ABSTRACT: Our previous experimental study showed that Na⁺-exchanged coal prepared from low-cost natural soda ash is an excellent catalyst for steam gasification of low-rank coals using fixed-bed quartz reactors. However, it is difficult to experimentally clarify the effect of Na ion exchange on low-rank coal. In order to investigate the influence of Na⁺ ions on low-rank coal, this study determined the electronic state between the Na⁺-exchanged coal model and raw coal model and compared them using RHF/6-311G* and B3LYP/6-31G*. The experiments revealed that Na ion exchange has a significant effect on low-rank coal gasification. The model structure of low-rank coal is considered to change significantly in terms of the electronic state before and after Na exchange even with a simple main molecular structure. Molecular models where H of COOH/OH was ion-exchanged with one, two, and three Na ions were developed, and quantum chemical calculations were performed. The results showed that when the number of Na⁺-exchanged sites is increased, the electron state on the coal molecule becomes more negatively charged in the case of the Na⁺-exchange coal model. It is presumed that this contributes to enhancing the reactivity of low-rank coal and water vapor. In addition, weak bonds in the Na⁺-exchanged coal molecule were examined by calculating the difference in the value of the Mulliken and Löwdin bond orders before and after Na⁺ exchange. The results showed that the increase in the number of exchanged Na⁺ in the low-rank coal molecule model increased the number of weak bonds in the molecule. It is presumed that this contributes to enhancing the decomposition of low-rank coal.

INTRODUCTION

Coal combustion accounts for about a fourth of the total world energy consumption, and coal plays an important role in satisfying the world’s primary energy demand. However, at the current rate of annual use, global coal deposits will last for about 150 years. One means of reducing coal consumption is improving the utilization efficiency of heat obtained from coal. To achieve this aim, various technologies, such as supercritical thermal power generation, integrated gasification combined cycle, and polygeneration, have been developed. The use of low-rank coal (brown coal), a potentially abundant resource, is also important for establishing stable energy supply in the future. Nevertheless, at present, the use of low-rank coal as energy source has few advantages because of high production costs. Low-rank coal is generally characterized by a high volatile component and moisture content and low ignition temperature. In addition, low-rank coal has a higher oxygen content (15−30%) in oxygen-containing functional groups than high-rank coal does. Therefore, since low-rank coal tends to adsorb moisture, a large amount of energy is required to remove it.

Accordingly, several attempts have been made to overcome this limitation. For example, the Strategic Technical Platform for Clean Coal Technology in Japan has aimed to achieve low-rank coal gasification at 900 °C or less using a catalyst. To achieve this aim, many studies have been conducted on the use of Ni or K carbonate catalysts in the gasification of low-rank coal. As an example, gasification at 600 °C using Ni-supported Yallourn low-rank coal with a fluid bed reactor
yielded high conversion rates (≥80 wt %). K catalysts also have excellent gasification properties, and Exxon has developed a pilot-scale fluidized-bed coal gasifier operating at 3 MPa and 700 °C using steam or H2 with K catalysts. However, this process has been shown to produce methane-rich products, and no commercially viable gasification catalysts have been developed hitherto.

Numerous studies have attempted to understand the chemical structure of coal to gasify coal. Mathews and Chaffee summarized the structures of many types of coal. Quantum chemical calculations of coal regarding the interaction between steam and benzene rings have been conducted, and C=O–K bonds in the benzene ring have been analyzed, completely neglecting differential overlap. Many studies have also investigated the interaction between water and coal through computer simulations. However, the influence of substituting H with Na in carboxyl or hydroxyl groups on the structure of low-rank coal has not been studied.
In a previous study, our group found that Na⁺ ion exchange of H in Austrian Loy Yang (LY) low-rank coal and Indonesian Adaro (AD) bituminous coal-promoted gasification. In particular, the samples used mainly had particle sizes of 250−500 μm, and ion exchange was performed at room temperature using natural soda ash powder (Na₂CO₃ > 99%) produced in the United States; a gasification test was also performed. Na⁺ was exchanged into LY and AD using the natural soda ash powder. According to the results, 2.7 mass % Na⁺-exchanged LY and 1.6 mass % Na⁺-exchanged AD were obtained. Table 1 presents char conversion during gasification after 1 and 2 h at 700 °C. The conversion was about 15−20% after 2 h irrespective of the coal type, but with the addition of Na⁺, the conversion of LY reached approximately 100% after 1 h, and that of AD also increased to 75%. As described above, our group clarified that Na⁺-exchanged coal remarkably promoted steam gasification.

