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The relationship between the microstructures and catalytic behaviors of iron–oxygen precursors during direct coal liquefaction

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ABSTRACT

A series of both unsupported and coal-supported iron–oxygen compounds with gradual changes in microstructure were synthesized by a precipitation-oxidation process at 20 to 70 °C. The relationship between the microstructures and catalytic activities of these precursors during direct coal liquefaction was studied. The results show that the microstructure could be controlled through adjusting the synthesis temperature during the precipitation-oxidation procedure, and that compounds synthesized at lower temperatures exhibit higher catalytic activity. As a result of their higher proportions of γ-FeOOH or α-FeOOH crystalline phases, the unsupported iron–oxygen compounds synthesized at 20–30 °C, which also had high specific surface areas and moisture levels, generate oil yields 4.5%–4.6% higher than those obtained with precursors synthesized at 70 °C. It was also determined that higher oil yields were obtained when the catalytically-active phase formed by the precursors during liquefaction (pyrrhotite, $Fe_{1-x}S$) had smaller crystallites. Feed coal added as a carrier was found to efficiently disperse the active precursors, which in turn significantly improved the catalytic activity during coal liquefaction.

1. Introduction

Direct coal liquefaction (DCL) is an effective method of utilizing coal to produce clean liquid fuels, especially for those countries that have limited oil resources but are rich in coal, such as China [1–3]. Oil yield is a key performance index for the DCL process, and 1% increase in oil yield can result in 20 000 tons of additional oil production or approximately 100 million RMB of additional profit for an industrial-scale DCL plant with a one million ton annual production capacity. A high-performance DCL catalyst can accelerate the pyrolysis of coal and promote the hydrocracking of macromolecular fragments, resulting in higher coal conversion and increased liquefied oil yield [4–6].

Iron-based materials applied as disposal catalysts during DCL have been widely employed due to their lower costs and moderate activities [7–11]. Pyrrhotite ($Fe_{1-x}S$), which is generated from iron-based catalysts during liquefaction, has been identified as the catalytically-active phase [12–15]. Red mud, natural iron ore, synthetic iron sulfide, synthetic iron oxides

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Table 1
Proximate, ultimate and petrographical analysis data for the Shenhua Shangwan coal.

w (wt%)			φ (vol%)			w(element) [a] (wt%)				
M_{ad}	A_d	V_{daf}	Vitrinite	Inertinite	Exinite	C	H	O [b]	N	S
4.46	5.86	34.89	54.2	44.2	0.4	79.16	4.38	15.21	0.98	0.27

M_{ad}—Air-dried moisture; A_d—Dry ash; V_{daf}—Volatiles on a dry-ash-free basis. [a] On a dry ash-free basis. [b] Determined by difference.

and oil- or water-soluble iron-containing materials have all been used in DCL. However, variations in properties such as crystalline phase, structure or dispersion will lead to pronounced differences in the resulting pyrrhotite and thus the catalytic activity [16–18].

Because DCL is a complicated three-phase reaction, it is very difficult to determine the relationship between catalytic precursors and oil yields. Linehan et al. [19] studied 11 different iron oxides, each having a single crystalline phase, during the catalytic cracking of a model coal compound, and found that the crystal structure was the key factor affecting the performance of the catalyst precursor. Kaneko et al. [20,21] assessed the physical properties and sulfidation activities of α-FeOOH, γ-FeOOH, ferrihydrite and two iron ores, and demonstrated that smaller pyrrhotite crystallite sizes correlate with higher oil yields. The particle size and extent of dispersion of the precursor are also important, and so ultrafine iron catalysts have been developed by numerous researchers [13,22]. Zhao et al. [23,24] has suggested that it is also important for the catalyst to maintain its dispersion at high temperatures, based on a comparative study of an ultrafine catalyst (with an average particle diameter of 3 nm) and two binary iron oxide catalysts (Si/ferrihydrite and Al/ferrihydrite, with average particle diameters of 5 and 10 nm, respectively). Cugini [25] reported that liquefaction feed coal not only promoted the generation of ultrafine FeOOH but also assisted in dispersing the $Fe_{1-x}S$ that was generated *in situ* during DCL. It is worth noting that ultrafine γ-FeOOH catalysts supported on coal have been successfully applied in the first megaton DCL industrial demonstration plant, operated by the Shenhua Group [26–28].

