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Room-Temperature Solid-State Preparation of CoFe_2O_4 @Coal Composites and Their Catalytic Performance in Direct Coal Liquefaction

Baolin Liu ¹, Yizhao Li ^{1,2,*} , Hao Wu ², Fengyun Ma ^{2,*} and Yali Cao ^{1,*}

¹ Key Laboratory of Energy Materials Chemistry, Ministry of Education, Key Laboratory of Advanced Functional Materials, Autonomous Region, Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, China; liubaolin6977@163.com

² Key Laboratory of Coal Clean Conversion & Chemical Engineering Process, Xinjiang Uygur Autonomous Region, School of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China; wuhaode123@eyou.com

* Correspondence: yizhao@xju.edu.cn (Y.L.); ma_fy@126.com (F.M.); caoyali523@163.com (Y.C.); Tel.: +86-991-8583083 (Y.L.); Fax: +86-991-8588883 (Y.L.)

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Abstract: Iron-based catalysts are promising catalysts in the direct coal liquefaction (DCL) process as they are inexpensive and environmentally friendly. However, most such iron-based catalysts show relatively low activity in coal conversion and oil yield. Common techniques for the synthesis of these catalysts with excellent catalytic performance remain a substantial challenge. We present a simple solid-state synthesis strategy for preparing CoFe_2O_4 nanoparticles and CoFe_2O_4 nanoparticles supported on coal (CoFe_2O_4 @coal) composites for DCL. The obtained bimetallic oxide CoFe_2O_4 nanoparticles show an enhanced catalytic performance in the DCL compared with monometallic components Fe_2O_3 and $\text{Co}(\text{OH})_2$ nanoparticles. The synergistic effect between Co and Fe of CoFe_2O_4 nanoparticles promotes the catalytic hydrogenation of coal during the DCL process. Moreover, the catalytic performance of CoFe_2O_4 nanoparticles is further improved when they are loaded on the coal. The conversion, oil yield, liquefaction degree, and gas yield of Dahuangshan lignite are 99.44, 56.01, 82.18 and 19.30 wt %, respectively, with the CoFe_2O_4 @coal composites involved. The smaller particle size and high dispersion of CoFe_2O_4 supported on coal are of great benefit to full contact between coal and active components. The in-situ solid-state synthesis with coal as support shows great potential to prepare effective iron-based catalysts toward DCL in practice.

Keywords: direct coal liquefaction; iron-based catalysts; CoFe_2O_4 @coal composites; solid-state reaction

1. Introduction

Direct coal liquefaction (DCL) in the presence of the catalyst, as one of the most effective utilization manners for convert coal resources into clean liquid fuel, has been paid to increasing attention [1–4]. Proper catalysts play a significant role in cracking C–C bonds and facilitating the hydropyrolysis of coal to oil [5]. Therefore, catalysts with a high efficiency not only could promote higher coal conversion and oil yield but also reduce the operating severity in the DCL process. Many types of catalysts have shown excellent catalytic performance for DCL, such as molybdenum-based catalysts [6–8], molten metals/halides (Sn or ZnCl_2) [9,10], and iron-based catalysts [5,11]. Nevertheless, one of the main obstacles for DCL is to develop cost-efficient and high-active catalysts to further improve the efficiency and reduce the cost of DCL processes in consideration of its pervasive application.

