

Study on Reaction Sites of Active Structures in Coal Based on the ReaxFF Reactive Force Field

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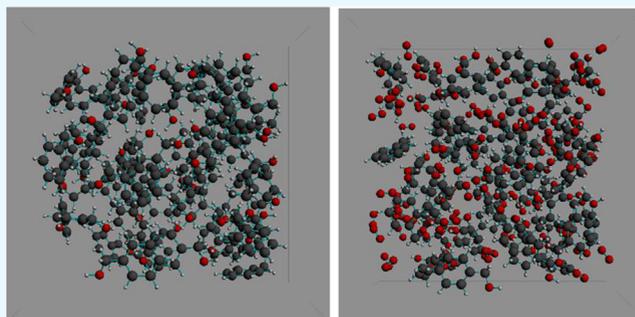
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ABSTRACT: To study the reaction paths and reaction mechanisms of the active structures in coal during the oxidation process, the oxygen-free pyrolysis and oxygen-containing combustion were simulated for nine active structures in coal based on the ReaxFF MD method. A separate simulation analysis of the active structure yielded that O₂ inhibited the reaction of H1. As the branched chain grows, the reaction paths of C2 and Q2 follow the direction of the reaction of carboxyl and aldehyde groups to CO₂ and CO. Considering the reaction rates and reaction process products of A1, B1, and B3 structures, it is obtained that O₂ has the greatest contribution to the decomposition reaction of aliphatic hydrocarbon structures. This is due to the strong electron-absorbing property of O₂ that attracts H radicals to generate HO₂, which in turn affects the reaction path of the active structure. Tracing the reaction process reveals that OH and oxygen-containing radicals under oxygen-free conditions greatly influence the active structural reaction.



1. INTRODUCTION

For a long time, prevention of coal spontaneous combustion is one of the key issues concerned by industry scholars. Coal spontaneous combustion will not only cause energy waste but also may lead to the occurrence of coupled disasters such as underground gas explosions, affecting the safety of enterprise production. Therefore, the study of coal spontaneous combustion mechanism is the key to prevent coal spontaneous combustion in advance. Generally speaking, coals that are prone to spontaneous combustion contain abundant organic active groups, such as oxygen bridges, carbonyl groups, carboxyl groups, and hydroxyl groups, which have a significant impact on coal spontaneous combustion.^{1–3} Many scholars have analyzed from an experimental perspective that the participation of active groups in oxidation heat release is the main factor affecting coal spontaneous combustion.^{4–6} Some scholars also studied the influence of active groups such as hydroxyl⁷ and aldehyde⁸ on coal oxidation reaction characteristics from the perspective of quantum chemistry.^{9,10} From the above studies it can be inferred that the organic reactive group reaction in coal is important for coal spontaneous combustion from macroscopic experimental point of view and quantum chemical analysis. However, it is difficult to obtain the detailed reaction path and reaction mechanism of the active structure in coal accurately from the molecular point of view by macroscopic experimental methods and quantum chemical simulation methods. In this work, based on the ReaxFF reactive force field, we used AMS software to simulate and

study the reaction sites and reaction sequences of reactive groups and bridge bonds in coal, to further understand the organic structure reaction mechanism of coal during spontaneous combustion.

The ReaxFF reactive force field is a force-field method capable of describing bond breaking, bond formation, and chemical reactivity.^{11–15} Molecular dynamics (MD) simulations using this reaction force field have been shown to describe precise processes during chemical reactions in large systems (>1000 atoms) at the atomic level.^{16–18} ReaxFF can calculate and explain the formation and breaking of chemical bonds and atomic reaction pathways and has also been widely used to determine the mechanism of chemical reactions during coal combustion and pyrolysis.^{19–21} Bhoi et al.¹⁹ used ReaxFF to explore the pyrolysis and combustion process and mechanism of lignite and found that the intermediates produced during the simulation were consistent with the experimental results. Qiu et al.²² conducted ReaxFF MD simulations to investigate the microscopic reaction behavior of lignite burning in an O₂/CO₂ environment. Chen et al.²³

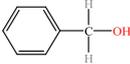
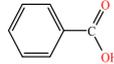
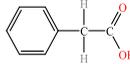
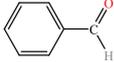
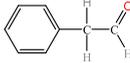
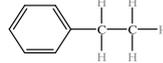
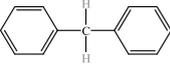
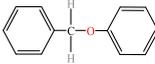
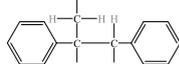
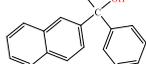
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Table 1. Active Structure Models in Coal

model	Hydroxyl structure		carboxyl	
compound				
molecular structure				
condensed formula	Ph-CH ₂ -OH	Ph-OH	Ph-COOH	Ph--CH ₂ -COOH
label	H1	H2	C1	C2
model	aldehyde group		alkyl	
compound				
molecular structure				
condensed formula	Ph-CHO	Ph-CH ₂ -CHO	Ph-CH ₂ -CH ₃	
label	Q1	Q2	A1	
model	methylene bridge	methylene ether	subalkyl bridge bond with	alkyl bridge bond
compound	bond	bridge bond	branched-chain	with the hydroxyl
molecular structure				
condensed formula	Ph-CH ₂ -Ph	Ph-CH ₂ -O-Ph	Ph-CH(CH ₃)-CH ₂ -Ph	Ar-CH(OH)-Ph
label	B1	B2	B3	B4

applied the ReaxFF method to study the mechanism behind the reaction leading to spontaneous combustion of lignite, and the simulation showed that O₂ abstracts hydrogen atoms from phenolic hydroxyl groups, followed by the formation of HO₂. Li et al.²⁴ analyzed the thermal reaction mechanism of coal with the ReaxFF kinetic method, obtained the distribution of common products and elementary reactions in the coal reaction process, and then explained the mechanism of reaction processes such as coal pyrolysis, oxidation, and hydrothermal treatment. Most of the above scholars used the organic macromolecular model of coal to simulate the pyrolysis and combustion reactions of coal to obtain the reaction mechanism of the organic structure in coal. However, these studies could not accurately obtain the reaction path of the active structure in coal and could not explain the reaction mechanism of the active structure more clearly. Therefore, a detailed exploration of the reaction sites and reaction pathways of each active structure in coal can further reveal the reaction mechanism of coal.

The structure of coal is extremely complex. A coal molecular structure is composed of thousands of atoms, so the reaction path of the active structure in the coal macromolecular structure cannot be well tracked in the macromolecular simulation calculation of coal. In this paper, a periodic box is

established by taking active groups and bridge bonds in coal as the research objects. The model was simulated by the ReaxFF reactive force field for pyrolysis and combustion, the reaction paths in the reaction process were analyzed at the molecular level, and the reaction sites and mechanisms of the active structures in the coal were obtained. It provides some theoretical support for the study of the reaction mechanism during the natural oxidation of coal.

2. MODELING AND COMPUTATIONAL DETAILS

The reactions occurring in the natural oxidation process of coal at low temperatures have been confirmed to be mainly oxidative exothermic reactions involving active groups and bridge bond structures.^{2,5} And it is generally believed that the active groups involved in the exothermic oxidation of coal at low temperatures are mainly hydroxyl, carboxyl, aldehyde, and aliphatic hydrocarbons.^{6,25,26} The bridge bond structure mainly includes methylene bridge bond, methylene ether bridge bond, subalkyl bridge bond with branched chain, and alkyl bridge bond with the hydroxyl.^{27–29} The active structures studied in this paper are shown in Table 1. The reaction sequence of organic structures in coal at high temperatures also follows the law of chemical reaction, that is, the smaller the activation energy is, the faster the reaction rate is. Therefore, the ReaxFF

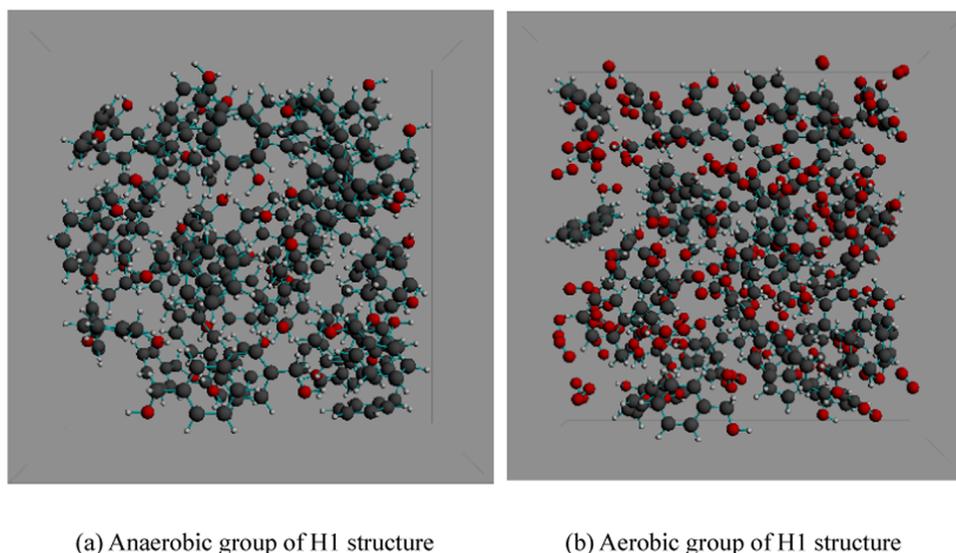


Figure 1. Periodic box of H1 structure.

