Experimental Study on Organic Sulfur Removal in Bituminous Coal by a 1-Carboxymethyl-3-methyl Imidazolium Bisulfate Ionic Liquid and Hydrogen Peroxide Solution

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Cite This: ACS Omega 2020, 5, 21127−21136

ABSTRACT: In order to improve the total sulfur removal rate in coal combustion, an acidic ionic liquid (IL) 1-carboxymethyl-3-methylimidazolium hydrogen sulfate ([HOOCCH2mim][HSO4]) as the extractant combined with the oxidant 30% hydrogen peroxide (H2O2) was applied to reduce the total sulfur content, and its microscopic mechanism of desulfurization was analyzed. The experimental results show that the desulfurization rate of the [HOOCCH2mim][HSO4]−H2O2 (1:10) solution was 45.12% and the organic sulfur removal rate was 16.26%, which were significantly higher than those of only H2O2 or pure [HOOCCH2mim][HSO4]. Fourier-transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy analyses showed that the mercaptan −SH and disulfide −S−S− in coal decreased after being treated with IL−H2O2. In particular, the results of FTIR spectroscopy indicated that the relative proportion of −S−S− and −SH treated with IL−H2O2 (1:10) decreased by 31.9 and 27.2%, respectively, compared with that of a pure IL. This is due to H2O2 oxidation; −SH and −S−S− were oxidized to sulfoxide and then the sulfoxide transferred from the coal phase to the IL phase, which improved organic sulfur removal from coal. Therefore, the combination of an ionic liquid and H2O2 could increase the total desulfurization rate. In addition, the thermogravimetric analysis of coal is divided into four different stages; the weight loss during the combustion stage and the residues show that the IL−H2O2 could improve the coal combustion because of good previous swelling and destruction of bridge bonds and hydrogen bonding of coal. Besides, the fewer residues in IL−H2O2-treated coals also indicate that a less amount of inorganic substance is left in coal after IL−H2O2 desulfurization, which is consistent with the desulfurization results.

1. INTRODUCTION

Coal is the primary energy source with the largest reserves and the largest consumption in China. Through combustion, sulfur compounds present in the coal are converted to SOx, which causes air pollution and acid rain.† Moreover, the combustion of coal is the precursor to the formation of sulfate aerosols that cause respiratory diseases, and the acid rain is harmful to both soil and marine life.‡

In order to reduce the above-mentioned pollution and harm to humans, it is necessary to remove sulfur present in coal to reduce SOx production. Wei et al. stated that the inorganic sulfur in coal is mainly found as pyrite, and the organic sulfur content is mainly composed of thiophene, mercaptan, sulfoether, sulfone, and sulfoxide.§ The structure of organic sulfur in coal is complex and usually covalently linked by intermolecular forces, for example, hydrogen −bonds and π−π bonds, in the aromatic structures of coal, which are difficult to be broken.∥ Generally, there are three common desulfurization methods, that is, the physical method,¶ chemical method,§ and microbial method.¶ Chemical desulfurization has become the main desulfurization method because of its short reaction time and high desulfurization rate. Ma et al.¶ treated high-sulfur coal

Received: June 12, 2020
Accepted: August 3, 2020
Published: August 12, 2020

© 2020 American Chemical Society
ACS Ômega 2020, 5, 21127–21136
https://dx.doi.org/10.1021/acsomega.0c02795
ACS Ômega 2020, 5, 21127–21136
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with 0.25 mol/L sodium hydroxide and then with a hydrochloric acid (HCl) solution and obtained an organic sulfur removal rate up to 73%. Although chemical methods such as hydrogenation catalysis and acid−base desulfurization are efficient in desulfurization, they suffer from harsh conditions of high temperatures and pressures during hydrogenation catalytic processes and even reduce the caloric value of coal by damaging coal molecular structures during acid−base treatments. Therefore, removing the sulfur in coal under mild conditions and maintaining the caloric value of coal are important challenges in coal desulfurization.

