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Effects of ash/ K_2CO_3/Fe_2O_3 on ignition temperature and combustion rate of demineralized anthracite

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Abstract: The effects of ash/ K_2CO_3/Fe_2O_3 and their interactions on the ignition temperature and combustion rate of acid-washed anthracite were examined. The coal ashes from combustion of anthracite at different temperatures showed very different properties such as chemical compositions, color and morphology. Reactivities of demineralized anthracite with and without catalysts were measured by thermo-gravimetric analyzer (TG-DTG). The results indicate that ash itself has no catalytic effects on ignition temperature while the combustion rate is improved, especially by the ash prepared at high temperatures. The use of ash with K_2CO_3 (or Fe_2O_3) together as combustion catalysts reveals that the interactions (i. e. sintering reactions) between them have caused the reduction in combustion rate, compared with the cases when K_2CO_3 or Fe_2O_3 was employed individually. Similarly, the synergistic effect between K_2CO_3 and Fe_2O_3 was also observed to lower the combustion rate of demineralized anthracite.

Key words: ash; catalyst; K_2CO_3/Fe_2O_3 ; ignition temperature; combustion rate

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Catalytic coal combustion is one of the most promising approaches to improve energy utilization efficiency in a pulverized coal boiler. For a given type of catalyst, not only organic compositions and structure in coal would affect the catalytic performance of the catalysts, but also the inorganic matters inherently existing in coal may play a vital role during the combustion process. Ash is the main derivatives of mineral matters in coal from combustion reaction. From inherent mineral matters to coal ash, it experiences a serial of changes/reforms, including structures, compositions and phases^[1,2]. The deposit of ash on reactor surfaces reduces the heat transfer rate, resulting in undesirable interruptions as well as decrease in lifetime of boilers^[3]. On the other hand, compounds in ash normally have some catalytic effects on coal combustion. Effects of inherent minerals in coal on combustion were often evaluated by comparing combustion reactivities between raw coal and demineralized coal^[4,5]. Some researchers found that the inherent minerals have improved coal combustion reactivity^[6-8], while others stated that the existence of inorganic matters could actually show no or even suppressing effects on coal combustion^[9,10]. Lemaigen et al^[11] studied links between coal

gasification reactivity and the amounts/compositions of mineral components in the samples including raw coal, acid-washed coal and acid-washed coal being impregnated with salts of Ca, K, Na and Fe, suggesting that it was almost impossible to develop a predictive tool for linking catalytic activity with those mineral matters.

As a matter of fact, it is very hard to conclude exact effects of the inherent mineral matter in coal by comparing combustion behavior of raw coal and demineralized coal, because the process of demineralization could also have induced the changes in physicochemical properties of coal^[8], such as the content of humic acid materials and the physical structure of coal particles. More importantly, due to the possible formation of new substances/phases during combustion process, these catalytic or suppressive effects (if any) did not simply result from the originally inherent minerals itself, but derived from those transition matters during combustion process. The “real” forms of inorganic materials showing catalytic activity during combustion may also vary, depending on the combustion conditions^[12], particularly the temperatures. Therefore, the insight into the characteristics of ash prepared from different

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combustion temperatures may facilitate to capture the actual catalytically-active matters during coal combustion. In theory, different characteristics of ash would mean different catalytic activities.

Catalytic combustion of pulverized coal can not only increase combustion reactivity^[13,14], but also decrease contaminant emission^[15,16], such as SO_x and NO_x . At present, catalysts used for coal combustion are mainly AAEM (alkali and alkaline earth metals) and some transition metal compounds, such as iron or its oxides^[16,17]. Besides the ash itself, information about the effect of interactions between ash and these externally-added catalysts on combustion behavior is practically important as they usually exist at the same time in pulverized coal boilers. The interactions between catalyst with different ashes (featuring different properties due to preparing conditions) could be vastly varied, leading to different catalytic activities for combustion reactions.

In this work, anthracite ashes were prepared at different combustion temperatures and were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) and fourier transform-infrared spectroscopy (FT-IR), respectively. To gain insights into the catalytic effects of transformed components of the different ashes on combustion reactivity of demineralized coal, the demineralized coal with different ashes were examined by TG-DTG. Furthermore, the influence of mixture (ash/ K_2CO_3 / Fe_2O_3) on the combustion behavior of acid-washed anthracite was investigated for observing their possible synergistic interactions.

1 Experimental

1.1 Sample preparation

An anthracite was ground to 0.10 ~ 0.15 mm and then demineralized. Properties of the anthracite are listed in Table 1. The procedure of demineralization is as follows: 10 g coal sample was mixed with 150 mL of 6 mol/L HCl; the slurry was stirred for 24 h at room temperature. After filtering, 150 mL of HF (40%) was added to HCl-washed coal and this mixture was stirred for 24 h and filtered again. Then the acid washed coals were continuously washed with boiling deionized water till no chloride ion was detected before being dried at 80 °C in vacuum oven for 24 h.

2 g of coal samples were burned in a muffle furnace in air at 15 °C/min from room temperature to 800 ~ 1300 °C with an interval of 100 °C, respectively, holding for 60 min at each final temperature. And the resultant ash was then taken out for use. All ash samples were ground to -0.10 mm, and were manually mixed into demineralized anthracite (10% ash) for

10 min in a mortar. The percentage of single or mixed catalysts in the demineralized anthracite was kept as 10% in this work.

