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Technical Report

Analysis of Low Temperature-oxidation Mechanism for Coal by Using High Resolution Solid State NMR and Gas Analysis

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Abstract

Spontaneous combustion property of low rank coal, an important issue in coal science, has been studied extensively. However, there are few studies discussing the quantitative chemical structural changes of coal during its oxidization under 80°C. In the present study, low rank coals of X and Y were oxidized in an adiabatic vessel where their temperature was increased due to spontaneous heating. Generated gases of H_2O, CO_2, and CO were analyzed by gas chromatography during the oxidization. As a result, coal Y, which was more easily oxidized than coal X, showed higher generation rates of CO_2 and CO gas than coal X. Some of the H_2O generated during the oxidation must have remained in coal as adsorbed water since the amount of water in the oxidized coal was higher than that before oxidation. ^{13}C MAS NMR spectra of coal X and Y indicated that the chemical reaction producing carboxyl acid in coal Y is more activated than that in coal X. Furthermore, the number of aromatic carbons was reduced during the oxidization. It implied that aromatic carbon might contribute to the oxidization reaction. Coal Y before oxidation had a smaller number of aromatic carbons per one cluster than coal X, while the structural parameters of aliphatic carbons in coal X and Y were almost the same. It is considered that the smaller number of aromatic carbons destabilize carbon radicals more to generate "active" species. Such active carbon radicals are suggested to also react with oxygen in the atmosphere.

1. Introduction

Coal is a fossil resource that is extensively used throughout the world as a raw material for steelmaking and fuel for power generation. Japan relies on imports for these fossil resources, which require lengthy marine transportation of resources as well as its storage and management in factories. In particular, coal requires appropriate safety management because it reacts with oxygen in the air to generate heat (spontaneous heating), which can lead to ignition.[1)]

In recent years, driven by soaring prices due to rising global demand for coking coal, the steel industry has increasingly utilized low-grade coal with abundant reserves and low carbonization. However, expanding the use of low-grade coal also means an increased risk of spontaneous heating. Furthermore, biomass resources, which are expected to play a crucial role in CO_2 reduction measures, are also known to exhibit spontaneous heating characteristics similar to coal.[2)] Therefore, technology for the suppression of spontaneous heating is essential not only for the immediate use of low-grade coal but also for the future CO_2 reduction measures.

Many studies[1, 3–20)] have been conducted on the spontaneous heating of coal. For example, Miyakoshi et al.[6)] reported a tendency for lower-grade coal to have a higher calorific value. Furthermore, they reported correlations between the calorific value and the specific surface area, oxygen content, and water content of low-grade coal. In addition, there exists correlations between oxygen content and specific surface area as well as between oxygen content and water content, all of which have unclear causal relationships with calo-

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rific value.

Moreover, spontaneous heating is essentially an oxidation reaction that involves chemical structural changes, such as the formation and decomposition of oxygen functional groups, in coal. Although there have been studies observing various reactions, they have focused on oxidation reactions at high temperatures above 100°C, and there have been few studies on oxidation reaction mechanisms from near room temperature to 80°C, which is an important range for heat generation countermeasures. It is also believed that the water content in coal is considered to have an effect on these oxidation reactions.[13)] However, as previous studies have shown[13, 14)], the actual reaction system is complicated by the addition of water produced by the oxidation reaction in excess to that originally contained in the coal.

Therefore, to elucidate the spontaneous heating mechanism, we considered it necessary to first clarify the oxidation reaction mechanism of dry coal, in which the water that is originally retained by the coal has been eliminated, and then elucidate the oxidation reaction mechanism of coal by retaining the original water.

In this study, two types of coal with different spontaneous heating properties were dried as previously reported,[16)] and their self-heating temperature rise behavior up to 80°C was analyzed using the R70 method. Gas analysis was performed on the gases generated during the oxidation. Furthermore, chemical structure analysis of the recovered oxidized coal was conducted using nuclear magnetic resonance (NMR) spectroscopy, and the differences in the oxidation reaction mechanisms between the two coal types were examined based on the chemical structural changes.[17)]

2. Experiments

2.1 Sample preparation and evaluation of coal self-heating properties

After pulverizing all of coal X and Y to a particle size of 212 μm or less, 180 g of the coal sample was promptly filled into the sample container of the R70 test apparatus[18)]. To remove water in the coal, it was dried for 24 hours under a nitrogen atmosphere at 107°C, then held until the sample temperature reached and stabilized at 40°C. Subsequently, the coal was oxidized by switching the feed gas from 100% nitrogen to 100% oxygen, while operating the system to maintain the flow gas temperature at the coal temperature and the process of raising the temperature to 100°C by coal spontaneous heating was evaluated. In practice, multiple tests with different target temperatures were conducted to prepare oxidized coal samples at various oxidation temperatures. The nitrogen and oxygen gas supply rates were both set to 50 ml/min during this process. A schematic of the R70 test apparatus is shown in **Fig. 1**[17)]. CO and CO_2 were determined by an Agilent 490 micro-GC after passing the gas through the sample vessel. The property values of coal samples X and Y before and after the R70 test are shown in **Table 1**[17)].

