Oxygen chemisorption and low-temperature oxidation behaviors of sub-bituminous coal

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Abstract

The effective utilization of sub-bituminous coals should be extended as an energy source for power generation because of their low cost and long minable years. However, sub-bituminous coal may undergo spontaneous combustion owing to high reactivity with oxygen in low-temperature air compared with bituminous coal. Therefore, the objective of this study is to elucidate the low-temperature oxidation behaviors of sub-bituminous coal. In particular, transition from oxygen chemisorption to low-temperature oxidation of sub-bituminous coal has been experimentally examined in detail. Isothermal gravimetric analyses are conducted for several bituminous and sub-bituminous coal samples at temperatures varying between 356 K and 476 K in oxygen-enriched air. The chemical compositions of emission gas are continuously monitored under low-temperature oxidation conditions. The changes in the chemical structure of the coals are analyzed using Fourier transform infrared (FTIR) spectrometry. The experimental results show that the mass of all tested coals, including those of bituminous and sub-bituminous coals, increases at temperatures below 426 K as a result of oxygen chemisorption. At 476 K, the mass of sub-bituminous coal increases slightly with low H_2 and CO_2 emissions at the beginning and subsequently decreases with high CO and CO_2 emissions. This mass change indicates that the transition from oxygen chemisorption to low-temperature oxidation occurs during this period. In addition, the FTIR spectra of sub-bituminous coals show the existence of carbonyl groups even in raw coal samples. These carbonyl groups are considered to contribute to the formation of CO_2 and H_2 from the beginning of reactions, triggering the transition from oxygen chemisorption to low-temperature oxidation.

Keywords : Sub-bituminous coal, Oxygen chemisorption, Low-temperature oxidation, Isothermal gravimetric analysis

1. Introduction

A large amount of bituminous coal is consumed as fuel for coal-fired power generations globally. However, bituminous coal reserves are limited when compared with other low-rank coal resources. Thus, we need to use sub-bituminous coal effectively. However, sub-bituminous coal has a disadvantage in that it easily reacts with oxygen at low temperature, increasing the risk of spontaneous firing at coal stockyards. To predict and control the spontaneous combustion in coal stockpiles, various field tests and large-scale experiments have been conducted in which gas temperature variations and gaseous emissions were analyzed (Fierro et al., 1999, and Deng et al., 2015). Numerical simulations of the spontaneous combustion in coal stockpiles have been also conducted to clarify the dominant reactions for temperature rise in these stockpiles. In these simulations, the evaporation of moisture from coal was found to play a critical role in heating coal stockpiles (Zhang et al., 2016). Miura (2016) pointed out that the amount of heat generated by the adsorption of water vapor was larger than that generated by initial coal oxidation in stockpiles. This means that the adsorption of moisture by coal particles is the main trigger for the initial temperature increase in coal stockpiles. Once the temperature locally increases in a part of a coal stockpile, surrounding coal particles in the

stockpile are heated and dried subsequently, leading to reaction with oxygen. It has been reported that lignite, preheated and dried in inert gas, showed higher spontaneous combustion propensities than raw lignite (Tang and Xue, 2015, and Fei et al., 2009). In a fundamental research on the low-temperature oxidation of coal conducted by Nugroho et al., (2000), particle sizes were found to affect the self-heating characteristics in high-rank coal samples but not in low-rank coal samples. In the case of high-ash coals, the ash content inhibited low-temperature oxidation reactions of coal owing to both a heat sink effect and physicochemical effects (Beamish, 2008). To investigate the fundamental reaction mechanisms of the low-temperature oxidation of coal in detail, conventional thermogravimetric (TG) analyses under elevated temperature conditions have been conducted by many researchers. In some of these TG analyses, the process of oxygen chemisorption on coal was observed prior to mass reduction caused by coal combustion. This oxygen chemisorption was explained as the formation of surface oxygen-containing complexes (Li et al., 2014, and Slovak and Taraba, 2010). Chemical phenomena taking place during coal oxidation at temperatures below 373 K were reviewed and systematically summarized by Wang et al. (2003a). CO and CO₂ emissions from the low-temperature oxidation of coal were measured under isothermal conditions (Wang et al., 2003b, Yuan and Smith, 2011, and Zhang et al., 2015) as well. The generation of CO and CO₂ has been regarded as evidence of low-temperature oxidation, which should be distinguished from oxygen chemisorption. However, to the best of the authors' knowledge, there are no reports explaining the detailed changes in coal mass and emissions of gaseous products during this simultaneous transition from oxygen chemisorption to low-temperature oxidation.