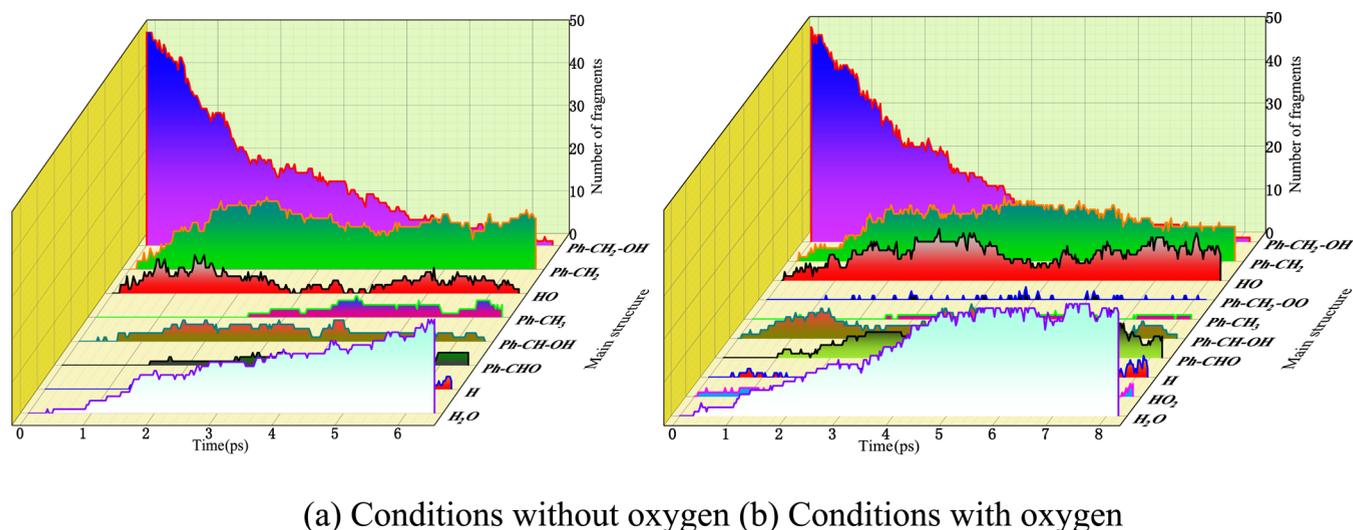


Figure 2. Reaction process of H1 and its products.

MD simulations of pyrolysis and combustion of active structures in coal were performed separately to obtain the detailed evolution mechanism of chemical reactions of active structures associated with spontaneous combustion.

For the same model compound, the periodic box containing 50 molecules and 100 O_2 molecules is the combustion group. The periodic box without O_2 is the pyrolysis group. The periodic box density is 0.5 g/cm^3 . The model results are shown in Figure 1.

Before the simulations were conducted, the reaction system was minimized using a 10 ps NVT Berendsen ensemble MD simulation. The volume and temperature parameters of this step are consistent with those under simulation conditions. No interactions between reactants occurred at this stage, as the Polak–Ribiere version of the conjugate gradient algorithm was used to prevent overlapping atoms. Subsequently, a simulation with a duration of 125 ps was performed at 5000 K with a step size of 0.25 fs. The simulation here adopts the NVT Berendsen ensemble and H/C/O/N/S/B field. This force field is often used by scholars to study the process of coal pyrolysis or coal combustion and has high adaptability.²³

3. RESULTS AND DISCUSSION

3.1. Analysis of Active Sites of Active Functional Groups in Coal. **3.1.1. Reaction Site of the Hydroxyl Structure.** Hydroxyl is one of the most active functional groups in the natural oxidation process of coal.³⁰ Studies have shown that the hydroxyl content in low-rank coal can account for up to one-quarter of the oxygen-containing functional groups.^{31,32} Therefore, a simulation study of hydroxyl-active groups was first carried out. In this paper, the alcoholic hydroxyl group (H1) and the phenolic hydroxyl group (H2) were selected as the research objects to analyze their reaction sites and pathways.

3.1.1.1. Ph-CH₂-OH (H1). First, the anaerobic and aerobic molecular dynamics simulations of the Ph-CH₂-OH (H1) structure are carried out, and the simulation results are shown in Figure 2.

Temperature only affects the reaction rate, not the reaction path. Since chemical reactions are usually more likely to occur at high temperatures, to reduce the simulation time, the set simulation reaction temperature of 5000 K is far higher than

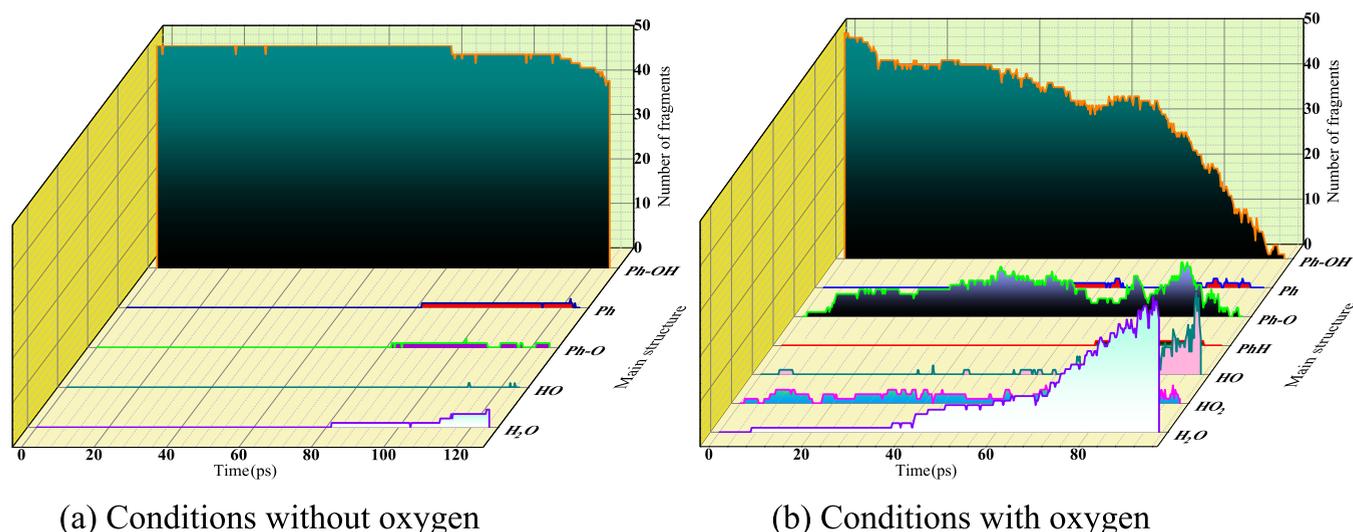


Figure 3. Reaction process of H2 and its products.