2.2 Solid-state NMR measurement

NMR measurements[21)] were performed on the coal samples before oxidation and on samples that reached temperatures of 60°C, 70°C, 80°C, and 100°C by the R70 test. Solid-state ^{13}C MAS (MAS: magic angle spinning) NMR spectra were measured using an Agilent INOVA500 spectrometer at magnetic field strength of 11.75 T. The Spin–Echo method with 90° and 180° pulses was used for the measurement, with a MAS rotation rate of 20 kHz, 90° pulse width of 3.2 μs, pulse repetition time of 100 s, and cumulative number of 4 096 times.

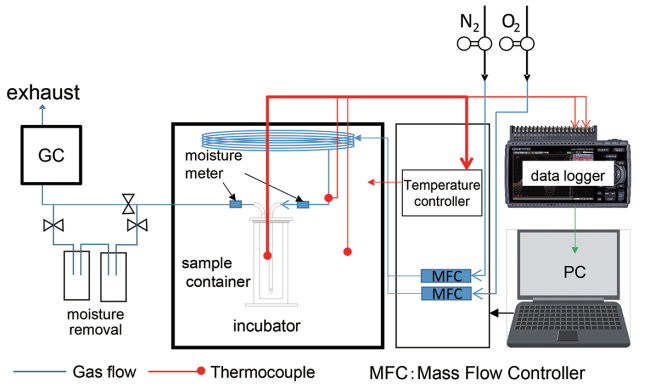

Fig. 1 Schematic explanation of the R70 apparatus for coal oxidation evaluation

Table 1 Proximate and ultimate analysis (d.b.; dry base) of original coal X, original coal Y, oxidized coal X, and oxidized coal Y treated at various temperatures using the R70 apparatus.

Coal		Proximate analysis (d.b. mass%)			Ultimate analysis (d.b. mass%)		
		Water	Ash	V.M.	C	H	Odir
X	Original	8.1	6.2	41.6	69.0	4.8	15.9
	Dry	1.3	5.6	42.1	70.6	4.6	16.1
	Oxidized at 60°C	2.6	5.5	42.3	71.9	4.6	15.9
	Oxidized at 70°C	2.3	5.7	41.6	71.2	4.5	15.6
	Oxidized at 80°C	4.6	4.5	49.9	72.2	4.6	16.4
	Oxidized at 100°C	2.8	5.7	42.0	70.0	4.8	16.2
Y	Original	19.9	2.0	49.7	69.0	4.6	21.5
	Dry	0.9	2.2	47.7	68.9	4.5	22.0
	Oxidized at 60°C	2.9	1.9	47.1	69.2	4.7	21.6
	Oxidized at 70°C	3.4	1.9	47.4	69.6	4.5	21.6
	Oxidized at 80°C	4.0	2.3	48.6	68.0	4.5	22.4
	Oxidized at 100°C	2.7	1.9	48.0	68.1	4.9	22.0

V.M.: Volatile mater, Odir: Oxygen concentration directly measured

Solid-state ^{1}H MAS NMR spectra were measured using a Bruker ASCEND800 spectrometer with magnetic field strength of 18.8 T was and a 0.7 mm diameter double resonance probe at the MAS rotation frequency of 100 kHz. The Depth method[21)] was used for the measurements to sufficiently reduce the ^{1}H signal derived from the probe member. The 90° pulse width was 1.3 μs, pulse repetition time was 5 s, and cumulative number was 3 200.

3. Results and Discussion

3.1 Evaluation of coal self-heating properties

The temperature rise curves for coal X and Y obtained from the R70 test are shown in **Fig. 2**[17)]. The time required for the temperature to rise from 40°C to 80°C was approximately 13 hours for coal X and approximately 4 hours for coal Y, and the rates of temperature increase were 3.1°C/h and 10°C/h, respectively. That is, industrial and elemental analysis showed that coal Y, which has a higher moisture content and oxygen content, has a higher spontaneous heating threshold than coal X. For both coal types, immediately after the start of the test, the temperature rapidly increased. The rate of temperature rise then slowed to become constant, and after approximately 60°C it increased gradually. The mechanism of the oxidation reaction changed around these temperature ranges.

