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Short Communication

Synthesis and catalysis of oleic acid-coated Fe_3O_4 nanocrystals for direct coal liquefaction

Yizhao Li [a], Fengyun Ma [a], Xintai Su [a,*], Chao Sun [a], Jianchao Liu [a], Zhiqiang Sun [a], Yanglong Hou [b]

[a] *Ministry Key Laboratory of Oil and Gas Fine Chemicals, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China*
[b] *Department of Advanced Materials and Nanotechnology, College of Engineering, Peking University, Beijing 100871, China*

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ABSTRACT

Oleic acid-coated Fe_3O_4 nanocrystals have been prepared by thermal decomposition of iron–oleate complex in the presence of oleic acid. The nanocrystals were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), transmission electron microscopy (TEM) and Fourier transform infrared spectrometry (FTIR). The results show that the oleic acid-coated Fe_3O_4 nanocrystals are spherical, around 15 nm in diameter. The as-synthesized Fe_3O_4 nanocrystals are highly effective catalysts for the direct liquefaction of Jiangjunmiao coal. With 1.5 wt.% Fe of dry and ash-free (daf) coal added as the synthesized nanocatalysts, the conversion, oil yield, and liquefaction degree reached 97.2, 86.5, and 92.0%, respectively.

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1. Introduction

Direct coal liquefaction (DCL) is one of the most effective techniques to transform coal to clean liquid fuel [1]. In the process of DCL, the catalyst plays an important role in cracking C-C bonds and promoting hydrogen transfer [2]. In particular, Fe-based catalysts have received considerable attention as they are cheap, environmentally benign, and disposable [3,4]. However, most such Fe-based catalysts with a hydrophilic surface show relatively low conversion and oil yield because they do not come into sufficient contact with coal in a DCL system. Furthermore, Fe-based nanoparticles have still not been extensively adopted as catalysts for DCL, despite their large surface area and high surface activity.

It is expected that small-sized Fe-based nanomaterials with a hydrophobic surface have great potential for application in DCL because they provide both high surface area and increased dispersion. Previous works have shown the dispersion performance of the Fe-based catalysts in DCL strongly influences their catalytic activity [5,6]. The FeNi catalysts supported on carbon nanoparticles which provide intimate contact between catalysts and coal have shown a high oil yield [7]. The iron oxides treated with sulfate anion, which increases the dispersion of catalysts in coal, have exhibited an enhanced catalytic activity for DCL [8]. Furthermore, it is quite encouraging that nanometer-sized Fe and FeS_2 with high surface areas and increased contact with coal can display good catalytic activity for coal hydropyrolysis and liquefaction [9]. However, little research has been conducted into applying nanometer-sized Fe_3O_4 with a hydrophobic surface to DCL, despite its high surface area and increased dispersion.

Here, we report for the first time the use of oleic acid-coated Fe_3O_4 nanocrystals in DCL. Fifteen nanometer-sized magnetite nanocrystals have been synthesized by a pyrolyzation of the iron–oleate complex. The DCL experiments indicate that the synthesized Fe_3O_4 nanocrystals exhibited higher catalytic activity compared with commercial Fe_3O_4 and modified commercial Fe_3O_4 powders. It demonstrates that the synthesized oleic acid-coated Fe_3O_4 nanocrystals are promising catalytic materials for DCL.

2. Experimental section

2.1. Preparation of the Fe_3O_4 nanocrystals

The preparation method of Fe_3O_4 nanocrystals was similar to that of Hyeon's group [10]. Typically, $FeCl_3 \cdot 6H_2O$ (2.7 g, 10 mmol) and sodium oleate (9.1 g, 30 mmol) were mixed with 15 mL of distilled water, 20 mL of ethanol and 35 mL of hexane. The resulting solution was heated to 70 °C and kept for 4 h while stirring. Then, the upper organic layer containing the iron–oleate complex was separated and washed with distilled water. Subsequently, the solvent was evaporated off, resulting in iron–oleate complex in a reddish-brown viscous oil form. Then a mixture of the synthesized iron–oleate complex (9.0 g, 10 mmol), oleic acid (1.4 g, 5 mmol) and 1-octadecene (50 g) was heated up to 100 °C under vacuum for 30 min while stirring. The resulting solution was then heated to 320 °C and kept for 3 h under N_2 atmosphere. The solution containing the nanocrystals was then cooled down to room temperature, and excess ethanol was added into the solution to make the nanocrystals precipitate. Then the

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* Corresponding author. Tel./fax: +86 991 8581018.
E-mail address: suxintai827@163.com (X. Su).