Iron-based catalysts with moderate activity and abundant reserves are promising catalysts in the DCL process [12]. However, most such iron-based catalysts (iron-bearing mineral, ferric salt, and ferric compounds) show relatively low coal conversion and oil yield [13]. In recent years, the research on liquefaction has mainly focused on the production of organic materials from coal [14], optimizing the hydrogen donor solvent [15], understanding the liquefaction mechanism [16,17], as well as designing catalyst with excellent performance, which can efficiently facilitate the coal liquefaction and promote the coal cracking. Many efforts have been devoted to improving its catalytic activities toward hydropyrolysis of coal, such as constructing composite [1], reducing size [18,19], and improving the dispersity of catalysts [20]. Small-sized Fe_3O_4 nanoparticles exhibited high coal conversion and oil yield as catalysts for DLC [18]. The oleic acid-coated Fe_3O_4 and Fe_2O_3 nanoparticles have presented a superior performance in catalytic DCL [21,22]. Meanwhile, research shows that cobalt and compounds containing cobalt have an excellent hydrodecarbonation activity [23–25]. However, few studies have been presented for cobalt-based catalysts in the DCL process [5,26,27]. Specifically, the research of the interaction between iron and cobalt in coal hydrocracking for iron-based composite catalysts has not been reported. Moreover, the supported catalysts loaded with active components have also exhibited an enhanced catalytic property because they provide a high surface area and increased active sites [20,28,29]. However, supported iron-based catalysts are fabricated generally by an immersion method in liquid, which is time-consuming and tedious. Therefore, it is a high demand for effective construction of supported iron-based catalysts with improved performance in DCL through a facile and scalable method.

Herein, aiming to further improve the catalytic performance of iron-based catalysts in the DCL process, we report a highly efficiency method for the preparation of CoFe_2O_4 nanoparticles and CoFe_2O_4 nanoparticles supported on coal ($\text{CoFe}_2\text{O}_4@\text{coal}$) composites. The CoFe_2O_4 catalyst exhibits a significantly better DCL performance than individual Fe_2O_3 and $\text{Co}(\text{OH})_2$ particles, which can be ascribed to the interaction between iron and cobalt. The DCL performance was further improved by CoFe_2O_4 nanoparticles loaded over the coal. This simple solid-state method is applicable to large-scale synthesis of bimetallic catalysts and supported catalysts for DCL.

2. Results and Discussion

2.1. Structure and Morphology Characterization of Nanocatalysts

Figure 1a illustrates a schematic illustration of the synthesis process of $\text{CoFe}_2\text{O}_4@\text{coal}$ catalyst by straightforward grinding strategy in agate mortar at ambient temperature. This processing allows for the mass production of such samples without the calcination treatment. As shown in Figure 1b, the X-ray diffraction (XRD) characteristic peaks of raw coal show the two broad diffraction peaks at around 25° and 42° , corresponding to (002), (101) lattice planes of carbon [30]. The identical XRD diffraction pattern of CoFe_2O_4 samples is broad and diffuse diffractions features (Figure 1b), indicating a poor crystallinity and a fine grain size. The major diffraction peaks observed at $2\theta = 35.45$ and 62.72° belong to the (311) and (440) planes of CoFe_2O_4 (JCPDS 03-0864), respectively, suggesting the formation of the as-synthesized $\text{CoFe}_2\text{O}_4@\text{coal}$ samples by the room-temperature solid-state method. As can be seen in Figure S1, The XRD patterns of samples display characteristic peaks of as-prepared Fe_2O_3 and $\text{Co}(\text{OH})_2$. The appearance of peaks at 25° – 30° may be attributed to impurities from raw material. The lower diffraction intensity of the samples indicates poor crystallinity and fine grain size.

Figure 1. (a) Schematic illustration of solid-state preparation of CoFe_2O_4 @coal composites; (b) XRD pattern of coal, as-synthesized CoFe_2O_4 nanoparticles and CoFe_2O_4 @coal composites; (c) FTIR spectra of coal and as-synthesized CoFe_2O_4 @coal composites.

The Fourier transform infrared (FTIR) spectroscopy was implemented for CoFe_2O_4 and CoFe_2O_4 @coal samples (Figure 1c). Specifically, the absorption peaks at 3420 cm^{-1} are due to OH groups [31]. The absorbance in the range of $2913\text{--}2835\text{ cm}^{-1}$ is attributed to $-\text{CH}_x$ stretching vibrations in aliphatic [32]. The absorption peaks at about 1613 cm^{-1} and 1440 cm^{-1} belong to aromatic $\text{C}=\text{C}$ stretching vibrations and the stretching vibration of COO^- in carboxylates, respectively [32]. The stronger absorption peaks at 3420 cm^{-1} for CoFe_2O_4 @coal sample compared with raw coal are due to the chemisorbed water and/or hydroxyl groups contributed by CoFe_2O_4 nanoparticles, which often saw in many papers [33,34]. The absorption peaks at 604 cm^{-1} are presented compared with raw coal, which can be associated with the Fe–O vibration [31]. This result further implies that CoFe_2O_4 nanoparticles are loaded over the coal through the solid-state reaction.

