Graphical Abstract

Ag promoted porous Fe_3O_4 microspheres with tunable pore size were synthesized using one pot solvothermal method and employed as catalysts for Fischer-Tropsch synthesis. Pore size determined confined space impedes hydrogenation and transportation of long chain hydrocarbon, but facilitates hydrogen abstraction and chain growth via inserting CH_2 groups to form olefins, particular for C_{2-4} olefins. Furthermore, the effect of dispersion of Fe on lower olefins selectivity was also discussed.

Synthesis of Ag promoted porous Fe₃O₄ microspheres with tunable pore size as catalysts for Fischer-Tropsch production of lower olefins

Yulan Zhang^{ab}, Longlong Ma^a, Tiejun Wang^{*a}, Xinjun Li^{*a}

^a Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding author. Tel: 862087057751;

E-mail: wangtj@ms.giec.ac.cn; lixj@ms.giec.ac.cn.

Abstract

Ag promoted porous Fe₃O₄ microspheres with tunable pore size were synthesized via one-pot solvothermal method and employed as catalysts for Fischer-Tropsch synthesis. The introduction of Ag played important role in regulating the pore size of catalysts and the dispersion of Fe. Comparable to unmodified catalyst in this system, Ag promoted Fe-based catalysts displayed excellent selectivity to lower olefins, particular for Fe-0.9Ag with smaller pore size of 1.33 nm and Fe dispersion of 10.1 %. The maximum selectivity to C₂ through C₄ olefins was 43.0 wt%, and the selectivity to CH₄ was low to 14.8 wt%.

Keywords: porous Fe₃O₄ microspheres; Fischer-Tropsch synthesis; lower olefins

1. Introduction

Fischer-Tropsch (FT) synthesis has been reported as an effective route to produce lower olefins (C_{2-4}) directly from syngas without intermediate steps, especially for Fe-based catalysts [1,2]. Compared with cobalt, iron enable to use the CO rich syngas without strictly considering the ratio of H_2/CO . Moreover, unsupported iron oxide catalysts exhibit high selectivity to C_{2-4} (up to 70 wt%) when iron is modified by promoters [1]. However, this kind of catalysts prepared through coprecipitation reveal poor mechanical stability at high temperature resulting in lower selectivity to C_{2-4} . Moreover, carbon deposition is inevitable, and carburization can block the active site and deactivation of catalysts [3-5]. On the basis of this, ordered porous materials possessing high surface area and controllable pore size are used as supports to enhance the dispersion of active metal and improve the mechanical stability of Fe-based catalysts [6,7]. In addition, the porous materials used as nanoreactors are expected to control chain growth via inserting methylene monomer units (CH_2) in the confined space, and then regulate the product selectivity [1]. Furthermore, supported iron catalysts show high catalytic activity, but corresponding with a low selectivity to C_{2-4} [8-9]. It has been demonstrated that supported iron catalysts exhibit an inverse relationship between activity and selectivity [1].

To overcome the low catalytic activity and olefins selectivity problems, porous Fe_3O_4 microspheres were directly synthesized through one-pot solvothermal method. In particular, the pores were not provided by supports but resulting from the aggregation of small nanocrystals. It is proposed that the as-prepared porous structure could enhance the dispersion of active phase but not impede the activity of active sites, which would be promising for FT synthesis. In addition to porous Fe_3O_4 microspheres, Ag^+ was introduced as promoter to improve the dispersion of Fe and regulate the size of pores. For better comparison, Fe-0.6Ag, Fe-0.9Ag, and Fe-1.3Ag porous microspheres with different weight percent of Ag were synthesized and used as FT catalysts.

2. Experimental

2.1. Catalyst preparation

1.0 g polyvinylpyrrolidone and 0.17 g AgNO_3 were mixed with 30 mL ethylene glycol (EG) under magnetic stirring. Then, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.0 g), sodium acetate (2.0 g), and ethylenediamine (7.0 ml) were added with stirring at 50 °C for 30 min. The as-formed solution was transferred into a 100 mL Teflon-lined autoclave and maintained at 200 °C for 10 h. Black precipitates were collected after being washed with ethanol and dried at 60 °C.