3.2 Analysis of CO and CO_2 gases generated during spontaneous heat generation

The total amounts of H_2O, CO_2, and CO gases observed during the R70 test for coal X and Y are shown in **Fig. 3**(a) and (b)[17]. The total amounts of H_2O, CO_2, and CO gas generated were higher for coal X than coal Y, which has higher spontaneous heating properties. The reason for this may be that coal X took longer to reach 80°C than coal Y, resulting in a longer reaction time. Here, at 80°C for example, the molar ratios of H_2O, CO_2, and CO gases produced by coal X and Y were 1:7:3 and 1:9:6, respectively. Meanwhile, according to Wang et al.,[15] when subbituminous coal was subjected to low-temperature oxidation (60–90°C), the molar ratio of H_2O, CO_2, and CO gas generation was 21:3:1, indicating a higher water production compared to this study. This difference may be attributed not only to variations in coal type and temperature range but also to the larger coal mass (approximately 180 g) in the R70 apparatus and its layered state. In particular, the reason for the lower amount of water detected in coal Y than in coal X in this study may be because the adsorption of water by hydrogen bonding was more dominant in coal Y owing to its higher oxygen concentration as it has more oxygen functional groups. The O_2 gas concentration at the outlet of the R70 test was approximately 98% regardless of the oxidation temperature of the coal; and no difference could be detected in oxygen consumption rate because of the difference in oxidation temperature. This may be because the oxygen feed rate in the R70 test was much greater than the oxygen consumption rate of the coal.

Next, the gas generation rates for each coal type are shown in **Fig. 4**[17], and the gas generation rates for each gas type are shown in **Fig. 5**[17]. The CO generation rate increased rapidly at the start of the reaction, then decreased once, and subsequently increased slowly as the temperature rose to 50–60°C. The CO_2 and H_2O generation rates

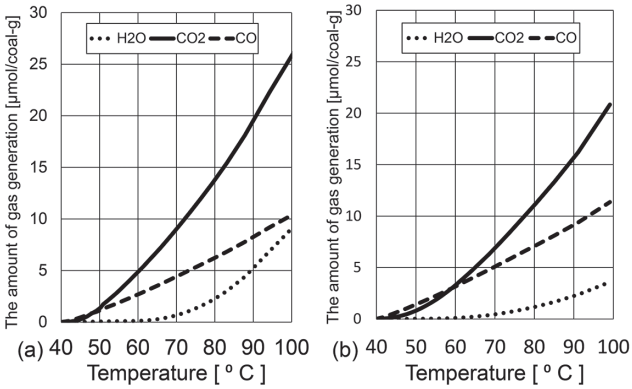

Fig. 3 The amount of gas generated from (a) coal X and (b) coal Y during oxidization

