COMPARISON OF SURFACE PROPERTIES OF ANTHRACITE COALS BEFORE AND AFTER HIGH TEMPERATURE HEATING PROCESS

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Abstract: Surface property plays a very important role on coal hydrophobicity which determines flotation behavior of fine coals. However, coal spontaneous combustion makes coal suffer both oxidation and high temperature heating processes. Coals from the outside of coal piles primarily suffer oxidation (or combustion process) while coals from the inside of coal piles primarily suffer high temperature heating process. It is necessary to investigate the changes in surface properties of coal before and after high temperature heating process. In this investigation, X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), surface area (BET) and contact angle measurements were used to indicate the changes in surface properties of anthracite coal before and after high temperature heating process. Throughout this study, surface properties of coal changed significantly after high temperature heating process. Meanwhile, coal hydrophobicity can be also reduced after high temperature heating.

Keywords: heating, coal hydrophobicity, XPS, SEM, BET, contact angle

Introduction

Coal has both inorganic and organic materials. Inorganic materials consist of silicate, pyrites and other clays. Organic materials consist of carbon, hydrogen, oxygen, nitrogen, organic sulfur and other elements. Surface properties of coals are determined by the ratio of inorganic materials to organic materials. Therefore, coal hydrophobicity is related to the surface properties of coal as well as the ratio of inorganic materials to organic materials on coal surface. In a way, organic materials usually make coal surface more hydrophobic while inorganic materials make coal surface more hydrophilic. Bituminous and anthracite coal usually have good natural hydrophobicity. Based on this natural hydrophobicity, bituminous and anthracite coal can be easy to float with only a little oily collector. However, coal oxidation processes can reduce this natural hydrophobicity and make fine coals difficult to float with the common oily

collectors (Wu et al., 1988; Bolat et al., 1998; Fuerstenau and Diao, 1992; Jia et al., 2000; Tao et al., 2002; Hao et al., 2013).

The types of coal oxidation processes generally include low temperature oxidation (weathering) and high temperature oxidation (combustion). Low temperature oxidation (weathering) process is considered as mild oxidation reaction and the surface properties of coal can be changed by this mild oxidation process (Kozlowski et al., 2002; Pilawa et al., 2002; Grzybek et al., 2002, 2006; Pietrzak and Wachowska, 2003; Pietrzak et al., 2004, 2007). In contrast, high temperature oxidation process is a fast oxidation process. During high temperature oxidation process of coal, coals from the outside of coal piles primarily suffer oxidation process (or combustion process) while coals from the inside of coal piles primarily suffer high temperature heating process. The phenomenon of coal spontaneous combustion can be seen in many coal mines or coal piles around the world. Coal spontaneous combustion makes coal suffer high temperature oxidation. However, the inner part of coal piles or coal mines may primarily suffer high temperature heating process during coal spontaneous combustion because there is only a little oxygen in the inner part of coal piles or coal mines. In contrast, the outer part of coal piles should primarily suffer combustion process because it is in contact with the atmosphere easily.

Taixi oxidized coal is primarily formed by high temperature heating process during coal spontaneous combustion. Meanwhile, Taixi oxidized coal is difficult to float using the common oily collectors (Xia et al., 2012; 2013; Xia and Yang, 2013). It is necessary to investigate the changes in both surface properties and hydrophobicity of coal before and after high temperature heating process. However, there are little literatures about the effects of high temperature heating process on the changes in both surface properties and hydrophobicity of coal. The aim of this paper is to reveal the changes in both surface properties and hydrophobicity of Taixi coal before and after high temperature heating process. Furthermore, this paper used a sample of anthracite coal with very low ash content to conduct this study. The low ash content anthracite coal may be more suitable for reveal accurate changes in both surface properties and hydrophobicity of coal before and after high temperature heating process.

Experimental section

Coal samples

In this investigation, a sample of fresh anthracite coal with very low ash content was selected prior by hand preparation and density separation. The density fraction of low ash content coal sample was 1.350~1.375 g/cm^3. These coal bulks were crushed and screened. The size fraction of 0.125-0.074 mm was selected to be used in this study. The proximate analysis of fresh coal samples is given in Table 1. Where Mad is the moisture matter content, Vad the volatile content, FCad the fixed carbon content, Aad is the ash content. The contents of elements (C, H, O, N and S) based on dry ash free are also shown in Table 1.

