Steam Gasification Runs and Quantum Chemical Calculations of Low-Rank Coals with Exchanged Sodium Cations

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Abstract: Previous our experiments showed that Na^+-exchanged coals prepared from a low cost natural soda ash was an excellent catalyst for the steam gasification of a low-rank coal using fixed bed quartz reactor. In this study, electronic states between Na^+-exchanged coal models and a row coal model were compared by quantum chemical calculations in order to study about effect of the Na^+ ions. As a result, it was clarified that Na^+-exchanged coal models became unstable states and had electronic localization states.

Keywords: Coal gasification, Ion-exchange catalyst, Quantum chemical calculation.

1. Introduction

The coal gasification at low temperature using catalysts has been studied for a long time because it has some kinds of advantage such as low reaction temperature and the reaction rate enhancement in addition to the control of the fuel gas composition, the creation of the high value chemical raw materials and so on.[1)] The catalysis which shows an activity to the gasification have been roughly separated into the following three types: the alkali metals, the alkali earth metals and the transition metals. However, our research group examined about an interplay between the Na^+ of low cost natural soda ash solution and the H^+ of the COOH groups in the coal and reviewed the effect of the Na catalyst to the steam gasification. As a result, the Na catalyst in brown coal showed a high gasification activity and the research clarified that the natural soda ash was a promising catalytic sauce.[2)] However, whether the Na^+ has an influence on the electronic state of the coal and how to change the molecular structure after Na^+-exchanged in the coal haven't been still clarified.

In this study, electronic states between Na^+-exchanged coal models and a raw coal model were compared by a quantum chemical calculation in order to study about the effect of the Na^+ ion. With this, the selection and the combination of the catalysts about the coal gasification will be possible to make estimates by the calculation.

2. Experiment and calculation

2.1 The ion exchange and the gasification

Austrian Loy Yang (denoted LY) brown coals and Indonesian Adaro (denoted AD) sub-bituminous coals were used. The size fraction of coal samples was mainly in the range of 250-500 μm and ion-exchanged at the room temperature using the natural soda ash powder (Na_2CO_3 > 99 %, American product). The steam gasification was conducted using a fixed-bed quartz reactor. Approximately 500mg of the test sample was heated at a rate of 300 ℃/min to the desired temperature in a stream of high-purity He, then held at this temperature for 10 min to remove volatile matter. Finally exposed to 50vol%/H_2O/He to gasify the resulting char in situ. Product gasses were analyzed by the micro gas chromatography. Char conversions were calculated from the weight of the sample before and after the reaction. Incidentally, the detail of these results was already reported. [2)]

2.2 Calculation methods

(1) Brown coal structures using calculations

The calculated models based on the analytical value of the Yallourn coal were used. [3)] As for the Yallourn coal, the molecular structure was studied and used by other author. [4)] Figure 1 shows a molecular structure of the Yallourn coal using this calculation. It has a small number of atoms, the small molecular weight compared with the bituminous coal, and the undeveloped aromatic ring structure. Consequently, this structure was adopted as the representative model of brown coals.

(2) Geometry optimizations and estimations of the electronic states

Spartan'16 V2.0.7 for Windows (Made by Wavefunction, Inc.) was used as a quantum chemical calculation program. First, as for the model structure of brown coal, the conformations were analyzed using a molecular dynamics method (MMFF) and five low energy structures were selected from the results, at the

same time, roughly different structures were chosen. Secondly, these structures were calculated using a geometry optimization by RHF/3-21G*. As for the Na^+-exchanged coal, every possible combination models which were exchanged by Na^+ in the raw col were constructed. As mentioned above, they were calculated by the geometry optimization. Finally, the structures calculated by RHF/3-21G* as the input data were calculated using RHF/6-311G* [5] and B3LYP [6]/6-31G* in order to obtain the accuracy results.

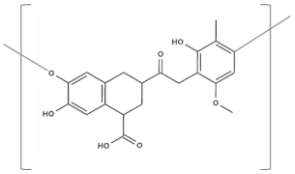

Figure 1. Yallourn brown coal unit structure.