In this study, isothermal gravimetric analyses combined with gaseous emission analyses are conducted to elucidate the low-temperature oxidation behaviors of sub-bituminous coal. Four sub-bituminous coals and four bituminous coals are selected as experimental samples. The temperature range tested in the experiments is between 356 K and 476 K. Oxygen-enriched air, in which O₂ concentration is 50 vol%, is utilized as the atmosphere gas. The initial oxygen chemisorption and subsequent low-temperature oxidation behaviors of coal samples are examined in isothermal gravimetric experiments. The variations in the chemical structure of coals are investigated using Fourier transform infrared (FTIR) spectrometry.

2. Experimental and analytical procedures

2.1 Coal samples

Four sub-bituminous coal samples (Coal Q, Coal R, Coal C, and Coal K) and four bituminous coal samples (Coal E, Coal D, Coal S, and Coal I) were selected as test samples in this study. All of them were pulverized, sieved to particle sizes smaller than 100 μm , and dried in a desiccator at room temperature for a few days. Table 1 and Table 2 list the proximate and ultimate analysis results and specific surface areas of eight coal samples taken from the desiccator. The fuel ratios are defined as Fixed Carbon (FC) / Volatile Matters (VM), and the carbon content is significantly different between the sub-bituminous and bituminous coals, as shown in these tables. Meanwhile, there is no systematic trend for the specific surface areas between the bituminous and sub-bituminous coals.

Table 1 Proximate analysis and specific surface ratios of coal samples (wt% in dry base)

Sample	Sub-bituminous coal				Bituminous coal			
	Coal Q	Coal R	Coal C	Coal K	Coal E	Coal D	Coal S	Coal I
Moisture [wt%]	23.53	16.59	8.50	4.60	2.92	3.50	0.83	3.30
Volatile matter [wt%]	49.63	47.37	44.84	44.50	34.21	32.62	18.51	19.10
Fixed carbon [wt%]	45.13	47.10	45.83	41.00	56.50	52.57	66.97	72.00
Ash [wt%]	5.24	5.53	9.33	14.50	9.29	14.81	14.52	8.90
Fuel ratio [-]	0.91	0.99	1.02	0.92	1.65	1.61	3.62	3.77
S.S.A [m^2/g]	6.55	1.85	3.61	3.55	1.41	6.62	4.77	3.17

Table 2 Ultimate analysis of coal samples (wt% in dry ash-free base)

Element	Sub-bituminous coal				Bituminous coal			
	Coal Q	Coal R	Coal C	Coal K	Coal E	Coal D	Coal S	Coal I
C	71.01	72.79	73.22	75.74	77.43	78.81	86.37	86.70
H	4.55	4.62	5.42	6.26	4.57	5.14	4.22	4.38
N	1.21	1.58	1.55	1.31	1.95	1.97	1.92	1.90
O	22.31	20.15	18.19	15.64	14.95	12.99	6.54	6.05
S	0.92	0.86	1.62	1.05	1.1	1.08	0.96	0.96

2.2 Experimental setups for isothermal gravimetric analysis

Two types of experimental setup were used for the isothermal gravimetric analysis of coal samples to observe low-temperature oxidation behaviors. One of them was a typical thermogravimetric (TG) analyzer (TG8120, RIGAKU). High-precision measurement of mass changes in low-temperature oxidation was conducted using this TG analyzer. The initial amount of coal samples charged into the platinum cell in the TG was approximately 5 mg. The procedures for conducting the isothermal gravimetric simulations in the TG are shown in Fig. 1, and the experimental conditions are summarized in Table 3. First, the coal sample in the cell was preheated at 356 K for approximately 2 h as a predrying process under N_2 atmosphere conditions. Then, it was heated to a given temperature at a heating rate of 20 K/min. In the case shown in Fig. 1, the sample was heated to 376 K. After the mass of the sample became almost stable at this temperature, the atmosphere was switched to oxygen-enriched air, that is, 50% N_2 and 50% O_2 , to start the low-temperature oxidation experiment. To understand the fundamental reaction behaviors in a short-term test, the concentration of O_2 was set to be higher than that of air. This was called an accelerated testing condition. The oxidation step of coal at low temperature is likely complex, but its reaction order has been defined as near unity in a lot of literatures (Hurt et al., 2005). Therefore, results under the accelerated testing condition in this study are of value for estimating reaction rates of coal under actual low oxygen concentrations. The mass changes of the coal samples were measured after switching atmospheres under an isothermal condition and was continuously recorded using a PC. If the mass increased, then the oxygen chemisorption on coal samples occurred. Otherwise, low-temperature oxidation caused gaseous emissions such as carbon oxides, resulting in a mass reduction. Gaseous products are discharged into the flue gas from the TG. However, concentrations of these gaseous products were too low to monitor them continuously during the TG experiments.