Table 1. Proximate analysis of fresh anthracite coal

Mad (%)	Vad (%)	FCad (%)	Aad (%)	Cdaf (%)	Hdaf (%)	Odaf (%)	Ndaf (%)	St,daf (%)
4.20	7.40	86.85	1.55	94.43	3.73	0.91	0.79	0.13

High temperature heating process

High temperature heating process was conducted in a quartz crucible and a muffle furnace. High temperature heating temperature was fixed at 800 °C. High temperature heating time was 120 minutes. After high temperature heating process, coal samples were cooled in a vacuum drying chamber and then stored in air for 48 hours.

XPS measurement

For the indication of surface properties of coals before and after high temperature heating process, coal samples were pressed into pellets firstly. The XPS experiments were carried out at room temperature in an ultra high vacuum (UHV) system with the surface analysis system (ESCALAB 250 Xi, America). The data processing (peak fitting) was performed with XPS Peak fit software, using a Smart type background subtraction and Gaussian/Lorentzian peak shapes. The binding energies were corrected by setting the C1s hydrocarbon (-CH$_2$-CH$_2$-bonds) peak at 284.6 eV.

SEM measurement

The FEI Quanta 250 SEM was used to analyze the surface morphology of coals before and after high temperature heating process. The coal samples were prepared by surface cleaning using absolute ethyl alcohol. After surface cleaning, the coal samples were dried in air. Before SEM, the coal samples were sputter-coated with a layer of gold.

BET measurement

Specific surface area measurements of coals before and after high temperature heating process were made by the Brunauer, Emmett and Teller (BET, BELSORP-max) method of adsorption of nitrogen gas. Surface area (m^2/g) was obtained from experimental data.

Contact angle measurement

Coal samples before and after high temperature heating process were pressed to form plates. The plates of coal samples were measured using water contact angle analyzer (JC2000D), such as a water droplet on the surface of coal plate in air. The contact angles were obtained while the water droplet contacts with the coal plate at the exact moment.

Results and discussion

XPS analysis

C1s peaks at binding energies of 284.6 eV, 285.6 eV, 286.6 eV and 289.1 eV correspond to the following groups: C-C or C-H, C-O (alcohol, phenol or ether), C=O (carbonyl or chinone) or O-C-O (in low rank coals) and COOH (carboxyl) (Desimoni et al., 1992; Fiedler and Bendler, 1992; Xia and Xie, 2014; Xia et al., 2014). C-C and C-H groups are the primary hydrophobic functional groups while C-O, C=O and COOH groups are the primary hydrophilic functional groups on coal surface (Cinar, 2009). The contents of C-C or C-H, C-O, C=O and COOH groups can be calculated (Table 2) by the analysis of C1s peaks shown in Figs. 1 and 2.
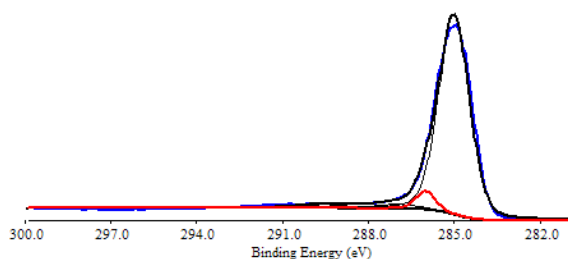

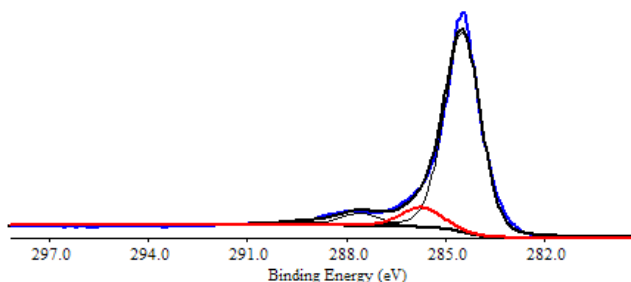Fig. 1. C1s peak for anthracite coal before high temperature heating process

Fig. 2. C1s peak for anthracite coal after high temperature heating process

Table 2. Fraction of C on the surface of anthracite coal before
and after high temperature heating process (relative % of C1s)