The element and valences of as-prepared samples were ascertained by X-ray photoelectron spectra (XPS). In the curve of XPS, the presence of C, O, Fe, and Co elements can be confirmed (Figure 2a). The increase in C content is due to the incorporation of coal. As shown in Figure 2b, the main peaks around 711 eV and 715 eV are assigned to $\text{Fe}^{2+} 2p_{2/3}$ and $\text{Fe}^{3+} 2p_{2/3}$. The peaks at 724 eV and 728 eV are attributed to $\text{Fe}^{2+} 2p_{1/2}$ and $\text{Fe}^{3+} 2p_{1/2}$ on the basis of their binding energies, respectively, which indicates the coexistence of Fe^{2+} and Fe^{3+} [33]. Co 2p spectra in Figure 2c exhibits the existence of Co^{2+} , Co^{3+} and their shake-up satellites (sat.) [33]. The spectra of O 1s for all the samples can be resolved into three peaks, which correspond to Co–O, Fe–O, and OH (surface oxygen), respectively [34,35]. The existence of OH in the CoFe_2O_4 @coal sample is consistent with the analysis of FTIR. Moreover, the presence of Co–O and Fe–O further proves the formation of CoFe_2O_4 through the solid-state reaction at ambient temperature.

Figure 2. (a) XPS survey spectrum of all elements; (b) Fe 2p; (c) Co 2p; and (d) O 1s for prepared samples.

The field emission scanning electron microscope (FESEM) images (Figure 3a,b) reveal that the average size of the synthesized CoFe_2O_4 nanoparticles is below 100 nm. $\text{CoFe}_2\text{O}_4@\text{coal}$ composites (Figure 3c,d) presents irregular bulks with a large size distribution of 300–500 nm. The CoFe_2O_4 nanoparticles with 10–50 nm are uniformly loaded over the coal through the solid-state reaction among ferric chloride, cobaltous chloride, sodium hydroxide, and coal. It can be seen that the surface of the raw coal is smooth and has no obvious particles. The irregular bulks for raw coal can be seen in Figure S2a,b. The irregular aggregation for FeCl_3 (Figure S2c,d) and CoCl_2 (Figure S2e,f) can be clearly seen. After grinding in the agate mortar, the coal particles became smaller (Figure 3c,d). The catalyst particles were more uniformly dispersed on the surface of coal, which further evidences that the CoFe_2O_4 nanoparticles are loaded over the coal through the solid-state reaction.

In addition, the morphology of Fe_2O_3 and $\text{Co}(\text{OH})_2$ particles was also acquired, as shown in Figures S3 and S4, displaying agglomerated nanoparticles with an average size of approximately 50–100 nm. It can be observed that the addition of coal is to help in reducing the size of CoFe_2O_4 nanoparticles and improving the dispersity of catalytic active components. This property of supported composites could guarantee that CoFe_2O_4 nanoparticles are easily fully of contact with coal in the DCL process, which is crucial for the catalytic hydrogenation of coal.

Figure 3. Typical FESEM images of as-synthesized (a,b) CoFe_2O_4 nanoparticles and (c,d) CoFe_2O_4 @coal composites.

