Chemical thermodynamics and kinetics of thiophenic sulfur removed from coal by microwave: A density functional theory study

Chen Yin[1], Shengfu Zhang[1,2,*], Jincheng Wang[1], Farooq Sher[3], Shuangshuang Cai[1], Jian Xu[1], Meilong Hu[1], Liangying Wen[1]

[1]College of Materials Science & Engineering, Chongqing University, Chongqing 400044, P.R. China

[2]Chongqing Key Laboratory of Vanadium-Titanium Metallurgy & Advanced Materials, Chongqing University, Chongqing 400044, P.R. China

[3] Department of Engineering, School of Science and Technology, Nottingham Trent University, Nottingham NG11 8NS, UK

Chen Yin, E-mail: yinchen@cqu.edu.cn

*Shengfu Zhang (Corresponding author), E-mail: zhangsf@cqu.edu.cn

Jincheng Wang, E-mail: wjc17307406593@163.com

Farooq Sher, E-mail: Farooq.Sher@ntu.ac.uk

Shuangshuang Cai, E-mail: 201809131196@cqu.edu.cn

Jian Xu, E-mail: jxu@cqu.edu.cn

Meilong Hu, E-mail: hml@cqu.edu.cn

Liangying Wen, E-mail: cquwen@cqu.edu.cn

Abstract

In this study, the feasibility of catalyzing removel of thiophenic sulfur from coal with microwave irradiation was evaluated by dielectric properties test, and the chemical thermodynamics and kinetics of thiophenic sulfur in coal with microwave irradiation was obtained by density functional theory calculation. Results suggested that the imaginary parts of dielectric constants ε" of benzothiophene and dibenzothiophene are higher than those of coal samples, meaning that thiophenic sulfur compounds in the coal can be selectively heated by microwave. Linear Synchronous Transit/Quadratic Synchronous Transit method indicated that the microwave field catalyzed the removel of thiophenic sulfur mainly affected the breaking of C–H and C–C bonds, thus reducing the energy barrier (E_b) and activation energy (E_a) and increasing the logarithm of rate constants (ln$k$) in the desulfurization process. Moreover, the optimal removel path of thiophenic sulfur changed from β(a) to α(b), and sulfur-containing products changed from carbon monosulfide (CS) to thioketene(C_2H_2S) after applied microwave field. These findings reveal the catalytic mechanism of microwave on the removel of thiophenic sulfur in coal from hydrogen migration and reaction changes, which is conducive to the clean utilization of coal.

Keywords: Thiophenic sulfur; Microwave; Dielectric properties; Coal desulfurization; DFT.

1. Introduction

In a long period of time in the future, blast furnace will still be the leading process of molten iron production. According to statistics [1], the molten iron production of blast furnace in China was about

8.88×10^8 t in 2020. Based on the coke ratio of 350 $kg\cdot t^{-1}$, the consumption of high-quality coking coal in China's metallurgical industry reached 5.0×10^8 t in 2020. Due to excessive development and consumption, the supply of high-quality coking coal with low ash and sulfur content have exceeded demand in recent years, and the coke price has increased by nearly 10% year on year [2-6]. As we know, for metallurgical industry, the direct utilization of high sulfur coal will not only produce SO_2, H_2S, COS and other gases, leading to extremely environment pollute and equipment corrosion, but also reduces the quality of coke and molten iron [2, 7-10]. Therefore, it is crucial important to remove sulfur from high sulfur coking coal to meet the resource allocation and realize the sustainable development of metallurgical industry [11-13].

The main existing form of sulfur in coal is inorganic sulfur and organic sulfur [14]. Some relative studies pointed out that the inorganic sulfur is mainly pyrite and sulfate, and it is mostly contained in coal in the form of fine particles [15], can be removed by physical and chemical methods [15-20]. The organic sulfur is a part of macromolecular structure of coal, including thiols, thioether, thiophene, etc. [21, 22]. Tang et al. [23] used peracetic acid to remove sulfur from coal, the removel rate of organic sulfur was 49%, this method would destroy the coal matrix while removing the organic sulfur. Results of these studies showed that it is very difficult to remove organic sulfur in coal desulfurization [24-29].

Microwave desulfurization is a novel coal desulfurization method, can selectively and rapidly heat sulfur components in coal [17]. The results show that microwave can accelerate the desulfurization reaction of coal without destroying the coal matrix, and has great application potential for the removel

of organic sulfur such as thiol, thioether and thiophenic sulfur in coal [30-35]. Under microwave irradiation, the removel of organic sulfur functional groups in coal is achieved by the dissociation of C–S bonds, and the degree of difficulty of its fracture is related to the dielectric properties of sulfur-containing substances. Previous studies have shown that the thioether in coal is easily oxidized to the corresponding sulfoxide or sulfone under microwave conditions, while the C-S bond in thiophene and thiophenone is difficult to break [36]. This is consistent with our previous studies, thiophenic sulfur accounted for more than 60% of the total organic sulfur, but the removel rate was the lowest among the three functional groups, only 18.9% [33]. These results indicate that the removel of thiophenic sulfur is the key to coal desulfurization. However, previous studies have focused more on the removel of thiol and thioether sulfur, and less analysis on the dielectric properties and removel mechanism of thiophenic sulfur.

The aim of this research was to clarify the dielectric property of thiophenic sulfur and mechanism of bond-breaking removel with microwave irradiation. Agilent N5244A network analyzer has been used to unravel the differences in dielectric properties between coal samples and thiophenic sulfur compounds. Using the Materials Studio package, the Linear Synchronous Transit/Quadratic Synchronous Transit (LST / QST) transition state search calculation of thiophenic sulfur in coal was carried out. The energy barrier curve and activation energy of thiophene hydrogen migration and pyrolysis under microwave electric field was obtained. The influence of microwave electric field on the thermodynamic and kinetic parameters of the sulfur-containing model compound was explored.

2 Experimental

2.1 Samples preparation

Two typical high-sulfur coking coals (NTC and LGC) with different coal ranks, sulfur contents and sulfur forms were selected as the study objection. **Table 1** presents the proximate, ultimate and sulfur form analysis of the coal samples. The sulfur contents of NTC and LGC were 2.83% and 2.99% on dry basis respectively, while the sulfur forms were significantly different. The organic sulfur content in NTC is much higher than LGC, accounting for 87.99% of the total sulfur. Considerable pyrite sulfur and sulfate sulfur occurs in LGC, which are 29.43% and 21.74% respectively. There is little difference in ash content between the two coals, hardly effecting their dielectric properties.

In addition, the two types of thiophenic sulfur compounds, thiophene and benzothiophene, used in this experiment were purchased from Bide Pharmatech Ltd., with a purity of 98%.

Table 1. Proximate, ultimate and sulfur form analysis of NTC and LGC

	Mass %	NTC	LGC
Proximate analysis	Moisture (air dry basis)	1.24	1.86
	Ash (dry basis)	10.37	8.46
	Volatile matter (dry basis)	17.92	30.11
	Fixed carbon (dry basis)	71.71	61.43
Ultimate analysis (dry basis)	C	87.62	84.67
	H	4.48	5.15
	N	1.39	1.42
	O	3.68	5.76
	S	2.83	2.99
Sulfur form analysis (dry basis)	Pyritic sulfur	10.60	29.43
	Sulfate sulfur	1.41	21.74
	Organic sulfur	87.99	48.83

2.2 Dielectric property test

A vector network analyzer was used to measure the dielectric constants of coal samples and thiophenic sulfur compounds by the transmission reflection method [35]. Before measurement test, each of samples dried were crushed and ground to a particle size less than 250 μm, then pressed into a circular cylindrical sample with 7±0.2 mm length, 3.04 mm inner diameter, and approximately 5.0 mm thickness. The dielectric constant ε_0 and permeability μ_0 were measured at 2-10 GHz frequency range according to Eq. (1) and (2) in reference [37].

$$\varepsilon_0 = \varepsilon' + \varepsilon''\cdot i \quad (1)$$

$$\mu_0 = \mu' + \mu''\cdot i \quad (2)$$

where ε' represents the dielectric constant real part, and the larger the value, the stronger the ability of sample to store electric field energy. ε'' represents the dielectric constant imaginary part, and the larger the value, the greater the ability of the sample to absorb electric field energy and convert it into heat energy. The meaning of μ' and μ'' are similar with ε' and ε'' respectively. The higher the value of ε'' and μ'', the more effective the microwave on the reaction.

2.3 Density functional theory (DFT) calculation

Thiophene is a common aromatic compound containing thiophenic sulfur in coal, which conforms to Schucker rule (4N + 2). Compared with thiols and thioethers, the removel of thiophenic sulfur involves not only the formation and breaking of chemical bonds, but also the transfer of H within the molecule.