However, many other studies have only experimentally shown that these additives are effective for coal gasification. The effect of Na catalyst ion exchange on the structure of coal has not been clarified. Since the reaction between water molecules and low-rank coal occurs at 700 °C, low-rank coal may decompose and react with water molecules. Consequently, determining the decomposition reaction between water molecules and low-rank coal via quantum chemical calculations involves many uncertainties, and the effect of Na addition has not been accurately evaluated. Therefore, this study focused on changes in the electronic state of low-rank coal before and after ion exchange and performed quantum chemistry calculations.

In this study, we used a molecular model based on analytical values of Yallourn low-rank coal (Australia), which is a typical structure of low-rank coal, and analyzed using the molecular orbital method. The chemical structure of Yallourn low-rank coal has been discussed in detail, and other researchers have used it for molecular dynamics calculations. In addition, low-rank coal has a smaller number of atoms and smaller molecular weight than bituminous coal, no large aromatic ring structure, and a unique minimum unit structure. Therefore, examining the interaction with the additive based on the minimum unit structure is significant because it can simplify the characterization of low-rank coal. In addition, the electronic state of Na⁺-ion-exchanged low-rank coal is considered to change before the gasification reaction. It is believed that changes in the electronic state facilitate reaction and promote gasification. Therefore, if changes in the electronic state and bond order during the exchange of H⁺ and Na⁺ in COOH and OH groups of simple low-rank coal are investigated, the influence of Na⁺ on low-rank coal molecules can be determined. Accordingly, this study extends the potential to the search for additional coal gasification catalysts and discovery of more catalyst species.

## RESULTS AND DISCUSSION

### Structure of low-rank coal used in the calculation and substitution position of Na⁺

In the gasification of low-rank coal, experimental results show that gasification of coal before and after ion exchange and performed quantum chemistry calculations.

In this study, we used a molecular model based on analytical values of Yallourn low-rank coal (Australia), which is a typical structure of low-rank coal, and analyzed using the molecular orbital method. The chemical structure of Yallourn low-rank coal has been discussed in detail, and other researchers have used it for molecular dynamics calculations. In addition, low-rank coal has a smaller number of atoms and smaller molecular weight than bituminous coal, no large aromatic ring structure, and a unique minimum unit structure. Therefore, examining the interaction with the additive based on the minimum unit structure is significant because it can simplify the characterization of low-rank coal. In addition, the electronic state of Na⁺-ion-exchanged low-rank coal is considered to change before the gasification reaction. It is believed that changes in the electronic state facilitate reaction and promote gasification. Therefore, if changes in the electronic state and bond order during the exchange of H⁺ and Na⁺ in COOH and OH groups of simple low-rank coal are investigated, the influence of Na⁺ on low-rank coal molecules can be determined. Accordingly, this study extends the potential to the search for additional coal gasification catalysts and discovery of more catalyst species.
promoted by ion exchange of the COOH group or OH group with an alkali metal, alkaline earth metal, or the like. Therefore, we adopted a molecular model constructed based on the analytical values of a typical low-rank coal, namely, Yallourn low-rank coal. The unit structure of the low-rank coal used for the calculations is shown in Figure 1. The ends of the bond were capped with hydrogen atoms without nitrogen and sulfur. Several possible combinations of reactions between Na\(^+\) and the COOH and/or OH groups of the Yallourn coal model structure exist, and all combinations are shown in Figure 2. Therefore, molecular orbital calculations were performed on structures with one (Na-1, Na-2, Na-3), two (2Na-1, 2Na-2, 2Na-3), and three Na ions exchanged (3Na) per Yallourn coal model structure (Figure 2).

Structure and total energy after structure optimization. Each structure substituted by Na\(^+\) was optimized, the most stable structure with the lowest energy and the same substitution number of Na\(^+\) were extracted, and their energies are shown in Figure 4. The relationship between the number of Na\(^+\) and total energy using B3LYP/6-31G\(^*\) is shown in Figure 4, and the relationship between the number of Na\(^+\) and electrostatic potential map using RHF/6-311G\(^*\) is shown in Figure 5.