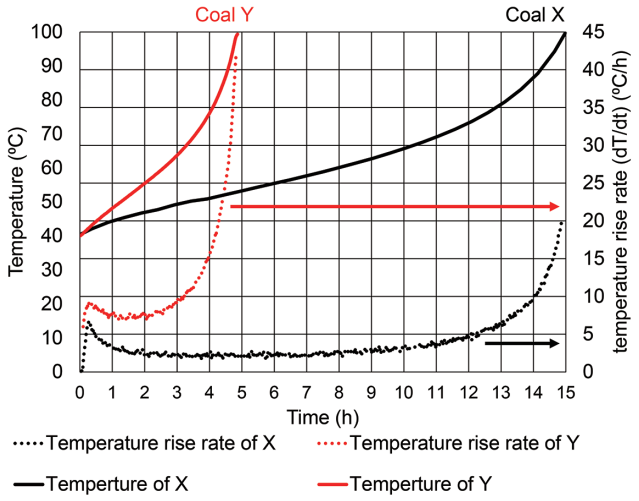

Fig. 2 Adiabatic self-heating curves of coal X and Y obtained by R70

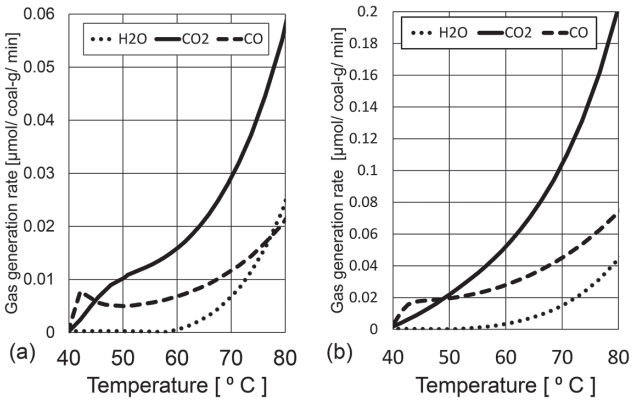

Fig. 4 Gas generation rate of (a) coal X and (b) coal Y during oxidization

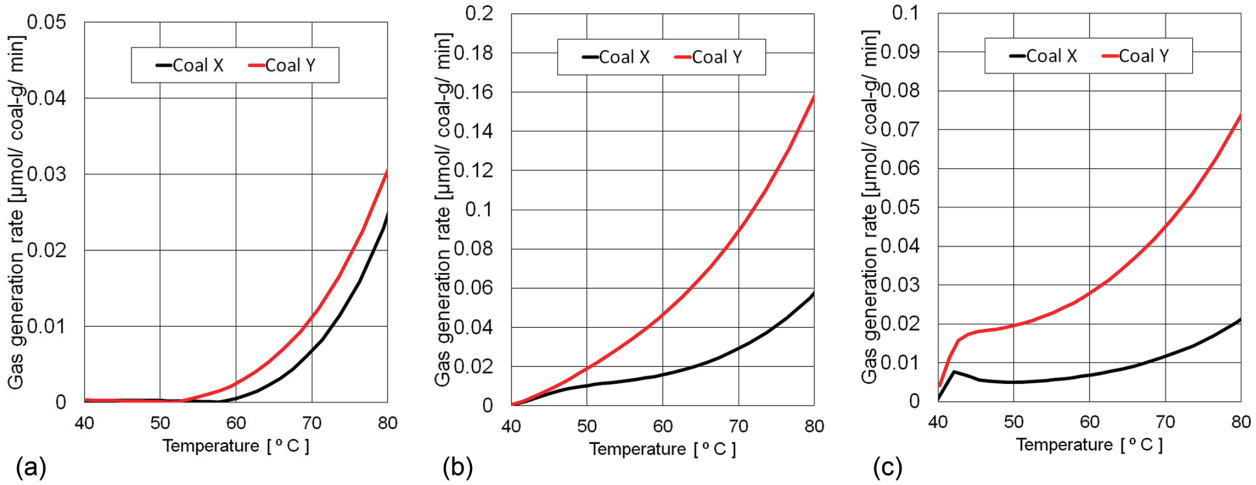

Fig. 5 Gas generation rate of (a) H_2O, (b) CO_2, and (c) CO during oxidization

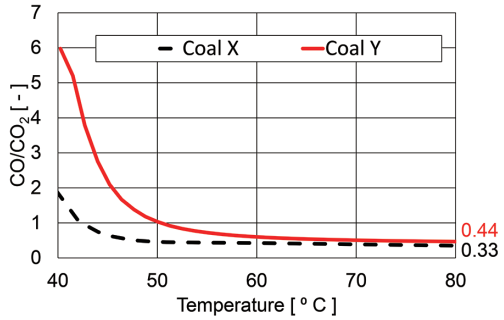

Fig. 6 CO/CO_2 ratio generated from coal X and Y during oxidization

increased monotonically with temperature. However, for most temperature ranges, both the CO_2 and CO generation rates were higher for Coal Y than for Coal X. This is because the oxidation rate of Coal Y is faster than that of Coal X, supporting previous findings[19] indicating that CO_2 and CO gases are generated by oxidation reactions. In this test, as coal heats up due to self-heating, the oxidation reaction rate is expected to accelerate further with increased heating rate. **Figure 6** shows the ratio of CO to CO_2 generation rates for each coal type. As temperature increased, the CO/CO_2 generation rate ratio approached a constant value specific to each coal type (X: 0.33, Y: 0.44). This trend was consistent with previous research[15] where the CO/CO_2 ratio approached a constant value for a given bituminous coal. These results suggest that: - During the initial oxidation phase, decomposition of the coal's inherent oxygen functional groups (1) primarily proceeds. - During the middle oxidation phase, decomposition of oxygen functional groups generated by oxidation (2) proceeds simultaneously with (1). - During the late oxidation phase, (2) primarily proceeds. Furthermore, H_2O generation commenced at approximately 60°C for both coal types. Thus, the trend of gas generation rate versus temperature was identical regardless of coal type. Since the temperature at which water generation became detectable as gas is close to the temperature where the heating rate shown in Fig. 2[17] began to rise sharply, it is possible that the water formation reaction contributes to the heat generation, or that the oxidation reaction accelerated sharply around 60°C, generating heat, which in turn accelerated water formation and led to its release as gas. This is likely because Coal Y has more oxygen functional groups than Coal X, enabling it to retain water even at high temperatures through hydrogen bonding. Therefore, to predict and evaluate the spontaneous heating of coal, it is considered necessary to determine the onset time and quantity of water generation.

3.3 Structural analysis of oxidized coal

To clarify chemical structural changes caused by spontaneous heating generation, ^{13}C MAS NMR spectra were measured for coal recovered after the R70 test. The ^{13}C MAS NMR spectra for coal samples X and Y are shown in **Fig. 7**(a) and (b)[17]. Coal before drying is labeled "original", coal after drying is labeled "dry", and coal recovered after the R70 test was stopped when the internal temperature reached 60°C, 70°C, 80°C, or 100°C due to self-heating is labeled "60°C", "70°C", "80°C", or "100°C", respectively.

Following previous literature[22], the functional groups in coal X and Y were quantified from the ^{13}C MAS NMR spectra and are shown as bar graphs in **Fig. 8**(a) and (b)[17]. The assignment of chemical shifts in the ^{13}C MAS NMR spectra to the coal structure is as shown in **Table 2**[17].