The thiophenic sulfur migration path varies with the hydrogen migration path, so hydrogen migration has been studied to reveal the catalytic effect of microwave on thiophene sulfur removel. According to the previous studies [38-40], the following reaction paths with hydrogen transfer process (α–H migration and β–H migration) were selected for the transition state search calculation, as shown in **Fig. 1**.

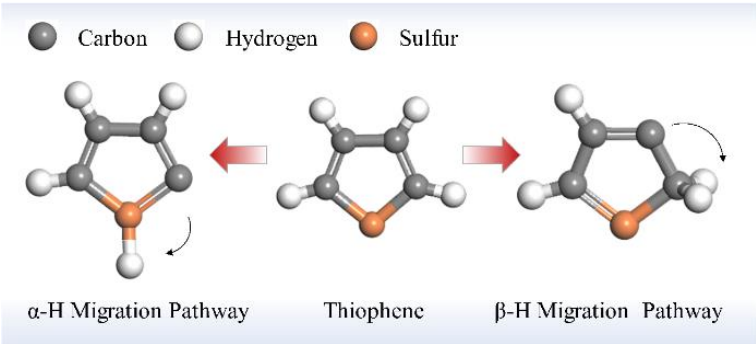

Fig. 1. Diagram of thiophenic hydrogen migration pathway during desulfurization.

All calculations were conducted by the Dmol^3 modules [7] of Materials Studio package (version 6.0). In the process of finding the transition state by conjugate gradient method (CG) and LST/QST, the key parameters were set as follows: Using GGA method with Perdew-Burke-Ernzerh of functional (PBE) with DND basis set, and the optimal convergence was obtained. The threshold value was the combination of medium parameters: the energy convergence was $2.0*10^5$ Ha, the energy gradient was $1.00*10^3$ (Ha·bohr^{-1}), the displacement was $1.00*10^3$ (Bohr), the spin multiplicity was octupole, the numerical integration accuracy and SCF convergence control was medium, and the electric field was set at (0 0 0.01) au [39-41].

3. Results and discussion

3.1 Dielectric properties of coal samples and thiophenic sulfur compounds

Fig. 2 shows the variation of dielectric constants of NTC, LGC, benzothiophene and dibenzothiophene with microwave frequency. As indicated in **Fig. 2** (a), the ε' value of dibenzothiophene increases with the increased microwave frequency, while that of benzothiophene is on the contrary. Moreover, the ε' values of NTC and LGC are higher than benzothiophene and dibenzothiophene. It is considered that coal can store more electric field energy than sulfur compounds in an alternating electromagnetic field [42-45]. **Fig. 2** (b) exhibits that the ε" values of thiophenic sulfur compounds are higher than coal samples, which indicated that sulfur compounds can better convert electric field energy into heat energy [42-45]. When microwave frequency reaches 2 GHz, the induced and oriented polarization occurs in the four samples. Since the microwave frequency is not high, the polarized dipoles have enough time to orient and arrange along the direction of the applied electric field. Most of the input energy of the microwave field is stored in a sample and converted into potential energy. Therefore, when the real part of dielectric constant ε' reaches a relatively high value, the imaginary part ε" is usually at a lower level.

With the increase of microwave frequency, the change rate of microwave electromagnetic field is accelerated, and the change rate of dipole begins to lag the change rate of microwave field. The interaction between dipoles take place, and the microwave energy is converted into heat energy. At this time, the energy storage decreases, and the energy loss increases [42-45]. There is a peak value of ε" near

4 GHz for the four samples, where the microwave frequency reaches the high frequency region above 5 GHz, the change rate of a dipole is completely disconnected from the microwave frequency. The dipole presents rigidity in the electromagnetic field, and the values of ε' and ε" are both in a lower position. Due to the ε" values of benzothiophene and dibenzothiophene are larger than coal samples, it shows that thiophenic sulfur compounds produce a dielectric response in the microwave field, and their response ability to microwave is greater than coal. Therefore, thiophenic sulfur is selectively heated by microwave, which is conducive to its removel [46].

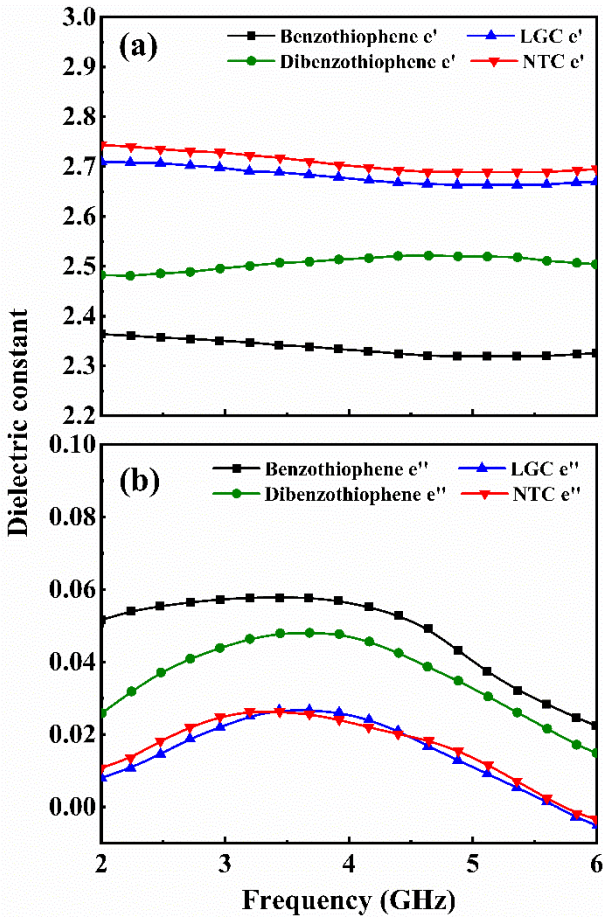

Fig. 2. The relation between dielectric constants and microwave frequency; (a) real part and (b) imaginary part.

The effects of microwave frequency on μ' and μ" values of four samples are shown in **Fig. 3** (a) and (b), respectively. The results indicate that the μ' value of four samples decrease slightly with the increased microwave frequency. The μ' value of LGC is the largest, while the μ" values of four samples have no significant difference. Due to the low magnetism properties of the samples, their μ' and μ" values are at a low level. Therefore, it is considered that both coal and sulfur compounds will not produce a large magnetic response and magnetic loss that is the reason, the influence of magnetic effect on microwave desulfurization of coal can be ignored.

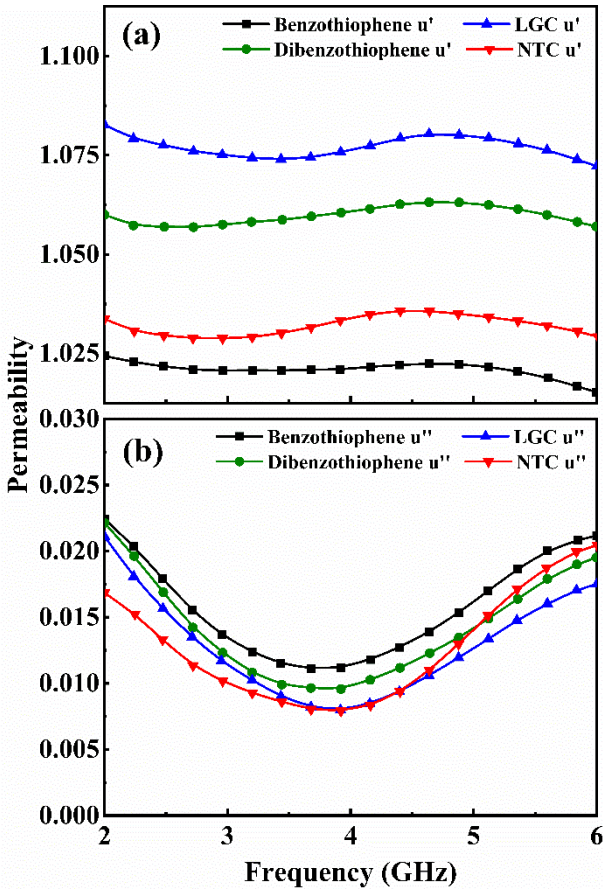

Fig. 3. The relation between permeability and microwave frequency; (a) real part and (b) imaginary part.