Coal types	C-C, C-H (%)	C-O (%)	C=O (%)	COOH
Before heating process	88.78	5.35	3.17	2.71
After heating process	82.49	9.25	6.11	2.15

The content of C-C/C-H groups is 88.78% in fresh anthracite coal. After high temperature heating process, the content of C-C/C-H groups is reduced to 82.49%. In contrast, the content of C-O group increases from 5.35% to 9.25% and the content of

C=O group increases from 3.17% to 6.11%. C-C and C-H groups can be cracked during high temperature heating process and can release gas (i.e. CO, CO_2 and CH_4) and coal tar. Therefore, the relative content of C-H and C-C groups on coal surface is reduced after high temperature heating process and the contents of C-O and C=O groups are increased. However, the content of COOH group decreases from 2.71% to 2.15% (Table 2). It seems that COOH group can also be cracked during high temperature heating process. COOH group can be cracked and can release CO, H_2O and CO_2 during the high temperature heating process. The thermal stability of COOH group is lower than C=O group as well as the thermal stability of C=O group is lower than C-O group. During high temperature heating process, COOH group will be cracked first and quickly (Schafer, 1979; Zhou et al., 2007). C-C and C-H groups are the primary hydrophobic functional groups while C-O, C=O and COOH groups are the primary hydrophilic functional groups on coal surface (Cinar, 2009). After high temperature heating process, the content of hydrophilic functional groups is increased while the content of hydrophobic functional groups is reduced, and hence the hydrophobicity of coal surface may be also reduced.

SEM analysis

Figures 3 and 4 are the SEM pictures for anthracite coal before and after high temperature heating process. It is obvious that heated coal surface is much rougher than the fresh coal surface. Meanwhile, some new cracks are produced by high temperature heating process. It indicates that anthracite coal may be expanded during high temperature heating process and constricted after high temperature heating process while it is cooled at room temperature. Furthermore, there are nearly no holes on the fresh coal surface while there are many holes on heated coal surface. The depth of these holes is very small. It seems that these holes have a bubble structure. The
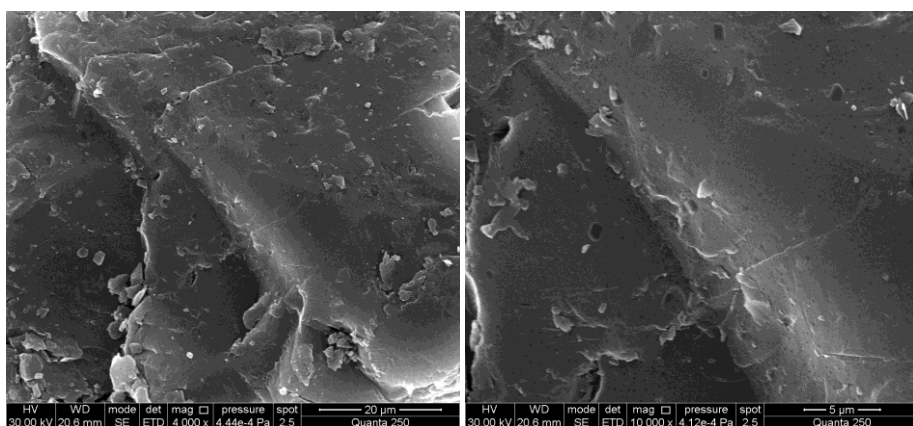