To overcome this difficulty in monitoring gaseous emissions during the low-temperature oxidation of coal, a second experimental setup larger than the TG was built, as shown in Fig. 2. An electric balance with a halogen heater (Shimadzu, MOC63u) was placed in a closed acryl box. Coal samples were thinly spread on an aluminum plate inside the electric balance, and the initial amount of coal samples for each experiment was approximately 10 g. A thermocouple was installed below the plate, and the temperature of the sample in the plate was controlled corresponding to a given temperature program. The cylinder gases of N_2 and O_2 were connected to the acryl box via mass flow controllers. The outlet gas from the acryl box was continuously analyzed for gaseous compositions by using a micro gas chromatograph (Agilent, 490-GC). This device contained two column modules: PoraPlot Q (He carrier) and Molsieve 5A (Ar carrier), equipped with thermal conductivity detectors. The former is used to measure CO_2 , C_2H_6 , C_2H_4 , and C_2H_2 , while the latter is used to measure H_2 , N_2 , O_2 , CO , and CH_4 . Temperature programs applied to this boxed electric balance with a heater were the same as those for the TG experiments shown in Fig. 1.

2.3 FTIR spectra of coal samples before and after experiments

Raw coal samples (after drying in a desiccator at room temperature for a few days) and coal samples after low-temperature oxidization experiments were analyzed for functional groups by FTIR spectroscopy. Both particle samples were directly applied to the analysis using Attenuated Total Reflection FTIR equipment (JASCO, FT/IR-4100). FTIR spectra were recorded between 3500 and 650 cm^{-1} , and were accumulated for 64 scans.

Fig. 1 Procedures for isothermal gravimetric experiments in TG

Fig. 2 Experimental setup for gaseous emission monitoring: boxed electric balance with halogen heater

Table 3 Experimental conditions of isothermal gravimetric analysis in TG

Sample	C, Q, R, D, E (and I, S, K only at 476 K)
Sample weight [mg]	5.00 ± 0.05
Atmosphere	N ₂ → N ₂ :O ₂ =1:1
Total gas flow rate [ml/min]	500
Heating rate [K/min]	20
Preheating temperature [K]	356
Oxidation temperature [K]	356, 376, 426, 476

3. Results and Discussion

3.1 Isothermal gravimetric analyses of coal samples in TG experiments

Figures 3(a), (b), and (c) show the experimental results of mass changes of two bituminous coals (D and E) and three sub-bituminous coals (C, Q, and R) at temperatures of 356 K, 376 K, and 426 K, respectively. The vertical axes in these figures indicate the mass changes normalized by the combustibles in the coal samples. Here, combustible means the sum of VM and FC in each coal. Because the mass changes shown in Figs. 3(a), (b), and (c) are all small but positive, oxygen chemisorption occurs for all coal samples in this temperature range. Higher temperatures resulted in greater oxygen chemisorption. However, there was no distinct difference in the behaviors between the bituminous coals and sub-bituminous coals.

Figure 4 shows the experimental results of mass changes of four bituminous coals (D, E, I, and S) and four sub-bituminous coals (C, K, Q, and R) at a temperature of 476 K. In the bituminous coals, the changes were still

positive, indicating that only oxygen chemisorption occurred even at 476 K. Oxygen chemisorptions in the bituminous coals were completed in several hours, and the mass of bituminous coal samples became almost stable. On the other hand, for the sub-bituminous coals, the changes were small and positive at the beginning and subsequently became large and negative. The mass continued to decrease during the test duration. This means that the transition from oxygen chemisorption to low-temperature oxidation occurred only in cases where sub-bituminous coals were used. It can be concluded that sub-bituminous coals have a distinctly higher reactivity to low-temperature oxidation when compared with bituminous coals. Because the amount of coal samples charged in the cell was small enough to dissipate the heat of reaction in the TG chamber, the temperature of the coal sample was kept constant at 476 K without reaching ignition. If the heat accumulated in a lump of coal particles, the oxidation reaction would promptly result in the ignition of coal.