It is revealed that in Coal X, the amount of aldehyde or ketone

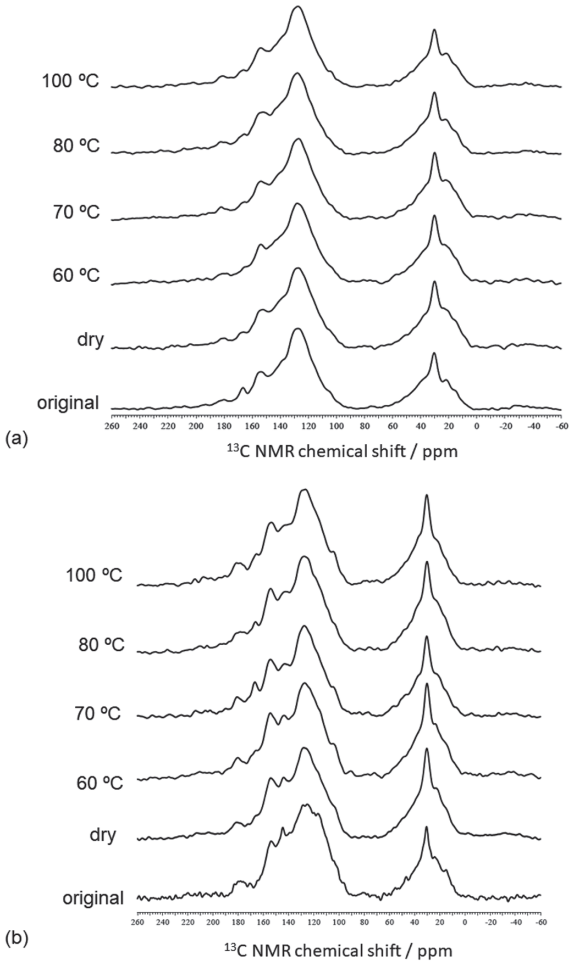

Fig. 7 ^{13}C MAS NMR spectra of (a) coal X and (b) coal Y

groups tended to increase as spontaneous heating progressed. Furthermore, the number of aromatic carbons bonded to hydrogen or carbons within the aromatic ring tended to decrease as oxidation progressed. Here, the structural changes in Coal X, particularly around the R70 test (comparing Coal X in its dry state before the R70 test with Coal X recovered when it reached 80°C during the R70 test), are shown in **Fig. 9**(a)[17]. The structural change rate (Δ) is calculated as follows and is defined by Equation (1) as the percentage change relative to the total functional group content of the coal before spontaneous heating.

$$\Delta(\%) = 100 \times ((\text{Functional group content after R70 test}) - (\text{Functional group content before R70 test}))/(\text{Total functional group content before R70 test}) \quad (1)$$

As a result, it was found that spontaneous heating up to 80°C produced 0.6 mmol of aldehyde or ketone groups per gram of coal (0.6 mmol/g-coal) in Coal X. This represented a change of Δ = +1.0% relative to the total functional group content of the coal prior to spontaneous heating. Furthermore, 0.3 mmol/g-coal of carboxyl groups were also generated (equivalent to Δ = +0.5%). On the other hand, the amount of hydrogen-bonded carbon atoms or carbon atoms within the aromatic ring decreased by 0.86 mmol/g-coal (Δ = −1.5%) due to spontaneous heating up to 80°C. This is estimated to be due to the difficulty in observing the decrease in hydrogen-bonded aromatic carbons or carbons within the aromatic ring, rather than an actual reduction. According to previous literature[23], it is clear

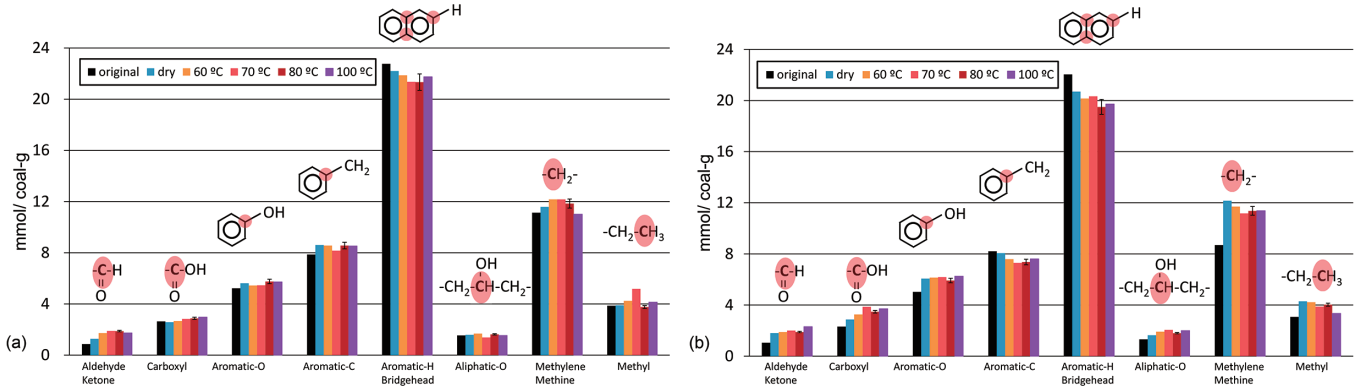

Fig. 8 Quantitative value of chemical structures of (a) coal X and (b) coal Y calculated by ^{13}C MAS NMR spectra