Figure 4. Relationship between the number of Na\(^+\) and total energy using B3LYP/6-31G\(^*\).

Figure 5. Relationship between the number of Na\(^+\) and electrostatic potential map using RHF/6-311G\(^*\).
were compared. Figure 3 shows the calculation results using the restricted Hartree−Fock method (RHF)/6-311G*, and Figure 4 shows those using Becke, 3-parameter, Lee−Yang−Parr (B3LYP)/6-31G* considering the interactions between electrons. According to the calculated total energies, structures with Na⁺ ions reacting with carboxyl groups were stable. The structure in which H in a COOH group was ion-exchanged with Na was found to be the most stable regardless of the
A previous study using infrared spectroscopy confirmed that the Ca\(^{2+}\) ion reacted with a carboxyl group. Therefore, this calculation result could be considered as correct. Furthermore, in the model with the substitution of 1, 2, and 3 Na ions, the electronic and bonding states were examined only for the structure in which H in the COOH group was ion-exchanged. These structures with the lowest total energies were compared using electrostatic potential maps.

Next, the electrostatic potential was superimposed on the structure of each low-rank coal. Figures 5 and 6 show the calculation results using RHF/6-311G* and B3LYP/6-31G*, respectively. The electrostatic potential map showed the interaction energy, which the positive charge of unit electric quantity exerted on the electron distribution of the molecule. It indicated the electrostatic potential at various points on an electron density surface corresponding to the overall molecular size. The map was used to determine the polar area of the Na\(^+\)-exchanged structures, encompassing the area of the electron density surface where the electrostatic potential is indicated in red (large negative values of potential) or blue (large positive values of potential). Comparing the low-rank coal before and after Na\(^+\) exchange, the Na\(^+\)-exchanged structure was found to be in the form of a horizontally elongated rod. The interaction of Na with the opposite O atom was found to stabilize the shape of the rod. Therefore, this part is blue when Na \(^+\) exchange increased. Furthermore, this part of the benzene ring is indicated in red. That is, the positive charge accumulated in this Na \(^+\) portion, and the negative charge was pushed out to the benzene ring. In the case of low-rank coal without ion exchange, the oxygen atom portion was negatively charged, and the electron state was not charged in the benzene ring portion. In addition, the charge of the benzene ring gradually became more negative in the case of two or three Na substitutions. This suggested an enhancement of the reactivity of the basic structure of low-rank coal, and
Na+-exchanged low-rank coal is considered to react with molecules, such as water vapor, during gasification to promote decomposition. It is presumed that decomposition due to gasification was likely to occur by increasing the Na+ ion exchange. In fact, although different types of coal were used in the experiment, the gasification of 2.7 mass % LY coal was higher than that of 1.6 mass % AD coal (Table 1).

Furthermore, to determine the part of the structure of low-rank coal affected by Na+, the strength of each bond in the coal structures was determined using Mulliken population analysis. Löwdin population analysis was also performed to support the Mulliken population analysis of symmetric orthogonal basis functions. In this study, the difference in bond order between the raw coal and ion-exchanged structure was determined. Although the bond state from the bond order may change, caution is required because absolute values have little physical significance. A bond that has a large difference in the Mulliken and Löwdin bond orders may have either a weak or strong bond. As a precaution, the bond orders of benzene, (1R)-1,2,3,4-tetrahydronaphthalene-1-carboxylic acid, 4-methylbenzene-1,3-diol, and raw low-rank coal were calculated using RHF/6-311G* (Figures 7 and 8). The calculations...
confirmed that raw low-rank coal had a bond order that was similar to that of each of the molecules that made up the structure. This suggested that the raw low-rank coal had a unit structure similar to that of a very stable single molecule.

The differences between the bond orders of Na⁺-exchanged and raw coal are indicated in Figures 9 and 10. The values in red indicate the bond order of Na⁺-exchanged coal, which is lower than that of raw coal by 0.05 or less. The blue characters indicate the bond order of Na⁺-exchanged coal, higher by 0.05 or more. From this point onwards, the red lines indicate weaker bonds. The blue characters mean that bonds became stronger. In addition, charge transfer was found to occur between the C=O and C−ONa bonds in the carboxyl group.