3.2 Comparison of theoretical microwave absorption power between coal samples and thiophenic sulfur compounds

Microwave heating refers to the process that the material absorbs and converts the microwave electric field energy and magnetic field energy into heat energy. In general, the electric field changes along with the space. In special cases, the electric field is regarded as a constant, by using the relation $E \cdot E^{*}=E^{2}$, there are Eq. (3) and (4) [47].

$$P_{\mathrm{av}} = \omega \varepsilon_0 \varepsilon'' \oint (E \cdot E^{*}) \cdot dV \tag{3}$$

$$P_{\mathrm{av}} = \omega \varepsilon_0 \varepsilon'' E_{\mathrm{rms}}^2 V \tag{4}$$

If the material also has a magnetic loss, then above equations is transformed into Eq. (5).

$$P_{\mathrm{av}} = \omega \varepsilon_0 \varepsilon E_{\mathrm{rms}}^2 V + \omega \mu_0 \mu H_{\mathrm{rms}}^2 V \tag{5}$$

Where P_{av} represents the microwave absorption power in W, E_{rms} represents the effective value of the electric field in V/m, H_{rms} represents the effective value of the magnetic field in A/m. ε_0 and μ_0 are the vacuum dielectric constant and vacuum permeability of sample, respectively, which are regarded as constants under certain conditions. V represents the volume of the sample in m^3.

In order to explain the dielectric response mechanism of coal desulfurization by microwave, the theoretical microwave absorption power of samples is estimated by the measuring dielectric constant and permeability value as in Eq. (5). The equivalent electromagnetic field is set based on the results of previous studies (15254.42 V/M and 2.33 A/M) [36], and the microwave input power is set at 1000 W [35].

Fig. 4 shows the heat generated by the dielectric loss (equivalent to the heat absorbed from the microwave electric field) and magnetic loss of coal samples as a function of microwave frequency. In 2.45 GHz region, the dielectric loss of coal samples occupy the dominant position and the generated heat is much greater than magnetic loss [42]. For example, the dielectric loss of NTC is about 92.68 W at 1000 W microwave power, while the magnetic loss is only 2.23 W. Similarly, the dielectric loss LGC is about 74.55 W at the frequency of 1000 W, while the magnetic loss is only 2.62 W.

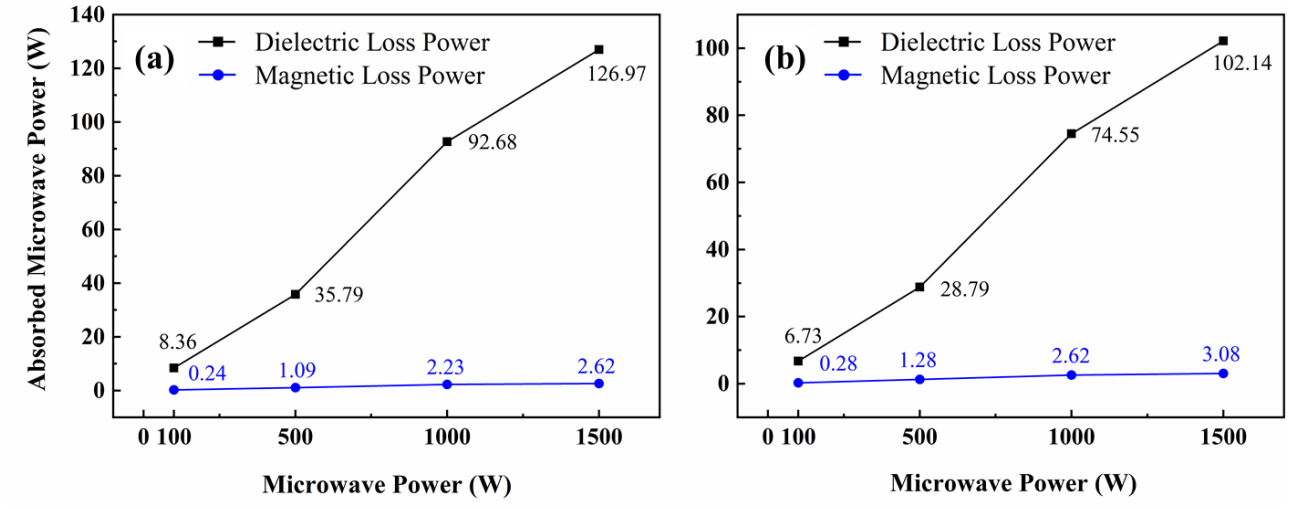

Fig. 4. Theoretical microwave absorption power at 2.45GHz; (a) NTC and (b) LGC.

The dielectric loss power of benzothiophene is higher than coal samples as shown in Fig. 5. For example, under 1000 W microwave power, the dielectric loss power of LGC is about 74.55 W, while benzothiophene is 284.72 W. Moreover, the heating power generated by the magnetic loss of benzothiophene is also relatively larger. The magnetic loss of LGC is 2.62 W while benzothiophene is 30.05 W at 1000 W. The dielectric loss of benzothiophene is still dominant [48]. Dibenzothiophene also

shows the same characteristics as benzothiophene, under microwave irradiation, its heat absorption is greater than coal sample; its own dielectric loss is much higher than the magnetic loss. At 1000 W microwave power, the dielectric loss power of dibenzothiophene is 233.43 W, and the magnetic loss power is 66.56 W. Due to the small value of the equivalent magnetic field, their magnetic loss is also very low. Due to the equivalent magnetic field values of coal samples and thiophenic sulfur compounds are very small, their magnetic losses are also very low. Therefore, the dielectric response is the main effect of microwave effect and the research on the microwave effect should focus on the influence of the microwave electric field [23, 33].

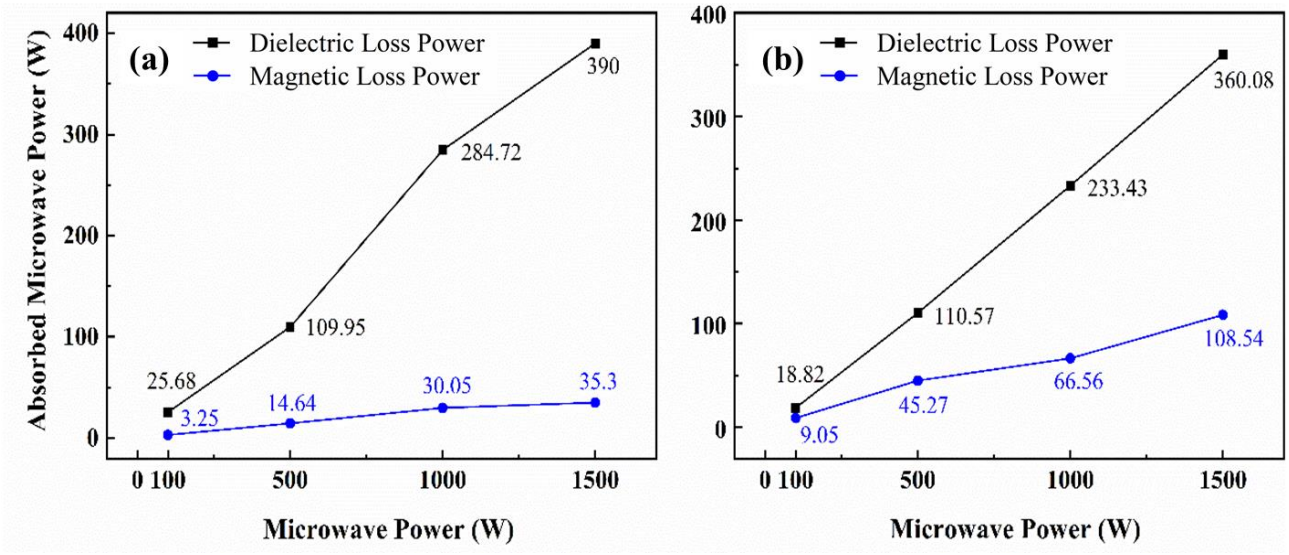

Fig. 5. Theoretical microwave absorption power at 2.45GHz; (a) benzothiophene and (b) dibenzothiophene.

According to the measured dielectric constants, the penetration depth D_p of the electromagnetic wave to the sample is calculated as follows Eq. (6) [49].

$$D_p = \lambda_0' / \left[2\pi(2\varepsilon')^{1/2}\right] * \left[(1 + (\varepsilon''/\varepsilon')^2)^{1/2} - 1\right]^{-1/2} \quad (6)$$

where λ_0' represents the wavelength of the incident wave in mm.

The calculated penetration depth is shown in **Fig. 6**. NTC has large microwave penetration depth at 5.75, 6.87 and 7.06 GHz, which are 610, 280 and 230 mm respectively; LGC has large microwave penetration depth at 5.67 and 7.18 GHz, which are 880 and 360 mm respectively. However, at 2.45GHz (Universal microwave frequency), the penetration depth of NTC and LGC can reach 180 mm and 220 mm respectively, which is larger than the general particle size of coal samples. The results indicate that the effect of microwave on desulfurization of coal is not only limited to the surface of coal but also has the same effect on sulfur groups in coal when the microwave frequency is appropriate [49, 50].