2.2. Fischer-Tropsch synthesis

Porous Fe-based catalysts were measured using Fixed-bed. Typically, 1.0 g catalyst and 1.0 g quartz granules were mixed together, and then load into the reactor tube which would be fixed in the reactor. Then, catalysts were reduced with syngas ($\text{H}_2/\text{CO}=1.0$, space velocity of $3000 \text{ ml}^{-1}\text{g}^{-1}\text{h}^{-1}$) at 300 °C for 12 h. After that, the pressure was elevated to 2.0 MPa at 150 °C, and then the reaction temperature was elevated to 280 °C and maintained for 48 hours.

3. Results and discussion

3.1 Synthesis and characterization of porous catalysts

Fig. 1 shows the XRD patterns of the fresh prepared catalysts. All the diffraction peaks in black line match well with the standard cubic Fe_3O_4 phase, and it is named as Fe catalyst in the following discussion. Notably, strong diffraction peaks at 38.1° , 44.6° , 64.7° , and 77.5° can be observed, indexing to the (111), (200), (220), and (311) planes of Ag cubic phase as shown in the red, blue, and green lines in Fig. 1, indicating that the corresponding catalysts are composed of Fe_3O_4 and Ag phases. The FT-IR spectra of the samples reveal a strong absorption peak at 606 cm^{-1} relating to the Fe-O lattice mode of Fe_3O_4 [10], no obvious Ag-O lattice mode can be observed (Fig. S1), suggesting that Fe_3O_4 is the unique oxide in this system.

The fresh prepared catalysts were also analysed by X-ray photoelectron spectroscopy to examine the surface composition of **products** (Fig. S2 and Fig. 2). Compared with the Fe catalyst, Ag promoted catalysts reveal obvious Ag3d peaks (Fig. S2), and the corresponding high-resolution spectra (Fig. 2, Ag3d) show two peaks at 367.3 and 373.4 eV ascribing to the metal Ag. The O1s spectra centred at 529.8 529.1, and 531.95

eV belong to O^{2-} from Fe_3O_4 . Therefore, it is accepted that Ag^+ cannot occupy the tetrahedral site of Fe^{3+} during the process of nucleation [11], and thus avoid the influence of intrinsic activity of Fe sites, and then improve the dispersion of Fe promising excellent catalytic performance.

Fig. 3a presents the SEM image of Fe catalyst, which maintain well-preserved and uniform morphology with diameter of 200 nm (Table S1). Fe-0.6Ag (Fig. 3b) matches with a mean size of 70 nm, Fe-0.9Ag (Fig. 3c) corresponds with a bigger size of 140 nm, and Fe-1.3Ag with the maximum content of Ag agrees to the biggest particle size of 170 nm (Fig. 3d). Specially, each single microsphere is consist of many nanoparticles (inset). On the other hand, the diameter of Ag promoted microspheres shows a linear relationship with the quality of Ag, but smaller than Fe catalyst. This phenomenon can be explained by the aggregation rate of Fe_3O_4 nanocrystals in the reaction system. It is known that Ag^+ can easily be reduced to Ag nanocrystals by EG [12,13], and which can be used as seeds to promote adjacent Fe_3O_4 nanocrystals in a common crystallographic orientation aggregating together along the (111) direction to form a spherical structure [14]. A higher quality of Ag seeds (Fe-1.3Ag) corresponds with a quicker aggregation rate, and thus results in bigger microspheres (170 nm). As for Fe-0.6Ag microspheres, although plenty of Fe_3O_4 nanocrystals can be formed through reducing and hydrolyzing reactions, it is difficult for small nanocrystals to migrate and aggregate together in such a high viscosity reaction solution. Then, Ostwald ripening process instead of the oriented aggregation plays the determining role in overcoming the size unbalance, and thus promotes the formation of Fe_3O_4 microsphere with smaller diameter (70 nm). A quicker aggregation rate produces a more compact structure, which is responsible for the decreasing dispersion of Fe from 18.0 % (Fe-0.6Ag) to 10.1 % (Fe-0.9Ag), and to 8.4 % (Fe-1.3Ag) as shown in Table S2. Furthermore, partly EG is used to reduce Ag^+ resulting in slower nucleation rate of Fe_3O_4 nanocrystals, indicating that the diameter of Ag promoted microspheres is smaller than Fe microspheres (200 nm).