As green solvents, ionic liquids (ILs) with low volatility, high stability, and strong extraction ability have been applied to efficiently remove sulfur in fuels. 21−23 Saikia et al.24 used formic acid (HCOOH) and hydrogen peroxide (H₂O₂), respectively, together with [Bmim][BF₄] and [Bmim][Cl] ILs during oxidative desulfurization, showing that the addition of ILs increased the total desulfurization rate up to 37.36% with the organic sulfur removal rate of 31.63%. Yi et al.25 used a mixed [Bmim][Cl]−NMP reagent to extract the residual solids after direct liquefaction of coal. The results showed that the total sulfur content decreased from 4.97 to 0.42%. Gong et al.26 added [Bmim][Br], [Bmim][Cl], and [Bmpy][Br] separately to remove the sulfur in coal water slurry at room temperature for 12 h and found that the desulfurization rate increased after the addition of ionic liquids, where [Bmim][Br] performed better desulfurization than [Bmim][Cl]. Li et al.27 selected four different types of ionic liquids (ILs), [Bmim][Br], [Bmim][BF₄], [Bmim][HSO₄], and [Bmim][H₂PO₄] and 30% H₂O₂ solutions for desulfurization experiments on high-sulfur coal samples under mild conditions. The results show that the addition of an IL enhanced the oxidative desulfurization ability of H₂O₂, and the pyrite sulfide and organic sulfide forms of sulfur in coal were significantly removed. Saikia et al.24 used [Bmim][BF₄] and [Bmim][Br], together with 13.2 mL of 20% HCOOH and 75 mL of 20% H₂O₂, to remove sulfur in coal at 70−80 °C temperature, and obtained 50.20% removal of the total sulfur and 48% of the organic sulfur. Wang et al.28 used 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim][HSO₄]) in combination with 30% H₂O₂ solution to remove sulfur at ambient temperatures and pressures and significantly reduced the content of sulfoether and thiophene in coal. They also found that the mixture of the [HOOCCH₂mim][HSO₄]−30% H₂O₂ solution can remove 16.76% of organic sulfur, and imidazolium ionic liquids are more efficient than the pyridinium ones.26

Table 1. Sulfur Contents of Coal Samples and Desulfurization Rates of H₂O₂ and IL−H₂O₂

| Sample          | IL/coal/H₂O₂ | S_TOC (%) | S_DSO₂ (%) | S_BSO₂ (%) | D (%)  |
|-----------------|--------------|-----------|------------|------------|--------|
| raw coal        |              | 2.15      |            |            |        |
| H₂O₂            |              |           | 1.32       | 2.44       | 86.96  | 38.61  |
| [HOOCCH₂mim][HSO₄] | 1:1\:\:1 | 1.54      | 43.08      | 8.70       | 28.37  |
| [HOOCCH₂mim][HSO₄]−H₂O₂ | 2:1:1 | 1.31      | 24.3       | 41.3       | 39.07  |
| [HOOCCH₂mim][HSO₄]−H₂O₂ | 1:1:3 | 1.24      | 12.20      | 82.61      | 42.33  |
| [HOOCCH₂mim][HSO₄]−H₂O₂ | 1:1:10 | 1.18      | 16.26      | 83.70      | 45.12  |
| [Bmim][BF₄]−HOOCOH−H₂O₂ | 1:1:4 | 1.32      | 2.44       | 86.96      | 38.61  |
| [Bmim][Cl]−HOOCOH−H₂O₂ | 1:1:4 | 1.32      | 2.44       | 86.96      | 38.61  |
| [Bmim][BF₄]−HOOCOH−H₂O₂−V₂O₅ | 1:4:1:1 | 1.24 | 12.20 | 82.61 | 42.33 |
| [Bmim][Cl]−HOOCOH−H₂O₂−V₂O₅ | 1:4:1:1 | 1.24 | 12.20 | 82.61 | 42.33 |