2.2. Catalytic Properties of Samples in DCL

The catalytic performances of the as-prepared CoFe_2O_4 @coal composites for the direct liquefaction of Dahuangshan coal from China were investigated. Figure 4 and Table 1 show the results of the catalytic hydrogenation of all prepared samples. The experiments of DCL were repeated three times to decrease the error. The conversion (86.28 wt %), oil yield (39.47 wt %), liquefaction degree (73.37 wt %) and gas yield (12.57 wt %) for Dahuangshan coal are presented without the catalysts involved, which indicates that the Dahuangshan coal is suitable for DCL under the current conditions. The Fe_2O_3 sample accomplished conversion (90.76 wt %), oil yield (37.78 wt %), liquefaction degree (77.41 wt %), and gas yield (14.28 wt %) for the DCL. The CoFe_2O_4 sample exhibits better catalytic activity compared with the Fe_2O_3 catalyst, which shows that the conversion, oil yield, liquefaction degree, and gas yield are 99.03%, 41.81%, 76.20% and 24.74%, respectively. This result indicates that the incorporation of Co species drastically promotes the catalytic activity of the Fe_2O_3 sample for the direct liquefaction of Dahuangshan coal. Even more surprisingly, the catalytic performance is further enhanced for the CoFe_2O_4 @coal composites. The conversion, oil yield, liquefaction degree, and gas yield of Dahuangshan coal increased to 99.44, 56.01, 82.18, and 19.30 wt %, respectively. The asphaltene and pre-asphaltene (APA) yield, residue yield dropped to 24.21 wt %, 0.11 wt %, respectively, while it was 33.57 wt %, 13.71 wt % compared to liquefaction without catalysts. The catalytic performance of $\text{Co}(\text{OH})_2$ sample applied to direct liquefaction of Dahuangshan coal was also investigated, which indicates poor performance in conversion, oil yield, liquefaction degree, and gas yield compared with CoFe_2O_4 @coal nanoparticles. Furthermore, they were compared with similar ones, as shown in Table 2, which exhibits higher conversion and oil yield. It is obvious that CoFe_2O_4 @coal composites exhibited a high catalytic activity toward DCL, and promoted the transform from APA to oil, which possess enhanced selectivity for oil components.

Figure 4. Results of the direct liquefaction of Dahuangshan coal with different catalysts (liquefaction degree label as LD).

Table 1. Results of the direct liquefaction of Dahuangshan coal with different catalysts.

Sample	Conversion/%	Oil Yiel/%	Liquefaction Degree/%	Gas Yield/%	APA/%	Residue Yield/%
/	86.28	39.47	73.37	12.57	33.57	13.71
Fe ₂ O ₃	90.76	37.78	77.41	14.28	38.35	9.65
Co(OH) ₂	95.59	40.71	77.54	18.49	38.89	4.84
CoFe ₂ O ₄	99.03	41.81	76.20	24.74	32.17	0.38
CoFe ₂ O ₄ @coal	99.44	56.01	82.18	19.30	24.21	0.11

The enhanced catalytic activity of CoFe₂O₄@coal composites may be attributed to the interaction between iron and cobalt. The incorporation of coal improves the dispersion of CoFe₂O₄ nanoparticles and decreases its particle size. The smaller particle size and high dispersion of CoFe₂O₄ supported on coal are of great benefit to full contact between coal and active components, which promote the catalytic hydrogenation of coal eventually. The reusability of CoFe₂O₄@coal is under consideration in our group. The coal mixed for the preparation of CoFe₂O₄@coal may have been liquefied, but the extra conversion for this catalyst in the liquefaction was deducted. Many studies [20,28,29] showed that active components supported by coal, which were usually obtained by impregnation, are good catalysts in DCL. Reusability is much more important in terms of the economical point of view. We propose a protocol for the reusability of catalysts. Because the liquefaction of coal mixed with CoFe₂O₄ for the preparation of CoFe₂O₄@coal, the active components contained in residue after DCL would be extracted by calcination and picking. They could be used to prepare the iron-based catalysts for reuse.

Table 2. Results of direct coal liquefaction reactions compared with previous literatures.