Table 1 Properties of the coal

| | Anthracite |
|---|------------|
| Proximate analysis, air dried basis w/% | |
| Moisture | 2.27 |
| Ash | 12.57 |
| Volatile matter | 10.77 |
| Fixed carbon | 74.39 |
| Ultimate analysis, air dried basis w/% | |
| Carbon | 74.97 |
| Hydrogen | 2.66 |
| Nitrogen | 0.94 |
| Sulphur | 0.62 |
| Oxygen (by difference) | 5.97 |
| Analysis of ash w/% | |
| SiO ₂ | 48.72 |
| Al ₂ O ₃ | 32.59 |
| TiO ₂ | 1.15 |
| Fe ₂ O ₃ | 5.20 |
| CaO | 4.09 |
| MgO | 0.74 |
| Na ₂ O | 0.96 |
| K ₂ O | 0.86 |
| P ₂ O ₅ | 0.63 |
| SO ₃ | 0.96 |
| Others | 4.10 |

To examine interactions between ash and catalyst during coal combustion, K_2CO_3 with purity of 99% was blended with ash (prepared from different temperatures) by mass proportion of 1:1. The mixture was then added into demineralized anthracite by above method. In addition, to explore influences of ash content on the interaction between ash and catalyst during coal combustion, ash prepared at 800 °C was firstly mixed with K_2CO_3 or Fe_2O_3 (over 99% in purity with particle size of -0.10 mm) by mass proportions of 10:0, 8:2, 6:4, 4:6, 2:8 and 0:10, respectively. The mixtures were then added into demineralized anthracite in the same way. Finally, to study influence of interaction between K_2CO_3 and Fe_2O_3 on the combustion reactivity, K_2CO_3 and Fe_2O_3 mixture (10:0, 8:2, 6:4, 4:6, 2:8, 0:10) were added into the demineralized anthracite, and the total content of inorganic matters in coal was still 10%.

1.2 Combustion

Combustion was carried out in a thermo-gravimetric analyzer (ZRY-2P, China) to show combustion reactivity of all coal samples. About 20 mg sample was

placed in an Al_2O_3 ceramic crucible (inner diameter 5 mm) and was burned under an O_2 atmosphere (100 mL/min) at $15\text{ }^\circ\text{C}/\text{min}$ from 100 to $1\,000\text{ }^\circ\text{C}$.

1.3 Evaluation of reactivity

Ignition temperature and combustion rate were determined to evaluate coal combustion reactivity. The lower ignition temperature and higher combustion rate would mean better reactivity. The ignition temperature was determined by TG-DTG, as shown in Figure 1. Temperature at the position of D was considered as the ignition temperature of sample. Combustion rate was calculated by Equation (1).

$$r = \frac{\Delta C}{\Delta t(1-w)} \quad (1)$$

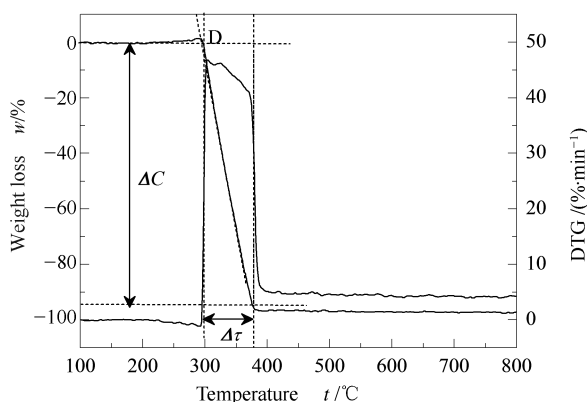


Figure 1 Determination of ignition temperature of char ("D" is the point for the ignition temperature of char)

where, r is the combustion rate; ΔC is the variation of conversion (dry-ash-free basis); Δt is time used for the conversion of ΔC ; w is the content

of inorganic matter in coal sample (dry basis).

1.4 Analysis of ash

The color and morphology of ash from different temperature were observed by camera (Canon) and scanning electron microscope (SEM, JEOL, JSM 6700F). The microcrystalline compositions of ash were characterized using X-ray diffraction (XRD, Philips X'pert PRO) equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.154\,187\text{ nm}$) at a scanning rate of $2\text{ }^\circ/\text{min}$ (2θ from 10° to 90°). X-ray tube voltage and current were set at 40 kV and 30 mA, respectively. The functional groups and structure on ash surface were analyzed by FT-IR. The FT-IR spectra in the range of $4\,000 \sim 400\text{ cm}^{-1}$ were recorded in KBr disk using an FT-IR 2000 Perkin-Elmer spectrophotometer.

2 Results and discussion

2.1 Effects of combustion temperature on ash characteristics

2.1.1 Color and morphology

Figure 2 shows pictures of ash obtained from anthracite combustion at different temperatures. From 800 to $1\,100\text{ }^\circ\text{C}$, color of ash changes from light pink into gray. At $1\,200\text{ }^\circ\text{C}$, it becomes light yellow, and then it turns into red brown at $1\,300\text{ }^\circ\text{C}$. The change in color was actually a reflection of changes in physicochemical properties of coal ash. The chemical compositions and proportions for ash prepared from different combustion temperatures could be different, which will be discussed in section 2.1.2.

