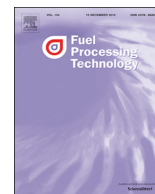




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Research article

Heterocyclic sulfur removal of coal based on potassium tert-butoxide and hydrosilane system

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ABSTRACT

The present work investigated the feasibility of heterocyclic sulfur (HS) removal for coal utilizing potassium tert-butoxide and hydrosilane system. Changes of sulfur forms with treatment time in Xinyu (XY) coal were determined by XANES. Results showed that reductions of total sulfur and organic sulfur for XY coal were 55% and 53%, respectively. > 85% sulfoether and thiophene sulfur were removed after treated for 4 h, suggesting that the HS could be removed to a high extent from coal. However, contents of sulfonate and sulfonic ester increased with treatment time due to the hydrolysis and oxidation of intermediate products containing Si–S bands. Furthermore, it indicated that the HS could be removed selectively from coal without destroying the macromolecular structure of coal based on analysis of desulfurization mechanism. These findings suggested that the desulfurization of refractory HS in coal could be obtained using the potassium tert-butoxide/hydrosilane reductive system, which provided a reference for desulfurization of high organic sulfur coal.

1. Introduction

In China, coal is a primary source of energy and still utilized in large numbers for the foreseeable future [1]. However, high quality coal reserves are gradually depleting and there are a lot high-sulfur coal reserves in China [2].

Although flue gas desulfurization technologies have been well developed, desulfurization of coal prior to combustion is still considered to be the most effective and economic method [3–5]. Among the primary coal desulfurization methods prior to combustion, including physical, physico-chemical, chemical, and microbial desulfurization, chemical-related desulfurization was considered to be the most effective methods for both inorganic and organic sulfur of coal [6]. A number of chemical methods with various chemical reagents and their sulfur removal efficiencies reported in literatures are listed in Table 1 [7–10].

Removal of pyrite from coal was effective for coal by nitric acid or peroxyacetic acid [32,33]. However, removal degrees of organic sulfur were not high, especially for coal with high organic sulfur content [6,14]. The amount of oxidized forms of sulfurs sulfoxides and sulfones in coal increased after treatment with oxidation assistants [34,35]. For

strong alkali or peroxyacetic acid, they removed organic sulfur from coal well combined ultrasound or microwave [13,16,17,19,22]. However, these auxiliaries could destroy the original characteristics of coal due to their strong oxidizing properties [36,37]. Although organic sulfur could be removed from coal utilizing the microbial desulfurization, the efficiency was low due to long leaching time [30,31].

40–60% organic sulfur could be removed from coal using metal boron hydrides (NaBH₄, KBH₄) with catalyzer (NiCl₂·6H₂O) and ultrasound [5,11]. However, these kinds of desulfurization reagents were not confirmed that the heterocyclic sulfur (HS) in coal could be removed efficiently. Reduction removal degree of organic sulfur in low rank coal reached 70% using pre-heat treatment and magnetic separation with reduced iron powder as a reducing agent, while the recovery rate of its cleaning coal was only 50–60% [38].

Sulfur atoms of refractory HS were removed from fuels by a robust potassium (K) alkoxide (O)/hydrosilane (Si)-based ('KOSi') system [39,40]. The content of refractory HS in coal usually accounted for about half of the organic sulfur in coal, and this part of organic sulfur was difficult to remove by existing desulfurization technologies [41–44]. For the existing chemical methods, their desulfurization effects were primarily the removal of pyrite, aliphatic sulfur and sulfur

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Table 1
Comparison of total sulfur and origin sulfur removal efficiencies of various methods with different reagents.

Reagents	Assisted method	Time	TS ^c (%)	OS ^d (%)	TR ^e (%)	OR ^f (%)	Ref.
NaBO ₂ and NaOH	Electroreduction	4 h	1.30	0.45	50.77	46.67	[5,11,12]
2.0 mM NaBH ₄	–	10 min	1.30	0.40	43.0	23.9	
NaBH ₄ with NiCl ₂ ·6H ₂ O	US ^a (25 kHz)	10 min	1.30	0.52	56.9	61.5	
HCOOH/H ₂ O ₂ , V ₂ O ₅ , ionic liquids	–	1 h	3.91	3.38	50.20	48.00	[13–16]
KOH/NaOH (1:1)	US (20 kHz)	3 h	3.51	2.71	18.80	6.64	
H ₂ O ₂	US (20 kHz)	3 h	4.47	3.44	31.09	33.72	
H ₂ O ₂	US (40 kHz)	3 h	2.06–2.89	1.66–2.51	70–77	67–81	
Peroxyacetic acid	US (43 kHz)	20 min	3.17	1.86	49–58	42–44	[17,18]
	MW ^b (300 W)	2 min	3.09	1.98	63.41	48.52	
Peroxyacetic acid	MW (1000 W)	2 h	1.44	0.67	73.43	51.21	[19,20]
HI	MW	20 min	5.0	3.4	62	–	[9]
NaBH ₄	–	1 min	2.77	1.23	40.8	15.0	[21]
NaOH, HCl (pH = 1)	–	5 h	3.15	0.79	81.0	73.4	[22]
H ₂ O ₂ with Sb ³⁺	–	24 h	5.7	3.6	–	31.12	[7,8,23–27]
Ni ²⁺ and naphthalene	–	4 h	–	–	–	18.7	
Peroxyacetic acid with Pd ²⁺	–	1–4 h	–	–	–	23–32	
Naphthalene with Hg ²⁺ or CoCl ₂	–	1 h	–	–	–	28.5	
K ₄ [Fe(CN) ₆]	–	1 h	–	–	–	36.4	
Methanol and KOH	–	4 h	4.20	2.23	20–42	33–62	[10]
H ₂ O ₂ with H ₂ SO ₄	–	4 h	4.27	3.11	38–49	26–31	[28]
Ionic liquids	–	3 h	0.94	–	84.0	–	[29]
<i>Rhodococcus</i> spp. (Eu-32)	–	15 days	7.5	5.0	40	60	[30]
<i>P. chrysosporium</i>	–	6 days	5.49	4.38	24.2	23.8	[31]