Many important results have been reported concerning the relationship between precursor catalyst properties and catalytic liquefaction activity, but these data have certain limitations because of variations in preparation methods as well as the compositions or sources of the catalyst precursors. In the present study, six unsupported iron–oxygen compounds having different microstructures were prepared by the same method and using the same raw materials, and the relationship between the microstructures of the catalyst precursors and their catalytic behaviors during coal liquefaction was systematically studied. In addition, a series of coal-supported catalyst precursors was prepared. The effects of the coal carrier and synthesis temperature on the formation of iron–oxygen compounds were assessed, with the aim of obtaining information of use during the future applications of industrial catalysts.

2. Experimental

2.1. Coal and recycle solvent

Table 2
The properties and ultimate analysis data for the recycle solvent.

ρ^{20} (g/cm^3)	f_a [a]	*PDQI* [b] (mg/g)	w (wt%)				
			C	H	S	N	O [c]
0.9905	0.49	18.88	89.490	9.718	0.003	0.021	0.768

[a] Aromaticity (f_a) calculated from the ^{1}H NMR spectrum and elemental composition. [b] Proton donor quality (*PDQI*) calculated from the ^{1}H NMR spectrum and elemental composition. [c] Determined by difference.

The coal sample employed in experimental trials was obtained from the Shenhua Shangwan coal mine, which provides the feedstock for the Shenhua DCL demonstration plant. The coal was first ground to obtain particle sizes below 150 μm, dried under vacuum at 100 °C for 6 h, and then stored in an airtight container. The results of the proximate, ultimate and petrographical analyses of the Shenhua Shangwan coal are shown in Table 1, while the properties of the recycle solvent produced by the demonstration plant are summarized in Table 2. The proton donor quality index (*PDQI*), as developed by Tanabe [29], reflects the hydrogen-donating ability of the solvent and is expressed in units of milliequivalents of β-naphthenic hydrogen per gram. The *PDQI* value of 18.88 mg/g in Table 2 indicates superior hydrogen-donating ability. The aromaticity (f_a) value of the solvent (0.49) was calculated based on its ^{1}H nuclear magnetic resonance (NMR) spectrum and elemental composition. These two parameters were calculated using the equations below [4,29,30].

$$PDQI = \frac{H_{N\beta}}{H_t} \times w(\mathrm{H})\% \times 10$$

$$f_a = \left[\frac{w(\mathrm{C})}{w(\mathrm{H})} - \frac{H_\alpha}{2H_t} - \frac{H_\beta}{2H_t} - \frac{H_\gamma}{3H_t}\right] / \frac{w(\mathrm{C})}{w(\mathrm{H})}$$

Here, $H_{N\beta}$, H_α, H_γ, H_β and H_t are the intensities of the β-naphthenic hydrogen, α-hydrogen, γ-hydrogen, β-hydrogen and total hydrogen peaks in the ^{1}H NMR spectrum, respectively, while w(H) and w(C) are the H and C mass concentrations in the recycle solvent, respectively.

2.2. Preparation of catalyst precursors

In a representative procedure, unsupported iron-oxygen compounds were synthesized by adding an ammonia solution (1.5 mol/L) dropwise to 500 mL of an aqueous ferrous sulfate solution (0.3 mol/L) with vigorous stirring until the pH value reached 7.5 ± 0.1. Subsequently, the precipitate was obtained and oxidized by bubbling air (600 mL/min) for 30 min, maintaining the pH value at 7.5 ± 0.1 with an ammonia solution. The temperature of the reaction solution was controlled so as to remain constant during both the precipitation and oxidation processes. The resulting precipitate was separated by centrifugation at 5000 r/min for 10 min and then dried at 120 °C under