

Study on the influence mechanism of acidic mineral components on the reaction behavior of ion-exchangeable Ca during coal pyrolysis

LI Hongsheng^{1,2,3}, HAO Pan^{1,3,*}, YAN Lunjing^{1,2,3}, KONG Jiao^{1,2,3}, WANG Meijun^{1,2,3},
BAO Weiren^{1,2,3}, CHANG Liping^{1,2,3}

¹ College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China;

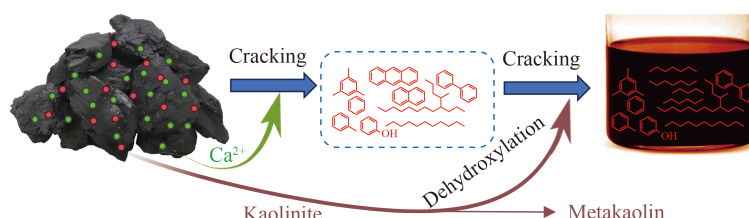
² State Key Laboratory of Clean and Efficient Coal-based Energy Utilization, Taiyuan University of Technology, Taiyuan 030024, China;

³ Key Laboratory of Coal Science and Technology of Ministry of Education, Taiyuan University of Technology, Taiyuan 030024, China

Abstract: Inherent minerals play a significant role in the thermal conversion of coal. However, the influence mechanism of the interactions among minerals on the generation of tar during coal pyrolysis remains unclear. To investigate the mechanism of the effect

of acidic mineral components on the behavior of Ca^{2+} during coal pyrolysis, several samples were prepared by HCl and HF washing and Ca^{2+} ion exchanging. The pyrolysis behaviors of the experimental coal samples were examined in a fixed-bed reactor. During the acid washing process, the ash content was effectively reduced, while the contents of organic elements such as carbon and hydrogen were also decreased. The loading of ion-exchangeable calcium enhanced the thermal weight loss rate of the coal sample in the 500–550 °C range, and the corresponding peak temperature shifted from 530 to 514 °C for the coal without Ca. When coal was pyrolyzed at a final temperature of 600 °C with a slow heating rate, kaolinite in acidic mineral components undergoes dehydroxylation to form metakaolin, and the content of small aromatic rings (<6 rings) in the char pyrolyzed by Ca-loaded coal sample was lower than that of the coal sample after acid washing. Due to the coexistence of acidic mineral components with ion-exchangeable Ca, the content of aliphatic hydrocarbons in the pyrolysis tar of YL-HCl-Ca reached 21.98%, significantly higher than 13.60% in the corresponding pyrolysis tar of YL-De-Ca. From the apparent results, it can be found that the acidic mineral components inhibit the adverse effect of ion exchangeable Ca^{2+} on the lightening of coal tar.

Key words: minerals; ion-exchangeable Ca; pyrolysis; coal tar



China is one of the world's largest producers and consumers of energy, and coal functions as the "Ballast stone" and "stabilizer" of energy security. Low rank coal is abundant in China; however, the high oxygen content and low calorific value of low rank coal limit the supply as power fuel. Pyrolysis is a suitable technology for low rank coal conversion, which can take advantage of its high volatile matter and reactivity to obtain semi-coke, gas and tar. After subsequent separation and processing, coal tar could be converted into high value-added products such as special fuels, fine chemicals and carbon materials^[1].

However, lower tar yield and the high content of heavy components in tar pose significant challenges to process equipment operation and subsequent product separation. Therefore, effective measures should be taken to increase the yield of coal tar and improve the product selectivity, by which a long-term stable operation of low rank coal pyrolysis can be effectively promoted.

Coal pyrolysis process involves complex reactions, and the inherent minerals in coal significantly influence the production of coal tar^[2–3]. Calcium-based minerals commonly occur as inherent mineral components in coal^[4],

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* Corresponding author. E-mail: haopan@tyut.edu.cn.