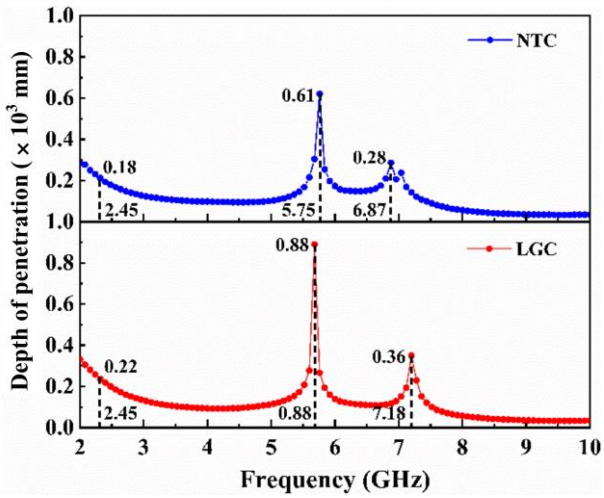

Fig. 6. Microwave penetration depth of NTC and LGC as a function of microwave frequency.

3.3 Thiophenic sulfur migration pathway

The transfers of α–H to S atom, referring to α(a) and α(b) are shown in **Fig. 7**. For the α(a) process, the α–H on thiophene first migrates to the adjacent S atom to form IM1, and then the thiophene ring

breaks twice to form hydrogen sulfide and 1,3-butanediyne (Product 1). In addition, H on the S atom of IM1 may continue to migrate to form ethylene radical and thioketene (Product 2), named as α(b) process.

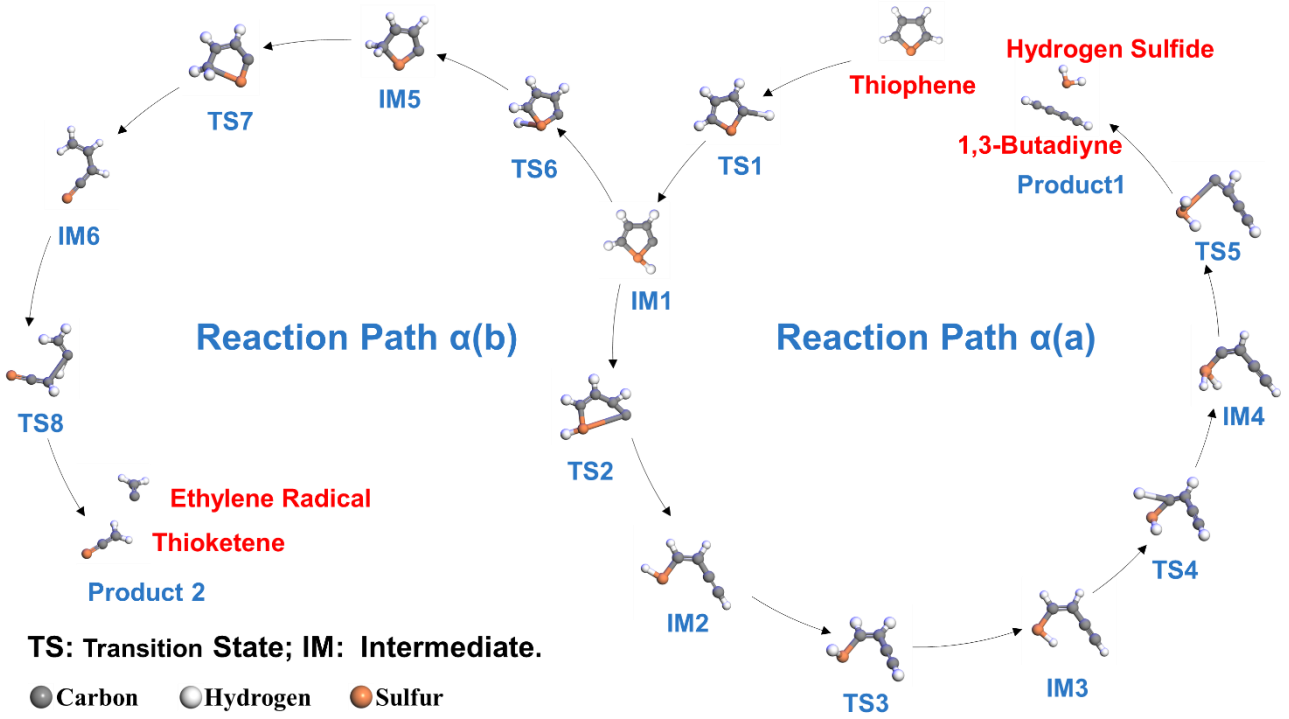

Fig. 7. α desulfurization reaction path; (a) generate H_2S and 1,3-butadiyne and (b) generate ethylene radical and thioketene.

Fig. 8 reveals the migration of β–H to α–C, referred to as β(a) and β(b) respectively. β(a) is that the β–H on thiophene first migrates to the adjacent α–C, at the same time, the C–S bond breaks to form IM7. In this step, the thiophene ring finally forms carbon monosulfide and propyne (product 3). Moreover, the H on another α–C of IM7 continues to migrate to form ethylene radical and thioketene (product 2), which is named β(b) process and its final product is the same as α(b) process.

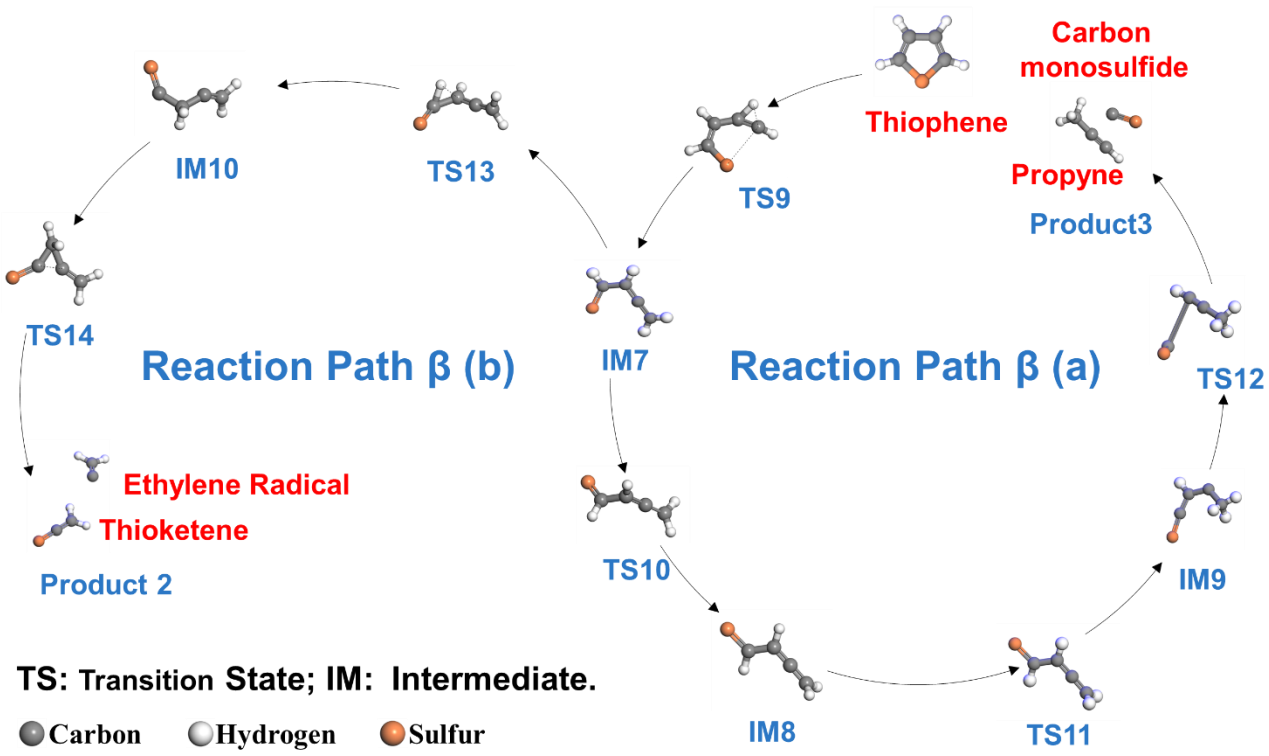

Fig. 8. β desulfurization reaction path; (a) generate carbon monosulfide and propyne and (b) generate ethylene radical and thioketene.