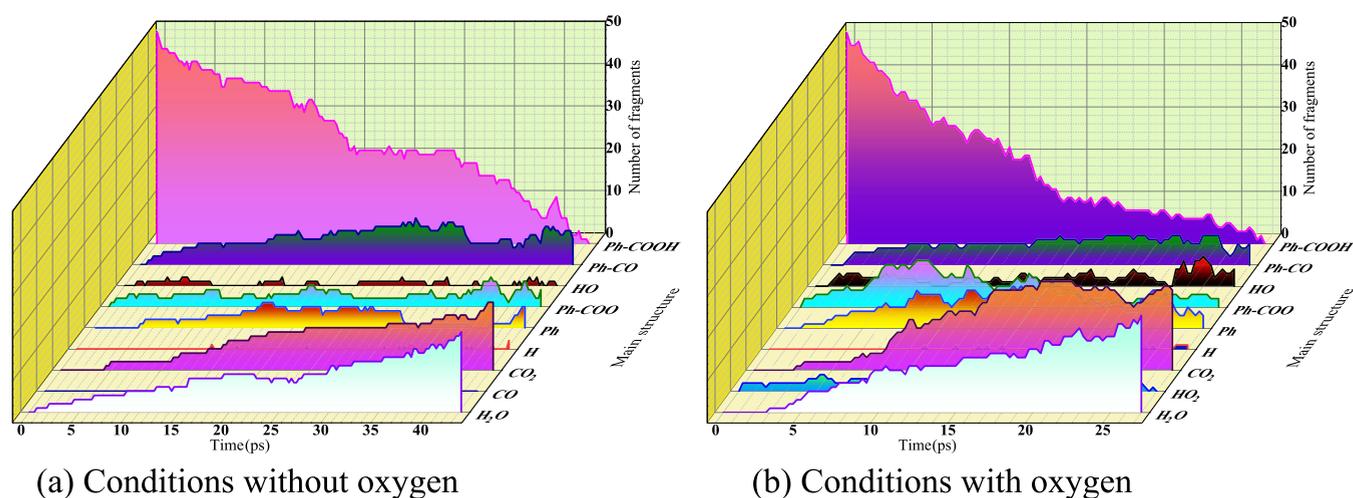


Figure 4. Reaction process of C1 and its products.

the experimental temperature.¹⁴ It can be seen from Figure 2a that H1 reacts completely in 6.45 ps under conditions without oxygen. Tracing the reaction process of H1 revealed that the structure reacted along two reaction paths. Reaction path 1 is that the H1 structure decomposes into Ph-CH₂ and OH radicals. The Ph-CH₂ content was relatively stable during the reaction. Over time, a small amount of Ph-CH₂ combines with H radicals to form a more stable Ph-CH₃. Reaction path 2 is the decomposition of H1 into Ph-CH-OH and H radicals. Subsequently, Ph-CH-OH further decomposes toward the more stable Ph-CHO structure. The active OH and H radicals decomposed form H₂O. This shows that the C-O bond in the alcoholic hydroxyl structure is the most easily broken under conditions without oxygen, followed by the C-H bond on the α -carbon atom.

It can be seen from Figure 2b that the reaction time of H1 is prolonged under oxygenated conditions, which is 8.23 ps. The reaction path of H1 under this condition is consistent with that under conditions without oxygen. Quantitatively, the addition of O₂ has a certain inhibitory effect on the decomposition of H1 into Ph-CH₂ and OH. This is because O₂ has a stronger electron-withdrawing property than OH and forms HO₂ with H atoms, which inhibits the reaction between OH and H.

There is always a certain content of OH radicals in the system, which inhibits the reaction of H1 along reaction path 1. The presence of O₂ also inhibited the formation of the Ph-CH₃ structure. The adsorption capacity of O₂ to H atoms increases the number of H1 structures along reaction path 2, which also leads to an increase in the content of Ph-CHO.

According to the above analysis, reaction path 1 is the easiest reaction path for the H1 structure, and it has high activity under conditions without oxygen.

3.1.1.2. Ph-OH (H2). The phenolic hydroxyl group is a relatively stable structure among oxygen-containing functional groups, but it exists in coals with different degrees of metamorphism. Therefore, this paper simulates Ph-OH (H2), and the results are shown in Figure 3.

As shown in Figure 3a, under conditions without oxygen, only a small amount of H2 reacts within the reaction time of 125 ps. Products of research significance have very little Ph and Ph-O. No PhH structure was generated. The simulation results reflect that the phenolic hydroxyl structure is a relatively stable oxygen-containing functional group in coal.

Under oxygenated conditions, H2 reacted completely after 95.25 ps, indicating that O₂ greatly promoted the reaction of H2. However, from the organic structure content in Figure 3b,

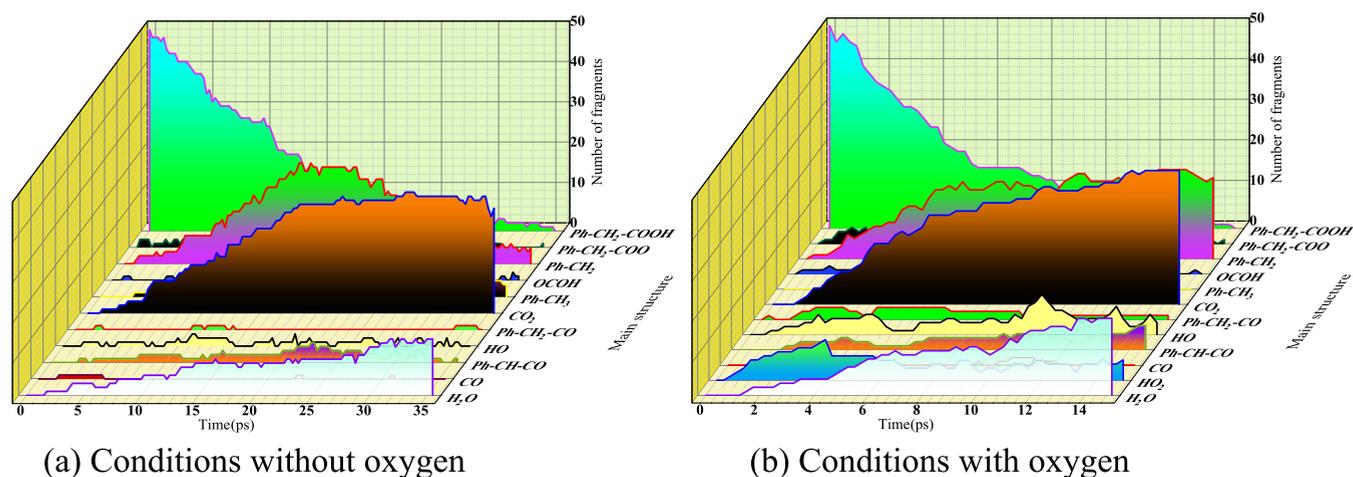


Figure 5. Reaction process of C2 and its products.

most of the H2 structure is split into structures that have no research significance under the action of O_2 . The strong electronegativity of O_2 promotes the reaction of H2 into Ph-O and HO_2 . HO_2 further generates H_2O . Subsequently, Ph-O decomposes into structures of no research significance. On tracking the source of OH, it can be found that OH originates from the reaction of O_2 and H radicals.

3.1.2. Reaction Site of the Carboxyl Structure. The carboxyl group is a highly active oxygen-containing functional group in the natural oxidation process of coal,²⁹ and the change of its structure content can reflect the oxidation exothermic situation of coal. In this paper, two carboxyl structures, Ph-COOH (C1) and Ph-CH₂-COOH (C2), were selected to analyze their reactions in the absence and presence of oxygen conditions.

3.1.2.1. Ph-COOH (C1). First, the reaction sites and pathways of Ph-COOH (C1) were analyzed, and the simulation results are shown in Figure 4.

As can be seen in Figure 4a, C1 reacted completely in 43.25 ps under conditions without oxygen. And C1 has two reaction paths. Reaction path 1 is that C1 decomposes to Ph-CO and OH. Ph-CO undergoes little further reaction until molecular cleavage. From Ph-CO it is difficult to generate CO because the large π bond on the benzene ring forms a conjugated system with the π bond of C=O, which makes the structure more stable. The OH radical reacts to form H_2O . H participates in the generation of H_2O , Ph-COO continues to generate CO_2 and C_6H_5 , and Ph splits with time. When C1 reaction is complete, the amount of H_2O (19) and CO_2 (16) generated is basically the same. By tracking the reaction process of generating H_2O and CO_2 , it can be obtained that the ability of C1 to undergo the reaction of reaction path 1 and reaction path 2 is basically the same.