The previously reported promising ionic liquids with tetrafluoroborate [BF₄]⁻ have a good sulfur removal ability, but they are instable with the formation of [HF]⁻ in the presence of water.27 To avoid the instability and environmental problems, halogen-free ionic liquids become optimal agents for extracting sulfur compounds. Here, we used 1-carboxymethyl-3-methylimidazolium bisulfate ([HOOCCH₂mim][HSO₄]) because of its ability for strong hydrogen bonding and providing an acidic medium. 28−30 In addition, Fang et al. and Ge et al.31,32 found that the anion [HSO₄]⁻ has a good effect on the removal of organic sulfur from oil, especially during the acidic extraction desulfurization process. Comprehensive, considering the nonhalogen and sulfur removal effect, [HOOCCH₂mim][HSO₄] was selected as the experimental reagent.

Compared to the strong basic and acid solvents, ILs have been believed to be relatively more environmentally friendly acting as sulfur removers under much more mild conditions. In order to reveal the role of ILs during desulfurization, here, we would use pure [HOOCCH₂mim][HSO₄] and mixed IL−H₂O₂ solutions to remove sulfur present in high-sulfur bituminous coal. The effects of the IL and binary IL−H₂O₂ on the functional groups and organic sulfur in coal will be analyzed by Fourier-transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) experiments, and the mechanism of oxidative desulfurization will be revealed.

2. RESULTS AND DISCUSSION

2.1. Effect of IL−H₂O₂ on Sulfur Content in Coal. It can be observed from Table 1 that the desulfurization rate of coal samples treated with H₂O₂ alone at a mass ratio of 1:1 is 38.61%, but the organic sulfur removal rate is only 2.44%. After being treated with only [HOOCCH₂mim][HSO₄] with a mass ratio of 1:1, the total desulfurization rate is 28.37% and the organic sulfur removal rate is 43.08%, while the inorganic sulfur removal rate is only 8.7%. Accordingly, ILs show priority for removing organic sulfur while H₂O₂ for inorganic sulfur reduction. Combining the advantages of both, [HOOCCH₂mim][HSO₄]−H₂O₂ solvent was applied to enhance sulfur removal on a synergistic basis. When the mass ratio of [HOOCCH₂mim][HSO₄]−H₂O₂ is 2:1, the desulfurization rate increased to 39.07% and up to 42.33% when the [HOOCCH₂mim][HSO₄]−H₂O₂ mass ratio is 1:3. This is close to the IL−H₂O₂−HOOCOH−V₂O₅ solution with a total desulfurization rate of 47.2%. 14 It shows that the mixed [HOOCCH₂mim][HSO₄]−H₂O₂ with an appropriate ratio can effectively reduce the total sulfur content in coal. In addition, it can be clearly seen from Figure 1 that the D of [HOOCCH₂mim][HSO₄]−H₂O₂ with a mass ratio of 1:3 is better than that of the mass ratio of 2:1, implying that a higher concentration of IL does not mean a better removal efficiency of total sulfur. The oxidation role of H₂O₂ cannot be ignored.
for achieving a satisfactory desulfurization result. Therefore, it is necessary to find an optimal ratio to achieve the best desulfurization efficiency. As shown in Figure 2 and Table 1, it is observed that as the mass ratio of H₂O₂ increases, the desulfurization rate of both inorganic sulfur and total sulfur increases. The organic sulfur removal ability becomes weaker when a less dose of [HOOCCH₂mim][HSO₄] is used. Clearly, the [HOOCCH₂mim][HSO₄] alone has the best organic sulfur removal ability, but its total desulfurization is very low because of its weak inorganic sulfur removal ability.