3.4 Comparison of E_b of thiophenic sulfur removel process before and after adding microwave field

E_b represents the zero-point energy difference between the activated complex and reactant. The larger the E_b is, the more difficult the reaction. As presented in **Fig. 9**, the external electric field hinders the α(a) process for Rea to IM2, and its E_b increases from 214.23 to 238.58 kJ·mol^{-1}. However, the process from IM3 to IM4 becomes easier under the external electric field and its E_b decreases from 477.73 to 253.76 kJ·mol^{-1}. For α(b) process, the E_b from Rea to IM5 is increased by the applied electric field, but the reaction process from IM5 to IM6 becomes an incompetent barrier reaction. The E_b of the process from IM6 to P2 is reduced from 374.60 to 242.88 kJ·mol^{-1}, which is the most difficult step in the

whole reaction process. Therefore, it is considered that the applied electric field can effectively reduce reaction difficulty. By comparing the maximum E_b of the above two reaction paths, it can be concluded that compared with α(a), α(b) is more suitable for H atom migration in the process of removing thiophenic sulfur from coal microwave [43].

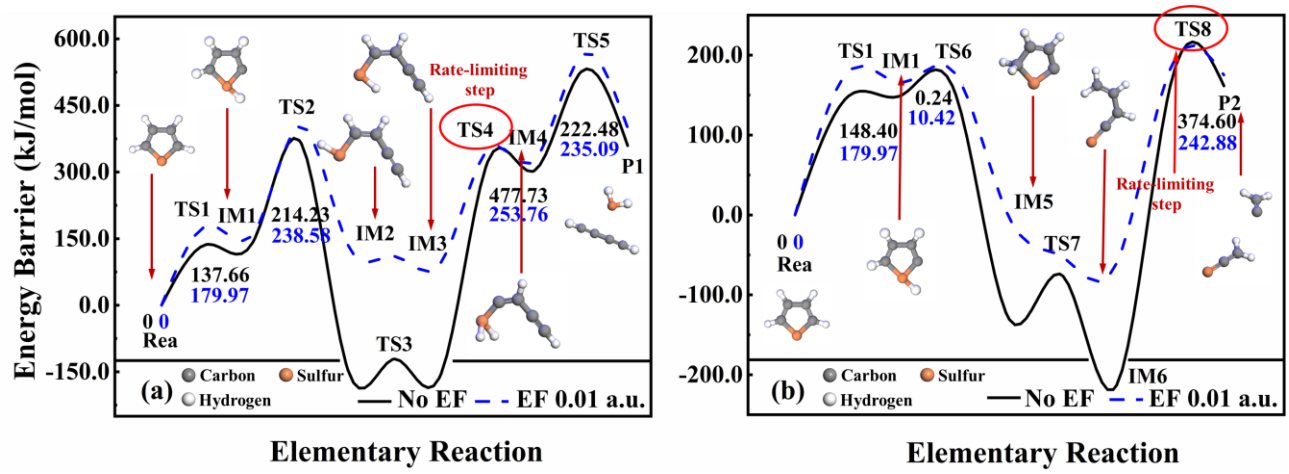

Fig. 9. The energy barrier E_b of thiophenic sulfur removel by pathway α; (a) α(a) pathway and (b) α(b) pathway.

Fig. 10 shows the change of E_b of thiophenic sulfur removel by pathway β. For the β(a) reaction path, the external electric field promotes the processes of Rea to IM7, IM7 to IM8 and IM9 to P3. The E_b decreases from 225.28 to 204.39 kJ·mol^{-1}, and 79.77 to 76.22 kJ·mol^{-1}, respectively. However, the reaction from IM8 to IM9 is inhibited by the applied electric field, which is the rate-limiting step of the β(a) path. The E_b of IM8 to IM9 is increased from 250.48 to 299.07 kJ·mol^{-1}. Therefore, it can be considered that microwave can inhibit the removel of thiophenic sulfur for this route. For the β(b) reaction path, the external electric field promotes the progress of all elementary reactions, especially in

the rate-limiting step IM7 to IM10, where the E_b decreases from 336.63 to 301.33 kJ·mol^{-1}. Comparing the above results, it is found that although microwave promotes the occurrence of the β(b) pathway, the E_b of rate-limiting step (301.33) is still higher than that of β(a) path (299.07). That is, the β–H atoms tend to migrate according to β(a), and this trend is inhibited under the microwave irradiation. Finally, combined with **Fig. 9** and **10**, it can be concluded from the E_b of rate-limiting step of different reaction path that under microwave irradiation, the optimal removel path of thiophenic sulfur will change from β(a) to α(b), and be catalyzed by microwave.

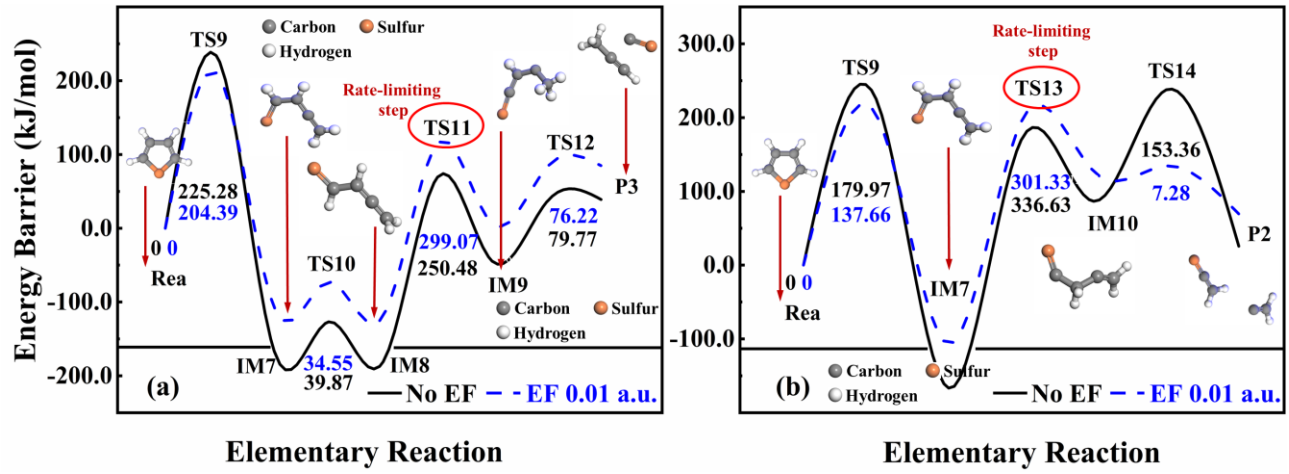

Fig. 10. The energy barrier E_b of thiophenic sulfur removel by pathway β; (a) β(a) pathway and (b) β(b) pathway.

3.5 Comparison of E_a and ln$k$ of thiophenic sulfur removel process before and after adding microwave field

E_a and ln$k$ represent the difficulty and speed of the chemical reaction respectively, which can be

calculated by Eq. (7) ~ (8). According to the transition state theory of Eyring chemical reaction, the molar statistical enthalpy ($\Delta_r H_m$) and entropy ($\Delta_r S_m$) of each elementary reaction in thiophenic sulfur migration path can be obtained. The calculation formula and obtained results are shown in Eq. (9) ~ (10) and supplementary Table S-1, respectively.

$$E_a = \Delta_r H_m + nRT \tag{7}$$

$$lnk = ln\left(\frac{KT}{h} e^{-\frac{E_a}{RT}} . e^{\frac{\Delta_r S_m}{RT}}\right) \tag{8}$$

where n, R, T, K and h represent the molar mass of substance, gas constant (8.314 J/mol·K), reaction temperature (K), Boltzmann constant (1.38×10^{-23} J/K) and Planck constant (6.63×10^{-34} J·s), respectively.

$$\Delta_r H_m = E_{total}(TS) + H_m^0(TS) - E_{total}(R) + H_m^0(R) \tag{9}$$

$$\Delta_r S_m = S_m^0(TS) - S_m^0(R) \tag{10}$$

Where E_{total}, TS and R represent the total energies, the transitions and the reactants, respectively.

Fig. 11 presents the process of α(a) reaction of thiophene to produce hydrogen sulfide and 1,3-butadiyne. It can be seen from the figure that except step 4, increasing temperature or applying electric field increases E_a and decreases ln$k$ in each step of the reaction, and the effect of electric field is more significant. Step 4 is the hydrogen transfer reaction. And this step is the rate-limiting step in α(a) reaction process, which needs to cross the highest E_b in **Fig. 9**. The whole reaction speed is determined by the speed of this step. Under the condition of no electric field, the ln$k$ in step 4 is 39.52 and 36.19 at 298.15 and 475 K respectively, which is the smallest in the whole reaction. After applying electric field, the ln$k$ of this step increases to 50.46 and 46.70 at 298.15 K and 475 K respectively. Therefore, combined with **Fig. 9 (a)**, it can be considered that the presence of microwave field not only reduces the difficulty of

hydrogen migration along α(a), but also speeds up the reaction, thus catalyzing removel of thiophenic sulfur [40-44, 48].