The surface area and porosity of the fresh prepared microspheres were determined by measuring the adsorption and desorption isotherms of N_2 . The BET surface area of the microspheres is respectively calculated to be 41.9, 43.9, 38.6, and 21.2 m^2g^{-1} , and

the corresponding pore size distribution is centred at 3.71, 1.62, 1.33, and 2.10 nm (Table S1). The bubbles formed during the reaction process can serve as “soft” template to promote the production of pores [15], which **are** partly responsible for the formation of pores on the surface of microspheres. Specially, the pore size changes between 1 and 4 nm, suggesting that microspheres are porous materials which can enhance the catalytic performance because of the pore determined transportation of products [16]. The effect of pore size on the product selectivity will be discussed later.

3.2. Fischer-Tropsch synthesis performance

The as-prepared porous catalysts were measured in FT reaction at 2.0 MPa and 280 °C using syngas ($H_2/CO=1$), and the corresponding activity and selectivity parameters after reaction for 48 h was summarized in Table 1. Catalytic activity is expressed as the molar of CO moles converted to hydrocarbons and CO_2 , and then the CO_2 selectivity for all the catalysts is nearly 45% (Table 1). Under the given reaction condition, all the catalysts display higher initial activity and gradually decrease with time on stream (Fig. S3). Moreover, Ag promoted catalysts exhibit considerable catalytic activity (~71.0 %). **Though** it is lower than unmodified Fe catalyst (80.1 %), the selectivity to olefins is significant enhanced and the undesired products has been suppressed to the lowest possible level. Furthermore, the dispersion of Fe has significant effect on the FT synthesis reaction. High dispersion of Fe (Fe-0.6Ag, 18.0 %) **can** strengthen CO adsorption **but** weaken H_2 **adsorption**, and then the hydrogen abstraction reaction is enhanced and the hydrogenation reaction is restrained, which promotes the selectivity to olefins. Whereas low dispersion of Fe (Fe-1.3Ag, 8.4 %) **is** significantly weaken the adsorption of CO and strengthen the adsorption of H_2 , and thus enhances the hydrogenation reaction and impedes the hydrogen abstraction reaction, resulting in higher selectivity to CH_4 and paraffin than Fe-0.6Ag. As shown in Table 1, Fe-0.9Ag with Fe dispersion of 10.1 % shows high selectivity toward C_2 through C_4 olefins (43.0 wt%), and a comparatively little carbon to CH_4 (14.8 wt%) and paraffin (7.5 wt%). Moreover, the ratio of $C_{2-4}^=$ to C_{2-4}^0 is high to 5.7 (Table 1). Fe-0.6Ag with higher Fe dispersion of 18.0 % also exhibits high selectivity to lower olefins (41.0 wt%),

but moderate ratio of olefins to paraffins (C_{2-4} , 4.2) is obtained. Nevertheless, Fe-1.3Ag with lower Fe dispersion of 8.4 % reveals a rather high selectivity to CH_4 (20.5 wt%), and then the weight percent of C_{2-4} olefins is low to 35.8 wt%. The result demonstrates that a balance exist between the dispersion of Fe and the olefins selectivity. Too high dispersion of Fe results in a moderate selectivity to olefins, too low dispersion of Fe leads to a poor selectivity to olefins.