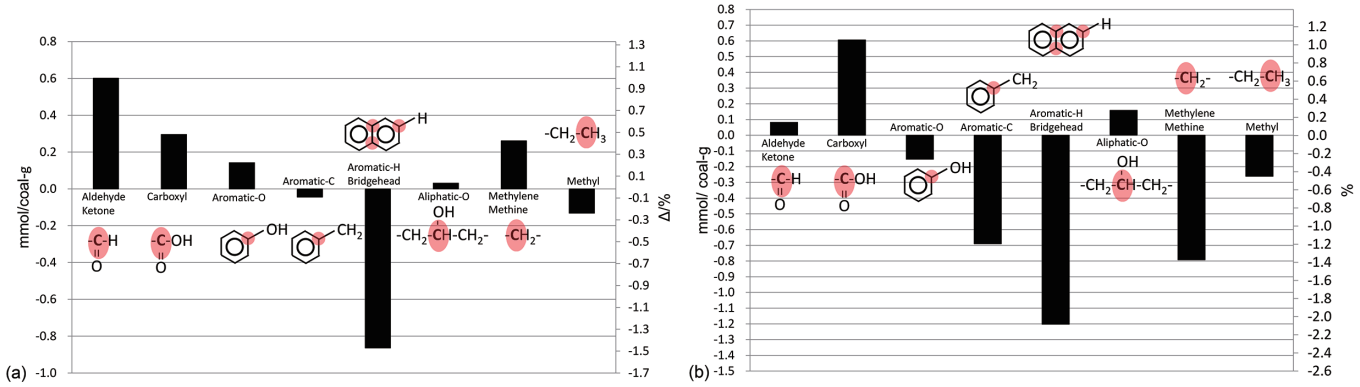

Fig. 9 Quantitative value of chemical structures of oxidized (a) coal X and (b) coal Y calculated by ^{13}C MAS NMR spectra at 80°C

Table 2 Chemical structural ratio of original coal X and Y calculated by ^{13}C MAS NMR spectra

Chemical shift (ppm)	Functional groups	Coal X	Coal Y
185 – 240	Aldehyde and Ketone groups	2.2	3.7
165 – 185	Carboxyl group	4.5	7.7
150 – 165	Aromatic O group	9.8	12.0
135 – 150	Aromatic C group	15.0	13.0
90 – 135	Aromatic H group	39.0	36.0
50 – 90	Aliphatic O group	2.8	4.5
22 – 50	Methylene and Methine groups	20.0	19.0
0 – 22	Methyl group	6.8	5.6

that when radicals are present, the spectrum originating from the nucleus species in their vicinity cannot be obtained. During coal oxidation reactions, carbon radicals and oxygen radicals are generated. Consequently, NMR signals originating from carbon near the generated radicals are lost, leading to a decrease in spectral intensity. Therefore, this experiment strongly suggests that new radicals were generated near the hydrogen-bonded aromatic carbon or carbon within the aromatic ring where spectral intensity decreased.

Based on the above analysis results, the spontaneous heating mechanism of dry coal X was estimated. The reaction mechanism is shown in **Fig. 10** (a)[17] and (b)[17]. First, it is thought that the previously reported reactions forming aldehyde or ketone groups proceeded, followed by the formation of carboxyl groups (a')[17]. At this stage, the carbon atoms in the coal that bonded with atmospheric

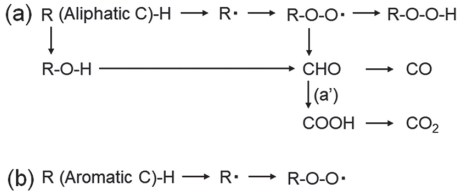

Fig. 10 Estimated oxidization reaction of dry coal

oxygen are considered to be aliphatic carbon atoms. Furthermore, since the formation of aldehyde or ketone groups is expected to yield the highest amount and also generate the largest amount of reaction heat, it is thought that the heat from this oxidation reaction was used to raise the temperature up to 80°C. Furthermore, the decrease in spectral intensity for aromatic carbon or carbon within the aromatic ring bonded to hydrogen strongly suggests formation of radicals. Since these radicals are considered to be aromatic carbon radicals, it is possible that an oxidation reaction of aromatic carbon, not previously observed in conventional findings as shown in Fig. 10 (b)[17], occurred.

As well as for Coal X, the ^{13}C MAS NMR spectra of unoxidized Coal Y and Coal Y recovered after the R70 test are shown in Fig. 7 (b)[17]. The quantitative analysis of each functional group at this stage is shown in Fig. 8 (b)[17]. These results indicate a tendency for the amount of carboxyl groups to increase as spontaneous heating progresses. Furthermore, it is found that the abundance of aromatic carbons bonded to carbon, methylene groups among aliphatic carbons, and carbons bonded to hydrogen or carbons within the aromatic ring among aromatic carbons tended to decrease as oxidation

progressed.