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Table 1
Analyses of the Jiangjunmiao coal sample.

Proximate analysis (wt %)				
Moisture (air dry basis)	Ash (dry basis)	Volatile matter (daf basis)	Fixed carbon (dry basis)	
5.42	3.93	34.40	63.02	
Elemental analysis (wt %, dry basis)				
C	H	O[a]	N	S
75.58	4.28	14.36	0.94	0.91
Petrographical analysis (vol. %)			H/C	
Vitrinite	Inertinite	Exinite	(atomic ratio)	
66.7	32.4	0.6	0.68	

[a] Obtained by difference.

nanocrystals were washed and centrifuged with ethanol three times. After that, the resultant nanocrystals were dried at 60 °C under ambient pressure for the next catalytic reaction. The mass fraction of iron in the Fe_3O_4 nanocrystals, which was determined by flame atomic absorption spectrophotometry (Hitachi Z-2000) after microwave digestion (Milestone ETHOS microwave system), was 41.2%. The weight of oleic acid in synthesized Fe_3O_4 nanocrystals was calculated by subtracting the weight of Fe_3O_4 from the weight of the synthesized catalyst.

2.2. Preparation of the modified commercial Fe_3O_4 powders

Commercial Fe_3O_4 powders were modified by oleylamine through a dispersion method [11]. Briefly, commercial Fe_3O_4 (2.315 g, 10 mmol) was dispersed in 300 mL ethanol under magnetic stirring. Then oleylamine (0.535 g, 2 mmol) was added to this solution. The resulting solution was heated to 75 °C for 1 h. The obtained samples were collected from the solution with an external magnet and washed with ethanol. Finally, the products were dried under ambient temperatures.

2.3. Characterization

The commercial Fe_3O_4, modified commercial Fe_3O_4 and as-synthesized nanocrystals were characterized by X-ray diffraction (XRD) using a Rigaku D/max-ga X-ray diffractometer with a scanning speed of $2° \min^{-1}$ ranging from 20° to 80° with Cu Kα radiation ($\lambda = 1.5418$ Å). The Brunauer–Emmett–Teller analysis (BET) measurements were performed on a JW-BK nitrogen adsorption apparatus at 77 K. The transmission electron microscopy (TEM) images were obtained on a Hitachi H-600 with an accelerating voltage of 100 kV. Fourier transform infrared (FTIR) spectra were collected with a Bruker EQUINOX55 spectrophotometer in the wave number interval between 4000 and 400 cm^{-1}.

2.4. Reaction of DCL

The raw coal used in this study is jet coal from the Jiangjunmiao mine in the Xinjiang Autonomous Region of China. Their properties are given in Table 1. In a typical procedure of DCL, 1.0 g (1.5 wt.% daf as Fe) of the as-prepared Fe_3O_4 nanocrystals, 0.3 g of sulfur (1.3 of S/Fe mole ratio), 30.0 g of pulverized Jiangjunmiao coal (200 mesh) and 60.0 g of tetralin were mixed ultrasonically for 30 min to produce a viscous suspension. The reaction mixture was then transferred into a CJF-1L autoclave reactor (Dalian Tongda Reactor Co.). Before the liquefaction experiment, the reactor was sealed and flushed several times with hydrogen followed by pressurizing the system to the initial hydrogen pressure of 6.5 MPa. Then the reactor was heated to 420 °C while stirring and kept for 75 min. The resulting product was extracted in sequence with hexane, toluene, and THF in Soxhlet extractor. The hexane-soluble (HS), hexane-insoluble but toluene-soluble, toluene-insoluble but THF-soluble, and THF-insoluble substances were defined as oil and solvent, asphaltene, preasphaltene, and residue, respectively. The direct liquefaction reactions of Jiangjunmiao coal with commercial Fe_3O_4, modified commercial Fe_3O_4, and without catalyst were also processed under a similar procedure. The conversion, oil yield and liquefaction degree of coal were determined using the following equations:

$$\text{Conversion}\ (\%) = [1-(W_r-W_{ash}-W_c)/W_{daf}] \times 100 \tag{1}$$

$$\text{Oil yield}\ (\%) = [(W_{HS}-W_s-W_o)/W_{daf}] \times 100 \tag{2}$$

$$\text{Liquefaction degree}\ (\%) = \text{Oil yield}\ (\%) + [(W_A+W_{PA})/W_{daf}] \times 100 \tag{3}$$

where W_{daf} is the dry and ash-free weight of coal; W_r is the weight of residue; W_{ash} is the weight of ash; W_c is the total weight of Fe_3O_4 and S; W_{HS} is the weight of HS; W_s is the weight of the solvent; W_o is the weight of oleic acid in the catalysts; W_A is the weight of asphaltene and W_{PA} is the weight of preasphaltene. Typically, W_{daf}, W_r, W_{ash}, W_c, W_{HS}, W_s, W_o, W_A, and W_{PA} are 27.2, 2.81, 1.18, 0.87, 83.96, 60.0, 0.43, 1.26, and 0.24 g, respectively.

3. Results and discussion

The phase of the commercial powders, modified commercial powders, and as-prepared nanocrystals was characterized by XRD. As shown in Fig. 1, all the diffraction peaks can be indexed as a cubic phase of magnetite, which are well matched with the values in the standard card (JCPDS 19–0629). No peaks from impurities are detected from this pattern, confirming the pure phase of all the samples. The crystallite sizes calculated using the Scherrer equation from the (311) reflections for commercial Fe_3O_4 powders, modified commercial Fe_3O_4 powders, and as-synthesized Fe_3O_4 samples, in Table 2, are about 33.2, 32.7, and 16.4 nm, respectively, which are consistent with the TEM results (Fig. 2).

The specific surface area of the three samples was determined by BET method. In Table 2, the specific surface area of the commercial Fe_3O_4 powders, modified commercial Fe_3O_4 powders, and as-synthesized Fe_3O_4 nanocrystals is 11.0, 22.0, and 65.6 m^2/g, respectively. The results of BET show the specific surface area of as-synthesized nanocrystals to be largest.

The size and morphology of the commercial Fe_3O_4, modified commercial Fe_3O_4, and as-synthesized Fe_3O_4 samples were further investigated by TEM. Fig. 2a and b presents the TEM images of the commercial Fe_3O_4 powders, indicating irregular spheres with a large size distribution of 30–200 nm. Fig. 2c and d displays the TEM images

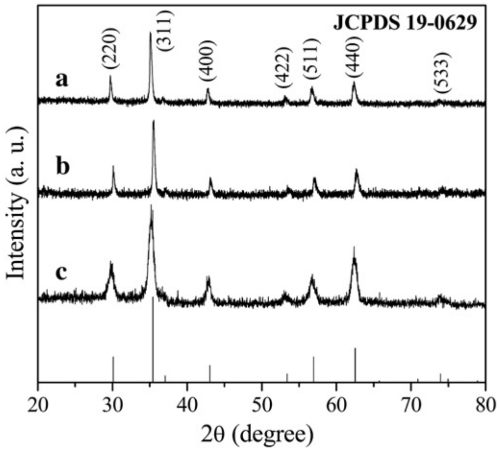

Fig. 1. XRD patterns of (a) commercial Fe_3O_4 powders, (b) modified commercial Fe_3O_4 powders and (c) as-synthesized Fe_3O_4 nanocrystals.

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