available at www.sciencedirect.com journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue for Excellent Research Work in Recognition of Scientists Who Are in Catalysis Field in China)

Iron catalyst encapsulated in carbon nanotubes for CO hydrogenation to light olefins

Xiaoqi Chen, Dehui Deng*, Xiulian Pan, Xinhe Bao #

State Key Laboratory of Catalysis, Collaborative Innovation Center of Chemistry for Energy Materials, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

ARTICLE INFO

Article history:

Received 30 March 2015

Accepted 5 May 2015

Published 20 September 2015

Keywords:

Fischer-Tropsch synthesis

Stability

Light olefins

Carbon nanotubes

Iron nanoparticles

ABSTRACT

Fe-based catalyst is an outstanding candidate for the Fischer-Tropsch reaction to get light olefins from syngas directly. However, exposed Fe species are susceptible to sintering and coking, which lead to deactivation. Here, we demonstrate that Fe nanoparticles encapsulated in pod-like carbon nanotubes (Pod-Fe) can be used as an efficient Fischer-Tropsch catalyst to produce light olefins. It gave a higher selectivity of light olefins (45%) and high stability over 120 h reaction ($P = 0.5$ MPa, $T = 320$ °C, $\text{CO:H}_2 = 1:2$, gas hourly space velocity = 3500 h^{-1}). A catalyst with exposed Fe particles on the outside of the Pod-Fe ($\text{FeO}_x/\text{Pod-Fe}$) catalyst showed a selectivity of light olefins of 42%, but had a significantly lower stability due to the agglomeration of Fe nanoparticles and carbon deposition. These results indicated that the graphene shell of Pod-Fe played an important role in protecting the Fe particles and provided a rational way to enhance the activity and stability of Fe-based catalysts in high temperature reactions.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Fischer-Tropsch synthesis (FTS) has attracted wide attention in recent years for its potential application in converting coal, natural gas or biomass to useful hydrocarbons and other chemicals [1–4]. Compared to other FTS catalysts like Co, Ni and Ru, a Fe-based catalyst has higher feedstock flexibility [5–8]. Fe-based catalysts can be used in CO-rich syngas directly with almost no need for further H_2/CO ratio adjustment because of their high water gas shift activity. The tunable selectivity makes an Fe-based catalyst a promising catalyst for generating hydrocarbons with different chain lengths [9–13]. However, a Fe-based catalyst faces a big problem as coking and sintering can easily happen with Fe and lead to the deactivation of the catalyst [14–16]. To stabilize Fe particles from aggregation,

different supports such as silica, alumina and zeolite are often used to disperse Fe particles [17–20]. But these oxide supports have a strong interaction with Fe, especially with highly dispersed Fe particles, and form iron aluminates [21] and iron silicates [22,23] which are hard to reduce and lead to low activity. On the other hand, when using weakly interactive supports like active carbon or carbon nanofibers, the weak physical binding between its surface and Fe nanoparticles does not protect Fe-based nanoparticles from aggregating and coking under reaction conditions [3].

To solve this, we recently propose the concept of “chainmail for catalyst”, namely, encapsulating a transition metal catalyst (such as Fe, Co, Ni, and their alloys) in carbon shells [24–27]. The stable carbon shell protect the inner metal particles from oxidizing in air or etching by acid, while the penetration elec-

* Corresponding author. Tel: +86-411-84686637; Fax: +86-411-84379128; E-mail: dhdeng@dicp.ac.cn# Corresponding author. Tel: +86-411-84686637; Fax: +86-411-84379128; E-mail: xhbaod@dicp.ac.cn

This work was supported by the National Natural Science Foundation of China (21321002 and 21303191) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA09030100).