Fig. 3 Mass changes of two bituminous coals (D, E) and three sub-bituminous coals (C, Q, R) at temperatures of (a) 356 K, (b) 376 K, and (c) 426 K

Fig. 4 Mass changes of four bituminous coals (D, E, I, S) and four sub-bituminous coals (C, K, Q, R) at 476 K

3.2 Monitoring of gaseous emissions during low-temperature oxidation of coal

To verify transitions from oxygen chemisorption to low-temperature oxidation of sub-bituminous coals from the viewpoint of gaseous emissions, a boxed electric balance with a heater was applied for gaseous emission analysis, as described above. However, the ignition of coal samples occurred in the boxed electric balance at 476 K because the heat dissipation from the coal samples charged in it was not large enough as compared with that in the TG experiments. Therefore, gaseous emissions during low-temperature oxidation of sub-bituminous coal were monitored in the boxed electric balance with a heater at 458 K, which was a little lower than the temperature in the TG experiments. Figure 5(a) shows the results of a gas analysis downstream of the oxygen chemisorption for coal I, one of the bituminous coal samples, at 458 K. The weight of the coal increased after switching the gas atmosphere from N_2 to 50% N_2 and 50% O_2 as well as that in the TG experiment. Meanwhile, gaseous emissions were barely observed at all. This means that the oxygen chemisorption in bituminous coal just captured oxygen without any emissions. On the other hand, figure. 5(b) shows the results of a gas analysis downstream of the low-temperature oxidation of coal Q, one of the sub-bituminous coal samples, at 458 K. The weight of the coal increased slightly just after switching gas atmospheres, and then gradually decreased in the same trend as the mass changes of sub-bituminous coals shown in Fig. 4. This means that a transition from oxygen chemisorption to low-temperature oxidation occurred. In the duration of oxygen chemisorption, small amounts of H_2 and CO_2 were discharged to the atmosphere gas. While H_2 emissions declined quickly, CO_2 emissions increased rapidly and had a peak during low-temperature oxidation. CO was emitted only after the transition from oxygen chemisorption to low-temperature oxidation. This implies that the oxygen chemisorption in sub-bituminous coal possibly includes substitution reactions of C and H with oxygen. The weight reduction of the coal was almost consistent with the total mass of C and H contained in the emitted gaseous compounds. H_2 emissions in the low-temperature oxidation process of coal was reported by Wang et al. (2017), in which the amount of H_2 emissions from sub-bituminous coal was greater than that from bituminous coal at temperatures higher than 373 K.

Fig. 5 Weight reduction and gas emissions from coal samples heated at 458 K:
(a) bituminous coal: coal I, (b) sub-bituminous coal: coal Q