It can be seen from Figure 4b that C1 reacts completely after 27 ps under oxygenated conditions, and the presence of O_2 accelerates the decomposition reaction of the C1 structure. And the reaction path is consistent with that under anaerobic conditions. From the simulation results, it can be concluded that the number of reactions of the C1 structure along reaction path 1 decreases, and the number of reactions along reaction path 2 increases. This is due to the adsorption of H by O_2 to form HO_2 , which promotes the formation of Ph-COO from the C1 structure, followed by the formation of CO_2 . The amount of H_2O produced under aerobic conditions is higher

than that under anaerobic conditions. Following the formation process of H_2O , it can be obtained that O_2 promotes the decomposition of unstable structures such as Ph into H radicals, and further forms H_2O .

3.1.2.2. Ph-CH₂-COOH. To further analyze the reactivity of the carboxyl structure, the Ph-CH₂-COOH (C2) structure was selected for comparative simulation, and the results are shown in Figure 5.

It can be seen from Figure 5a that under conditions without oxygen, C2 reacts completely after 35.5 ps, and there are two reaction paths. Reaction path 1 is that C2 decomposes to Ph-CH₂-COO and H. Ph-CH₂-COO decomposes to generate Ph-CH₂ and CO_2 . Then part of Ph-CH₂ generates Ph-CH₃, and another part of Ph-CH₂ decomposes into structures of no analytical significance. The amount of CO_2 produced by C2 under anaerobic conditions is greatly increased compared to C1 under pyrolysis conditions, which is due to the growth of the carbon chain, resulting in easier bonding of α -position C to carboxyl C. The appearance of the OCOH structure also reflects that the C-C bond between the carboxyl group C and the α -position C is easier to break. Reaction path 2 is that C2 decomposes into Ph-CH₂-CO and OH. Ph-CH₂-CO further dissociated H radicals to form a stable Ph-CH-CO structure. The OH radicals reacted to generate H_2O , but the amount of H_2O was much lower than that of C1 under conditions without oxygen.

Under oxygenated conditions, C2 reacted completely after 15 ps. In terms of process products, the addition of O_2 inhibited the formation of Ph-CH₃ in reaction path 1 and promoted the formation of Ph-CH-CO in reaction path 2. The amount of CO_2 and H_2O continued to increase, and the reason for this result is consistent with the interpretation of the results of the C1 simulation. Tracing the generation path of CO, it is found that under conditions without oxygen, the decomposition of the carbonyl structure in C2 will generate a small amount of CO. But since CO is highly unstable, further reactions take place. Under oxygenated conditions, CO is mainly formed from CO_2 at a later stage.

Comparing the reaction time of C1 and C2 and the number of reactions in each reaction path, it can be found that as the branch chain becomes longer, the reaction rate of the carboxyl structure increases and the amount of CO_2 produced increases.

3.1.3. Reaction Site of the Aldehyde Group. **3.1.3.1. Ph-CHO (Q1).** The change of aldehyde group content of coal

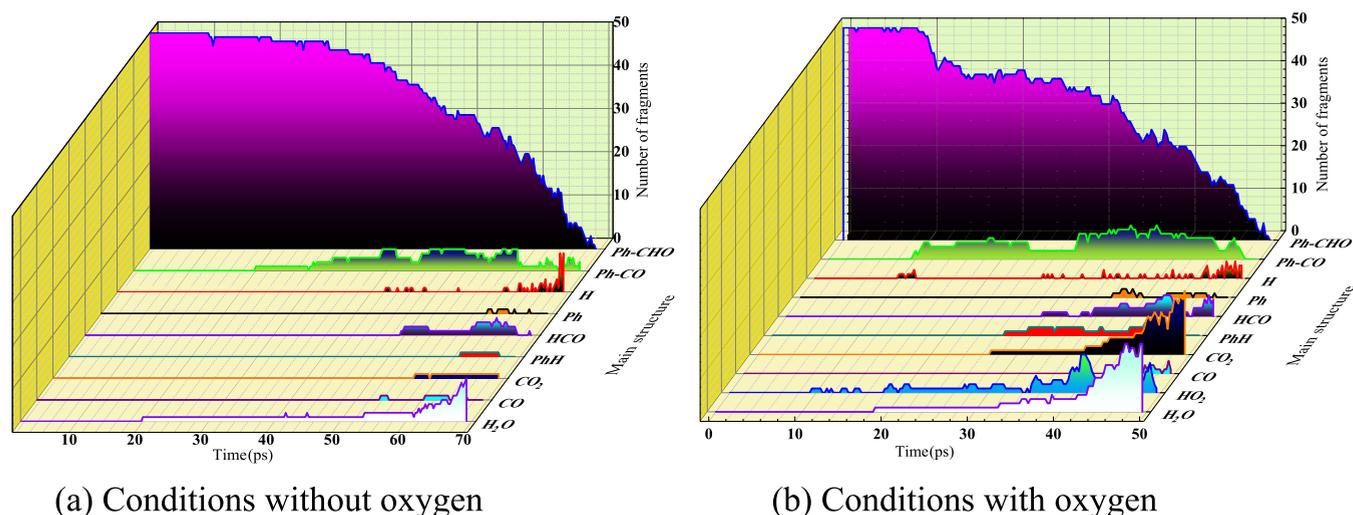


Figure 6. Reaction process of Q1 and its products.

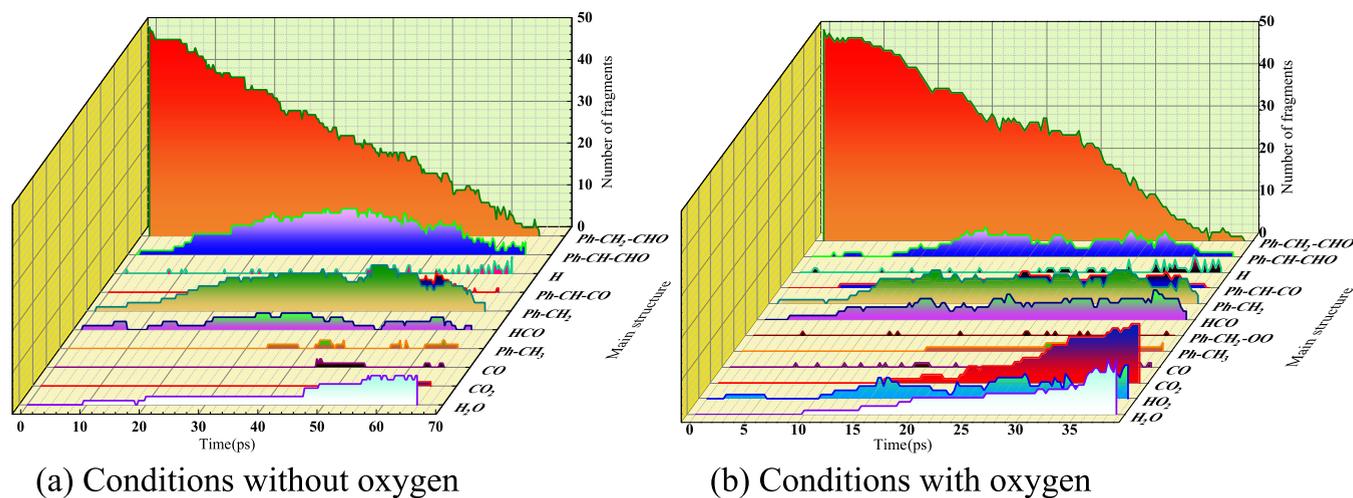


Figure 7. Reaction process of Q2 and its products.

during low-temperature oxidation can reflect the oxidation of coal.³³ In this paper, two aldehyde-containing structures Q1 and Q2 were selected for the ReaxFF molecular dynamics simulation. First, Q1 is simulated, and the results are shown in Figure 6.

As shown in Figure 6a, the reaction of Q1 was completed in 69.25 ps under conditions without oxygen. However, it can be seen from the overall reaction situation that Q1 has a certain stability so that the aldehyde group structure connected to the benzene ring did not participate in more pyrolysis reactions. Q1 is more prone to break down into irregular structures. A small amount of Q1 (5) can be decomposed into Ph-CO and H radicals. The Ph-CO structure will not continue to decompose to produce CO. This is because, from the point of view of the electronic effect, the large π bond on the benzene ring and the π bond of C=O form a π - π conjugated system, resulting in a certain stability of the structure. This makes it difficult to decompose CO from Ph-CO. In addition, there is a small amount of HCO decomposed from Q1.