3. Results and discussion

Na^+ was exchanged the LY and the AD using a natural soda ash powder, a 2.7 mass% Na^+-exchanged LY and a 1.6 mass% Na^+-exchanged AD were obtained. Table 1 showed the cha conversion of gasification after 1h and 2h at 700 °C. The conversion was about 15~20% after 2h in spite of coal types, but when Na^+ was existed, the conversion of LY was reached approximately 100% after 1h and also that of AD were went up to 75%. As described above, our group clarified that the Na^+-exchanged coal remarkably promoted the steam gasification.[2]

Therefore, molecular orbital calculations were performed to the structures which were one ($1Na^+$-exchanged coal), two ($2Na^+$-exchanged coal) and three Na-ions exchanged ($3Na^+$-exchanged coal) per the Yallourn coal model structure (Figure 1). Table 2 presents calculation results of electronic states about typical bonds (Mulliken bond orders [7-10]). **Boldface** means the Na^+-exchanged coal's bond order of 0.05 or less more than the raw coal's bond order. *Italic* means the bond order of 0.05 or above more than that. From table 2, it was proved that the larger the number of Na^+ in the Na^+-exchanged coal increase, the weaker the bond strengths become. Furthermore, the calculation results were shown that π-electron conjugation of the aromatic were spread and these electrons make localizations in the Na^+-exchanged coal. It is convenient to consider that the relaxation of this π-π interaction improves a reactivity with the other molecules.

Table 1. Changes in char conversion with the reaction time for the steam gasification of raw and Na^+-exchanged coals at 700℃.

Coal	Char conversion, mass% (dacf)	
	Reaction time (1h)	Reaction time (2h)
Raw AD coal	15-18	15-20
Raw LY coal	15-18	15-20
Na^+/AD coal	75	100
Na^+/LY coal	100	

Table 2. Comparisons between the raw coal and Na^+-exchanged coal models for Mulliken Bond Orders using RHF/6-311G*.

Coal model	Mulliken Bond Order											
Raw coal	1.53	1.40	1.39	1.41	1.39	1.52	1.35	1.37	1.51	1.38	1.46	1.29
$1Na^+$ -exchanged coal	**1.43**	1.39	1.38	1.40	1.39	1.51	1.35	1.39	1.50	1.38	*1.52*	1.30
$2Na^+$ -exchanged coal	**1.39**	*1.46*	1.41	1.39	1.38	1.53	**1.28**	1.37	**1.41**	*1.44*	1.48	*1.34*
$3Na^+$ -exchanged coal	**1.43**	*1.47*	1.41	1.38	1.38	1.53	**1.28**	1.36	**1.39**	*1.43*	**1.40**	1.25

4. Conclusions

As the results of the quantum chemical calculations about the brown coal models and the Na^+-exchanged models, it turned out that Na^+-exchanged models have weak bonds in compared with the bond strengths (the bond orders) of the raw coal model. Furthermore, it was proved that the larger the number of Na^+ in the Na^+-exchanged coal increase, the weaker the bond strengths become. The Na catalyst has influences on the electronic state of the brown coal molecule and on the intramolecular bonds to weak, and raises up electronic localizations. As a result, the progress of the thermal decomposition reactivity and the improvement of the steam gasification reactivity may have occurred. The analysis of the electronic states in the heating process by quantum chemical calculations will be an important research subject in the future.

References

1. Tomita, A. Catalytic Coal Gasification. *J. Fuel Soc. Jpn.* **1979**, 58, 332-342. 2. Tsubouchi, N.; Mochizuki, Y.; Byambajav, E.; Hanaoka, Y.; Kikuchi, T.; Ohtsuka, Y., *Energy Fuels* **2017**, 31, 2565-2571. 3. Murata. S.; Miura, M.; Nomura, M.; Takanohashi, T.; Iino, M.; kumagai, H.; Sanada, Y.; Nakamura, K., *J. Jpn Inst Energy*. **1995**, 74, 342-351. 4. Isoda, T.; Takagi, H.; Saiki, H.; Kusakabe, K.; Morooka, S. *J. Jpn Inst Energy*. **1998**, 79, 511-521. 5. A. Szabo, N. S. Ostlund "Modern Quantum Chemistr y: Introduction to Advanced Electronic Structure Theory", Dover, **1996**. 6. A.D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652. 7. R. S. Mulliken, *J. Chem. Phys.*, **1955**, 23, 1833-1840. 8. R. S. Mulliken, *J. Chem. Phys.*, **1955**, 23, 1841-1846. 9. R. S. Mulliken, *J. Chem. Phys.*, **1955**, 23, 2338-2342. 10. R. S. Mulliken, *J. Chem. Phys.*, **1955**, 23, 2343-2346.