^a Ultrasound-assisted extraction.

^b Microwave-assisted extraction.

^c TS Total sulfur.

^d OS Organic sulfur.

^e TR Total sulfur removal.

^f OR Organic sulfur removal.

ether in coal [8,33]. However, the thiophene sulfur was almost oxidized to sulfoxide and sulfone remained in coal [27,34]. To our knowledge, there have been few reports about thiophene sulfur removal in high organic sulfur coal. Especially the removal of sulfur atoms from thiophene in coal without destroying the carbon skeleton of coal has not been reported. Therefore, the potassium tert-butoxide and hydrosilane system was selected to explore the effect and mechanism of reduction removal for thiophene sulfur of coal.

The objective of this paper was to investigate the desulfurization effect of the HS of coal utilizing the potassium tert-butoxide and hydrosilane system as reducing agents. In the present work, some variables including the reductant concentration, reaction temperature and time were studied. Subsequently, the sulfur distribution of the coal samples before and after treatment were determined. XANES analyses were performed to investigate the variations of sulfur forms in coal.

2. Material and methods

2.1. Coal sample characterization

One high-sulfur coking coal used in this study was collected from Xinyu (XY) coal mine, in Shanxi province, China. Representative samples were dried in a vacuum drying oven, and then ground and sieved to the size of < 0.074 mm. The proximate analysis, ultimate analysis, and sulfur speciation determination were carried out. The corresponding characterization parameters are shown in Table 2. Potassium tert-butoxide (KO^tBu, > 95%), hydrosilane (> 98%), mesitylene (> 95%) and acetone (> 98%) were purchased from Aladdin (Shanghai, China).

For the raw coals with an ash content of < 10%, its sulfur content (dry ash-free basis) based on the ultimate analysis was 2.16%. Its organic sulfur content reached 1.93%, which accounted for 89.35% of the total sulfur in coal, suggesting that organic sulfur was the most dominant form of sulfur.

2.2. Apparatus and experimental procedure

In a nitrogen-filled glovebox, a 1 g coal sample, mesitylene (solvent, 10 mL), an appropriate amount of KO^tBu and hydrosilane were added to a 50 mL polytetrafluoroethylene digestion tank under the condition of electromagnetic stirring. The vial was sealed, and then removed from the glovebox. Subsequently, the mixture was stirred (300 rpm) at the indicated temperature for the indicated time.

The sample after treatment was allowed to cool to room temperature, filtered, washed with 50 mL acetone and 100 mL hot de-ionized water, and then dried for 3 h at 110 °C prior to analysis. The final sulfur content was analyzed using automatic coulomb sulfur analyzer. The data (error < 5%) are presented as the average of two replicates in each treatment.

2.3. XANES analysis

For studying the change of sulfur forms, the X-ray absorption near edge structure analysis (XANES) of samples was performed at 4W1B endstation, Beijing synchrotron Radiation Facility, which ran 2.5 GeV electron with current from 150 mA to 250 mA. The XANES data of the standard samples (diphenyl sulfide, dibenzothiophene, diphenyl sulfoxide, diphenyl sulfone, sodium dodecylsulphate, benzenesulfonic acid, zinc sulfate) and coal samples were processed by interpolating and normalizing, and then fitted by the Athena software [45].

3. Results and discussion

3.1. Effect of reductive assistant amount

With the increase of reductive assistant (KO^tBu/hydrosilane, 1/1) amount, as shown in Fig. 1, desulfurization degree increased. As the molar ratio of reductive assistant to sulfur in coal, n (reductive assistant)/n (S), increased from 3 to 15, the desulfurization degree increased from 9% to 55% rapidly, suggesting that the assistant amount was of

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