However, because the conjugation suggested charge transfer, only the change in the bond order of the main structure was considered here. Therefore, the difference in cleaving energy was estimated using B3LYP/6-31G* when the difference in Mulliken bond order was 0.06 (Löwdin bond order was 0.05). Figure 11 shows the bond order of the raw low-rank coal. It was calculated to separate bond A from 1.410 to 5.410 Å in 20 steps with respect to the most stable structure of raw coal. The relationship between the bond distance and total energy is also shown in Figure 11. In the raw coal, the energy for the cleaving bond A was 171.692 kcal/mol. Next, as shown in Figure 12, calculation was performed to cleave bond A in 20 steps from 1.425 to 5.425 Å in the model (2Na-1). The energy for
The experiments in the previous study showed that the steam gasification reaction proceeded readily via ion exchange between low-rank coal molecules and Na. The purpose of this study was to investigate the effect of Na in low-rank coal molecules on the molecule structure using quantum chemical calculations. As a result, according to the calculated total energies, structures with Na’ ions reacting with carboxyl groups were stable. The structure in which H in a COOH group was ion-exchanged with Na was found to be the most stable regardless of the number of Na’ ions. Previous research confirmed that Ca2+ ions reacted with carboxyl groups.

Therefore, the calculation results in this study can be considered correct. Moreover, the Na catalyst affected the electronic state and weak intramolecular bonding of low-rank coal molecules and caused electron localization. The quantum chemistry calculations for low-rank coal and Na’ exchange showed that the Na’-exchange model had a weak bond compared to the bond strength (bond order) of the raw coal model. Bond strength was found to decrease with increasing number of Na’ ions in Na’-exchanged coal. Although different types of coal were used in the experiments, gasification of 2.7 mass % LY coal occurred more readily than that of 1.6 mass % AD coal did. Consequently, both thermal decomposition and steam gasification reactivity may be improved. Analysis of the electronic state of the heating process through quantum chemical calculations will likely be an important research topic in the future.

### CALCULATION METHOD

For geometry optimization and estimation of the electronic states, Spartan’16 V2.0.7 for Windows (Wavefunction, Inc.) installed on DELL XPS 8930 (Intel Core i7−8700, system memory 16 GB Double-Data-Rate4 Synchronous Dynamic Random Access Memory 2666 MHz, and hard disk drive 1 TB, SSD 256 GB) was used for the quantum chemical calculation. For Na’-exchanged coal, all possible combination models exchanged with Na’ in the raw coal were constructed. These models were also subjected to geometrical optimization. Finally, the structures calculated with RHF/3-21G* were used as input data for the calculation using RHF/6-311G*, B3LYP (exchange-correlation functional), and 6-31G* to obtain accurate results. B3LYP included all electron interactions other than classical Coulomb interactions. Therefore, using B3LYP, an accurate solution considering the relationship between exchange interaction and electron correlation could be obtained, which is not included in the RHF method.
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NOMENCLATURE

B3LYP: Becke, 3-parameter, Lee—Yang—Parr
AD: Adaro
LY: Loy Yang
RHF: Restricted Hartree–Fock method

