Article

Room-Temperature Solid-State Preparation of CoFe$_2$O$_4$@Coal Composites and Their Catalytic Performance in Direct Coal Liquefaction

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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$_2$O$_4$ nanoparticles and CoFe$_2$O$_4$ nanoparticles supported on coal (CoFe$_2$O$_4$@coal) composites for DCL. The obtained bimetallic oxide CoFe$_2$O$_4$ nanoparticles show an enhanced catalytic performance in the DCL compared with monometallic components Fe$_2$O$_3$ and Co(OH)$_2$ nanoparticles. The synergistic effect between Co and Fe of CoFe$_2$O$_4$ nanoparticles promotes the catalytic hydrogenation of coal during the DCL process. Moreover, the catalytic performance of CoFe$_2$O$_4$ 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$_2$O$_4$@coal composites involved. The smaller particle size and high dispersion of CoFe$_2$O$_4$ 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$_2$O$_4$@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 hydrolysis of coal, such as constructing composite [1], reducing size [18,19], and improving the dispersity of catalysts [20]. Small-sized Fe₃O₄ nanoparticles exhibited high coal conversion and oil yield as catalysts for DLC [18]. The oleic acid-coated Fe₃O₄ and Fe₂O₃ 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 efficient method for the preparation of CoFe₂O₄ nanoparticles and CoFe₂O₄ nanoparticles supported on coal (CoFe₂O₄@coal) composites. The CoFe₂O₄ catalyst exhibits a significantly better DCL performance than individual Fe₂O₃ and Co(OH)₂ particles, which can be ascribed to the interaction between iron and cobalt. The DCL performance was further improved by CoFe₂O₄ 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 CoFe₂O₄@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 CoFe₂O₄ samples is broad and diffuse diffractions features (Figure 1b), indicating a poor crystallinity and a fine grain size. The major diffraction peaks observed at 2θ = 35.45 and 62.72° belong to the (311) and (440) planes of CoFe₂O₄ (JCPDS 03-0864), respectively, suggesting the formation of the as-synthesized CoFe₂O₄@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 Fe₂O₃ and Co(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.
The Fourier transform infrared (FTIR) spectroscopy was implemented for CoFe$_2$O$_4$ and CoFe$_2$O$_4$@coal samples (Figure 1c). Specifically, the absorption peaks at 3420 cm$^{-1}$ are due to OH groups [31]. The absorbance in the range of 2913-2835 cm$^{-1}$ is attributed to –CH$_x$ stretching vibrations in aliphatic [32]. The absorption peaks at about 1613 cm$^{-1}$ and 1440 cm$^{-1}$ belong to aromatic C=C stretching vibrations and the stretching vibration of COO– in carboxylates, respectively [32]. The stronger absorption peaks at 3420 cm$^{-1}$ for CoFe$_2$O$_4$@coal sample compared with raw coal are due to the chemisorbed water and/or hydroxyl groups contributed by CoFe$_2$O$_4$ 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$_2$O$_4$ 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 Fe$^{2+}$ 2p$_{2/3}$ and Fe$^{3+}$ 2p$_{2/3}$. The peaks at 724 eV and 728 eV are attributed to Fe$^{2+}$ 2p$_{1/2}$ and 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$_2$O$_4$@coal sample is consistent with the analysis of FTIR. Moreover, the presence of Co–O and Fe–O further proves the formation of CoFe$_2$O$_4$ 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$_2$O$_4$ nanoparticles is below 100 nm. CoFe$_2$O$_4$@coal composites (Figure 3c,d) presents irregular bulks with a large size distribution of 300–500 nm. The CoFe$_2$O$_4$ 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$_2$O$_4$ nanoparticles are loaded over the coal through the solid-state reaction.