Aside from the dispersion of Fe, more significant promoting effect on olefins selectivity may be closely related with the pore size because of the confinement effect. It is known that CO can be dissociated and hydrogenated to form alkyl during FT synthesis reaction, and then hydrogenation may compete with inserting CH_2 groups. The former is to produce methane, the latter is responsible for chain growth. The chain growth is terminated by hydrogen abstraction to produce olefins or hydrogenation to synthesize paraffin. Nevertheless, it is difficult for mesoporous and micropore catalysts in this system to transport long chain hydrocarbon through confined space to exterior. As shown in Fig.4, the products obey the Anderson-Schulz-Flory (ASF) distribution and show obvious decline tendency with the increasing of carbon number, and the selectivity to C_2 through C_{11} olefins is higher than that of paraffins. The former demonstrates that the as-prepared porous catalysts restrain chain growth to form long chain hydrocarbon. The latter shows that hydrogen abstraction is encouraged in this system, and thus improves the selectivity to olefins, particular for C_{2-4} olefins. As shown in Table 1, all the catalysts exhibit maximum selectivity to C_{2-4} olefins, indicating that smaller pore size impedes hydrogenation, but facilitates hydrogen abstraction and chain growth via inserting CH_2 groups to produce olefins with short chain. Especially, Fe-0.9Ag catalyst with pore size of 1.33 nm provides a high ratio of olefin to paraffin in the C_2 through C_4 range, and the corresponding value reaches to 5.7. With increasing the pore size from 1.33 to 1.62 nm, the ratio of olefins decreases to 4.2 (Fe-0.6Ag), and then to 3.4 (Fe-1.3Ag, 2.10 nm). Notably, unmodified Fe catalyst with bigger pore size of 3.72 nm results in poor ratio of lower olefins (2.4). The result reveals that the olefins selectivity displays an inverse relationship with pore size. Moreover, the ratio of olefins in C_{5-11} range also obeys above rule.

Generally, ASF model predicts that the maximum selectivity to short hydrocarbon ranging from C₂ to C₄ is up to 50 wt% when a chain growth probability (α) changes between 0.4 and 0.5, and then the CH₄ product fraction is approximately 30 wt% [1]. ASF plots in Fig. 5 provide α values of about 0.5 which are close to the optimal value to produce maximum selectivity to lower olefins from syngas. Furthermore, the plots show lower selectivity to CH₄ by comparison with the predicted value according to ASF model, which matches with the “alkyl” mechanism [1]. As shown in Table 1, the selectivity to CH₄ is lower in contrast to the speculated value from ASF model. Especially, Fe-0.9Ag displays low selectivity to CH₄ (14.8 wt%), but olefins selectivity in C₂₋₄ fraction is up to 43.0 wt% and the lower olefins ratio is high to 5.7. The result demonstrates that Ag as promoter can be viewed as an effective strategy to restrain the hydrogenation reaction, and thus retards the selectivity to CH₄, but enhances the selectivity to C₂₋₄ olefins with a high ratio of olefins. Moreover, the in-depth effect of Ag on catalytic mechanism needs to be further explored.

4. Conclusion

Ag promoted porous Fe₃O₄ microspheres were synthesized through one-pot solvothermal method and used as Fe-based FT catalysts. The content of Ag played significant effect on the dispersion of Fe and the pore size of porous microspheres. The former related to the chemisorption ability of CO, the latter was responsible for confinement effect. Furthermore, Ag promoted porous catalysts showed higher ratio of olefins and lower selectivity to CH₄ in comparison with unmodified Fe catalyst. Especially, Fe-0.9Ag with Fe dispersion of 10.1 % and pore size of 1.33 nm displayed maximum C₂₋₄ olefins selectivity (43.0 wt%), optimum ratio of C₂₋₄ olefins (5.7), and minimum CH₄ selectivity (14.8 wt%).