DOI: 10.1016/S1872-2067(15)60882-8 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 36, No. 9, September 2015

trons of the transition metals promote the catalytic reaction on the carbon surface [24,27,28]. This strategy can significantly enhance the activity and stability of non-precious metal catalyst under harsh conditions, as has been demonstrated by our group and other groups in the fields of the oxygen reduction reaction (ORR) in fuel cells [24,25,29,30], hydrogen evolution reaction (HER) [26,27], I_3^- reduction reaction in dye-sensitized solar cells (DSSCs) [31], and catalytic oxidation and reduction reactions in heterogeneous catalysis [32,33]. Inspired by this, we report that Fe nanoparticles encapsulated in the compartment of bean pod-like carbon nanotubes (Pod-Fe) can be used as a highly stable catalyst for CO hydrogenation to light olefins at high temperature. It can efficiently avoid the agglomeration and coking of Fe nanoparticles during the reaction.

2. Experimental

2.1. Catalyst preparation

$\text{FeO}_x/\text{Pod-Fe}$ was synthesized by the method of our previous report [24]. Briefly, 3.0 g ferrocene (Tianjin Bodi Chemical Holding Co., Ltd.) and 3.0 g sodium azide (BDH Chemicals Ltd. Poole England) were put into a 40 mL stainless steel autoclave in N_2 in a glove box. The reaction was then carried out at 350 °C for 6 h. The product was treated with distilled water at 90 °C, followed by washing with distilled water and ethanol, and drying at 120 °C for 12 h. The resulting sample was denoted as $\text{FeO}_x/\text{Pod-Fe}$. The Fe content of $\text{FeO}_x/\text{Pod-Fe}$ was 31.8% as measured by inductively coupled plasma atomic emission spectrometry (ICP-AES).

$\text{FeO}_x/\text{Pod-Fe}$ was further treated by refluxing in 25 wt% HCl aqueous solution at 90 °C for 4 h, followed by the same washing and drying process as for $\text{FeO}_x/\text{Pod-Fe}$. The resulting sample was denoted as Pod-Fe. The Fe content of Pod-Fe was 12.8% as measured by ICP-AES.

2.2. Characterization

The Fe concentration was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES,

ICPS-8100, Shimadzu, Japan). The sample for ICP-AES analysis was first heated at 900 °C for 2 h in air, and then dissolved in aqua regia. X-ray diffraction (XRD) was measured on a Rigaku D/Max 2500 diffractometer with a $\text{Cu } K\alpha$ ($\lambda = 1.541 \text{ \AA}$) monochromatic radiation source. Transmission electron microscopy (TEM) was carried out on a FEI Tecnai G2 microscope operated at an accelerating voltage of 120 kV.

2.3. Catalytic reaction

The Fischer-Tropsch reaction was carried out in fixed bed reactors with a quartz inner lining. The feed flow was a mixture of $\text{H}_2/\text{CO}/\text{Ar}$ (63.3/31.7/5, vol%) and Ar was used as an internal standard. Typically, 100 mg catalyst was used to react syn-gas under different gas hourly space velocities (GHSV) and temperatures. All gas lines after the reactor were kept at 140 °C. All products were analyzed by an online gas chromatography (Agilent 7890A) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Three chromatography columns were used, Porapak Q and 5 Å molecular sieves packed columns to analyze CO , CO_2 , CH_4 and Ar with a TCD, and a modified Al_2O_3 capillary column to analyze $\text{C}_1\text{--C}_8$ range hydrocarbons with a FID. The selectivity of the hydrocarbons was calculated on a carbon atom basis excluding CO_2 .

3. Results and discussion

The morphology of Pod-Fe and $\text{FeO}_x/\text{Pod-Fe}$ is shown in Fig. 1(a) and 1(b). One can clearly see that the Fe nanoparticles of Pod-Fe were completely encapsulated in the CNTs with usually one or two Fe particles in one compartment, while the iron nanoparticles of $\text{FeO}_x/\text{Pod-Fe}$ were distributed both inside and outside the carbon nanotube. The XRD patterns showed that Pod-Fe contained only metallic iron, while $\text{FeO}_x/\text{Pod-Fe}$ showed both metallic iron and characteristic iron oxide peaks (Fig. 1(c)). X-ray photoelectron spectroscopy (XPS) in our previous work also showed that the Fe in Pod-Fe was metallic, while both Fe^{3+} and Fe^0 were observed in $\text{FeO}_x/\text{Pod-Fe}$ [24]. The above results indicated that the exposed Fe particles on the