Under oxygenated conditions, Q1 reacted completely after 49.5 ps, and the reaction rate was significantly accelerated. It can be seen from Figure 6b that the adsorption of H atoms on Q1 by O₂ leads to the increase of Ph-CO. This can explain the

reason why the aldehyde group belongs to the active group, but the Q1 structure cannot easily generate CO.

3.1.3.2. Ph-CH₂-CHO (Q2). To further analyze the reaction characteristics of the aldehyde group structure during coal oxidation, the Q2 structure was simulated and analyzed, and the results are shown in Figure 7.

As can be seen in Figure 7a, under conditions without oxygen, Q2 reacted completely after 68.75 ps, mainly by two reaction paths. Reaction path 1 is that Q2 decomposes into Ph-CH-CHO and H. Part of Ph-CH-CHO was subsequently decomposed into Ph-CH-CO. The number of Q2 passing through this reaction path is about half of the total number of Q2. Reaction path 2 is that Q2 decomposes into HCO and Ph-CH₂. The unstable HCO structure participates in other reactions and rarely generates CO and CO₂. A small part of Ph-CH₂ generates Ph-CH₃, and most Ph-CH₂ is cleaved over time, forming a structure of no research significance. Quantitatively, the magnitude of Q1's ability to respond along the two reaction pathways is basically the same.

As shown in Figure 7b, the reaction time of the Q2 structure was greatly shortened to 38.75 ps under oxygenated conditions. The adsorption of H atoms in the Q1 structure by O₂ promotes the formation of HO₂. This results in Q2

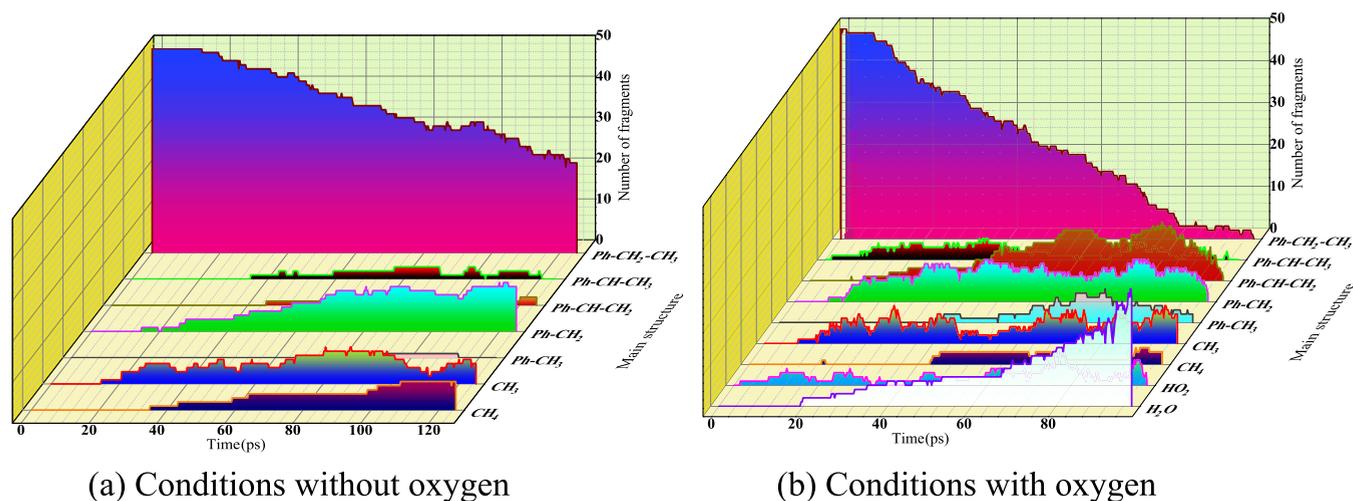


Figure 8. Reaction process of A1 and its products.

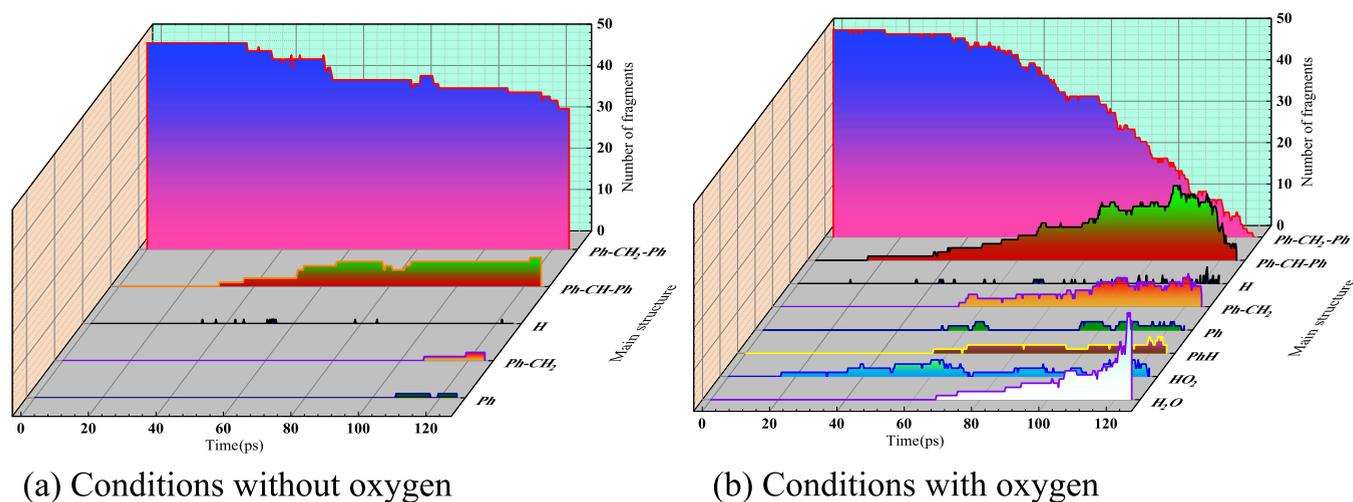


Figure 9. Reaction process of B1 and its products.

being more inclined to form Ph-CH-CO along reaction path 1. As can be seen from the figure, O₂ did not further promote the reaction of the Q2 structure along reaction path 2. Tracking the reaction process of HCO, it was found that O₂ occupies the adsorption sites of HCO and other active structures and promotes the decomposition of CO from HCO, but the unstable CO then forms more stable CO₂ with O atoms.

Comparing the simulation results of the Q1 and Q2 structures, it can be seen that the reaction rate of the aldehyde functional group increases with the distance from the benzene ring structure, and the amount of CO also increases.

3.1.4. Reaction Site of the Alkyl. Scholars believe that aliphatic hydrocarbons are the most active structures in the process of coal-oxygen reaction.³⁴ Therefore, the Ph-CH₂-CH₃ (A1) structure was established for simulation analysis. The results are shown in Figure 8.

It can be seen from Figure 8a that under conditions without oxygen, within 125 ps, the A1 structure reacted 31 times, indicating that the structure has low reactivity under pyrolysis conditions. There are two main reaction paths. The main reaction of A1 is reaction path 1, that is, the decomposition of A1 into Ph-CH₂ and CH₃ radicals. This is because the bond between the two aliphatic C atoms in A1 is the longest and

breaks first at high temperatures. From the generation amount of Ph-CH₃ and CH₄, it can be obtained that H radicals are more likely to form CH₄ with CH₃. Reaction path 2 is that H is decomposed from the α-position C atom of A1. The number of A1s reacting along this path is small. Compared with the number of H radicals decomposed by the α-position C atom of Ph-CH₂-CHO (Q2) and Ph-CH₂-OH (H1), the number of A1 decomposition is very small. This shows that the aldehyde and hydroxyl groups in Q2 and H1 can promote the decomposition of H from the α-position C atom.