In addition, the morphology of Fe$_2$O$_3$ and Co(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$_2$O$_4$ nanoparticles and improving the dispersity of catalytic active components. This property of supported composites could guarantee that CoFe$_2$O$_4$ nanoparticles are easily fully of contact with coal in the DCL process, which is crucial for the catalytic hydrogenation of coal.
2.2. Catalytic Properties of Samples in DCL

The catalytic performances of the as-prepared CoFe$_2$O$_4$@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 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. It is obvious that CoFe$_2$O$_4$ was 33.57 wt %, 13.71 wt % compared to liquefaction without catalysts. The catalytic performance (77.41 wt %), and gas yield (14.28 wt %) for the DLC. The CoFe$_2$O$_4$ (73.37 wt %) and gas yield (12.57 wt %) for Dahuangshan coal are presented without the catalysts. The conversion (8.03 wt %), oil yield (4.74 wt %), liquefaction degree (7.41 wt %), and gas yield (14.28 wt %) for the DLC. The CoFe$_2$O$_4$ sample exhibits better catalytic activity compared with the Fe$_3$O$_4$ 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$_3$O$_4$ sample for the direct liquefaction of Dahuangshan coal. Even more surprisingly, the catalytic performance is further enhanced for the CoFe$_2$O$_4$@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 Co(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$_2$O$_4$@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$_2$O$_4$@coal composites exhibited a high catalytic activity toward DCL, and promoted the transform from APA to oil, which possess enhanced selectivity for oil components.
CoFe$_2$O$_4$ extracted by calcination and picking. They could be used to prepare the iron-based catalysts for reuse. Because the liquefaction of coal mixed with CoFe$_2$O$_4$ 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 CoFe$_2$O$_4$ for the preparation of CoFe$_2$O$_4$@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. Many studies [20,28,29] showed that the interaction between iron and cobalt. The incorporation of coal improves the dispersion of CoFe$_2$O$_4$ nanoparticles and decreases its particle size. The smaller particle size and high dispersion of CoFe$_2$O$_4$ 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 CoFe$_2$O$_4$@coal is under consideration in our group. The coal mixed for the preparation of CoFe$_2$O$_4$@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 CoFe$_2$O$_4$ for the preparation of CoFe$_2$O$_4$@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.

The enhanced catalytic activity of CoFe$_2$O$_4$@coal composites may be attributed to the interaction between iron and cobalt. The incorporation of coal improves the dispersion of CoFe$_2$O$_4$ nanoparticles and decreases its particle size. The smaller particle size and high dispersion of CoFe$_2$O$_4$ 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 CoFe$_2$O$_4$@coal is under consideration in our group. The coal mixed for the preparation of CoFe$_2$O$_4$@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 CoFe$_2$O$_4$ for the preparation of CoFe$_2$O$_4$@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.

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 Yield/% | 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            |