Dehui Deng (Dalian Institute of Chemical Physics, Chinese Academy of Sciences) **received the Catalysis Rising Star Award in 2014**, which was presented by The Catalysis Society of China. Dr. Dehui Deng received his Ph.D. degree in Physical Chemistry from Dalian Institute of Chemical Physics, CAS in 2013, and he joined the same institute and was promoted to associate professor via "100 Talents Program" by DICP, CAS at the same time. He is also now a visiting scientist in Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Xiamen University, and a visiting scholar in Department of Chemistry, Stanford University since 2015. His research interests focus on the fields of catalysis, energy and materials, including: (1) Design of advanced nanocarbon catalyst, such as graphene, carbon nanotubes, SiC, carbon-encapsulated metal, et al.; (2) Non-precious metal-based two-dimensional layered nanocatalyst, involving of the synthesis and doping of single layer or few layer MoS_2 , WS_2 , et al.; (3) Fundamental research in heterogeneous catalysis and electrocatalysis, aiming at the highly efficient activation of small molecules such as O_2 , H_2 , H_2O , CH_4 and C_6H_6 . He has published more than 20 peer-reviewed papers including *Science* (1), *Angew. Chem. Int. Ed.* (3), *Energy Environ. Sci.* (2), *Adv. Mater.* (1), and *Chem. Sci.* (1) with over 800 citations. He also applied 13 patents.

Fig. 1. TEM images of Pod-Fe (a) and FeO_x/Pod-Fe (b). (c) XRD patterns of Pod-Fe compared with FeO_x/Pod-Fe.

Table 1

Effect of GHSV on the performance of Pod-Fe catalysts in CO hydrogenation.

GHSV/h ⁻¹	10000	3500	1000	500
CO conversion/%	1.3	2.4	8.9	19.4
CO ₂ selectivity/%	11.0	14.3	22.6	30.3
CH distribution/%				
CH ₄	31.6	32.3	29.8	28.1
C ₂ ⁰ –C ₄ ⁰	12.3	13.1	18.5	22.8
C ₂ ⁼ –C ₄ ⁼	38.9	39.4	35.3	32.5
C ₅ ⁺	17.2	15.2	16.4	16.6
C ₂ ⁼ –C ₄ ⁼ /C ₂ ⁰ –C ₄ ⁰	3.2	3.0	1.9	1.4

Reaction conditions: *P* = 0.5 MPa, *T* = 320 °C, CO:H₂ = 1:2.

outside of FeO_x/Pod-Fe were easily oxidized, while the Fe nanoparticles encapsulated in Pod-Fe were well protected by the graphene layer and remained in a metallic state.

We then evaluated the performance of the two catalysts in FTS. As the activity and selectivity of the FTS reaction are sensitive to the GHSV and reaction temperature, we investigated the reaction under different GHSVs and temperatures as shown in Tables 1 and 2 for Pod-Fe and FeO_x/Pod-Fe. With increased GHSV, the CO conversion of both catalyst decreased, which is consistent with the reported literature [7]. When the GHSV was higher than 3500 h⁻¹, both catalysts showed a selectivity towards light olefins of around 40%. At very low GHSV (lower than 500 h⁻¹), the selectivity towards light olefins slightly decreased.

The influence of the temperature for both samples are summarized in Fig. 2. Comparing the selectivity of Pod-Fe and FeO_x/Pod-Fe, one can find that although both catalysts showed

Fig. 2. Effect of temperature on the performance of Pod-Fe (a) and FeO_x/Pod-Fe (b) catalysts in CO hydrogenation. Reaction conditions: *P* = 0.5 MPa, CO:H₂ = 1:2, GHSV = 3500 h⁻¹.