In the case of IL–H₂O₂ solution with the mass ratio of 1:10, the total sulfur desulfurization rate is further increased to 45.12%, wherein the inorganic sulfur removal rate is 83.70% and the organic sulfur removal rate is 16.26%; compared with that treated with H₂O₂ alone, the inorganic sulfur removal rate is slightly reduced, while the organic sulfur removal rate is significantly improved. It implies that the removal rate of inorganic sulfur in coal mainly depends on the amount of H₂O₂, and the addition of an IL can significantly increase the removal rate of organic sulfur, which may be due to the ability of the IL to transfer the organic sulfur from coal to the liquid phase where the oxidation could be carried out more favorably. The H₂O₂ solution desulfurization mechanism is shown in Formulas 1 and 1. The H₂O₂ solution oxidized mercaptan to sulfoether and then the sulfoether was oxidized to sulfoxide and sulfone, which were converted into organic molecules (R¹ and R²) and SO₄²⁻. This mechanism has also been used to explain the removal mechanism of sulfur ether in coal by microwave irradiation with peroxyacetic acid.  

2.2. Spectroscopy Analysis of Functional Groups in Coal before and after Desulfurization. FTIR spectroscopy was used to measure the change in functional groups to explain the desulfurization mechanism from the microstructure perspective. The Gaussian–Lorentz method was used to fit and analyze the spectrum with a half-width of 10 and medium sensitivity. Figure 3 shows the infrared spectra and character-
Because different groups have different extinction coefficients, Xin et al.37 proposed an improved infrared spectroscopy calculation method to obtain the absorption peak area A of each functional group. The peak area of aromatic C=C was referenced to calculate the relative content W (%) according to eq 3, and the results are shown in Table 2.

\[ W\% = \frac{A_i}{R_i} \times \frac{A_{C=C}}{R_{C=C}} \]  

(3)

From Table 2 and Figure 4, it can be found that −CH2−OH, −SH, and −S−S− contents of coal decreased, while the

contents of aliphatic −CH2− and aromatic −CH increased after being treated with H2O2 and IL−H2O2.

Relative to the coal after being treated with H2O2 alone, −CH2− in the IL−H2O2-treated coal is increased because of the cleavage of the saturated alkane chain bridge leading to increased −CH2− exposure. This indicates that the addition of IL can significantly cause a destructive effect on the intermolecular forces and transfer the organic sulfur into the liquid phase, enhancing the oxidation ability of H2O2.

Based on the calculated relative contents of sulfur-containing structures, it can be clearly seen that the desulfurization rate of IL/coal/H2O2 (1:1:10)−treated coal is better than the use of coal/H2O2 (1:1) or IL/coal (1:1) alone, respectively. Compared to coal treated with IL/coal (1:1), the relative proportions of disulfide and mercaptan decreased to 31.9 and 27.2%, respectively, after being treated with IL/coal/H2O2 (1:1:10) (data are provided in Table S1 of the Supporting Information). It indicates that the IL has an ability to improve desulfurization, possibly because the IL can extract sulfur structures from coal into the liquid phase to increase the contact and further oxidize these sulfur structures with H2O2.

2.3. XPS Analysis of the Change in the Organic Sulfur Form before and after Desulfurization. The FTIR measurements detect only the changes in two sulfur-containing functional groups while providing no information about the sulfur−form changes, especially thiophene, before and after desulfurization, which can be compensated by the XPS measurements.

The electron binding energy of XPS characteristic peaks corresponds to various forms of sulfur in coal, that is, 162.2−163.6 eV for mercaptan and sulfoether (S1); 164−164.4 eV for thiophene (S2); 165−168 eV for sulfone and sulfoxide (S3), and >168.7 eV for inorganic sulfur (S4).8−40

The fitted XPS spectrum of the raw coal and that after desulfurization treatment are shown in Figure 5a−d, where the ordinate is the S2p electron intensity and abscissa is the electron binding energy (eV). The relative areas of all peaks of each sulfur form in all coal samples were calculated and shown in Figure 6.