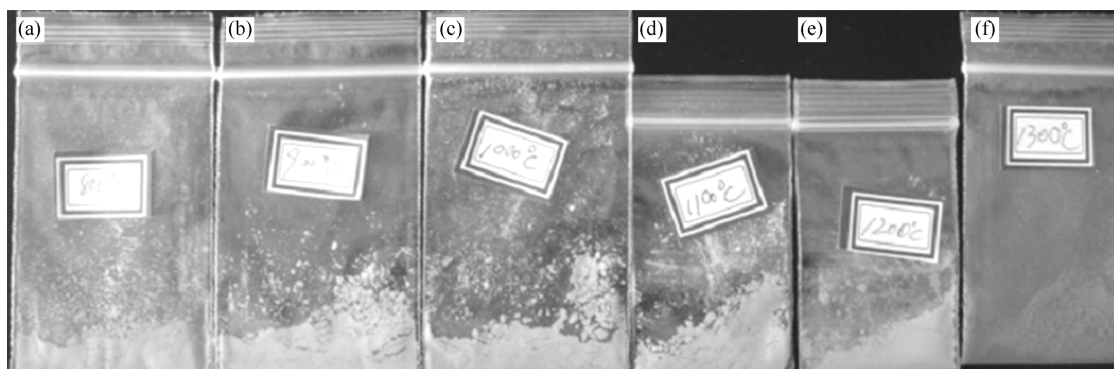


Figure 2 Color change of coal ash from different temperatures ($800 \sim 1\,300\text{ }^\circ\text{C}$)
(a): $800\text{ }^\circ\text{C}$; (b): $900\text{ }^\circ\text{C}$; (c): $1\,000\text{ }^\circ\text{C}$; (d): $1\,100\text{ }^\circ\text{C}$; (e): $1\,200\text{ }^\circ\text{C}$; (f): $1\,300\text{ }^\circ\text{C}$

Figure 3 shows ash morphology by SEM. The ash particles tend to be accumulated with increasing combustion temperature. When the temperature is above $1\,000\text{ }^\circ\text{C}$, it seems that sintering phenomenon takes place and larger particles are formed at $1\,300\text{ }^\circ\text{C}$.

2.1.2 Microcrystalline phases

Figure 4 shows XRD patterns of ashes prepared from the anthracite combustion at different temperatures. As the combustion temperature increases, diffraction peak intensity of quartz (SiO_2) decreases, and that of portlandite ($\text{Ca}(\text{OH})_2$) disappears gradually. With

increasing temperature, gehlenite ($2CaO_2 \cdot Al_2O_3 \cdot SiO_2$) in ash also reduces, melts and then disappears at $1\ 300\ ^\circ C$. Formation of mullite ($3Al_2O_3 \cdot 2SiO_2$) is observed at $1\ 000\ ^\circ C$, and its content in ash slightly increases from $1\ 000$ to $1\ 100\ ^\circ C$, and then keeping nearly constant until $1\ 300\ ^\circ C$. Formation of anorthite [$(Ca, Na)(Si, Al)_4O_8$] also occurs at around $1\ 100\ ^\circ C$ and still be clearly seen at $1\ 300\ ^\circ C$. The

slight reduction in the content of anorthite with increasing temperature to $1\ 300\ ^\circ C$ is due to the conversion from crystalline to non-crystalline structure. Indeed, most of them will be in amorphous structure when the temperature is above $1\ 400\ ^\circ C$ [12, 18-20]. In addition, the XRD spectral indicates that hematite and hedenbergite are detectable for the ash prepared at high combustion temperatures.