Under oxygenated conditions, A1 reacted completely within 98 ps, and the reaction path was consistent with that under anaerobic conditions. Under this condition, A1 mainly reacts through path 2. Under the strong electronegativity of O₂, A1 generates Ph-CH-CH₃ and H radicals. Ph-CH-CH₃ continues to be affected by O₂ to form a more stable Ph-CH-CH₂ structure, which also reflects the strength of chemical bonds in the A1 structure. This path forms a large number of unstable HO₂ radicals, which subsequently form H₂O. Under this condition, the number of reactions passing through path 1 accounts for about one-third of the A1 structure, which is greatly reduced compared with the number of reactions in this path under anaerobic conditions. From the perspective of quantum chemistry, the H atom on the methine

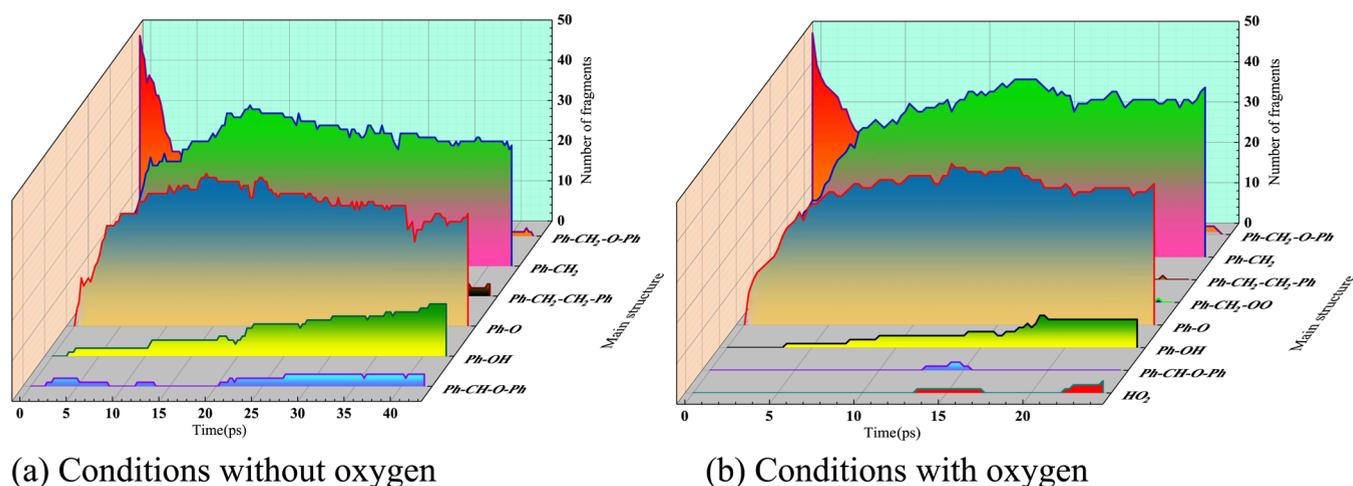


Figure 10. Reaction process of B2 and its products.

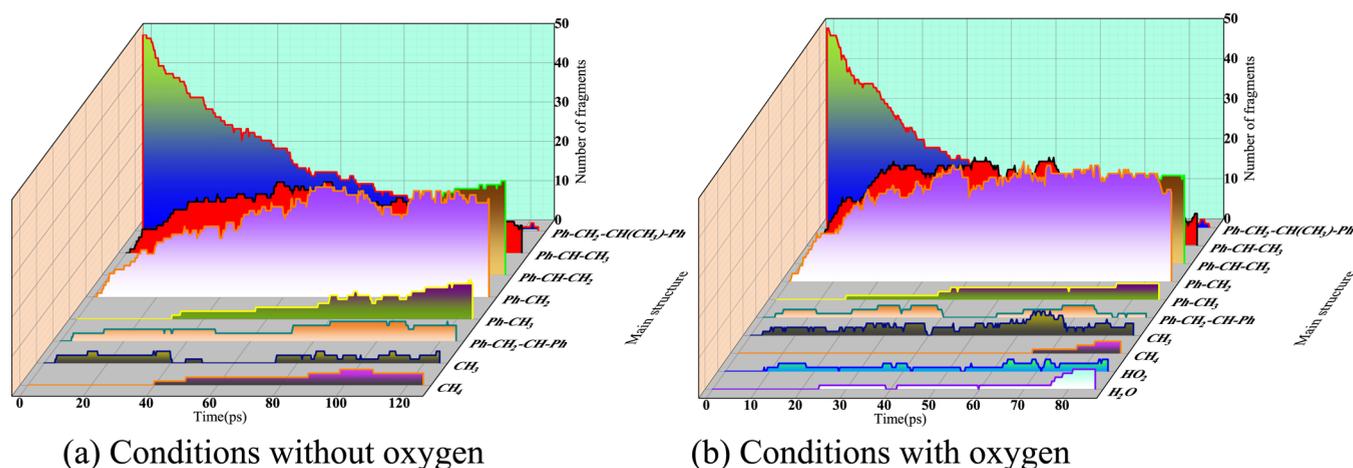


Figure 11. Reaction process of B3 and its products.

group in the $\text{Ar}-\text{CH}_2-\text{CH}_3$ structure has the lowest charge density and has a high ability to lose electrons.³³ Therefore, O_2 adsorbs the H atom on the methine group to form $\text{Ph}-\text{CH}-\text{CH}_3/\text{Ph}-\text{CH}-\text{CH}_2$.

It can be seen from the simulation results that the presence of O_2 has a great influence on the A1 reaction, which promotes the A1 structural reaction and generates a large amount of H_2O . During the reaction, a small amount of $\text{Ph}-\text{CH}(\text{OO})-\text{CH}_2$ and $\text{Ph}-\text{CH}(\text{OO})-\text{CH}_3$ structures appeared in small amounts and at high frequency. Due to the high activity of these structures, they can only appear for a short time under high-temperature conditions, which is consistent with studies on low-temperature natural oxidation of coal.^{29,35}

3.2. Analysis of Active Sites of Bridge Bonds during Coal Oxidation. The bridge bond is also an active structure that is easy to react with oxygen at room temperature.²⁹ The following four structures are selected for calculation and analysis.

3.2.1. Methylene Bridge Bond (B1). First, the simulation analysis of $\text{Ph}-\text{CH}_2-\text{Ph}$ (B1) under anaerobic and aerobic conditions is carried out, and the results are shown in Figure 9.

It can be seen from Figure 9a that B1 reacted 26 times within 125 ps under conditions without oxygen. This indicates that the activity of the B1 structure in coal is low under pyrolysis conditions. Among them, seven of B1 structures are

decomposed into the $\text{Ph}-\text{CH}-\text{Ph}$ structure. There are few $\text{Ph}-\text{CH}_2$ and Ph structures, indicating that the C–C bond between the aromatic ring and the methine group is not easily broken under pyrolysis conditions. Other structures produced by the B1 reaction do not have better analytical significance.

It can be seen from Figure 9b that the B1 structure reacts completely within 125 ps after adding O_2 . The 18 B1 structures are promoted to form $\text{Ph}-\text{CH}-\text{Ph}$ structures due to the adsorption of H atoms by O_2 . Over time, the $\text{Ph}-\text{CH}-\text{Ph}$ structure cleaved, but no more analytically meaningful structures were formed. Second, under this condition, the amount of $\text{Ph}-\text{CH}_2$ and Ph formed by B1 also increased. This indicates that the presence of O_2 promotes the cleavage of the C–C bond between the aromatic ring and the methine group. From the simulation results, B1 is a relatively stable bridge bond structure in coal. But with the increase of O_2 , the reaction of this structure is also promoted.

3.2.2. Methylene Ether Bridge Bond (B2). Molecular dynamics simulations were performed on the $\text{Ph}-\text{CH}_2-\text{O}-\text{Ph}$ (B2) structure in the absence and presence of oxygen, and the results are shown in Figure 10.