According to the relative area (data are provided in the Supporting Information), the inorganic sulfur in coal treated with only 30% H2O2 solution has the smallest relative peak area, while thiophene has the highest, indicating that H2O2 shows superior activity in removing inorganic sulfur and inferior activity for thiophene. From Figure 6, it is observed that the proportions of mercaptan and sulfoether in IL−treated coal are the lowest, while those of thiophene and inorganic sulfur are relatively high, which indicate that [HOOCCH2mim][HSO4] is favorable for mercaptan and sulfoether removal but inferior for thiophene and the inorganic one. In addition, because of the lack of oxidation process by H2O2, the conversion of mercaptan or sulfoether into soluble sulfone or sulfoxide is relatively low. Therefore, using only the IL is not applicable for increasing the organic sulfur reduction rate. Combining the extracting effect of IL and the oxidizing ability of H2O2 should be more ready for removing sulfur from coal.

As being expected, the relative area ratios of sulfoxide, sulfoether, thiophene, and sulfone are significantly reduced after the addition of the IL compared to the case of only H2O2 solution. The addition of acidic [HOOCCH2mim][HSO4] actually enhances the oxidizing ability of H2O2, as stated by ref 24. On the other hand, the presence of H2O2 could provide some H+ and reduce the intramolecular interaction between the cation and the anion, which makes the [HSO4]− anion more active. The activated [HSO4]− has more power to destroy the hydrogen bonding networks, π−π bonds, and van der Waals forces in coal and makes the coal swell, so that more
organic sulfur structures could significantly be exposed and dissolved in IL–H$_2$O$_2$ and then be oxidized into sulfone and sulfoxide.\textsuperscript{41–43}

Figure 7 demonstrates the plausible dissolution and oxidizing process of $\text{−SH}$ and $\text{−S−S−}$ in the ionic liquid. It is shown that the form of $\text{−SH}$ can be directly oxidized by H$_2$O$_2$ and converted to sulfone and sulfoxide after being extracted from coal into the ionic liquid phase. Differently, the $\text{−S−S−}$ bonds could be first broken and enabled accepting a H$^+$ from H$_2$O$_2$, and then could be oxidized into sulfone or sulfoxide, which can be washed away by water.

According to the analysis results of XPS, compared with the raw coal, all forms of organic sulfur decreased obviously after IL–H$_2$O$_2$ treatments, indicating that the combined action of IL and H$_2$O$_2$ is beneficial for coal desulfurization.

Figure 5. (a–d) XPS spectrum of coal before and after desulfurization.

Figure 6. Relative sulfur content of various forms in coal.

Figure 7. Mercaptan and sulfone removal mechanism in a IL–H$_2$O$_2$ solution.
Combining the experimental analyses of FTIR and XPS, the addition of IL is able to improve the oxidative desulfurization efficiency of H$_2$O$_2$, especially the removal of organic sulfur. It is deduced that the IL can act as a hydrogen bond receptor which destroys the intermolecular forces such as hydrogen bonding network structures, π−π bonds, and van der Waals forces in coal, leading to the expansion and collapse of the coal structure. Therefore, it is beneficial for the organic sulfur structure to be transferred from the coal phase to the ionic liquid phase and then oxidized by H$_2$O$_2$.

2.4. TG-DSC Analysis of Bituminous Coal after Desulfurization of IL−H$_2$O$_2$. Through thermogravimetric analysis, the combustion and calorific values of coal samples after desulfurization by ILs can be analyzed. Zhang et al. found that the thermogravimetric analysis of coal can be divided into four different stages, as illustrated in Figure 8a−c. Stage 1, that is, dehydration and desorption stage, mainly causes the desorption of primitive gases (CO$_2$, CH$_4$, N$_2$, etc.) and water molecules in coal pores. The desorption of gas and water molecules in coal pores is an endothermic process. As can be seen from Table 3, the endothermic heat of coal treated with IL−H$_2$O$_2$ is clearly less than that of the raw coal, possibly because some gas molecules and bound water have been released during the desulfurization process.