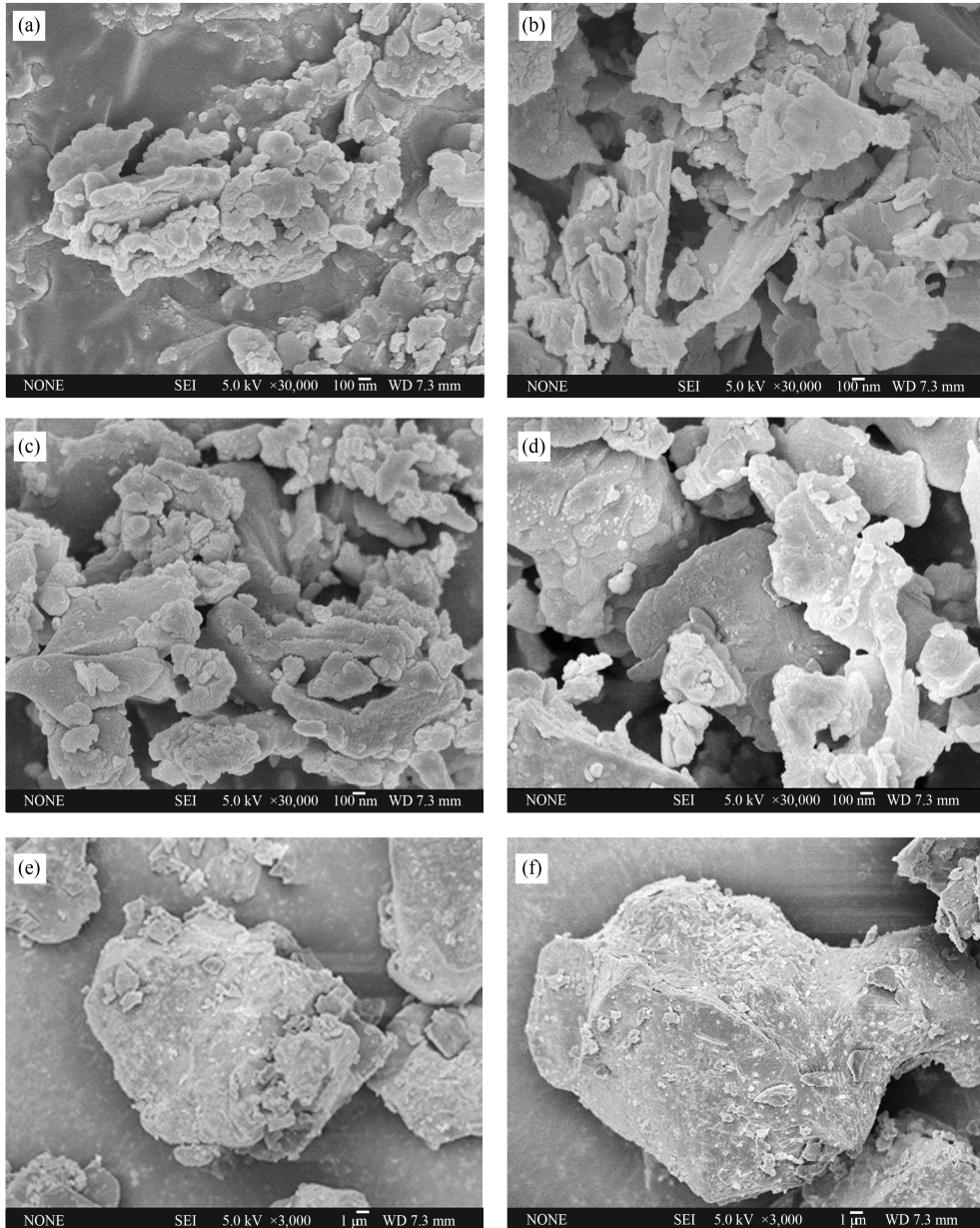


Figure 3 Variation of coal ash morphology prepared from different temperatures ($800 \sim 1\ 300\ ^\circ C$)
(a): $800\ ^\circ C$; (b): $900\ ^\circ C$; (c): $1\ 000\ ^\circ C$; (d): $1\ 100\ ^\circ C$; (e): $1\ 200\ ^\circ C$; (f): $1\ 300\ ^\circ C$

According to SEM and XRD analyses of ash from varied combustion temperatures, bulk of inherent mineral matters originally existing in coal have firstly decomposed into small units or layer structure at initial stage of combustion. As increasing

temperature, these structural units of nascent ash could sinter together and form new crystalline phases while some originally-existing crystalline phases disappear. The process was schematically described in Figure 5. The evolution of crystalline phases is the

basic reason for the change in the color and particle size of ash shown in Figures 2 and 3.

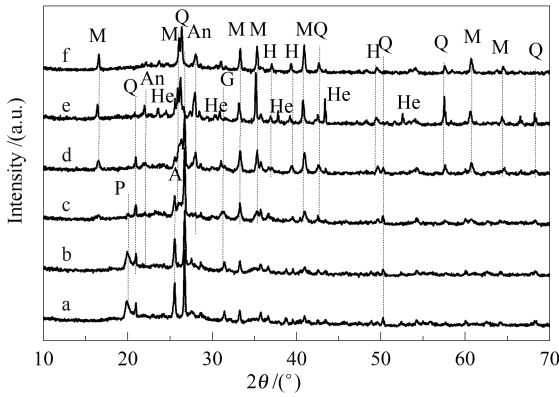


Figure 4 XRD patterns of ash at different temperatures

a: 800 °C; b: 900 °C; c: 1000 °C;
d: 1100 °C; e: 1200 °C; f: 1300 °C;
Q: quartz; A: anhydrite; P: portlandite;
G: gehlenite; L: lime; An: anorthite;
M: mullite; H: hematite; He: hedenbergite

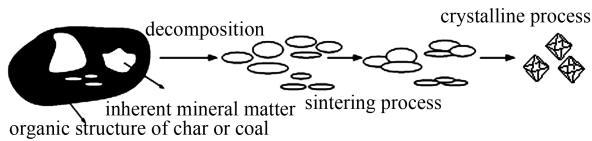


Figure 5 Schematic diagram of inherent mineral evolution during coal thermal conversion

2.1.3 Functional groups on the ash surface

The FT-IR spectra of ash generated from different temperatures are shown in Figure 6 (a). And Figure 6 (b) shows the most informative part of spectrum of ash at 900 °C for the purpose of better denoting and observation. The bands in the region around 3500 and 1620 cm^{-1} are commonly assigned to O-H in the planar water. The band at 1040 cm^{-1} is due to anti-symmetric Si-O-Si or Si-O-Al stretching vibrations. And the broad band with two shoulder peaks at 915 and 845 cm^{-1} is attributed to Al-O stretching.

The vibration of Si-O is around 667 cm^{-1} , whereas the Si-O-Al vibrations are around 800 and 720 cm^{-1} [12,18]. The band peak/area of Fe-O (560 cm^{-1}) also increases with increasing temperature, reaching the maximum at 1200 °C. As the combustion temperature for preparing ash increases, the FT-IR peaks of ash are generally getting weak, again indicating the rearrangement of surface elements and the formation of new crystal phases.

2.2 Effects of ash on demineralized anthracite combustion reactivity

Figure 7 shows variations of ignition temperatures and combustion rates of demineralized anthracite

loaded with ashes prepared at different temperatures. Compared with ignition temperature (300 °C) of demineralized coal (the dash line), the variation in ignition temperature due to the presence of ash is not obvious, meaning that the addition of ash into the coal has no catalytic effects on the coal ignition. Previous researchers reported that one of the main purposes for developing catalytic combustion of pulverized coal was to reduce ignition temperature [21]. But the ash used as additives in this study did not benefit the reduction in ignition temperature. Generally, catalysts should be decomposed to show good catalytic activity for lowering ignition temperature of coal [14].