It is obtained from Figure 10a that the reaction of the B2 structure is complete in 42.5 ps under conditions without oxygen. The reaction that takes place for B2 to decompose into $\text{Ph}-\text{O}$ and $\text{Ph}-\text{CH}_2$. Subsequently, part of $\text{Ph}-\text{O}$ forms a

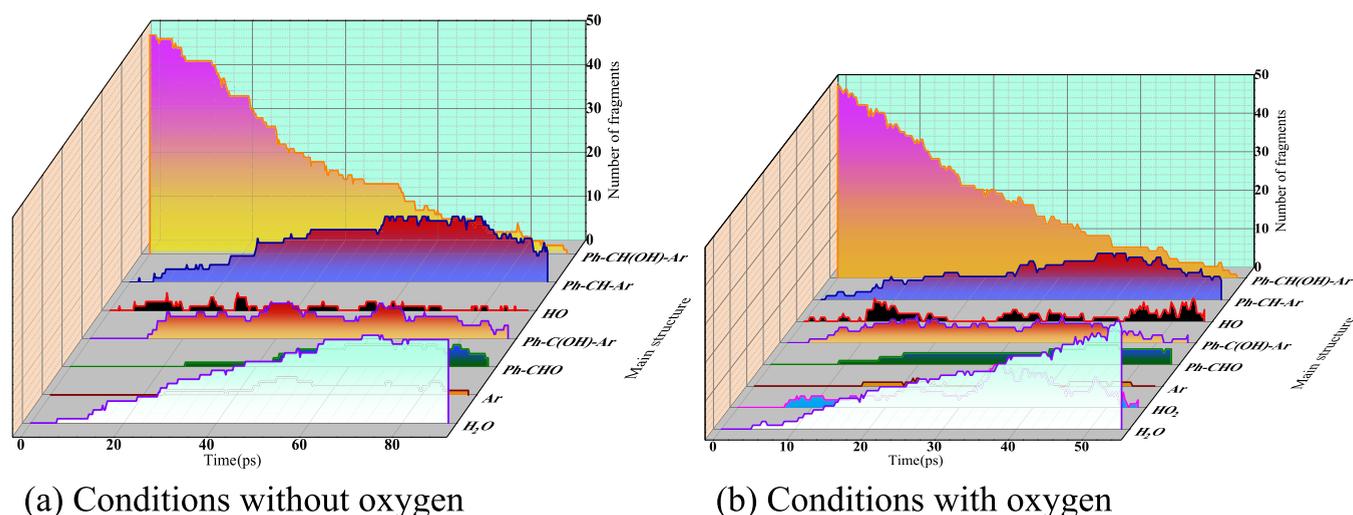


Figure 12. Reaction process of B4 and its products.

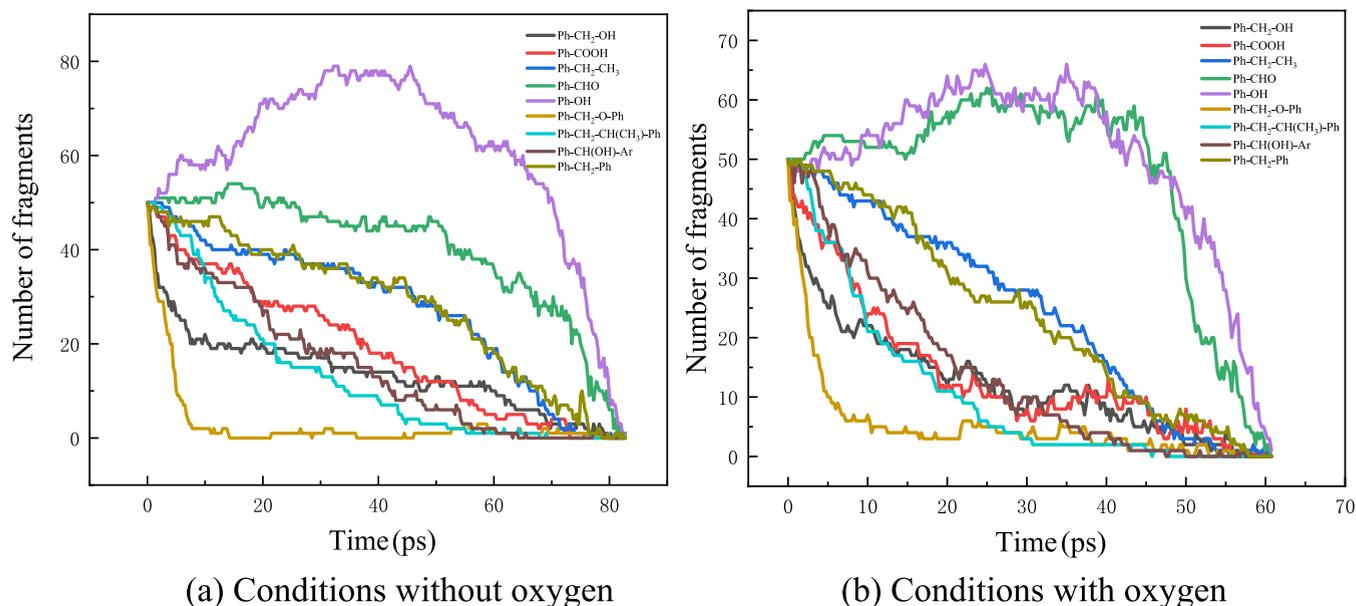


Figure 13. Reaction rates of nine types of structures.

more stable Ph-OH. Part of Ph-CH₂ forms the Ph-CH₂-CH₂-Ph structure. The simulation results show that the B2 structure has a higher reaction rate. From the point of view of the electronic effect, O has stronger electronegativity than C and has a strong negative induction effect. The large π bond of the benzene ring and the p orbital of O form a p- π conjugation effect. This results in the easy breakage of the C-O bond.

It can be seen from Figure 10b that the reaction rate of B2 is further accelerated under oxygenated conditions. The increase in the number of Ph-O and Ph-CH₂ indicates that O₂ accelerates the breaking of C-O bonds in B2. Ph-CH₂ is more inclined to form the Ph-CH₂-OO structure with O₂, which inhibits the formation of the Ph-CH₂-CH₂-Ph structure. However, the Ph-CH₂-OO structure is unstable, so the content has been kept very small. The content of Ph-OH decreases, which indicates that the adsorption capacity of O₂ for H atoms is stronger.

3.2.3. Subalkyl Bridge Bond with Branched Chain (B3). Ph-CH(CH₃)-CH₂-Ph (B3) is also one of the main bridge structures in coal, and the simulation results are shown in Figure 11.

It is obtained from Figure 11a that the B3 structure under conditions without oxygen just reacts completely at 125 ps, and there are two reaction paths. Reaction route 1 is the most important reaction route of B3, that is, B3 decomposes into Ph-CH₂ and Ph-CH-CH₃. This shows that the inductive effect of the benzene ring on the α -carbon atom is stronger, and the C-C bond of the bridge bond is easily broken. Ph-CH-CH₃ then forms the more stable Ph-CH-CH₂. Part of Ph-CH₂ forms Ph-CH₃. Reaction route 2 is that a small fraction of B3 forms Ph-CH₂-CH-Ph and CH₃. CH₃ reacts to form CH₄.

Under oxygenated conditions, the B3 structure reacted completely after 86 ps. It can be seen from Figure 11b that O₂ accelerates the decomposition reaction of B3, but the reaction site of the structure does not change. From the changing trend

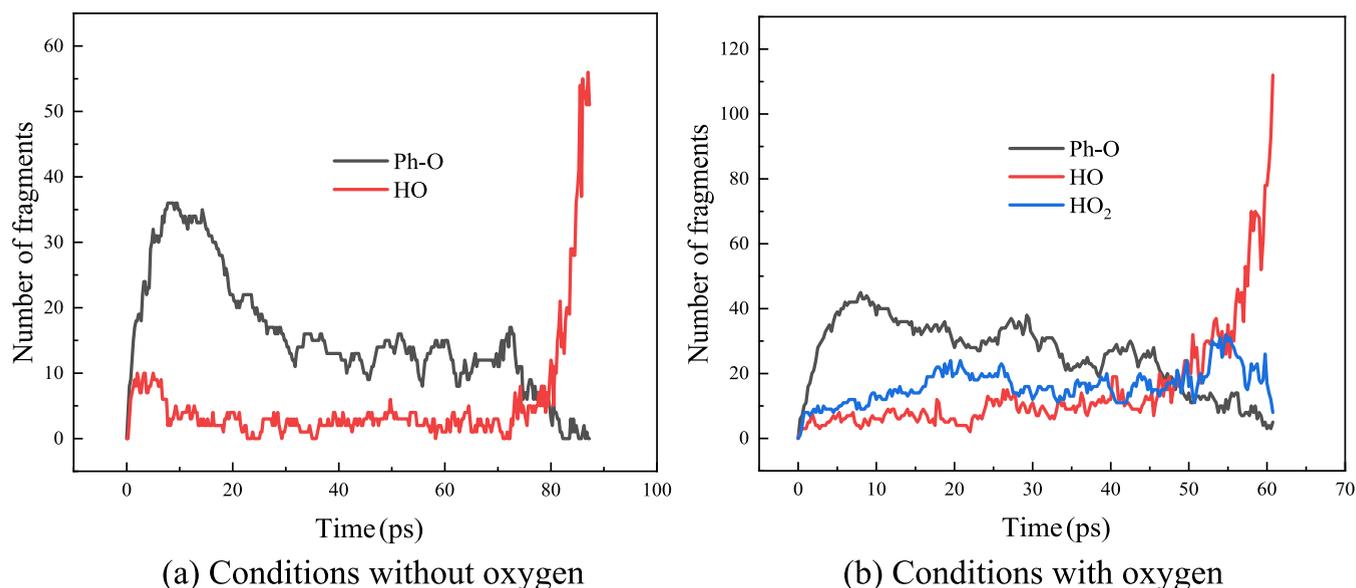


Figure 14. Free radicals in the reaction process of nine types of structures.