As the temperature increases, after the release of primitive gases, more space is available for oxygen to come in contact with coal and then the stage 2 oxidation starts. During this stage, the chemical adsorption of oxygen onto the coal surface should increase dramatically, so the coal mass should start to increase during the early stage of oxygen absorption. However, three samples show different mass increases, especially the IL−H$_2$O$_2$-treated coals show less oxygen adsorption than the raw coal, which is ascribed to the oxidation of surface-active groups in advance and the breaking of some bridge bonds due to previous H$_2$O$_2$ oxidation.

Table 3. Effect of IL and H$_2$O$_2$ Treatment on Thermal Parameters of Coal Samples

| Sample       | Endothermic/J·g$^{-1}$ | Exothermic/J·g$^{-1}$ | Net Released Heat/J·g$^{-1}$ |
|--------------|------------------------|-----------------------|------------------------------|
| raw coal     | 116.5                  | −14,127               | −14,010.5                    |
| IL/coal/H$_2$O$_2$ 1:1:3 | 89.44                  | −11,333               | −11,243.6                    |
| IL/coal/H$_2$O$_2$ 1:1:10 | 91.1                   | −13,809               | −13,717.9                    |

Table 4. Weight Loss in Different Stages before and after Coal Treatment with IL−H$_2$O$_2$

| Sample       | Dehydration and desorption stage/% | Oxidation adsorption/% | Combustion adsorption stage/% | Residual mass/% |
|--------------|------------------------------------|------------------------|-------------------------------|-----------------|
| raw coal     | 1.05                               | −1.16                  | 90.22                         | 9.38            |
| IL/coal/H$_2$O$_2$ 1:1:3 | 1.32                               | −0.67                  | 92.53                         | 7.27            |
| IL/coal/H$_2$O$_2$ 1:1:10 | 1.02                               | −0.92                  | 93.97                         | 5.80            |
swelling and the destruction of bridge bonds and hydrogen-bonding of coal. The swelling and destruction of ionic liquids on coal structures had been confirmed by many references so far.45-48

In addition, according to Table 4 and Figure 9, both IL−H$_2$O$_2$-treated coals have a less residue ratio than that of the raw coal, indicating that less inorganic substances were left in coal after full combustion. It is consistent with the inorganic sulfur removal ability of the two IL−H$_2$O$_2$ solutions. The IL−H$_2$O$_2$ (1:10) performed best in removing the inorganic structures including the inorganic sulfurs. In comparison, the IL−H$_2$O$_2$ (1:3) solution with much less H$_2$O$_2$ insufficiently preoxidized the coal, especially the inorganic sulfur, leading to a larger ratio of inorganic structures being left than IL−H$_2$O$_2$ (1:10).

3. CONCLUSIONS

In order to reduce the sulfur oxide emission after coal combustion, a pure IL [HOOCCCH$_2$mim][HSO$_4$], 30% H$_2$O$_2$, and mixed [HOOCCCH$_2$mim][HSO$_4$]−H$_2$O$_2$ solutions were applied to remove inorganic and organic structures from the high-sulfur bituminous coal, and the changes in functional groups and sulfur forms were analyzed by FTIR spectroscopy and XPS experiments.

The results show that H$_2$O$_2$ can remove most of the inorganic sulfur and a small part of organic sulfur from bituminous coal. The pure [HOOCCCH$_2$mim][HSO$_4$] could remove organic sulfur efficiently but has a very weak ability to reduce inorganic sulfur, while only 30% H$_2$O$_2$ acts inversely. However, the mixed IL−H$_2$O$_2$ solutions performed better regarding total sulfur, especially the organic ones. The desulfurization rate of the [HOOCCCH$_2$mim][HSO$_4$]−H$_2$O$_2$ (1:10) solution was 45.12% and the organic sulfur removal rate was 16.26%, which were significantly higher than those of only H$_2$O$_2$ or pure [HOOCCCH$_2$mim][HSO$_4$].