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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/$\gamma$-Al$_2$O$_3$     | 89.40%     | -         | -                   | -         | [29]      |
| g-FeOOH                         | 32.00%     | -         | -                   | -         | [37]      |
| Fe$_2$S$_3$                     | 62.60%     | 54.20%    | -                   | -         | [20]      |
| Fe$_2$O$_3$                     | 79.00%     | 47.00%    | -                   | -         | [20]      |
| Fe$_3$O$_4$ nanoparticles       | 87.00%     | 44.00%    | -                   | -         | [20]      |
| Oleic acid-coated Fe$_2$O$_3$   | 97.20%     | 86.50%    | 92.00%              | -         | [21]      |
| Oleic acid-coated Fe$_3$O$_4$   | 97.20%     | 86.50%    | 92.00%              | -         | [21]      |
| Fe$_2$O$_3$                     | 83.67%     | -         | -                   | -         | [22]      |
| Co$_2$S$_3$                     | 89.60%     | 65.10%    | 77.3%               | -         | [20]      |
| Co$_2$S$_3$                     | 79.00%     | 47.00%    | -                   | -         | [20]      |
| Fe$_2$S$_3$                     | 87.00%     | 44.00%    | -                   | -         | [20]      |
| Co$_2$S$_3$                     | 62.60%     | 54.20%    | -                   | -         | [20]      |
| Co$_2$S$_3$                     | 79.00%     | 47.00%    | -                   | -         | [20]      |
| Fe$_2$S$_3$                     | 87.00%     | 44.00%    | -                   | -         | [20]      |
| Oleic acid-coated Fe$_2$O$_3$   | 97.20%     | 86.50%    | 92.00%              | -         | [21]      |
| Oleic acid-coated Fe$_3$O$_4$   | 97.20%     | 86.50%    | 92.00%              | -         | [21]      |
| Fe$_2$O$_3$ 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 (FeCl$_3$·6H$_2$O, 99.7%), cobalt (II) chloride hexahydrate (CoCl$_2$·6H$_2$O, 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 %) | Ultimate Analysis (wt %, daf) | H/C  | O/C  |
|--------|---------------------------|------------------------------|------|------|
|        | $M_{ad}$  | $A_d$  | $V_{daf}$ | $F_{C_d}$ | $C$  | $H$  | $O^3$ | $N$  | $S$  |------|
| 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; $F_{C_d}$, the fixed carbon content of air-dried coal. 2. daf, dry and ash-free coal. 3. Obtained by difference.

3.2. Preparation of CoFe$_2$O$_4$@coal, CoFe$_2$O$_4$, Fe$_2$O$_3$, and Co(OH)$_2$ Nanoparticles by Solid-State Reaction

CoFe$_2$O$_4$@coal, CoFe$_2$O$_4$, Fe$_2$O$_3$, 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 CoFe$_2$O$_4$ in the composite catalyst is fixed to 40 wt %. In a typical procedure for the synthesis of CoFe$_2$O$_4$@coal, FeCl$_3$·6H$_2$O (1.08 g, 4 mmol), CoCl$_2$·6H$_2$O (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 CoFe$_2$O$_4$@coal was acquired. Moreover, the same method was applied to prepare CoFe$_2$O$_4$ nanoparticles without coal.

As a comparison, the bulk Fe$_2$O$_3$ and Co(OH)$_2$ particles were also obtained by straightforward grinding FeCl$_3$·6H$_2$O or CoCl$_2$·6H$_2$O 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\(\alpha\) (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. In a typical experiment, 7.0 g of coal, 14.0 g of tetralin as a solvent, CoFe\(_2\)O\(_4\)@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 \(^\circ\)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\(_2\)O\(_3\) and Co(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:

\[
\text{residue yield/wt %} = \frac{(W_r - W_{ash} - W_c)}{W_{daf}} \times 100
\]
\[
\text{conversion/wt %} = [1 - (W_r - W_{ash} - W_c)/W_{daf}] \times 100
\]
\[
\text{oil yield/wt %} = [(W_{HS} - W_s)/W_{daf}] \times 100
\]
\[
\text{APA yield/wt %} = (W_{APA}/W_{daf}) \times 100
\]
\[
\text{gas yield/wt %} = \text{conversion - oil yield - APA yield}
\]

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\(_2\)O\(_4\)@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\(_2\)O\(_4\) nanoparticles and CoFe\(_2\)O\(_4\)@coal composites were developed via a facile and green method under ambient conditions. The synergistic effect between Co and Fe of CoFe\(_2\)O\(_4\) nanoparticles promote the catalytic hydrogenation of coal during the DCL process. The incorporation of coal improves the dispersion of CoFe\(_2\)O\(_4\) 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\(_2\)O\(_4\)@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\(_2\)O\(_4\)@coal composites for DLC.

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\(_2\)O\(_3\) and Co(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 Co(OH)\(_2\) particles; Figure S4: Typical FESEM image of as-synthesized Fe\(_2\)O\(_3\) particles.
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Conflicts of Interest: The authors declare no conflict of interest.

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