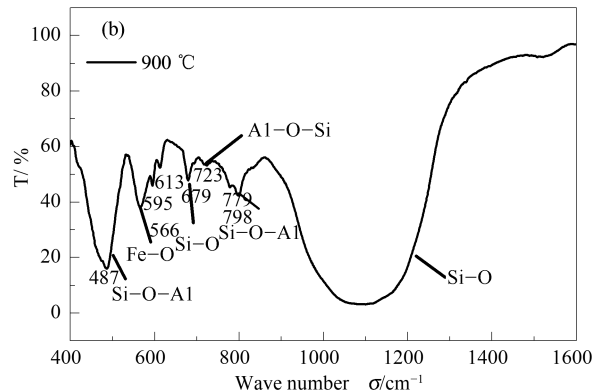
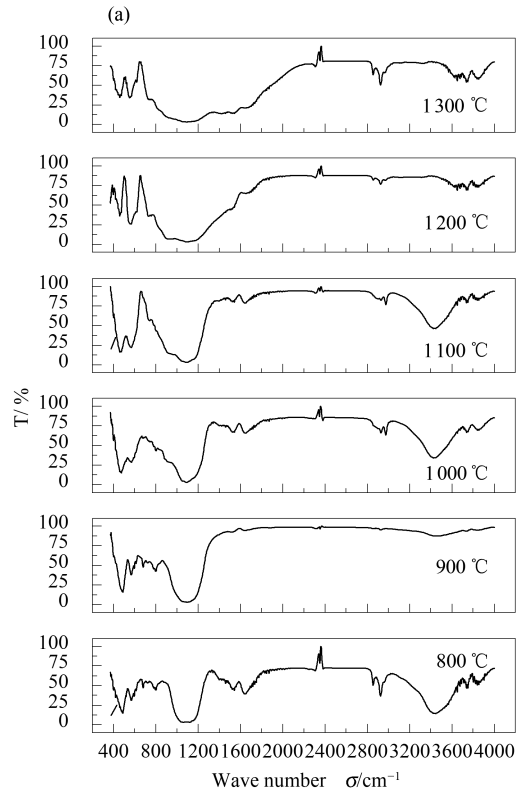


Figure 6 (a) FT-IR analysis of ash from different temperatures;
(b) part of FT-IR analysis of ash prepared at 900 °C

Figure 7 shows ignition temperature of demineralized anthracite is only about 300 °C. The ashes are prepared above 800 °C, which is much higher than 300 °C. In other words, the ash employed as catalysts has been thermally-annealed at high temperatures and the inert structure may not be possible to decompose at low temperatures, thus its effect on the ignition temperature is minor. In addition, the inert ash components on coal surface may negatively affect the contact between carbon and oxygen and even raise ignition temperatures^[22].

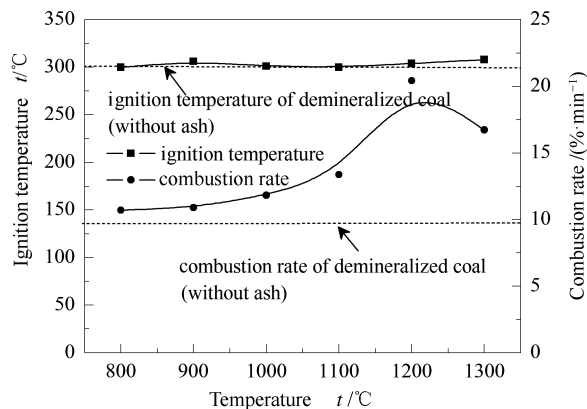


Figure 7 Effects of ash prepared from different temperatures on demineralized anthracite combustion reactivity

However, the combustion rate of acid-washed anthracite has apparently increased when being loaded with ash, especially with the ash prepared at high temperatures. This means that the ash could show activity for carbon-oxygen reaction after ignition takes place. The sintering structure and new crystalline phases formed in ash at high combustion temperatures could effectively improve demineralized anthracite combustion reaction rate because the transfer from one crystalline phase to another could produce new lattice

defects in ash. These defects may favor the oxygen adsorption and dissociation, hence improving the carbon and oxygen reaction (combustion) rate. However, when the ash preparation temperature is above 1 200 °C, some crystalline units (catalytically-active) disappear due to the fairly high temperature, thus catalytic effects of ash is decreasing. For example, FT-IR spectra of ash indicates that the amount of Fe–O on ash from 1 300 °C is less than that from 1 200 °C; while XRD analysis shows that the ash from high temperature contains more anorthite and mullite with less content of portlandite, compared with the ash prepared at low combustion temperatures.

2.3 Effects of interactions of inorganic matters

2.3.1 Interaction between coal ash and K_2CO_3 with fixed ratio

Figure 8 shows effects of interaction of K_2CO_3 and ashes (from different combustion temperatures) on combustion reactivity of demineralized anthracite. The total content of ash and K_2CO_3 in coal is kept 10% and the mass ratio of ash to K_2CO_3 is 1 : 1. From Figure 8 (a), compared with 10% ash addition (square dots), 5% ash plus 5% K_2CO_3 (circle dots) in coal have seen about 13 °C lower in ignition temperature. And the ignition temperature with using 10% K_2CO_3 in coal shows the lowest value (approximately 275 °C). The net reduction of ignition temperature by 10% K_2CO_3 is roughly twice of that by 5% K_2CO_3 coupling with 5% ash. Ash itself does not show any effects on the ignition point, agreeing with the results mentioned above. It may be concluded that the effect of interaction between K_2CO_3 and ash on the ignition temperature is also negligible.