3.3 Comparison of FTIR spectra before and after oxygen chemisorption

To understand the reaction mechanisms in detail, the FTIR spectra were compared between bituminous coal and sub-bituminous coal. The peaks in the FTIR spectra from the coal samples were specified based on a previous work (Worasuwannarak et al., 2002). Figure 6 shows FTIR spectra of all raw coal samples tested in the present study: (a) bituminous coals (D, E, I, S), (b) sub-bituminous coals (C, K, Q, R). Peaks of carbonyl groups are clearly observed in spectra from sub-bituminous coals, while those are very small or not detected in spectra from bituminous coals. Figure 7 shows the FTIR spectra of coal I, one of the bituminous coal samples, before and after oxygen chemisorption. The solid line indicates a spectrum from a raw coal sample, and the dashed line indicates a spectrum from the sample after oxygen chemisorption at 476 K in the TG experiment. These are drawn separately in two ranges to observe the peaks of aliphatic C–H groups and carbonyl groups (dividing into ester, aldehyde, and carboxyl groups). As shown in Fig. 7, the peaks of the aliphatic C–H groups became smaller after oxygen chemisorption, while the peaks of the carbonyl groups became larger. This implies that aliphatic C–H groups in coal capture oxygen molecules in gas and then change to carbonyl groups, resulting in oxygen chemisorption. On the other hand, figure 8 shows the FTIR spectra of coal Q, one of the sub-bituminous coal samples. In this graph, the spectrum from the sample after low-temperature oxidation at 476 K is compared with that from its raw coal sample. Because raw coal Q contained substantial moisture even after air drying at room temperature, as shown in Table 1, a broad peak of O–H around 3300 nm was observed in the FTIR spectrum of raw coal Q in Fig. 8. Then, the peak became smaller after low-temperature oxidation. The peaks of the aliphatic C–H groups also became smaller after low-temperature oxidation, indicating that oxygen chemisorption occurred in a similar manner to coal I. However, unlike coal I, peaks of carbonyl groups were observed even in the raw coal Q sample. In addition, a peak from aldehyde markedly became larger after low-temperature oxidation. It has been reported that the aldehyde group is a functional group that produces not only CO₂ but also H₂ by its oxidation reaction (Wang et al., 2017). This fact is consistent with the H₂ emissions observed in the low-temperature oxidation of coal Q shown in Fig. 5(b). Because CO₂ formation is an exothermic reaction, the oxidation of aldehyde groups is considered to be the trigger for the transition from oxygen chemisorption to low-temperature oxidation in the sub-bituminous coal samples. The temperatures for the transition depend on the balance between the heat generation and heat dissipation of the coal samples. Heat generation is dependent on the physicochemical properties of the coal sample, while heat dissipation is affected by the experimental setup and surrounding conditions. It is difficult to determine the specific value of the transition temperature for each coal sample. However, the transition temperatures of the sub-bituminous coals were found to be distinctly lower than those of the bituminous coals in this study. We concluded that this resulted from the larger amount of carbonyl groups, in particular aldehyde group, of the sub-bituminous coals. As shown in Fig. 6(a), peaks of carbonyl groups from coal D and E are slightly larger than those from the other two bituminous coals. It means that oxygen chemisorption of coal D and E are relatively easier to transition to the low temperature oxidation than that of coal S and I. Meanwhile, as shown in Fig. 6(b), peaks of carbonyl groups from Q and R are larger than

those from the other two sub-bituminous coals. It means that oxygen chemisorption of coal Q and R are further easier to transition to the low temperature oxidation than that of coal C and K. These considerations are well consistent with experimental results shown in Fig. 4.

Fig. 6 FTIR spectra of raw coal samples: (a) bituminous coals (D, E, I, S), (b) sub-bituminous coals (C, K, Q, R)

Fig. 7 FTIR spectra from raw coal I (solid line) and sample after oxygen chemisorption at 476 K in TG experiment (dashed line)

Fig. 8 FTIR spectra from raw coal Q (solid line) and sample after low-temperature oxidation at 476 K in TG experiment (dashed line)

4. Conclusions

The objective of this study was to understand differences in low-temperature oxidation behaviors between sub-bituminous coal and bituminous coal. To achieve this, two isothermal gravimetric analyses were conducted for different coal samples. One of them was a standard TG for the precise measurement of mass changes in coal samples, while the other consisted of a boxed electric balance with a heater and a micro gas chromatograph for simultaneous measurements of mass change and emission gas compositions. All tests were conducted under an oxygen-enriched-air condition in which the O_2 concentration was 50 vol% balanced with N_2 . The results are summarized as follows:

- 1) At temperatures below 426 K, the mass of all coal samples, including those of bituminous and sub-bituminous coals, increased slightly as a result of oxygen chemisorption.
- 2) At 476 K, in the TG experiments, the mass of sub-bituminous coal samples increased only at the beginning and then decreased drastically, indicating transitions from oxygen chemisorption to low temperature. By contrast, the mass of bituminous coal samples increased and became stable even at 476 K.
- 3) At 458 K, in a boxed electric balance experiments, emissions of H_2 , CO_2 , and CO were observed only for the sub-bituminous coal samples. Although H_2 emissions rapidly declined, CO_2 emissions had a large peak after the transition from oxygen chemisorption to low-temperature oxidation. CO emissions occurred only after the transition.
- 4) The FTIR spectra of bituminous coals implied that aliphatic C–H groups were converted to carbonyl groups owing to oxygen chemisorption. On the other hand, the FTIR spectra of sub-bituminous coals showed the existence of carbonyl groups even in the raw coal samples. In particular, the aldehyde group is considered to contribute to the formation of CO_2 and H_2 at the beginning of the reactions, triggering the transition from oxygen chemisorption to low-temperature oxidation.

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