Acknowledgements

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References

- [1] H.M. Torres Galvis, J.H. Bitter, C.B. Khare, M. Ruitenbeek, A.I. Dugulan, K.P. de Jong, *Science* 335 (2012) 835-838.
- [2] C. Wang, L. Xu, Q. Wang, *ChemCatChem* 2 (2010) 1030-1058.
- [3] B.H. Davis, *Catal. Today* 84 (2003) 83-98.
- [4] S. Soled, E. Iglesia, R.A. Fiato, *Catal. Lett.* 7 (1990) 271-280.
- [5] Y. Jin, A.K. Datye, *J. Catal.* 196 (2000) 8-17.
- [6] X. Zhang, R. Hirota, T. Kubota, Y. Yoneyama, N. Tsobaki, *Catal. Commun.* 13 (2011) 44-48.
- [7] H. Xiong, Y. Zhang, S. Wang, K. Liew, J. Li, *J. Phys. Chem. C* 112 (2008) 9706-9709.
- [8] V.K. Jones, L.R. Neubauer, C.H. Bartholomew, *J. Phys. Chem.* 90 (1986) 4832-4839.
- [9] Y. Liu, J. Chen, K. Fang, Y. Wang, Y. Sun, *Catal. Commun.* 8 (2007) 945-949.
- [10] T. Fan, D. Pan, H. Zhang, *Ind. Eng. Chem. Res.* 50 (2011) 9009-9018.
- [11] A. Yan, X. Liu, R. Yi, R. Shi, N. Zhang, G. Qiu, *J. Phys. Chem. C* 112 (2008) 8558-8563.
- [12] Y. Sun, Y. Xia, *Adv. Mater.* 14 (2002) 833-837.
- [13] Y. Xia, Y. Xiong, B. Lim, S.E. Skrabalak, *Angew. Chem. Int. Ed.* 47 (2008) 2-46.
- [14] B. Jia, L. Gao, *J. Phys. Chem. C* 112 (2008) 666-671.
- [15] G.C. Maiti, R. Malessa, M. Baerns, *Appl. Catal.* 5 (1983) 151-170.
- [16] H. Li, Z. Bian, J. Zhu, D. Zhang, G. Li, Y. Huo, H. Li, Y. Lu, *J. Am. Chem. Soc.* 129 (2007) 8406-8407.

Table 1 FT performance of Fe-based catalysts after reaction for 48 h.

Fig. 1. XRD patterns of fresh prepared catalysts.

Fig. 2. XPS spectra of fresh prepared catalysts: O1s (a) and Ag3d (b).

Fig. 3. SEM image of fresh prepared catalysts: Fe (a), Fe-0.6Ag (b), Fe-0.9Ag (c) and Fe-1.3Ag (d).

Fig. 4. Product distribution of Fe-based catalysts.

Fig. 5. ASF plots for Fe-based catalysts.

Table 1

Run no.	Fe	Fe-0.6Ag	Fe-0.9Ag	Fe-1.3Ag
CO conversion (%)	80.1	73.0	71.4	74.1
CO ₂ (% of CO converted)	47.5	45.0	45.6	49.7
Product selectivity (wt%)				
CH ₄	20.8	16.9	14.8	20.5
C ₂₋₄ ⁼	38.5	41.0	43.0	35.8
C ₂₋₄ ⁰	11.6	9.7	7.5	10.6
C ₅₋₁₁ ⁼	16.8	23.1	24.3	22.6
C ₅₋₁₁	7.1	6.5	6.5	7.6
C ₁₂₊	5.2	2.7	3.9	2.9
Olefin/paraffin				
C ₂₋₄ ⁼ /C ₂₋₄ ⁰	3.3	4.2	5.7	3.4
C ₅₋₁₁ ⁼ /C ₅₋₁₁ ⁰	2.4	3.6	3.7	3.0

Fig. 1.

Fig.2.

Fig. 3.

Fig.4.

Fig.5