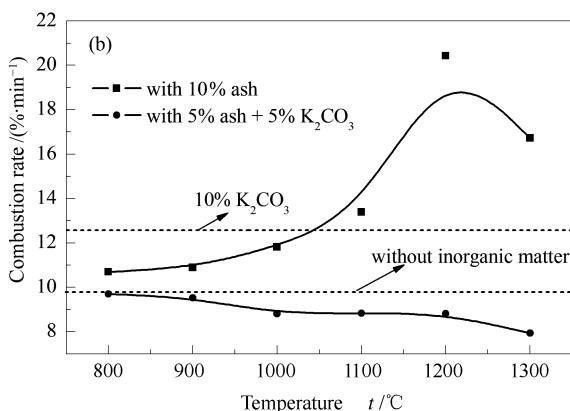
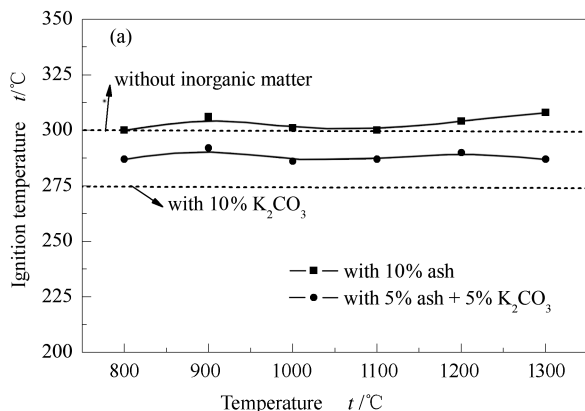


Figure 8 Effects of mixture of ash and K_2CO_3 (fixed ratio) on demineralized anthracite combustion reactivity (a): ignition temperature; (b): combustion rate

However, Figure 8 (b) demonstrates that the

synergistic effect between ash and K_2CO_3 on combustion

rate is very significant. Adding only 10% ash or K_2CO_3 , the combustion rates are all considerably improved. In contrast, when the ash (5%) and K_2CO_3 (5%) are used together, the combustion rate is going down in most cases. The interaction of K_2CO_3 and ash has inhibited catalytic effects of K_2CO_3 or ash on the combustion reaction.

The higher temperature used for ash preparation is, the stronger inhibiting effect could be seen. Compared with the ash prepared at low temperatures, the new materials/phases present in the ash from high temperature combustions (see Figure 4) may easily react with K_2CO_3 and form some inert substances (i. e. $K_2O \cdot nAl_2O_3 \cdot mSiO_2$) during the combustion process^[23]. The new compounds were produced at higher gasification above 700 °C^[24]. However, combustion process in this study was at much lower temperature in TGA (below 500 °C), and thus it is very difficult to form the inert substances. The potassium ion has strong diffusing ability to migrate into the ash pores^[25], deteriorating the contact between carbon and potassium and thus contributing to the observed lower catalytic activity for combustion reaction^[26].

2.3.2 Interaction of coal ash with K_2CO_3 or Fe_2O_3 with varied ratio

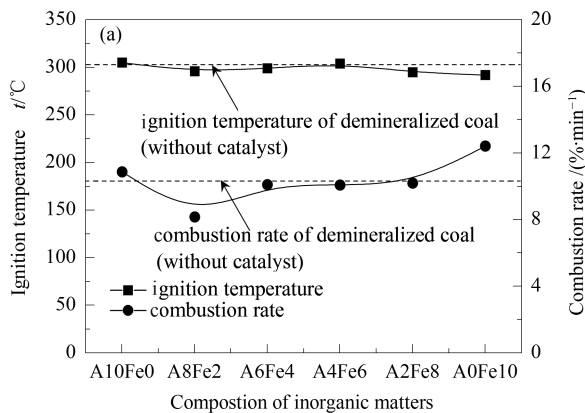


Figure 9 (a) and (b) illustrate the effect of interactions of ash and K_2CO_3 (or Fe_2O_3) with different ratios on changes in ignition temperature and combustion rate, respectively. The ash is prepared from anthracite combustion at 800 °C. When only Fe_2O_3 or K_2CO_3 is used as catalysts, it shows the better catalytic ability to lower ignition temperature and increase combustion rate than ash does. With the mixture of ash with Fe_2O_3 or K_2CO_3 , the ignition value gradually decreases with increasing contents of Fe_2O_3 or K_2CO_3 . It seems that the ash in mixture is not playing a role for the change in ignition point, indicating again that the interaction of ash and Fe_2O_3 or K_2CO_3 is nearly ignorable with respect to the variation in ignition temperature. However, the mixture of ash with Fe_2O_3 or K_2CO_3 performs very poor catalytic role in improving the combustion rate, even reducing it in some cases, particularly when the portion of ash in the mixture is high. This implies that the co-existence of ash and K_2CO_3 or Fe_2O_3 hinders their individual effects on combustion rate. The finding from Figure 9 (a) and (b) is essentially in agreement with that indicated in Figure 8 (a) and (b) although the extents are very different.

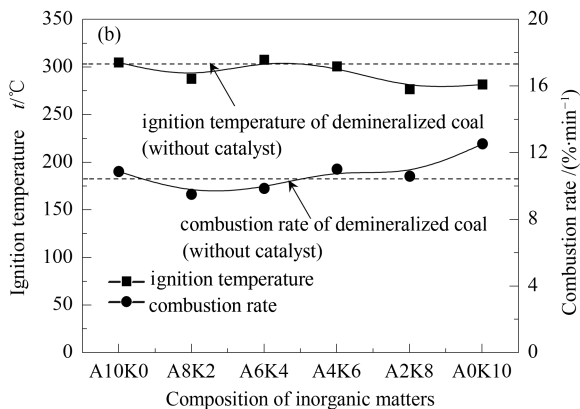


Figure 9 Effects of ratio of ash and catalysts on demineralized anthracite combustion reactivity
(a): ash and Fe_2O_3 ; (b): ash and K_2CO_3

2.3.3 Interactions of K_2CO_3 and Fe_2O_3 with different ratios

Figure 10 shows effects of K_2CO_3 , Fe_2O_3 and their mixture on combustion behavior of demineralized anthracite. Given the total content of 10%, the change in the portion of K_2CO_3 or Fe_2O_3 in the mixture does not obviously change its catalytic effect on ignition temperature.

