



Short communication

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

Yulan Zhang^{a,b}, 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

ARTICLE INFO

Article history:

Received 25 November 2014

Received in revised form 24 January 2015

Accepted 29 January 2015

Available online 30 January 2015

Keywords:

Porous Fe₃O₄ microspheres

Fischer–Tropsch synthesis

Lower olefins

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 an 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, particularly 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.%.

© 2015 Elsevier B.V. All rights reserved.

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 enables to use the CO rich syngas without strictly considering the ratio of H₂/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 reveals 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 (CH₂) in the confined space, and then regulate the product selectivity [1]. Furthermore, supported iron catalysts show high catalytic activity, but correspond 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 olefin selectivity problems, porous Fe₃O₄ microspheres were directly synthesized through one-pot solvothermal method. In particular, the pores were not provided by supports, 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 Fe₃O₄ 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 AgNO₃ were mixed with 30 mL ethylene glycol (EG) under magnetic stirring. Then, FeCl₃·6H₂O (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 (H₂/CO = 1.0, space velocity of 3000 mL⁻¹ g⁻¹ 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 h.

* Corresponding authors.

E-mail addresses: wangtj@ms.giec.ac.cn (T. Wang), lixj@ms.giec.ac.cn (X. Li).

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 analyzed 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 centered 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 avoids the influence of intrinsic activity of Fe sites, and then improves the dispersion of Fe promising excellent catalytic performance.

Fig. 3a presents the SEM image of Fe catalyst, which maintains well-preserved and uniform morphology with a 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 consists 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

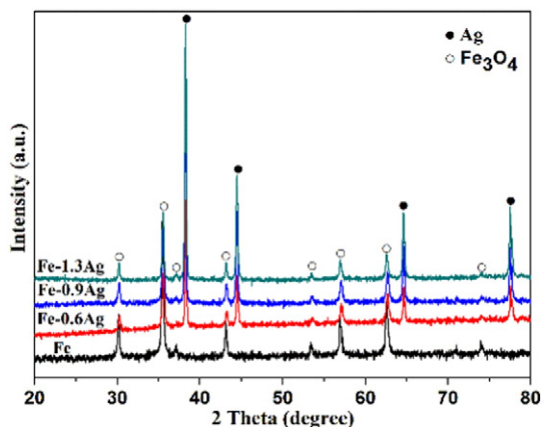


Fig. 1. XRD patterns of fresh prepared catalysts.

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 $21.2\text{ m}^2\text{ g}^{-1}$, and the corresponding pore size distribution is centered 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 ($\text{H}_2/\text{CO} = 1$), and the corresponding activity and selectivity parameters after reaction for 48 h were 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 significantly 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%) significantly weakens the adsorption of CO and strengthens 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 by 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 exists between the dispersion of Fe and the olefin 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 olefin 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 while 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,

Download English Version:

<https://daneshyari.com/en/article/49873>

Download Persian Version:

<https://daneshyari.com/article/49873>

[Daneshyari.com](https://daneshyari.com)