Table 2

Effect of temperature and GHSV on the performance of FeO_x/Pod-Fe catalysts in CO hydrogenation.

Temperature (°C)	GHSV/h ⁻¹	CO conversion (%)	CO ₂ selectivity (%)	CH distribution (%)				
				CH ₄	C ₂ ⁰ –C ₄ ⁰	C ₂ ⁼ –C ₄ ⁼	C ₅ ⁺	C ₂ ⁼ –C ₄ ⁼ /C ₂ ⁰ –C ₄ ⁰
300	15000	4.0	46.8	18.7	4.0	36.2	41.1	9.1
300	10000	8.5	49.0	18.6	4.7	36.6	40.1	7.8
300	3500	26.8	56.0	20.6	7.5	40.5	31.4	5.4
320	15000	3.4	48.1	25.7	4.4	40.2	29.7	9.2
320	10000	6.4	46.0	22.7	4.1	36.0	37.2	8.8
320	3500	20.7	51.9	26.2	6.4	41.4	26.0	6.5

Reaction conditions: *P* = 0.5 MPa, CO:H₂ = 1:2.

similar selectivities towards light olefins at different temperatures, the distributions of products were quite different. Pod-Fe showed much higher methane selectivity (30.6%) and lower C_{5+} selectivity (18.6%) at 300 °C (Fig. 2(a)). With increasing temperature up to 380 °C, the methane selectivity was 47.8% while the C_{5+} selectivity dropped to 6.3%. In contrast, FeO_x /Pod-Fe showed a lower methane selectivity (20.6%) and higher C_{5+} selectivity (31.4%) at 300 °C (Fig. 2(b)). These results indicated that the Pod-Fe catalyst could limit carbon chain growth as compared to FeO_x /Pod-Fe. Note that there was also an obvious difference of selectivity towards CO_2 over the two catalysts. During FTS, the production of H_2O is unavoidable. This is because FeO_x particles on FeO_x /Pod-Fe promoted the water gas shift reaction leading to a higher CO_2 selectivity since Fe_3O_4 is an active phase in the water gas shift reaction [34–36].

More importantly, the CO conversion of the catalysts was quite different with increasing temperature. Although the Pod-Fe sample showed a lower CO conversion than FeO_x /Pod-Fe due to the lower Fe content in Pod-Fe, the conversion increased with increasing temperature (Fig. 2(a)). Surprisingly, it still worked even at 380 °C without any deactivation. In contrast, the CO conversion of FeO_x /Pod-Fe steadily increased from 0.7% at 240 °C up to 26.8% at 300 °C (Fig. 2(b)). However, with further increasing temperature, the CO conversion dropped to 6.9% at 340 °C. It showed poor stability at higher temperature. These results demonstrated that the Pod-Fe catalyst significantly enhanced the catalytic stability compared to FeO_x /Pod-Fe.

To find the reason for the deactivation of FeO_x /Pod-Fe at high temperature, we carried out TEM characterization on both samples. The TEM images of Pod-Fe catalyst (Figs. 3(a) and 3(b)) showed that it still kept the morphology of the pod-like structure even after reaction at 380 °C for 10 h. No obvious agglomerated iron and carbon filaments were observed. How-

Fig. 3. (a, b): TEM images of Pod-Fe catalyst after reaction for 10 h at 380 °C. (c, d): TEM images of FeO_x /Pod-Fe catalyst after reaction for 10 h at 340 °C. Reaction conditions: $P = 0.5$ MPa, $CO:H_2 = 1:2$, GHSV = 3500 h^{-1} .

ever, for FeO_x /Pod-Fe after 10 h reaction at 340 °C (Figs. 3(c) and 3(d)), the tube morphology of the FeO_x /Pod-Fe was hardly observed. The Fe particles of the sample were agglomerated and the tubular structure was covered by carbon filaments and flakes, which would be the reason for the decrease of the catalytic activity. This confirmed that the carbon shells could protect the encapsulated Fe particles and maintain stability at high temperature.