of the curve, it can be seen that Ph-CH-CH₃ in path 1 is more likely to form Ph-CH-CH₂ under the O₂ atmosphere. Under oxygenated conditions, the amount of B3 reacted through route 2 did not increase. Under oxygenated conditions, the reaction of CH₃ into CH₄ is inhibited, forming a CH₃OO structure. CH₃OO is a highly reactive free radical, so it did not appear significantly. The simulations show that CH₃ and Ph-CH₂ radicals tend to combine with O₂.

3.2.4. Alkyl Bridge Bond with Hydroxyl (B4). Molecular dynamics simulations of Ar-CH(OH)-Ph (B4) in the absence and presence of oxygen were performed, and the results are shown in Figure 12.

It can be seen from Figure 12a that B4 reacts completely after 90 ps under conditions without oxygen, and there are two reaction paths. Path 1 is that B4 generates Ph-CH-Ar and OH radicals. Later in the reaction, Ph-CH-Ar is cleaved over time. Path 2 is that B4 generates Ph-C(OH)-Ar and H. There is a small amount of Ph-C(OH)-Ar in the later stage to generate Ph-CHO and Ar. OH and H radicals generate H₂O. Comparing with the reaction times of the H1 structure, the step size of the B4 reaction increases significantly under anaerobic conditions. This is because the C atom in the B4 structure is affected by the δ - π hyperconjugation effect of the benzene rings connected on both sides, which makes the structure more stable, so the C-O bond is not easily broken.

Under oxygenated conditions, B4 reacted completely after 54.25 ps, the reaction rate was accelerated, and the reaction path did not change. But from the content of free radicals OH and HO₂, it can be seen that O₂ promotes the further reaction of the two reaction paths.

3.3. Reaction Rate Analysis of Active Structures during Coal Oxidation. To further analyze the reaction rate of each active structure, nine types of structures were placed in the same periodic box for simulation. The results are shown in Figure 13.

It can be seen from Figure 13a that the nine types of structures react completely within 82.75 ps under conditions without oxygen. The reaction rate for each structure changed considerably compared to the pyrolysis reaction under separate conditions. The specific reaction sequence size of each

structure is of the order B2 > H1 > B3 > B4 > C1 > A1 = B1 > Q1 > H2. The results of this reaction sequence are consistent with Shi's³⁴ research results from the perspective of quantum chemistry. This indicates that the interaction between the active structures in coal can promote the oxidation reaction of coal.

In the absence of oxygen, the A1, B1, B2, B3, and B4 structures in the mixed periodic box reacted faster than their own reaction rates under pyrolysis conditions, and their reaction rates are consistent with their reactions under oxygenated conditions alone. This indicates that the active structures in the periodic box interact with each other under conditions without oxygen to promote the reaction. By tracing their reaction paths and production amounts, it can be found that the reaction paths under this condition are consistent with their reactions under oxygenated conditions alone. This indicates that the oxygen-containing functional group structure and OH radicals play an important role in the reaction process. As shown in Figure 14a, OH radicals are generated in a certain amount at the beginning of the structural reaction and remain in the form of high-frequency vibration throughout the reaction process. By tracking the process of the OH radical reaction, it can be found that the OH radical greatly participate in the reaction of the adsorption of H atoms in the active structure. Comparing the reaction rates of the Ph-O structure in the absence and presence of oxygen, it can also be concluded that the structure plays an important role in conditions without oxygen in the self-reaction process of coal.

The reaction rates of H1 and C1 are somewhat delayed compared to their reactions alone under conditions without oxygen. This is due to its high reactivity, and the generated OH and H radicals can participate in their own further reactions when under reaction conditions alone. Under the condition of the mixed structure, the periodic box structure becomes larger, and the free radicals decomposed by H1 and C1 are not able to further affect their own reactions. This explanation can be further corroborated by the apparent decrease in the H1 reaction rate after 8.25 ps.

The reaction rate of Q1 and H2 was the lowest among the nine structures. It can be seen from Figure 13a that the number

of Q1 and H2 both increased significantly during the reaction, which indicates that the Q1 and H2 structures are more stable than other structures. During the reaction, the O in Ph–O formed after the decomposition of the B2 structure adsorbs the H atoms of the surrounding structure to form the H2 structure. The increase in the Q1 structure is mainly generated by a small amount of H1 and C1 structures.

In general, the reaction rate of each structure can reflect that the coal molecular structure has a high self-reaction ability under conditions without oxygen.

Under oxygenated conditions, all of the structures reacted completely within 60.75 ps, and the reaction rates all increased. The specific reaction sequence is of the order B2 > H1 > B3 > C1 > B4 > B1 = A1 > Q1 > H2, indicating that the reaction sequence of each active group changes little after adding O₂. The reaction sequence of C1 was advanced after the addition of O₂, indicating that the addition of O₂ could further promote the formation of CO₂. The amount of H2 decreases. This is because O₂ has stronger electronegativity, desorbing H radicals as well as occupying the active sites of the structure. This reason can be reflected in the decrease in the reactivity of Ph–O in Figure 14b. It is also due to the strong electronegativity of O₂ that the H1 and B4 structures generate more Q1 structures. This result is consistent with the results of individual reactions of each structure under oxygenated conditions.

4. CONCLUSIONS

In this paper, the oxygen-free pyrolysis and oxygen-containing combustion of nine types of active structures in coal were simulated by the ReaxFF molecular dynamics method. The reaction paths and mechanisms of active structures in coal were obtained by analysis. The main conclusions are as follows:

- (1) By analyzing the individual simulations of active functional groups, it is found that the reactive sites of active functional groups are basically the same in the absence and presence of oxygen, but the presence of O₂ greatly changes the number of reactions of each structure along different paths. O₂ has a certain inhibitory effect on the reaction of H1. As the branched chain grows, the reaction paths of C2 and Q2 follow the direction of the reaction of carboxyl and aldehyde groups to CO₂ and CO. The H2 and Q1 structures were the least reactive. Due to the strong electronegativity of O₂, it is more inclined to generate HO₂, which in turn affects the change of the reaction path of functional groups.
- (2) The simulation analysis of the bridge structure alone simulated that O₂ accelerates the reaction of the bridge structure, but does not change its reaction path. B2 is the most active bridge bond structure. Combining the reaction rates and reaction process products of A1, B1, and B3 structures, it is obtained that O₂ has the greatest promotion effect on the reaction of aliphatic hydrocarbon structures. Due to the hyperconjugation of the B4 structure, its reactivity is weaker than that of H1.
- (3) Analysis of the simulation results of the mixed periodic box with nine structures shows that the reaction sequence under conditions without oxygen is B2 > H1 > B3 > B4 > C1 > A1 = B1 > Q1 > H2. This order does not change much from the reaction order of the active structure under oxygenated conditions. By tracing the

reaction path of the structure, it was found that the OH radical and oxygen-containing radicals in the absence of oxygen have a great influence on the reaction of the active structure. The reaction rates of the A1, B1, B2, B3, and B4 structures under anaerobic conditions were accelerated, consistent with those of their aerobic conditions alone. The more stable H2 and Q1 structures are formed when some oxygen-containing structures in coal react.

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Notes

The authors declare no competing financial interest.

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