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especially for the abundant coal resources discovered in Zhundong, Xinjiang, with the content of CaO in the ash reaching over 40%^[5]. As a common occurrence form of Ca, the ion-exchangeable calcium forms chemical bonds with organic matter, and its mechanism of action is closely related to both the primary cracking of coal and the secondary reactions of volatiles. Scholars have done a lot of work on the effect of Ca^{2+} on the coal pyrolysis. However, due to the complexity of coal structure and pyrolysis processes, the addition method of Ca and pyrolysis conditions significantly influence the pyrolysis mechanism. The conclusion obtained from research varies with literature. The main methods of Ca addition include ion exchange, impregnation and mechanical mixing. Compared to coal samples without Ca addition, the coal loaded with ion exchanged Ca^{2+} shows a declining trend in the yields of semi-coke and tar under low-temperature slow pyrolysis conditions^[6–7], while Ca-impregnated coal results in an increased semi-coke yield^[8–9]. The coal mixed with calcium acetate by mechanical mixing exhibits a decreased semi-coke yield and an increased tar yield in the high-temperature pyrolysis^[10]. Also, the addition method of Ca affects the physicochemical structure of coal. Coal undergoes impregnation and rinsing by Ca^{2+} solution during ion exchanging reaction, leading to the formation of $-\text{COOCa}$ bonds and more pore structure. Calcium compounds disperse on the coal surface and within the pores uniformly during impregnation, which may lead to pore blockage. The mechanical mixing method mixes solid samples containing calcium compounds with coal powder, which cannot achieve complete uniform dispersion and only allows surface contact between Ca and coal. Pyrolysis conditions such as heating rate, final pyrolysis temperature, and residence time regulate the heat and mass transfer processes during coal pyrolysis and influence the effect of $\text{Ca}^{6-7,11-12}$. Bao et al.^[13–15] found that ion-exchangeable Ca undergoes different chemical reactions with temperature rising. The form of Ca is transformed, accompanied by organic matter cracking, resulting in the varying yield and composition of volatiles. As a divalent ion, Ca^{2+} acts as a cross-linking site in the coal structure. During pyrolysis, the tight structure inhibits the release of volatiles. Ca combines with $-\text{COO}$ in coal or the carbon matrix in semi-coke and decomposes continually, causing secondary reactions of tar precursor, which may crack into gases or form coke. Additionally, during slow low-temperature pyrolysis, Ca^{2+} increases the proportion of polycyclic aromatic hydrocarbons in tar, enhancing the content of heavy fraction^[6]. The research also indicates that Ca^{2+} has an adverse effect on the yield and light fraction of coal tar under slow low-temperature pyrolysis conditions.

Acidic components of minerals in coal are compounds containing Si and Al, such as SiO_2 , kaolinite and Al_2O_3 , etc. SiO_2 is stable during low temperature pyrolysis, primarily exhibiting a physical effect on the coal pyrolysis, i.e., the

mineral particles are doped between organic substances, which hinder the contact of organic substances, thus affecting the mass transfer process^[16]. Kaolinite can facilitate the release of tar precursors from the surface of coal char to form tar during low-temperature pyrolysis. Acid-modified kaolinite can promote the generation of light components in tar through catalytic effects^[17]. By adding Al_2O_3 to a coal, the thermal reactivity of coal is significantly enhanced at 580 °C, and the release of volatile matter increases^[18]. From the above studies, it can be concluded that the acidic mineral components exhibit inert or beneficial effects on the coal tar production under low-temperature pyrolysis conditions.

The affecting mechanisms of minerals on the coal pyrolysis are not completely the same. During the thermal conversion, minerals have many effects on organic matter evolution, resulting in changes in the primary cracking of coal and the secondary reaction of volatile matter^[8,19–20]. Researchers have employed diversified minerals to regulate the thermal transformation process^[21–22]. Currently, most studies about the interaction between minerals focus on the gasification process, while the influence mechanism of minerals on the tar generation in the coal pyrolysis process is still unclear. Therefore, further research on the combined effect of different types of minerals on the generation and transformation of tar during coal pyrolysis is necessary to provide theoretical basis for improving the quality of coal tar. This study aims to investigate the influence of acidic components of minerals on the reaction behavior of ion-exchangeable Ca in the coal pyrolysis process, especially on the generation mechanism of pyrolysis tar. Coal samples under minerals removing completely or removing metal minerals by hydrochloric acid to retain the acidic components of minerals are selected as the samples for loading Ca^{2+} . Calcium acetate is used as the ion-exchange material, and the calcium is loaded into the organic structure of the coal by ion exchangeable reaction. The pyrolysis behavior and products of different coal samples are tested to explore the influence of mineral types on the generation mechanism of tar.