REFERENCES

(1) Zhang, Y.; Schauer, J. J.; Zhang, Y.; Zeng, L.; Wei, Y.; Liu, Y.; Shao, M. Characteristics of particulate carbon emissions from realworld Chinese coal combustion. Environ. Sci. Technol. 2008, 42, 5068–5073.
(2) Thiemann, T.; Schmidt, S.; Peter Gerling, J. Lignite and hard coal: energy suppliers for world needs until the year 2100—An outlook. Int. J. Coal Geol. 2007, 72, 1–14.
(3) Jia, R.; Harris, G. H.; Fuerstenau, D. W. An improved class of universal collectors for the flotation of oxidized and / or low-rank coal. Int. J. Miner. Process. 2000, 58, 99–118.
(4) Tahmasebi, A.; Yu, J.; Han, Y.; Zhao, H.; Bhattacharya, S. Thermogravimetric study and modeling for the drying of a Chinese lignite. Asia-Pac. J. Chem. Eng. 2013, 8, 793–803.
(5) Tomita, A.; Tamai, Y. Low-temperature gasification of Yallourn coal catalysed by nickel. Fuel 1981, 60, 992–994.
(6) Tomita, A.; Ohtsuka, Y.; Tamai, Y. Low-temperature gasification of brown coals catalysed by nickel. Fuel 1983, 62, 150–154.
(7) Ohtsuka, Y.; Tomita, A.; Tamai, Y. Catalysis of nickel in low temperature gasification of brown coal. Appl. Catal. 1986, 28, 105–117.
(8) Tomita, A.; Watanabe, Y.; Takarada, T.; Ohtsuka, Y.; Tamai, Y. Nickel-catalysed gasification of brown coal in a fluidized bed reactor at atmospheric pressure. Fuel 1985, 64, 795–800.
(9) Nahas, N. C. Exxon catalytic coal gasification process: Fundamental to flowsheets. Fuel 1983, 62, 239–241.
(10) Jintgen, H. Application of catalysts to coal gasification processes. Incentives and perspectives. Fuel 1983, 62, 234–238.
(11) Mathews, J. P.; Chaffee, A. L. The molecular representations of coal - A review. Fuel 2012, 96, 1–14.
(12) Chen, S. G.; Yang, R. T. The active surface species in alkali-catalyzed carbon gasification: phenolate (C-O-M) groups vs clusters (particles). J. Catal. 1993, 141, 102–113.
(13) Kumagai, H.; Hayashi, J.; Chiba, T.; Nakamura, K. Change in physical and chemical characteristics of brown coal along with a progress of moisture release. In: Abstracts of papers of the American Chemical Society, vol. 218. American Chemical Society: Washington, DC, 1999; pp U611-U611.
(14) Given, P. H. The Distribution of Hydrogen in Coal and Its Relation to Coal Structure. Fuel 1960, 39, 147–153.
(15) Vu, T.; Chaffee, A.; Yarovsky, I. Investigation of lignin-water interactions by molecular simulation. Mol. Simul. 2002, 28, 981–991.
(16) Gao, Z.; Ding, Y.; Yang, W.; Han, W. DFT study of water adsorption on lignite molecule surface. J. Mol. Model. 2017, 23, 27.
(17) Tsubouchi, N.; Mochizuki, Y.; Byambajav, E.; Hanaoka, Y.; Kikuchi, T.; Ohtsuka, Y. Steam gasification of low-rank coals with iron-exchanged sodium catalysts prepared using natural soda ash. Energy Fuels 2017, 31, 2566–2571.
(18) Murata, S.; Miura, M.; Nomura, M.; Takanohashi, T.; Ino, M.; kumagai, H.; Sanada, Y.; Nakamura, K. Application of computer chemistry to the study of coal chemical structure. J. Jpn. Inst. Energy. 1995, 74, 342–351.
(19) Isoda, T.; Takagi, H.; Saiki, H.; Kusakabe, K.; Morooka, S. Analysis for initial stage reaction of coal pyrolysis by molecular orbital calculation. J. Jpn. Inst. Energy. 2000, 79, 511–521.
(20) Nabatame, T.; Ohtsuka, Y.; Takarada, T.; Tomita, A. Steam gasification of brown coal impregnated with calcium hydroxide. J. Fuel Soc. Jpn. 1986, 65, 53–58.
(21) Spartan’16 for windows; Wavefunction, Inc. Spartan16Manual, https://www.wavefun.com/.
(22) Mulliken, R. S. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. I. J. Chem. Phys. 1955, 23, 1833–1840.
(23) Löwdin, P.-O. Quantum Theory of Many-Particle Systems. I. Physical Interpretations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction. Phys. Rev. 1955, 97, 1474–1489.
(24) Halgren, T. A. Merck molecular force field. I. Basis, form, scope, parameterization, and performance of MMFF94. J. Comput. Chem. 1996, 17, 490–519.
(25) Szabo, A.; Ostlund, N. S. Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory; Courier Corporation 1996, ISBN 0–486–69186-1.
(26) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648–5652.
(27) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. J. Phys. Chem. 1994, 98, 11623–11627.