Nevertheless, the catalytic impact by only K_2CO_3 or Fe_2O_3 on combustion rates is similarly higher than any ratios of their mixture. For the mixture of K_2CO_3 and Fe_2O_3 , the improvement of

combustion rate can not be observed, compared with the combustion rate of the acid-washed anthracite in the absence of catalysts. This well proves that the strong interactions between K_2CO_3 and Fe_2O_3 have also taken place during the combustion process. The effects of the mixture of K_2CO_3 and Fe_2O_3 on changes in the ignition temperature and the combustion rates are different. At initial stage of combustion, K_2CO_3 and Fe_2O_3 are well distributed inside the anthracite and their contacts with coal particles are good, which is important for a redox reaction^[26,27]. More importantly, at the low temperature each catalyst

could keep their chemical forms with catalytic ability, resulting in the improvement of ignition temperature via the possible catalytic pyrolysis as well as better absorption and dissociation of oxygen. However, combustion rate is calculated at high temperature after pulverized coal ignition. Sintering of two catalysts might be a reason that resulted in lower catalytic activity when they are mixed during demineralized coal combustion. Less likely, new compounds are formed as $K_2CO_3-Fe_2O_3$ reactions need higher temperature^[28].

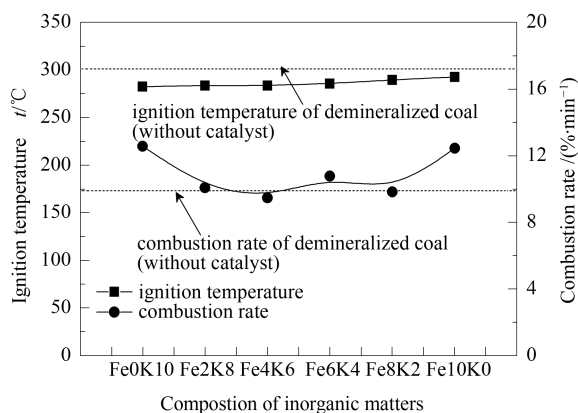


Figure 10 Effects of mixture of K_2CO_3 and Fe_2O_3 on demineralized anthracite combustion reactivity

However, the continuous carbon consumption with combustion preceding, the contact between K_2CO_3 and Fe_2O_3 become more compact and intimate. The interaction between K_2CO_3 and Fe_2O_3 could suffocate their catalytic activities, and further study is needed for understanding the exact mechanism.

3 Conclusions

Coal ash experienced a serial of changes with increasing combustion temperature, such as the formation of new crystalline phases and the accumulation of particles.

Ash prepared from different temperatures had no effects on the ignition temperature for demineralized anthracite. However, combustion rate was greatly improved by the introduction of ash prepared at 1 200 °C.

The presence of ash did not suppress the effect of K_2CO_3 or Fe_2O_3 on the reduction in ignition temperature, but reduced their positive effects on the combustion rate. Similarly, the synergistic effect of K_2CO_3 and Fe_2O_3 on anthracite ignition temperature was not observed while co-effects of K_2CO_3 and Fe_2O_3 lowered the combustion rate, compared with the effect when K_2CO_3 or Fe_2O_3 was used individually.