We then further performed the stability test of both catalysts at a constant reaction temperature. As shown in Fig. 2, both Pod-Fe and FeO_x /Pod-Fe have good activity and selectivity at 320 °C, 0.5 MPa, GHSV = 3500 h^{-1} , so the stability test was carried out at this reaction condition. For Pod-Fe, as shown in Fig. 4(a), the CO conversion increased in the first 6 h, from 0.8% up to 4.2%, up to about 5 times. Then the CO conversion dropped a bit and kept stable in the next 120 h. The variation of selectivity towards light olefins was the opposite to the CO conversion. It decreased in the first 6 h and then increased and kept around 45%. It was quite different for FeO_x /Pod-Fe and the CO conversion dropped more than 50% in first 6 h, i.e., from 16.9% to 7.9% and then was constant afterwards (Fig. 4(b)). Meanwhile the selectivity towards light olefins kept around 42% as the reaction time increased, which was a little lower than the selectivity of Pod-Fe. These results further con-

Fig. 4. Stability test of the Pod-Fe (a) and FeO_x /Pod-Fe (b) catalysts for CO hydrogenation. Reaction conditions: $P = 0.5$ MPa, $T = 320$ °C, $CO:H_2 = 1:2$, GHSV = 3500 h^{-1} .

firmed that Pod-Fe had a better catalytic stability compared to $\text{FeO}_x/\text{Pod-Fe}$.

In order to get a better understanding of the different behavior and active phase of the two catalysts, XRD patterns were used to examine the crystal structure of the used catalysts. As shown in Fig. 5, the main phase of Pod-Fe remained metallic. Only trace amount of iron carbide species can be observed. For $\text{FeO}_x/\text{Pod-Fe}$, there were mainly two kinds of iron carbides, namely, Hägg carbide (Fe_5C_2) and Cohenite (Fe_3C) after reaction. Both iron carbides were claimed to be active for FTS in the literature [14,37]. It can be concluded that the iron oxide outside $\text{FeO}_x/\text{Pod-Fe}$ will convert into iron carbides, which is easily formed for exposed iron under the FTS reaction condition [14,16,38].

The different performance of the two catalysts mainly originated from the deactivation of the Fe particles outside the carbon nanotube. $\text{FeO}_x/\text{Pod-Fe}$ showed a higher activity at the beginning due to the higher Fe content and a large number of bare Fe particles outside the tube that formed iron carbide under the FTS reaction condition. But without the protection of the carbon shell, the activity of the Fe particles outside the CNTs dropped quickly due to carbon deposition and Fe agglomeration. In contrast, Fe particles encapsulated in the CNTs were efficiently prevented from structure damage and showed a high catalytic stability. According to our previous work, there is a strong interaction between encapsulated non-precious metals and the carbon shell, which lead to electron transfer from Fe to the carbon shell and reduced the local work function of the carbon surface where the Fe particles were located [24]. Molecules such as O_2 , H_2O , I_3^- , etc. can be adsorbed on the carbon shell surface of these catalysts and be activated [24,26,27,31]. In this system, similarly, the penetrated electron from the Fe to the outside carbon surface probably promoted the adsorption of CO and H_2 , and their subsequent activation since the Fe was encapsulated inside the compartment of the pod-like carbon nanotubes and cannot directly contact the reaction molecules. Meanwhile, the stable carbon shells efficiently protected the inner Fe from agglomeration. It should be noted that FTS reaction is very complex and the reaction

mechanism on these catalysts still needs further study.

4. Conclusions

Pod-like carbon nanotubes with encapsulated Fe nanoparticles can be used as an efficient Fischer-Tropsch catalyst. The Pod-Fe catalyst showed good selectivity towards light olefins and excellent anti-sintering performance, especially at high temperature. It was superior to a supported Fe-based catalyst because the Fe particles in Pod-Fe were well protected by the carbon shells. This result provides a practical approach to stabilize metal nanoparticles for reactions at high temperature in heterogeneous catalysis.