Here, the amount of structural change in coal Y and its change rate (Δ) are shown in Fig. 9 (b)[17], particularly around the time of the R70 test (comparing dry coal Y before the R70 test with coal Y recovered when it reached 80°C during the R70 test).The results revealed that natural heating (oxidation) up to 80°C increased the carboxyl group content in coal Y by 0.61 mmol/g-coal (Δ = +1.0%). Since more carboxyl groups formed in coal Y than in coal X, it is considered that the oxidation reaction generating carboxyl groups via the aldehyde group, as shown in Fig. 10 (a')[17], proceeded more extensively. On the other hand, the aromatic carbon to which carbon is bonded, the methylene group among the aliphatic carbon, and the aromatic carbons with hydrogen-bonded carbons or carbons within the aromatic ring decreased by 0.69 mmol/g-coal (Δ = −1.2%), 0.79 mmol/g-coal (Δ = −1.4%), and 1.2 mmol/g-coal (equivalent to Δ = −2.1%), respectively, due to spontaneous heating (oxidation) up to 80°C. Thus, the decrease in spectral intensity in the region corresponding to hydrogen-bonded aromatic carbon in the ^{13}C MAS NMR spectrum of Coal Y is considered to be due to radical generation, similar to Coal X. On the other hand, considering radical stability, the decrease in methylene groups among aliphatic carbons and in aromatic carbons bonded to carbon may indicate not only radical generation but also the formation of oxygen functional groups at these carbon positions.

Furthermore, the ^{1}H MAS NMR spectra of Coal X and Y before and after the spontaneous heating test are shown in **Fig. 11** (a)[17] and (b)[17]. No significant changes in the ^{1}H MAS NMR spectrum were observed with temperature. Additionally, the signal expected to originate from free water around 4.8 ppm was not observed in any temperature range. From the elemental analysis and industrial analysis values of each sample shown in Table 1[17], it was found that during oxidation up to 80°C, moisture increased with rising temperature. This suggests either the generation of new water during the oxidation reaction or the adsorption of atmospheric moisture during sample handling. However, the moisture content at 100°C decreased compared to 80°C, indicating that some of the generated moisture may have evaporated and been lost. In any case, despite containing 2.3–4.6% and 2.9–4.0% moisture after spontaneous heating for coal X and Y, respectively, no peaks originating from free water were observed in the ^{1}H MAS NMR spectra. Therefore, the water generated during spontaneous heating is thought to have existed as water interacting with the coal surface, where molecular motion is constrained (adsorbed water). This indicates that, in addition to the water detected in the gas analysis as a gas phase, water adsorbed onto the coal exists.

Based on the above analytical results, the estimated spontaneous heating mechanism of dry coal is as shown in Fig. 10[17]. While the oxidation reaction in Coal X was dominated by aldehyde group formation, in Coal Y the reaction progressed further, and it is considered that carboxyl group formation, as shown in Fig. 10 (a')[17], became dominant. Considering that the carboxyl groups generated by the oxidation reaction are formed via aldehyde groups, it is thought that at least an equivalent amount of aldehyde groups was generated alongside the carboxyl groups, and corresponding exothermic heat was also produced. Therefore, one of the main differences in the spontaneous heating mechanisms of dry coal X and Y lies in the reactivity (reaction rate or occurrence) of the aldehyde groups generated by the oxidation reaction.

3.4 Structural analysis of raw coal

The spontaneous oxidation reaction of coal is a chemical reaction between coal and oxygen. Therefore, the molecular structure of coal before oxidation is thought to significantly contribute to its spontaneous heating properties. We thus analyzed the molecular structure of coal before oxidation. To understand the average molecular structures of Coal X and Y, molecular structure parameters such as the degree of aromatic ring development, aliphatic side chain length, and number of chains as shown in **Table 3**[17] were calculated from the ^{1}H MAS NMR spectra, ^{13}C MAS NMR spectra, and elemental analysis values, following previously reported methods[24, 25]. Furthermore, average molecular structure models satisfying these parameters were constructed and are shown in **Fig. 12**[17]. These results revealed that, regarding the structural parameters related to aliphatic side chains—which have been previously implicated in the oxidation reaction—there were no significant differences between Coal X and Coal Y in terms of average side chain length or number of side chains.

Therefore, we investigated the possibility that differences in molecular structure other than aliphatic carbon might contribute to spontaneous heating. The results showed that Coal X has 11.5 aro-

