两个小峰, 说明铁以 $\alpha\text{-Fe}_2\text{O}_3$ 形式存在(PDF #85-0987). NW-FS催化剂的氧化铁衍射峰更弱, 说明其结晶度更差, 即铁颗粒更小, 与TEM结果一致. 图5为两种催化剂的 N_2 吸附脱附曲线. 可以看出, 经胺处理后, 母体催化剂上的介孔基本消失, 在纳米线化的过程中形成了大量堆积介孔, 与SEM结果类似. 在0.65 MPa下将NW-FS样品压片, 再用SEM观察发现, 超过80%的NW-FS小球(图6)保持球体形貌, 说明NW-FS的机械强度足以支持在固定床反应器中的反应.

3.1.3. 铁物种的表征

负载的 Fe_2O_3 用XPS, ESR和TPR表征. 图7为NW-FS和indus-FS样品的Fe 2p区域的XPS谱, 在分峰后, 根据自旋耦合Fe 2p可以分为 $2p_{3/2}$ (712.9 eV)和 $2p_{1/2}$ (725.8 eV)两个峰, 说明两个样品中Fe物种均以Fe(III)形式存在^[28]. 图8为两个催化剂的ESR谱, 可见它们均仅在 $g \approx 2.0$ 处出现一个信号, 说明铁以氧化铁形式存在^[29]. 图9为它们的TPR谱, 低温区的还原峰对应于从 Fe_2O_3 还原至 FeO_x , 而高温区对应于从 FeO_x 还原至Fe^[30]. 可以看出, 这两个样品的峰位置类似, 说明两者氧化铁的状态类似.

3.2. 费托反应结果

表2为NW-FS和indus-FS催化剂上费托反应的结果. 控制质量空速(0.75 h^{-1})和CO转化率(约为10%, 通过调节质量空速实现)相同, 以比较两种催化剂的催化性能. 保持相对低的CO转化率可以清晰看出两种催化剂上初级产物反应过程的不同, 并减少反应中水的影响. 可以

发现: (1) NW-FS催化剂倾向于生成低碳烃类, CH_4 和 C_2 烃类的选择性更高, C_{3+} 产物选择性更低, 且没有 C_{6+} 产物出现; (2) NW-FS催化剂倾向于产生低碳烯烃, 乙烯选择性甚至为indus-FS催化剂的2倍, 乙烷选择性更低, 导致其 C_2 的烯烷比(1.7)和 $\text{C}_2\text{--C}_4$ 烃类的烯烷比(3.3)都高于indus-FS催化剂(大约分别是0.7和2).

基于此, 我们提出了如图10所示的反应机理. 根据费托合成反应机理研究, 初级产物主要是低碳烯烃, 它们会发生二次反应如加氢和链增长^[19,22,31]. 有两个因素对产物分布非常重要: (1) 产物的扩散, 高的扩散速度非常有利于富产烯烃, 因为初级产物中的烯烃容易扩散离开, 从而减少其发生二次反应的几率^[31]; (2) 催化活性中心的尺寸, 减少活性中心尺寸会增加低碳烃类选择性^[6–8]. 由于工业催化剂上介孔的存在(图5), 初级产物烯烃在催化剂的内壁经历了一个较长的扩散周期, 从而导致初级烯烃容易吸附在内壁上并发生二次反应(图10(a)). 然而, 由于纳米线催化剂的敞开载体结构(图10(b)), 初级烯烃产物容易从表面逸散, 所以趋向于不发生加氢和碳链增长等二次反应.

表2给出了不同空速下工业催化剂的反应结果, 证明了上述结论, 也与文献^[31]结果一致. 可以看出, 当空速增加时, 烯烷比和低碳产物选择性均增加. 此外, 纳米线载体也改变了活性中心, 即得到高分散的氧化铁组分(图1(f), 图2), 促进了较短链长烃类产物的生成^[6–8].

许多研究认为^[19,21,31], 随着碳链长度的增加, 各种产物的选择性分布逐渐减少, 但 C_2 产物例外, 因为乙烯在二次反应中活性很高, 因而很容易发生链增长反应生成较长链的产物. 但是, 纳米线催化剂表现出更高的乙烯选择性, 甚至高于 C_3 , 这也是因为初级产物乙烯容易离开催化剂避免发生二次反应, 也就是说, 随着产物更有效地离开催化剂, 二次反应得到抑制. 因此, 由于较高的扩散性能和小尺寸的负载铁活性组分, 纳米线催化剂上低碳烯烃选择性增大.

4. 结论

在铁的辅助下, 使用有机胺蒸气相转化法合成了纳米线铁硅球体催化剂. 纳米线载体的敞开体系提高了产物扩散速度, 同时也使得氧化铁活性组分高度分散. 在费托合成反应中, 纳米线催化剂实现了富产烯烃的效果. 该材料不仅提供了全新的设计与合成费托催化剂的思路, 而且提供了一种新的催化剂设计方案, 即在连续反应中设计限制二次反应的催化剂结构.