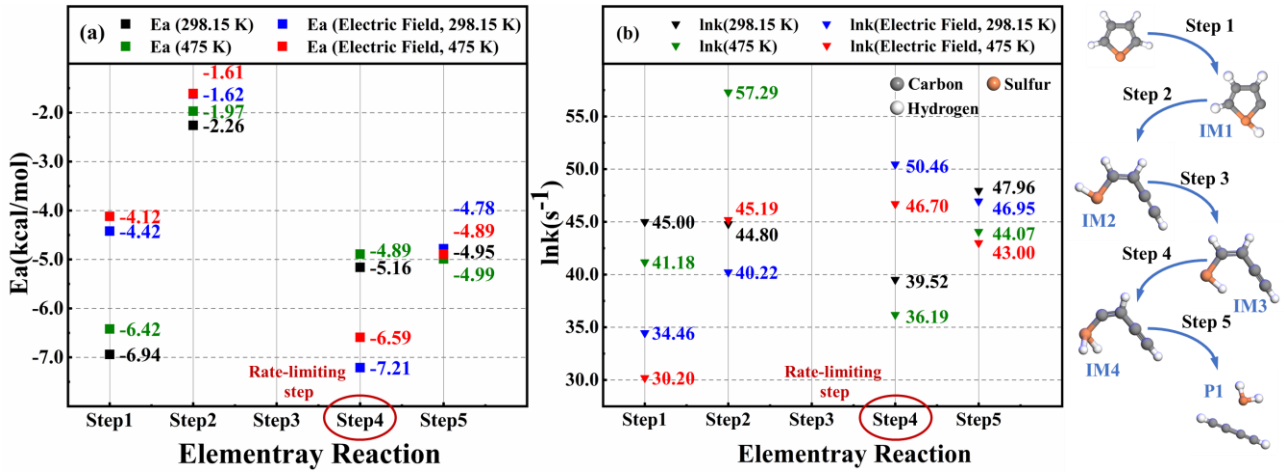

Fig.11. E_a and ln$k$ of elementary reactions in α(a) reaction pathway; (a) E_a and (b) ln$k$.

Fig. 12 reflects E_a and ln$k$ of elementary reactions in α(b) pathway, and the change of temperature has little effect on E_a and ln$k$. After the addition of electric field, the E_a of Step 1 and step 2 increases, while that of step 3 and step 4 decreases, indicating that the electric field inhibits the progress of the first two reactions and promotes the latter two reactions. This is consistent with the results of previous studies [23, 40]. Reviewing **Fig. 9 (b)**, step 3 and 4 are C–S and C–C bond-breaking reaction respectively, and step 4 is the rate limiting step of α(b) pathway. Therefore, it is believed that the microwave field promotes the C-C bond breaking, thus catalyzing the removel of thiophenic sulfur along α(b) pathway.

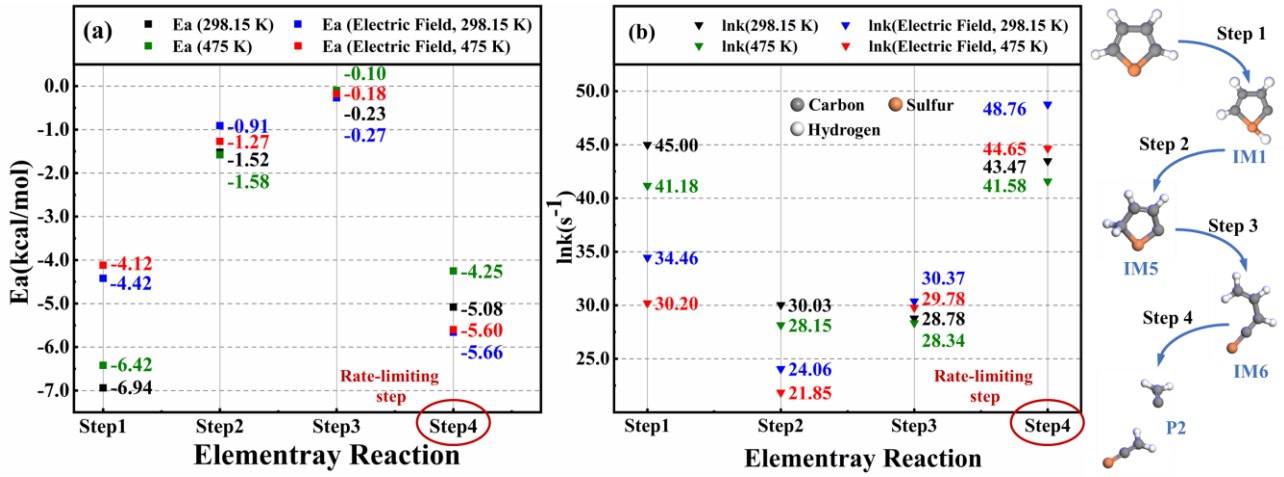

Fig. 12. E_a and ln$k$ of elementary reactions in α(b) reaction pathway; (a) E_a and (b) ln$k$.

E_a and ln$k$ of elementary reactions in β(a) reaction pathway to produce carbon monosulfide and propyne are illustrated in **Fig. 13**. Elevated temperature has little effect on E_a and ln$k$ of the reaction, but the applied electric field obviously improves ln$k$ of step 1 and lowers that of step 2, 3 and 4. In combination with **Fig. 10 (a)**, step 3 representing the hydrogen migration between carbon atoms is the rate limiting step of β(a) pathway. It is assumed that the external microwave not only improves E_b of hydrogen migration along β (a), but also reduces its reaction rate, thus inhibiting removel of thiophenic sulfur.

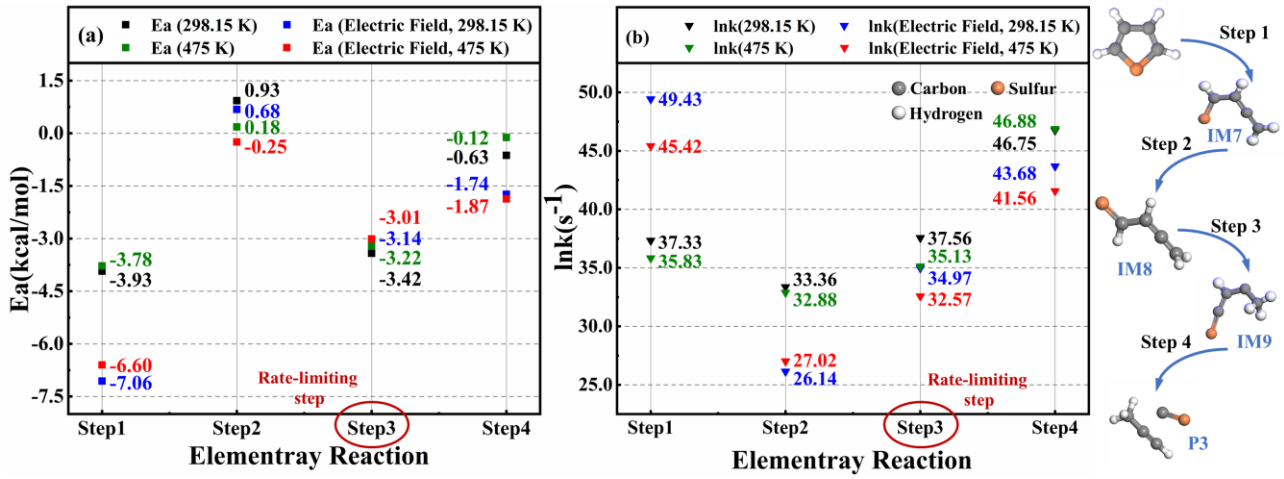

Fig. 13. E_a and ln$k$ of elementary reactions in β(a) reaction pathway; (a) E_a and (b) ln$k$.

Fig. 14 shows the E_a and ln$k$ of elementary reactions in β(b) reaction pathway that represents thiophene generates ethylene radicals and thioketene. E_a of each step of the pathway decreases after the addition of electric field, which indicates that the applied microwave field promotes the reaction rate of each step. Combining with **Fig. 10 (b)**, it shows that step 2 of hydrogen migration between carbon atoms is the rate limiting step of β(b) pathway. Therefore, it is considered that microwave can improve the removel of thiophenic sulfur from coal along β(b) pathway by catalytic cracking of C–H bonds [40-44, 48].