Sample	Conversion	Oil Yield	Liquefaction Degree	Gas Yield	Reference
CoFe ₂ O ₄ @coal	99.44%	56.01%	82.18%	19.30%	This work
Fe ₃ O ₄	89.60%	65.10%	77.3%	-	[31]
Fe ₂ (MoS ₄) ₃	78.20%	70.50%(oil+gas)	-	-	[36]
g-FeOOH	32.00%	-	-	-	[37]
FeNi-S/γ-Al ₂ O ₃	89.40%	-	-	-	[29]
Oleic acid-coated Fe ₂ O ₃	83.67%	-	-	-	[22]
Fe ₂ S ₃	62.60%	54.20%	-	-	[20]
Co/SiO ₂	99.00%	55.00%	-	44.00%	[5]
FeS ₂	79.00%	47.00%	-	32.00%	[5]
Fe/SiO ₂	87.00%	44.00%	-	43.00%	[5]
Oleic acid-coated Fe ₃ O ₄	97.20%	86.50%	92.00%	-	[21]
Fe ₃ O ₄ nanoparticles	76.40%	53.80%	-	13.90%	[18]

3. Experimental Methods

3.1. Starting Materials

All chemicals were used without further purification. Ferric (III) chloride hexahydrate (FeCl₃·6H₂O, 99.7%), cobalt (II) chloride hexahydrate (CoCl₂·6H₂O, 99.7%) and sodium hydroxide (NaOH, 96.0%) were purchased from Tianjin Zhiyuan Chemical Reagents Co., Ltd (Tianjin, China). The raw coal in this study was obtained from the Dahuangshan mine in the Xinjiang Autonomous Region of China. Its proximate analysis and ultimate analysis results are given in Table 3. The coal was ground to fine particles with about 200 mesh before its use.

Table 3. Proximate and ultimate analysis of Dahuangshan lignite.

Coal.	Proximate Analysis (wt %) ¹				Ultimate Analysis (wt %, daf ²)					H/C	O/C
	M _{ad}	A _d	V _{daf}	FC _d	C	H	O ³	N	S		
Dahuangshan	1.22	17.57	48.34	42.58	63.17	3.63	14.30	1.11	0.20	0.69	0.17

¹ M_{ad}, moisture content of air-dried coal; A_d, the ash content of air-dried coal; V_{daf}, volatile content; FC_d, the fixed carbon content of air-dried coal. ² daf, dry and ash-free coal. ³ Obtained by difference.

3.2. Preparation of CoFe₂O₄@coal, CoFe₂O₄, Fe₂O₃, and Co(OH)₂ Nanoparticles by Solid-State Reaction

CoFe₂O₄@coal, CoFe₂O₄, Fe₂O₃, and Co(OH)₂ were fabricated through a simple solid-state chemical approach at ambient temperature. Given the uniform dispersion of active components on the coal, the mass percent of CoFe₂O₄ in the composite catalyst is fixed to 40 wt %. In a typical procedure for the synthesis of CoFe₂O₄@coal, FeCl₃·6H₂O (1.08 g, 4 mmol), CoCl₂·6H₂O (0.48 g, 2 mmol) and coal (0.67 g) were sufficiently mixed by grinding in an agate mortar. Subsequently, NaOH (0.64 g, 16 mmol) was added into the agate mortar. After grinding for about 30 min, the color of mixtures changed to dark brown due to the metal ions react with sodium hydroxide. The resulting solid products were washed with distilled water and absolute ethanol several times, then dried at 80 °C for 3 h, and the CoFe₂O₄@coal was acquired. Moreover, the same method was applied to prepare CoFe₂O₄ nanoparticles without coal.

As a comparison, the bulk Fe₂O₃ and Co(OH)₂ particles were also obtained by straightforward grinding FeCl₃·6H₂O or CoCl₂·6H₂O with NaOH, respectively. The obtained product was washed and filtrated with distilled water and dried at 80 °C for 3 h.

3.3. Characterization

The crystal structure of the obtained samples was characterized by XRD using a Bruker D8 X-ray diffractometer (Bruker Corporation, Karlsruhe, Germany) with Cu-Kα radiation (λ = 1.5418 Å). FESEM images were obtained on a Hitachi S-4800 scanning electron microscope (Hitachi Limited, Tokyo,

Japan) with an accelerating voltage of 15 kV. FTIR spectra were obtained on a Bruker EQUINOX55 spectrophotometer (Bruker Corporation, Karlsruhe, Germany) in the wave interval between 4000 and 400 cm^{-1} . XPS were acquired on a Thermo Fisher Scientific ESCALAB250Xi (Thermo Fisher Scientific, Waltham, Massachusetts, USA) employing Al K α (1486.6 eV).