References

- [1] Schulz H. *Appl Catal A*, 1999, 186: 3
- [2] Tijmensen M J A, Faaij A P C, Hamelinck C N, van Hardeveld M R M. *Biomass Bioenergy*, 2002, 23: 129
- [3] Torres Galvis H M, Bitter J H, Khare C B, Ruitenbeek M, Dugulan A I, de Jong K P. *Science*, 2012, 335: 835
- [4] Torres Galvis H M, de Jong K P. *ACS Catal*, 2013, 3: 2130
- [5] Khodakov A Y, Chu W, Fongarland P. *Chem Rev*, 2007, 107: 1692
- [6] Davis B H. *Ind Eng Chem Res*, 2007, 46: 8938
- [7] Van Der Laan G P, Beenackers A A C M. *Catal Rev-Sci Eng*, 1999, 41: 255
- [8] Iglesia E, Soled S L, Fiato R A. *J Catal*, 1992, 137: 212
- [9] Li S Z, Li A W, Krishnamoorthy S, Iglesia E. *Catal Lett*, 2001, 77: 197
- [10] Zhang Q H, Kang J C, Wang Y. *ChemCatChem*, 2010, 2: 1030
- [11] Yang Z Q, Guo S J, Pan X L, Wang J H, Bao X H. *Energy Environ Sci*, 2011, 4: 4500
- [12] Janardana Rao M. *Ind Eng Chem Res*, 1990, 29: 1735
- [13] Chen W, Fan Z L, Pan X L, Bao X H. *J Am Chem Soc*, 2008, 130: 9414
- [14] de Smit E, Weckhuysen B M. *Chem Soc Rev*, 2008, 37: 2758
- [15] Koeken A C J, Torres Galvis H M, Davidian T, Ruitenbeek M, de Jong K P. *Angew Chem Int Ed*, 2012, 51: 7190
- [16] Niemantsverdriet J W, Van der Kraan A M, Van Dijk W L, Van der Baan H S. *J Phys Chem*, 1980, 84: 3363
- [17] Wan H J, Wu B S, Zhang C H, Xiang H W, Li Y W, Xu B F, Yi F. *Catal Commun*, 2007, 8: 1538
- [18] Zhang C H, Yang Y, Teng B T, Li T Z, Zheng H Y, Xiang H W, Li Y W. *J Catal*, 2006, 237: 405
- [19] Pour A N, Zamani Y, Tavasoli A, Kamali Shahri S M, Taheri S A. *Fuel*, 2008, 87: 2004
- [20] Pour A N, Shahri S M K, Zamani Y, Irani M, Tehrani S. *J Nat Gas Chem*, 2008, 17: 242
- [21] Perrichon V, Charcosset H, Barrault J, Forquy C. *Appl Catal*, 1983, 7: 21
- [22] Raupp G B, Delgass W N. *J Catal*, 1979, 58: 337
- [23] Zhang C H, Wan H J, Yang Y, Xiang H W, Li Y W. *Catal Commun*, 2006, 7: 733
- [24] Deng D H, Yu L, Chen X Q, Wang G X, Jin L, Pan X L, Deng J, Sun G Q, Bao X H. *Angew Chem Int Ed*, 2013, 52: 371
- [25] Deng J, Yu L, Deng D H, Chen X Q, Yang F, Bao X H. *J Mater Chem A*, 2013, 1: 14868
- [26] Deng J, Ren P J, Deng D H, Yu L, Yang F, Bao X H. *Energy Environ Sci*, 2014, 7: 1919
- [27] Deng J, Ren P J, Deng D H, Bao X H. *Angew Chem Int Ed*, 2015, 54: 2100
- [28] Chen X Q, Xiao J P, Wang J, Deng D H, Hu Y F, Zhou J G, Yu L, Heine

Fig. 5. XRD patterns of Pod-Fe and $\text{FeO}_x/\text{Pod-Fe}$ after 120 h stability test. Reaction conditions: $P = 0.5$ MPa, $T = 320$ °C, $\text{CO:H}_2 = 1:2$, GHSV = 3500 h^{-1} .