Fig. 3. SEM pictures for anthracite coal before high temperature heating process

surface topography of heated anthracite coal surface looks like the surface topography of unburned carbon particles in the fly ash from the literatures (Niewiadomski et al., 1999; Kutchko and Kim, 2006). It is well known that unburned carbon particles in fly ash are difficult to float with the common oily collectors due to its low hydrophobicity. Therefore, heated coal may be much more hydrophilic than fresh coal.
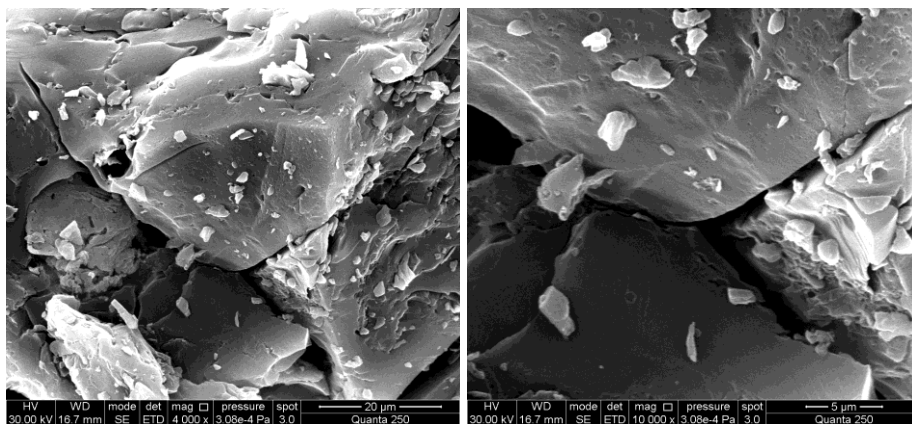

Fig. 4. SEM pictures for anthracite coal after high temperature heating process

BET analysis

Table 3 shows surface area (m^2/g) of anthracite coal before and after high temperature heating process. Surface area of fresh anthracite coal is much lower than that of heated anthracite coal. Figure 3 shows that there are nearly no cracks and holes on fresh coal surface. As shown in Fig. 4, there are many cracks and holes on heated coal surface. Therefore, the BET results mach the SEM results very well.

Table 3. BET results for anthracite coal before and after high temperature heating process

Coal types	Surface area (m^2/g)
Before heating process	0.24
After heating process	44.78

Contact angle analysis

Figure 5 and 6 are the pictures of contact angles of anthracite coal before and after high temperature heating process. The contact angle of fresh coal is about 112° while that of heated coal is only about 45°. After high temperature heating process, anthracite coal surface becomes more hydrophilic. From the above-mentioned results, heated anthracite coal surface has much more holes, cracks and hydrophilic functional groups. Hydrophilic functional groups make coal surface easy to be wetted. Meanwhile, the infiltration of water into the cracks and holes is also occurred during the measurements of contact angles. Therefore, the contact angle of heated anthracite

coal is much lower than that of fresh anthracite coal. The hydrophilicity of anthracite coal surface is increased by high temperature heating process.
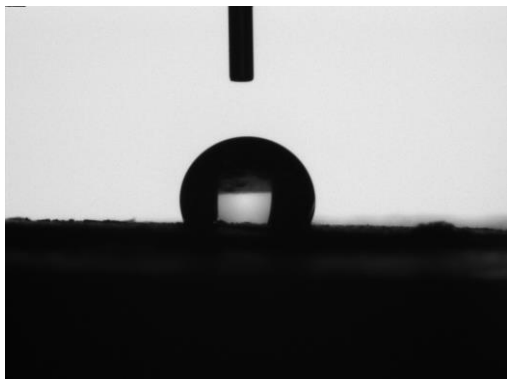

Fig. 5. Contact angle of anthracite coal before high temperature heating process
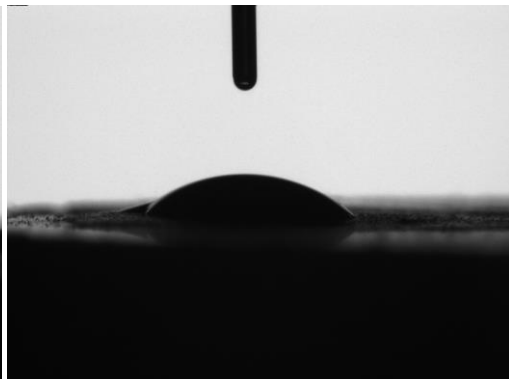
Fig. 6. Contact angle of anthracite coal after high temperature heating process

Conclusions

- The results of XPS, SEM, BET and contact angle measurements indicate that high temperature heating process not only changes the surface properties of anthracite coal but also reduces the hydrophobicity of coal surface.
- Compared with fresh anthracite coal surface, there are more holes, cracks and hydrophilic functional groups on heated anthracite coal surface.
- Both surface area and pore volume of fresh anthracite coal are much lower than those of heated anthracite coal.
- The contact angle of heated anthracite coal is much lower than that of fresh anthracite coal, and hence anthracite coal becomes much easier to be wetted after high temperature heating process than fresh anthracite coal.

Acknowledgment

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