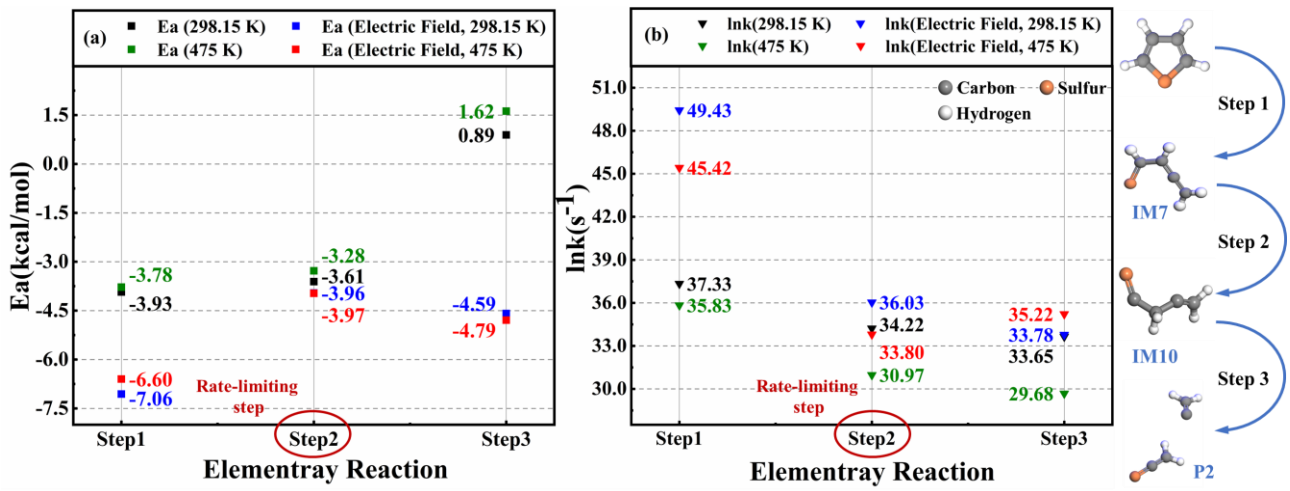

Fig. 14. E_a and ln$k$ of elementary reactions in β(b) reaction pathway; (a) E_a and (b) ln$k$.

Based above result, After the application of microwave field, the minimum E_b path of thiophene sulfur remove from coal is transferred from β(a) to α(b), and the E_a of rate-limiting step for β(a) is increased and the ln$k$ is decreased, while the α(b) is on the contrary. On the whole, the E_a and ln$k$ of α(b) with microwave is better than that of β(a) without microwave.

Table 2 Thermodynamics and kinetics parameters of rate-limiting step at 298.15 K

Reaction path	Thermodynamics and kinetics parameters of rate-limiting step at 298.15 K					
	E_b	E_b-EF	E_a	E_a-EF	ln$k$	ln$k$-EF
α(a)	477.73	253.76	-5.16	-7.21	39.52	50.46
α(b)	374.60	242.88	-5.08	-5.66	43.47	48.76
β(a)	250.48	299.07	-3.42	-3.14	37.56	34.97
β(b)	336.63	310.33	-3.61	-3.96	34.22	36.02

EF: Electric field

4 Conclusions

By measuring the dielectric properties, it is found that the imaginary part of dielectric constants ε" of benzothiophene and dibenzothiophene is higher than coal samples, which means that thiophenic sulfur compounds in coal can generate more heat with microwave irradiation. So, thiophenic sulfur can be selectively heated by microwave. In addition, due to the weak magnetic properties of coal samples and thiophenic sulfur, the heating value from magnetic loss is far lower than the dielectric loss, so the microwave field is simplified to an electric field in the simulation. Linear Synchronous Transit/Quadratic Synchronous Transit transition state search shows that under microwave irradiation, the cleavage of C–H or C–C bond in paths α(a), α(b) and β(b) was catalyzed and the cleavage of C–H bond in path β(a) was inhibited, resulting in the change of the optimal removel path of thiophenic sulfur from β(a) to α(b) and sulfur-containing products changed from carbon monosulfide (CS) to thioketene (C_2H_2S). Overall, the calculated thermodynamic and kinetic parameters of rate limiting steps of each reaction pathway indicated that that the applied microwave can catalyze the removel of thiophenic sulfur by reducing E_b and E_a and increasing ln$k$.

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Conflict of interest statement

On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

[1] NBOS. China, The 2019 National economic and social development statistics bulletin of the people's republic of China (PRC), NBS, Beijing, 2019, https://doi.org/10.38309/n.cnki.nzgxx.2020.000341.

[2] Tang Y, He X, Chen A, Li W, Deng X, Wei Q, Occurrence and sedimentary control of sulfur in coals of China, J. China Coal Soc 2015;40:1977-1988.

[3] Liu J, Reflection on low-carbon development of coal energy in China, Journal of China University of Mining and Technology (Social Science edition), 2011, 13, 5-12.

[4] Lotfian S, Ahmed H, Samuelsson C. Alternative reducing agents in metallurgical processes: devolatilization of shredder residue materials. J SUST METALL 2017;3(2):311-21. https://doi.org/10.1007/s40831-016-0094-0

[5] Nomura S. Use of waste plastics in coke oven: a review. J SUST METALL 2015;1(1):85-93. https://doi.org/10.1007/s40831-014-0001-5

[6] Delley B. From molecules to solids with the DMol(3) approach. J Chem Phys 2000;113(18):7756-64. https://doi.org/10.1063/1.1316015.

[7] Yang N, Guo H, Liu F, Zhang H, Hu Y, Hu R. Effects of atmospheres on sulfur release and its transformation behavior during coal thermolysis. Fuel 2018;215:446-53. https://doi.org/10.1016/j.fuel.2017.11.099.

[8] Kawashima H. Changes in sulfur functionality during solvent extraction of coal in Hyper-coal production. Fuel Process Technol 2019;188:105-9. https://doi.org/10.1016/j.fuproc.2019.02.011.

[9] Chen H, Huo Q, Wang Y, Han L, Lei Z, Wang J, et al. Upcycling coal liquefaction residue into sulfur-rich activated carbon for efficient Hg^0 removel from coal-fired flue gas. Fuel Process Technol 2020;206. https://doi.org/10.1016/j.fuproc.2020.106467.

[10] Meng X, Li L, Li K, Zhou P, Zhang H, Jia J, et al. Desulfurization of fuels with sodium borohydride under the catalysis of nickel salt in polyethylene glycol. J Clean Prod 2018;176:391-8. https://doi.org/10.1016/j.jclepro.2017.12.152.

[11] Tang L, Chen S, Wang S, Tao X, He H, Zheng L, et al. Heterocyclic sulfur removel of coal based on potassium tert-butoxide and hydrosilane system. Fuel Process Technol 2018;177:194-9. https://doi.org/10.1016/j.fuproc.2018.04.031.

[12] Zhang B, Zhu G, Lv B, Dong L, Yan G, Zhu X, et al. A novel high-sulfur fine coal clean desulfurization pretreatment：Microwave magnetic separation, high-gradient effect and magnetic strengthen. J Clean Prod 2018;202:697-709. https://doi.org/doi.org/10.1016/j.jclepro.2018.08.088.

[13] Tao X, Xu N, Xie M, Tang L. Progress of the technique of coal microwave desulfurization. Int J Coal Sci Technol 2014;1(1):113-28. https://doi.org/10.1007/s40789-014-0006-5.

[14] Pecina ET, Camacho LF, Herrera CA, Martinez D. Effect of complexing agents in the desulphurization of coal by H_2SO_4 and H_2O_2 leaching. Miner Eng 2012;29:121-3. https://doi.org/10.1016/j.mineng.2011.10.011.

[15] Blaesing M, Melchior T, Mueller M. Influence of temperature on the release of inorganic species during high temperature gasification of Rhenish lignite. Fuel Process Technol 2011;92(3):511-6. https://doi.org/10.1016/j.fuproc.2010.11.005.

[16] Joriani E, Rezai B, Vossoughi M, Osanloo M, Abdollahi M. Oxidation pretreatment for enhancing desulfurization of coal with sodium butoxide. Miner Eng 2004;17(4):545-52. https://doi.org/10.1016/j.mineng.2003.12.007.

[17] Jorjani E, Chelgani SC, Mesroghli S. Application of artificial neural networks to predict chemical desulfurization of Tabas coal. Fuel 2008;87(12):2727-34. https://doi.org/10.1016/j.fuel.2008.01.029.