FTIR spectroscopy and XPS analyses showed that −SH and −S−S− in coal decreased after treated with IL−H$_2$O$_2$. However, the conversion of −SH and −S−S− in treated coal is lower in the case of pure [HOOCCCH$_2$mim][HSO$_4$] because of the lack of H$_2$O$_2$ oxidation process. Therefore, the combination of ionic liquid and H$_2$O$_2$ could increase the total desulfurization rate. In addition, the thermogravimetric analysis, the weight loss during the combustion stage and residues, shows that the IL−H$_2$O$_2$ could improve the coal combustion because of well previous swelling and destruction of bridge bonds and hydrogen bonding of coal. Besides, the fewer residues in IL−H$_2$O$_2$-treated coals also indicate less inorganic substances were left in coal after IL−H$_2$O$_2$ desulfurization, which is consistent with the desulfurization results.

Generally, the acidic [HOOCCCH$_2$mim][HSO$_4$] IL is favorable for reducing the organic −SH and −S−S−; however, thiophene removal is still a big problem in the future investigation. Another problem is the possible introduction of sulfur by using the [HSO$_4$]$^-$ anion. Therefore, the nonsulfur acidic ILs could be the future consideration for desulfurization.

4. EXPERIMENTAL PROCESS

4.1. Experimental Materials. 1-Carboxymethyl-3-methylimidazolium hydrogensulfate IL ([HOOCCCH$_2$mim][HSO$_4$]), whose structure is shown in Figure 10, was used as the experimental reagent. The IL was purchased from Shanghai Chengjie Chemical Company with a purity of 98%. Hydrogen peroxide with a purity of 30% was from the Tianjin Fuchen Chemical Reagent Factory. The middle−high-sulfur bituminous coal was collected from Chenjiashan Colliery, Shanxi Province, and its proximate and ultimate analyses are shown in Table 5. S$_{O,C}$ and S$_{I,C}$ were calculated using eqs 4 and 5.

4.2. Coal Sample Treatment and Preparation. The coal was crushed and ground into particles with a diameter of 0.1−0.15 mm and then dried at 40 °C in a DZF-6210 vacuum oven for 48 h. The dose of all experimental reagents and coal samples were weighed using a German SARTORIUS BT-224S balance, and the preparation mass ratio is shown in Table 6.

A certain amount of IL−H$_2$O$_2$ was mixed with coal in a flask using an RE-5000 type rotary evaporator with a rotation speed of 200 rpm in a water bath of 30 °C for 6 h. After the reaction, the coal sample was filtered until there were no Cl$^-$ and Fe$^{3+}$ ions in the filtrate at neutral pH = 7 using deionized water at room temperature and then dried in a vacuum oven for 48 h. The total sulfur content was measured using an automatic sulfur analyzer.

4.3. Experiments. The organic sulfur content, inorganic sulfur content, and desulfurization rate in the coal were measured and calculated according to the method described in ref 49. The nitric acid solution can remove the inorganic sulfur in coal and leave the organic ones. Here, 1 g of dried coal sample was taken and immersed in 50 mL of nitric acid solution (HNO$_3$/H$_2$O = 1:7) at room temperature for 24 h. After that, the coal sample was washed with deionized water and filtered until there were no Cl$^-$ and Fe$^{3+}$ ions in the filtrate when tested with AgNO$_3$ and KSCN solutions separately. Then, it was dried for 48 h and weighed; the yield rate of the coal sample $\gamma_y$ was calculated. A SE-8S/All Sulfur Meter was applied to measure the total sulfur content $S_{T,C}$. A total amount of 45 mg of coal was put into the crucible of an automatic
sulfur analyzer and then tungsten trioxide was added. When the sulfur analyzer temperature increased to 1500 °C, the measurement of S_{T,C} started and the analytical error was 0.001%. The organic sulfur content (S_{O,C}) and the inorganic sulfur content (S_{I,C}) of coal after [HOOCCH2mim][HSO4] ionic liquid treatment were calculated using eqs 4 and 5. The sulfur data in Table 5 were also measured by this method.