Graphical Abstract

Chin. J. Catal., 2015, 36: 1631–1637 doi: 10.1016/S1872-2067(15)60882-8

Iron catalyst encapsulated in carbon nanotubes for CO hydrogenation to light olefins

Xiaoqi Chen, Dehui Deng*, Xiulian Pan, Xinhe Bao*
Dalian Institute of Chemical Physics, Chinese Academy of Sciences

Pod-like carbon nanotubes with encapsulated iron particles were used as an efficient Fischer-Tropsch catalyst for light olefins, giving high selectivity of light olefins and good stability.

- T, Pan X L, Bao X H. *Chem Sci*, 2015, 6: 3262
- [29] Wang J, Wang G X, Miao S, Jiang X L, Li J Y, Bao X H. *Carbon*, 2014, 75: 381
- [30] Hu Y, Jensen J O, Zhang W, Cleemann L N, Xing W, Bjerrum N J, Li Q F. *Angew Chem, Int Ed*, 2014, 53: 3675
- [31] Zheng X J, Deng J, Wang N, Deng D H, Zhang W H, Bao X H, Li C. *Angew Chem, Int Ed*, 2014, 53: 7023
- [32] Fu T, Wang M, Cai W M, Cui Y M, Gao F, Peng L M, Chen W, Ding W P. *ACS Catal*, 2014, 4: 2536
- [33] Luo J, Yu H, Wang H J, Peng F. *Catal Commun*, 2014, 51: 77
- [34] Keiski R L, Salmi T, Niemistö P, Ainaslahti J, Pohjola V J. *Appl Catal A*, 1996, 137: 349
- [35] Rhodes C, Peter Williams B, King F, Hutchings G J. *Catal Commun*, 2002, 3: 381
- [36] Edwards M A, Whittle D M, Rhodes C, Ward A M, Rohan D, Shannon M D, Hutchings G J, Kiely C J. *Phys Chem Chem Phys*, 2002, 4: 3902
- [37] Yang C, Zhao H B, Hou Y L, Ma D. *J Am Chem Soc*, 2012, 134: 15814
- [38] de Smit E, Beale A M, Nikitenko S, Weckhuysen B M. *J Catal*, 2009, 262: 244

碳纳米管封装铁纳米粒子催化剂上CO加氢制低碳烯烃

陈晓琪, 邓德会*, 潘秀莲, 包信和[#]

中国科学院大连化学物理研究所, 能源材料化学协同创新中心, 催化基础国家重点实验室, 辽宁大连116023

摘要: 由于石油资源的逐步枯竭, 近年来费托(F-T)反应因其可以高效将煤、天然气和生物质等转化成液体燃料和高值化学品而越来越受到人们的关注. 相比于Co, Ni和Ru等F-T催化剂, Fe基催化剂因其价格低廉, 产物分布广而被广泛研究. 以合成气直接制备低碳烯烃的F-T过程为例, 铁基催化剂通常会因积碳和烧结的问题, 而导致失活. 因此, 人们通常使用一些氧化物载体, 比如氧化硅, 氧化铝或者分子筛来分散并稳定铁粒子. 但是这类氧化物载体通常与铁有非常强的相互作用, 特别是在铁粒子较小的情况下, 容易生成一些难于还原的硅酸铁和铝酸铁. 而活性炭、碳纤维等惰性载体与铁的相互作用较弱, 不足以稳定小的铁粒子而在反应过程中聚集. 近来, 我们组提出了利用石墨烯碳层封装过渡金属粒子作为催化剂, 利用“穿透”的金属电子来催化反应, 从而可以使活性中心和反应介质隔离, 有效地增强了非贵金属催化剂的活性和稳定性. 在此基础上, 我们组和其他课题组的研究表明, 一系列石墨烯碳层封装的非贵金属催化剂在燃料电池阴极氧还原反应, 电催化析氢反应, 染料敏化太阳能电池中的 I_3^- 还原反应以及催化氧化还原反应中都有着广泛的应用前景. 这种材料中碳层不仅能在氧化气氛、酸性介质中保护包覆的金属, 防止其被氧化或者腐蚀, 还与包覆的金属有着较强的相互作用, 可以促进非贵金属的电子向碳层表面的转移, 有望在一些苛刻的反应条件下实现对贵金属催化剂的替代. 本文进一步拓展了其在高温反应中的应用, 发现豆荚状碳纳米管封装的金属铁纳米粒子在合成气制备低碳烯烃中可以有效防止金属铁纳米粒子的烧结和聚集, 因此表现出优异的低碳烯烃选择性和催化稳定性.