[18] Wijaya N, Choo TK, Zhang L. Generation of ultra-clean coal from Victorian brown coal - Sequential and single leaching at room temperature to elucidate the elution of individual inorganic elements. Fuel Process Technol 2011;92(11):2127-37. https://doi.org/10.1016/j.fuproc.2011.05.022.

[19] Zhang B, Ma Z, Zhu G, Yan G, Zhou C. Clean coal desulfurization pretreatment: microwave magnetic separation, Response Surface, and Pyrite Magnetic Strengthen. Energy Fuels 2018;32(2):1498-505. https://doi.org/10.1021/acs.energyfuels.7b03561.

[20] Wiser WH. Conversion of bituminous coal to liquids and gases: chemistry and representative processes. In: Petrakis L, Fraissard JP, editors. Petrakis L, Fraissard JP Springer Netherlands Dordrecht; 1984, p. 325-50. https://doi.org/10.1007/978-94-009-6378-8_12.

[21] Zhang L, Wang Y, Li X, Wang S. Region-of-interest extraction based on spectrum saliency analysis and coherence-enhancing diffusion model in remote sensing images. Neurocomputing

2016;207:630-44. https://doi.org/10.1016/j.neucom.2016.05.045.

[22] Tang L, Long K, Chen S, Gui D, He C, Li J, et al. Removel of thiophene sulfur model compound for coal by microwave with peroxyacetic acid. Fuel 2020;272:117748. https://doi.org/10.1016/j.fuel.2020.117748.

[23] Jorjani E, Chelgani SC, Mesroghli S. Prediction of microbial desulfurization of coal using artificial neural networks. Miner Eng 2007;20(14):1285-92. https://doi.org/10.1016/j.mineng.2007.07.003.

[24] Qin ZH, Zhang HF, Dai DJ, Zhao CC, Zhang LF. Study on occurrence of sulfur in different group components of Xinyu clean coking coal. Journal of Fuel Chemistry and Technology 2014;42(11):1286-94.

[25] Tang L, Chen S, Wang S, Tao X, He H, Fan H. Exploration of the combined action mechanism of desulfurization and ash removel in the process of coal desulfurization by microwave with peroxyacetic acid. Energy Fuels 2017;31(12):13248-58. https://doi.org/10.1021/acs.energyfuels.7b02112.

[26] Yao Q, Sun M, Gao J, Wang R, Zhang Y, Xu L, et al. Organic sulfur compositions and distributions of tars from the pyrolysis of solvent pretreatment vitrinite of high sulfur coal. J Anal Appl Pyrolysis 2019;139:291-300. https://doi.org/10.1016/j.jaap.2019.03.002.

[27] Saikia BK, Khound K, Baruah BP. Extractive desulfurization and deashing of high sulfur coals by oxidation with ionic liquids. Energy Convers Manage 2014;81:298-305. https://doi.org/10.1016/j.enconman.2014.02.043.

[28] Mursito AT, Hirajima T, Sasaki K. Alkaline hydrothermal de-ashing and desulfurization of low quality coal and its application to hydrogen-rich gas generation. Energy Convers Manage 2011;52(1):762-9. https://doi.org/10.1016/j.enconman.2010.08.001.

[29] Bichot A, Lerosty M, Radoiu M, Méchin V, Bernet N, Delgenès J-P, et al. Decoupling thermal and non-thermal effects of the microwaves for lignocellulosic biomass pretreatment. Energy Convers Manage 2020;203. https://doi.org/10.1016/j.enconman.2019.112220.

[30] Mong GR, Chong CT, Ng JH, Chong WWF, Lam SS, Ong HC, et al. Microwave pyrolysis for valorization of horse manure biowaste. Energy Convers Manage 2020;220. https://doi.org/10.1016/j.enconman.2020.113074.

[31] Wu Q, Wang Y, Peng Y, Ke L, Yang Q, Jiang L, et al. Microwave-assisted pyrolysis of waste cooking oil for hydrocarbon bio-oil over metal oxides and HZSM-5 catalysts. Energy Convers Manage 2020;220. https://doi.org/10.1016/j.enconman.2020.113124.

[32] Cai SS, Zhang SF, Wei Y, Sher F, Wen LY, Xu J, et al. A novel method for removing organic sulfur from high-sulfur coal: Migration of organic sulfur during microwave treatment with NaOH-H_2O_2. Fuel 2021;289:119800. https://doi.org/10.1016/j.fuel.2020.119800.

[33] Liu J, Wang Z, Qiao Z, Chen W, Zheng L, Zhou J. Evaluation on the microwave-assisted chemical desulfurization for organic sulfur removel. J Clean Prod 2020;267:121878. https://doi.org/10.1016/j.jclepro.2020.121878.

[34] Wu Y, Zhang SF, Cai SS, Xiao X, Yin C, Xu J, et al. Transformation of organic sulfur and its

functional groups in nantong and laigang coal under microwave irradiation. J Comput Chem 2019;40(31):2749-60. https://doi.org/10.1002/jcc.26051.

[35] Tao X, Tang L, Xie M, He H, Xu N, Feng L, et al. Dielectric properties analysis of sulfur-containing models in coal and energy evaluation of their sulfur-containing bond dissociation in microwave field. Fuel 2016;181:1027-33. https://doi.org/10.1016/j.fuel.2016.05.005.

[36] Nicolson AM, Ross GF. Measurement of the intrinsic properties of materials by time-domain techniques. IEEE Trans Instrum Meas 1970;IM-19(4):377-82. https://doi.org/10.1109/TIM.1970.4313932.

[37] Song X, Parish CA. Pyrolysis mechanisms of thiophene and methylthiophene in asphaltenes. J Phys Chem A 2011;115(13):2882-91. https://doi.org/10.1021/jp1118458.

[38] Ling LX, Zhang RG, Wang BJ, Xie KC. DFT study on the sulfur migration during benzenethiol pyrolysis in coal. J M Struc-Theochem 2010;952(1-3):31-5. https://doi.org/10.1016/j.theochem.2010.04.001.

[39] Ling LX, Zhang RG, Wang BJ, Xie KC. Density functional theory study on the pyrolysis mechanism of thiophene in coal. J M Struc-Theochem 2009;905(1-3):8-12. https://doi.org/10.1016/j.theochem.2009.02.040.

[40] Zhang F, Guo H, Liu Y, Liu F, Hu R. Theoretical study on desulfurization mechanisms of a coal-based model compound 2-methylthiophene during pyrolysis under inert and oxidative atmospheres. Fuel 2019;257:116028. https://doi.org/10.1016/j.fuel.2019.116028.

[41] Fan W, Jia C, Hu W, Yang C, Liu L, Zhang X, et al. Dielectric properties of coals in the low-terahertz frequency region. Fuel 2015;162:294-304. https://doi.org/10.1016/j.fuel.2015.09.027.

[42] Ge T, Cai C, Chen P, Min F, Zhang M-X. The characterization on organic sulfur occurrence in coking coal and mechanism of microwave action on thiophene. Spectroscopy and Spectral Analysis 2020;40(4):1321-7. https://doi.org/10.3964/j.issn.1000-0593(2020)04-1321-07.

[43] Ge T, Deng N, Min F. The dielectric properties of thiophene model compounds: insights for microwave desulfurization of coking coal. Energy Fuels 2020;34(11):14101-8. https://doi.org/10.1021/acs.energyfuels.0c03001

[44] Quan B, Liang XH, Ji GB, Cheng Y, Liu W, Ma JN, et al. Dielectric polarization in electromagnetic wave absorption: Review and perspective. J ALLOY COMPD 2017;728:1065-75. https://doi.org/10.1016/j.jallcom.2017.09.082.

[45] Ge T, Li F, Li Y. Influence of dielectric property of organic sulfur compounds on coal microwave desulfurization. ASIA-PAC J CHEM ENG 2020. https://doi.org/10.1002/apj.2581.

[46] Sutton WH. Microwave processing of ceramic materials. Am Ceram Soc Bull 1989;68(2):376-86.

[47] Ge T, Zhang M. Dielectric properties of the model compounds of thiophene sulfur in coals and its relation to molecular polarity. Journal of China University of Mining and Technology 2016;45(6):1245-50.

[48] Peng ZW, Hwang JY, Mouris J, Hutcheon R, Huang XD. Microwave penetration depth in materials with non-zero magnetic susceptibility. ISIJ Int 2010;50(11):1590-6.

https://doi.org/10.2355/isijinternational.50.1590.

[49] Peng ZW, Lin XL, Li ZZ, Hwang JY, Kim BG, Zhang YB, et al. Dielectric characterization of Indonesian low-rank coal for microwave processing. Fuel Process Technol 2017;156:171-7. https://doi.org/10.1016/j.fuproc.2016.11.001.