\[
S_{O,C} = S_{O,C} \times Y_{T} \times 100\% 
\]

\[
S_{I,C} = (S_{T,C} - S_{O,C}) \times 100\% 
\]

The organic sulfur removal rate S_{R,O,C} inorganic sulfur removal rate S_{R,I,C} and total desulfurization rate D_S were calculated using eqs 6–8.

\[
S_{R,O,C} = \frac{S_{Raw,O,C} - S_{O,C}}{S_{Raw,O,C}} \times 100\% 
\]

\[
S_{R,I,C} = \frac{S_{Raw,I,C} - S_{I,C}}{S_{Raw,I,C}} \times 100\% 
\]

\[
D_S = \frac{S_{T,C} - (S_{O,C} + S_{I,C})}{S_{T,C}} \times 100\% 
\]

In order to analyze the microscopic mechanism of extraction and oxidation of coal samples by IL and H_2O_2, infrared functional spectroscopy (FTIR) and nondestructive X-ray photoelectron spectroscopy (XPS) experiments were conducted to analyze the functional groups and morphological sulfur changes in the IL–H_2O_2 reaction system.

An in situ FTIR Spectrometer TENSOR-37 was used to detect the functional groups of nonpretreated coals (i.e., raw coal), H_2O_2-pretreated coals (H_2O_2-tcs), and IL–H_2O_2 pretreated coals (IL–H_2O_2–tcs). The dried 2 mg of coal was mixed with 300 mg of potassium bromide (KBr) and then the mixture was ground in a mortar (mass ratio of coal to KBr was 1:150). Each coal–KBr sample was dried in vacuum for 24 h at 105 °C and then scanned 64 times in the range 400 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). The noise target was set to 10. The peak areas were fitted using Omnic software.

XPS is a direct and efficient method in specifying the forms of sulfur, including aliphatic and aromatic sulfur. Here, XPS measurements were carried out using an AXIS ULTRA DLD equipped with Mg K\(_\alpha\) radiation. The spectrometer is a hemispherical energy analyzer (HMA) with a pulse counting mode. The test voltage was 15 kV with a power of 400 W and a resolution of 0.8 eV. All data were corrected by the C 1s (284.8 eV) peak. The S_2p peak curves were resolved using a mixed Lorentzian–Gaussian line shape with XPSpeak 4.1 software.

In order to evaluate whether desulfurization reduces the calorific value of coal, TG-DSC experiments were conducted from room temperature to 800 °C using a STA449C synchronous thermal analyzer manufactured by NETZSCH, Germany. Around 25 mg of bituminous coal sample was used, and the heating rate was set to 10 °C/min. The atmospheric N_2 and O_2 gas flow rates were 20 mL/min and 10 mL/min, respectively. According to the TG and DSC curves, the change in the calorific value of all coal samples can be calculated.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acsomega.0c02795](https://pubs.acs.org/doi/10.1021/acsomega.0c02795).

Coal relative proportion after IL/coal 1:1 and IL/coal/ H_2O_2 1:1:10 treated; analysis of peak area and relative content of organic sulfur in raw coal by XPS; analysis of peak area and relative content of organic sulfur in IL/ H_2O_2 1:1 by XPS; analysis of peak area and relative content of organic sulfur in coal/ H_2O_2 1:1 by XPS; and analysis of peak area and relative content of organic sulfur in IL/coal/H_2O_2 1:1:10 by XPS (PDF)

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### Notes

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (no. 51874124), the Doctoral Fund of Ministry of Education of China (no. 2018T110725), Program for Innovative Research Team of Henan Polytechnic University (T2018-2), Fund for Distinguished Young Scholars (J2019-5), the Education Department of Henan Province (19A440009), and Fundamental Research Funds for the Central Universities (2017CXNL02).

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