我们利用一步化学反应法合成了豆荚状碳纳米管封装的铁纳米粒子催化剂(Pod-Fe), 并通过酸洗除去碳管外面裸露的铁粒子. 透射电镜(TEM)和X射线衍射(XRD)表明酸洗后铁粒子被包覆在碳管内, 并且呈金属态, 而酸洗前, 则还有大量的氧化铁粒子分布于碳管外部(FeO_x /Pod-Fe). 将酸洗前后的两个催化剂用于固定床气相F-T反应中. 通过调节空速和温度考察了它们的催化反应性能, 结果表明两个催化剂在不同的反应条件下都有着良好的低碳烯烃选择性. 不同反应温度下, 它们表现出不同的变化趋势: Pod-Fe活性随着温度的升高而缓慢增长, 至380 °C都没有明显的失活现象; 而对于 FeO_x /Pod-Fe催化剂, 随着温度的升高, CO的转化率先升高, 在300 °C时达最高, 但随着温度进一步升高, 活性迅速降低, 呈现一个火山型曲线. TEM结果发现, 反应后 FeO_x /Pod-Fe催化剂粒子上产生了很多杂乱的碳丝, 并且铁粒子有着明显的聚集长大. 而Pod-Fe催化剂即使在380 °C反应后, 其形貌仍然保持完好, 没有积碳产生, 粒子也没有发生聚集和长大. 进一步在320 °C下120 h的寿命试验发现, Pod-Fe催化剂的初始活性较低, 但经20 h的活化阶段, 活性会先增加后略有下降, 20 h后趋于稳定. 而 FeO_x /Pod-Fe催化剂在反应初始虽然表现出较高的活

性,但是随着时间进行,活性迅速下降一半以上,最后趋于稳定.同时结合反应后TEM和XRD的结果发现碳管外部裸露的铁粒子会在反应过程中形成碳化铁物种,并随着反应进行产生聚集,并伴有大量积碳,导致活性迅速下降;而碳层的包覆对于铁粒子有着很好的稳定作用,使得铁粒子能够在高温反应中保持稳定,并且没有积碳的产生.由此可见石墨烯碳层可以有效保护其包覆的金属粒子,并且能够提高其在高温反应下的低碳烯烃选择性和稳定性.此类催化剂有望在一些苛刻条件下的多相催化反应中得到广泛应用.

关键词: 费托合成; 稳定性; 低碳烯烃; 碳纳米管; 铁纳米粒子

收稿日期: 2015-03-30. 接受日期: 2015-05-05. 出版日期: 2015-09-20.

*通讯联系人. 电话: (0411)84686637; 传真: (0411)84379128; 电子信箱: dhdeng@dicp.ac.cn

#通讯联系人. 电话: (0411)84686637; 传真: (0411)84379128; 电子信箱: xhbao@dicp.ac.cn

基金来源: 国家自然科学基金(21321002, 21303191); 中国科学院战略性先导科技专项(A类)资助(XDA09030100).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).