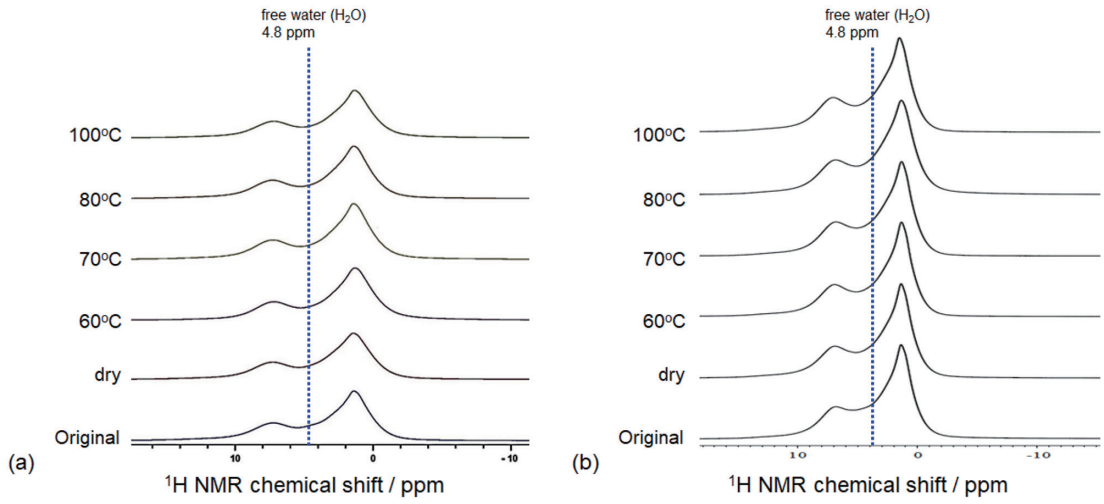

Fig. 11 ^{1}H MAS NMR spectra of (a) coal X and (b) coal Y

Table 3 Average of chemical structural parameters for coal X and coal Y

Coal	Number of aromatic carbons	Side chain length*	Number of side chains	Bridged chain length**	Ratio of aldehyde and ketone carbon	Ratio of carboxylic carbon
X	11.5	2.8	1.2	3.3	2.2	4.5
Y	8.0	2.9	1.0	2.3	3.5	7.7

*Side chain length: The number of an aliphatic side chain carbon, **Bridged chain length: The number of an aliphatic bridging chain carbon

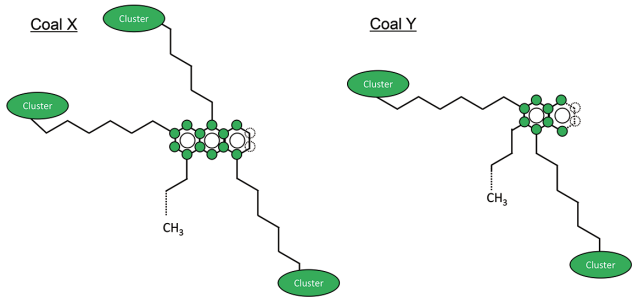

Fig. 12 Estimated average chemical structure of coal X and Y

matic carbon atoms, corresponding to 2-3 aromatic rings, while Coal Y has 8 aromatic carbon atoms, corresponding to 1-2 aromatic rings. Thus, Coal Y has an average aromatic ring number, which is smaller than Coal X by approximately one. The smaller the number of aromatic rings, the lower the resonance stabilization effect, making radicals less stable and increasing reactivity.[26] When reactions involving direct interaction between these aromatic carbon radicals and atmospheric oxygen (Fig. 10(b)) occur, coal Y, with fewer aromatic rings, is expected to exhibit enhanced reactivity. Therefore, it is thought that more oxidation reactions involving aromatic carbon, not previously known, occurred in coal Y. However, it is unclear whether oxygen functional groups such as aldehyde or carboxyl groups were generated as a result of the reaction of the aromatic carbon radical. Further investigation is needed regarding the stable structure ultimately reached by this aromatic carbon radical.

4. Conclusion

To elucidate the oxidation reaction mechanism below 80°C, which is critical for managing coal's spontaneous heating risk, we investigated two types of dry coal, X and Y. This involved monitoring temperature rise behavior by the R70 test, quantitative analysis of generated gases, and chemical structure analysis of oxidized carbon using solid state NMR. The results showed that the heating rate for coal Y is significantly higher than that for coal X, and both coals have a sharp increase in temperature around 60°C.

Gas generation analysis revealed that while CO_2 and CO generation rates are higher for coal Y than coal X across all temperature ranges, the total generation are nearly equivalent when comparing the same final temperatures reached. Chemical analysis of the oxidized carbon suggested higher amounts of adsorbed water in coal Y compared to coal X, a finding supported by ^{1}H MAS NMR analysis indicating adsorbed water as the main component.

Furthermore, carbon structure analysis using ^{13}C MAS NMR suggested that oxidation of both coals generates aldehyde and carboxyl groups, with the reaction from aldehyde to carboxyl group being accelerated particularly in Coal Y. Contrary to previous knowledge, it was newly indicated that aromatic carbon may contribute to the oxidation reaction.

Analysis of the average molecular structures of unoxidized coal X and coal Y revealed that the primary difference lay in the number of aromatic rings. This disparity is likely to have led to differences in the stability of aromatic carbon radicals, which in turn may have caused the variation in spontaneous heating properties. Actually, reports using electron spin resonance (ESR) spectroscopy on coal indicate the presence of numerous radicals in coal, and that the quantity of radicals changes with heating and reaction with oxygen.[27–29] In the future, elucidating the radical species and quantities in oxidized coal using methods such as ESR is expected to enable a more detailed understanding of low-temperature oxidation reactions in coal.

Acknowledgments

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