References

- [1] SAMIT M, SUNIL K S. Minerals transformations in Northeastern region coals of India on heat treatment[J]. *Energy Fuels*, 2006, **20**(3): 1089-1096.
- [2] VAN-DYK J C, WAANDERS F B, BENSON S A, LAUMB M L, HACK K. Viscosity predictions of the slag composition of gasified coal, utilizing FactSage equilibrium modelling[J]. *Fuel*, 2009, **88**(1): 67-74.
- [3] MCLENNAN A R, BRYANT G W, STANMORE B R, WALL T F. Ash formation mechanisms during pf combustion in reducing conditions [J]. *Energy Fuels*, 2000, **14**(1): 150-159.
- [4] LIU Y H, CHE D F, XU T M. The effects of indigenous minerals in a coal on the emissions of NO and SO₂ during combustion[J]. *Combust Flame*, 2004, **138**(4): 404-406.
- [5] ÖZTAS N A, YÜRÜM Y. Pyrolysis of Turkish Zonguldak bituminous coal. Part 1. Effect of mineral matter[J]. *Fuel*, 2000, **79**(10): 1211-1227.
- [6] RALF K, HENRYK Z. Catalytic effects of ash components in low rank coal gasification. 1. Gasification with carbon dioxide[J]. *Fuel*, 1991, **69**(3): 275-281.
- [7] MÉNDEZ L B, BORRERO A G, MARTINEZ-TARAZONA M R, MENÉNDEZ R. Influence of petrographic and mineral matter composition of coal particles on their combustion reactivity[J]. *Fuel*, 2003, **82**(15): 1875-1882.
- [8] RUBIERA F, ARENILLAS A, PEVIDA C, GARCÍA R, PIS J J, STEEL K M, PATRICK J W. Coal structure and reactivity changes induced by chemical demineralization[J]. *Fuel Process Technol*, 2002, **79**(3): 273-279.
- [9] SUJANTI W, ZHANG D K. A laboratory study of spontaneous combustion of coal: The influence of inorganic matter and reactor size[J]. *Fuel*, 1999, **78**(5): 549-556.
- [10] CRELLING J C, HIPPO E J, WOERNER B A, WEST J D P. Combustion characteristics of selected whole coals and macerals[J]. *Fuel*, 1992, **71**(2): 151-158.
- [11] LEMAIGNEN L, ZHOU Y, REED G P, DUGWELL D R, DANDIYOUTI R. Factors governing reactivity in low temperature coal gasification. Part II. An attempt to correlate conversions with inorganic and mineral constituents[J]. *Fuel*, 2002, **81**(3): 315-326.
- [12] BAI J, LI W, LI B Q. Characterization of low-temperature coal ash behaviors at high temperatures under reducing atmosphere[J]. *Fuel*, 2008, **87**(4): 583-591.
- [13] HEDDEN K, WILHELM A. Catalytic effects of inorganic substances on reactivity and ignition temperature of solid fuels[J]. *Ger Chem Eng*, 1980, **3**(2): 142-147.
- [14] WU Z H, XU L, WANG Z Z, ZHANG Z R. Catalytic effects on the ignition temperature of coal[J]. *Fuel*, 1998, **77**(8): 891-893.
- [15] LIU Y H, CHE D F, XU T M. Effects of NaCl on the capture of SO₂ by CaCO₃ during coal combustion[J]. *Fuel*, 2006, **85**(4): 524-531.
- [16] ZHAO Z B, LI W, QIU J S, WANG X Z, LI B Q. Influence of Na and Ca on the emission of NO_x during coal combustion[J]. *Fuel*, 2006, **85**(5): 601-606.
- [17] MCKEE D W. Mechanisms of the alkali metal catalyzed gasification of carbon[J]. *Fuel*, 1983, **62**(2): 170-175.
- [18] BAI J, LI W, LI C Z, BAI Z Q, LI B Q. Influences of minerals transformation on the reactivity of high temperature char gasification[J]. *Fuel Process Technol*, 2010, **91**(4): 404-409.
- [19] VAN-DYK J C, BENSON S A, LAUMB M L, WAANDERS B. Coal and coal ash characteristics to understand mineral transformations and

- slag formation[J]. Fuel, 2009, **88**(6): 1057-1063.
- [20] VARGAS S, FRANDSEN F J, DAM-JOHANSEN K. Rheological properties of high-temperature melts of coal ashes and other silicates[J]. Prog Energy Combust Sci, 2001, **27**(3): 237-429.
- [21] GONG X Z, GUO Z C, WANG Z. Reactivity of pulverized coals during combustion catalyzed by CeO_2 and Fe_2O_3 [J]. Combust Flame, 2010, **157**(2): 351-356.
- [22] GURURAJAN V S, WALL T F, GUPTA R P, TRUELOVE J S. Mechanisms for the ignition of pulverized coal particles[J]. Combust Flame, 1990, **81**(12): 119-132.
- [23] LOTHAR K, HORST P. Reaction of catalysts with matter during coal gasification[J]. Fuel, 1983, **62**(2): 205-208.
- [24] FORMELLA K, LEONHARDT P, SULIMMA A, VANHEEK K H, JÜNTGEN H. Interaction of mineral matter in coal with potassium during gasification[J]. Fuel, 1986, **65**(10): 1470-1472.
- [25] PRANDA P, PRANDOÁ K, HLAVACEK V. Combustion of fly-ash carbon Part I. TG-DTA study of ignition temperature[J]. Fuel Process Technol, 1999, **61**(3): 211-221.
- [26] AN H M, MCGINN P J. Catalytic behavior of potassium containing compounds for soot combustion[J]. Appl Catal B: Environ, 2006, **62**(1): 46-56.
- [27] JIMÉNEZ R, GARCÍA X I, CELLIER C, RUIZ P, GORDON A L. Soot combustion with K/MgO as catalyst[J]. Appl Catal A: Gen, 2006, **297**(2): 125-134.
- [28] HAO Z Z, WU S L, WANG Y C, LUO G P, WU H L, DUAN X G. Acting mechanism of F, K, and Na in the solid phase sintering reaction of the Baiyunebo iron ore[J]. Int J Miner Metal Mater, 2010, **17**(2): 137-142.

煤灰/ K_2CO_3 / Fe_2O_3 对脱矿无烟煤燃点与燃烧速率的影响

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摘要:考察了煤灰/ K_2CO_3 / Fe_2O_3 及其之间的相互作用对酸洗无烟煤燃点和燃烧速率的影响。不同温度下制备的煤灰显示了不一样的性质(如化学组成、颜色和形貌)。脱矿无烟煤(负载和非负载催化剂)的燃烧反应性测试在热重分析仪(TG-DTG)中完成,结果表明,煤灰本身对酸洗无烟煤的燃点几乎没有影响,而高温下制备的煤灰能够明显提高酸洗无烟煤的燃烧速率。当煤灰和 K_2CO_3 或者 Fe_2O_3 的混合物加入酸洗无烟煤中作为燃烧催化剂时,可以看出与单独使用 K_2CO_3 或 Fe_2O_3 相比,煤灰的加入明显导致酸洗煤的燃烧速率下降,而对其燃点影响不大。同样, K_2CO_3 和 Fe_2O_3 之间的相互作用也能够对酸洗无烟煤的燃烧速率产生负面影响。

关键词: 煤灰; 催化剂; K_2CO_3 / Fe_2O_3 ; 燃点; 燃烧速率

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