3.4. The Catalytic Process of DCL

Liquefaction reactions were conducted in a 0.1 L batch stirred autoclave. The process of DCL catalyzed by obtained catalysts and the separation procedure of products were similar to the previous studies. [18,21,31] In a typical experiment, 7.0 g of coal, 14.0 g of tetralin as a solvent, CoFe_2O_4 @Coal (Fe is 1.4 wt % of dry and ash-free (daf) coal) as a catalyst, and sulfur (S/Fe mole ratio is 1.8) as a cocatalyst were mixed and charged into the reactor.

After replacing air in the autoclave with H_2 (99.99%), the reactor was pressurized with H_2 to 6 MPa at room temperature and heated to 430 $^\circ\text{C}$. Then, the mixture was stirred with 300 rpm for 60 min at that temperature. After the autoclave was rapidly cooled by blowing to room temperature, the resulting liquid and solid product were extracted in sequence with *n*-hexane and tetrahydrofuran (THF) in a Soxhlet extractor. The *n*-hexane-soluble (HS), *n*-hexane-insoluble, but THF-soluble, and THF-insoluble substances were defined as oil, asphaltene and pre-asphaltene (APA), and residue, respectively. The catalytic hydrogenation of Dahuangshan coal with Fe_2O_3 and $\text{Co}(\text{OH})_2$ nanoparticles and without catalysts were also conducted, respectively. The conversion, oil yield, APA yield, and gas yield of coal were determined using the following equations:

$$\text{residue yield/wt \%} = (W_r - W_{\text{ash}} - W_c)/W_{\text{daf}} \times 100$$

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

$$\text{oil yield/wt \%} = [(W_{\text{HS}} - W_s)/W_{\text{daf}}] \times 100$$

$$\text{APA yield/wt \%} = (W_{\text{APA}}/W_{\text{daf}}) \times 100$$

$$\text{gas yield/wt \%} = \text{conversion} - \text{oil yield} - \text{APA yield}$$

where W_{daf} is the weight of dry and ash-free coal; W_r is the weight of the residue; W_{ash} is the weight of ash; W_c is the total weight of CoFe_2O_4 @Coal and sulfur; W_{HS} is the weight of HS substances; W_s is the weight of solvent, and W_{APA} is the weight of APA.

4. Conclusions

In conclusion, aiming to improve the catalytic performances of the iron-base catalysts for the DLC, CoFe_2O_4 nanoparticles and CoFe_2O_4 @coal composites were developed via a facile and green method under ambient conditions. The synergistic effect between Co and Fe of CoFe_2O_4 nanoparticles promote the catalytic hydrogenation of coal during the DCL process. The incorporation of coal improves the dispersion of CoFe_2O_4 nanoparticles and decreases its particle size in the composite catalyst. The obtained composite exhibited better catalytic performance in the direct liquefaction of Dahuangshan coals, which can achieve the conversion, oil yield, liquefaction degree, and gas yield of Dahuangshan coal to 99.44, 56.01, 82.18, and 19.30 wt %, respectively. The APA yield and residue yield dropped to 24.21 wt % and 0.11 wt %, respectively with the CoFe_2O_4 @coal composites in the catalytic hydrogenation of Dahuangshan coal under the conditions. This simple solid-state method is applicable to the large-scale synthesis of CoFe_2O_4 @coal composites for DCL.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/5/503/s1>, Figure S1: XRD pattern of as-synthesized Fe_2O_3 and $\text{Co}(\text{OH})_2$ nanoparticles; Figure S2: Typical FESEM image of (a,b) raw coal; (c,d) FeCl_3 and (e,f) CoCl_2 ; Figure S3: Typical FESEM image of as-synthesized $\text{Co}(\text{OH})_2$ particles; Figure S4: Typical FESEM image of as-synthesized Fe_2O_3 particles.

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