1 Experimental

1.1 Experimental material

The coal used in the experiment was from Yili, Xinjiang, with particle sizes of 0.15–0.18 mm, which was denoted as YL. The coal sample was dried in a vacuum oven at 105 °C for 12 h before using. The proximate and ultimate analyses of YL was carried out in accordance with the standards of GB/T212—2008 and GB/T31391—2015, and the results are shown in Table 1. The analysis of ash composition was carried out in accordance with the GB/T1574—2007 standard, and the results are shown in Table 2.

Table 1 Proximate and ultimate analyses of coal

Sample	Proximate analysis w/%		Ultimate analysis w _{daf} /%				$S_{t,d}$	Atomic ratio	
	A_d	V_{daf}	C	H	O ^a	N		H/C	O/C
YL	9.29	36.46	76.47	4.01	>17.69	0.77	1.06	0.63	>0.17
YL-HCl	3.71	34.99	75.58	4.05	>18.73	1.03	0.46	0.64	>0.19
YL-De	1.10	34.54	76.10	3.88	>18.50	1.03	0.48	0.61	>0.18
YL-HCl-Ca	6.09	38.01	76.32	3.73	>18.36	1.01	0.58	0.59	>0.18
YL-De-Ca	5.26	37.55	75.79	3.69	>19.06	1.00	0.45	0.58	>0.19

^a: by difference.

Table 2 Ash composition analysis of YL

Ash composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	SO ₃	K ₂ O	Na ₂ O	P ₂ O ₅
Content w/%	13.95	9.36	23.98	18.98	5.30	0.38	26.71	0.52	0.25	0.042

The inherent minerals in coal are removed by the stepwise acid leaching method. The specific steps are as follows. Coal sample and 5 mol/L HCl solution were mixed in a ratio of 1:10 (g:mL) in a beaker at room temperature. After stirring evenly, let the mixture stand still. Then, the mixture was stirred for 3 min every 3 h with a total reaction time of 12 h. Afterwards, filtration was conducted and the chloride ions were completely washed away by deionized water. The obtained coal was dried in a vacuum oven at 105 °C for 24 h, which is denoted as YL-HCl. Subsequently, YL-HCl and 12 mol/L HF solution were mixed in a ratio of 1:10 (g:mL) in a plastic beaker. The next operating process is the same as HCl treating. The filter cake was washed with deionized water until the filtrate became neutral, and the washed coal was dried in a vacuum drying oven at 105 °C for 24 h, which is denoted as YL-De.

The specific steps of ion exchangeable reaction are as follows. YL-HCl and YL-De were mixed with 1.5 mol/L calcium acetate solution in a ratio of 1:10 (g:mL) in a beaker respectively. After stirring for 12 h, the mixture was washed with a large amount of water and filtered. Then the filter cake was dried at 105 °C for 24 h. The coal samples prepared by ion exchanging are denoted as YL-HCl-Ca and YL-De-Ca.

1.2 Pyrolysis experiments

5.00 g coal sample was placed in a fixed bed reactor with a quartz plate. Argon gas was introduced, and the gas flow rate was maintained at 100 mL/min. The reactor was heated at a rate of 10 °C/min to 600 °C, and retained for 30 min. The resulting volatile products flowed into a gas-washing bottle containing CH₂Cl₂ for collecting tar, and the pyrolysis gas was collected in a gas bag after filtration and drying. The tar and char yields were obtained by weighing, the water content was determined by Karl Fischer water analyzer, and the collected gas was analyzed by a gas chromatography (GC). The chars obtained from the fixed bed pyrolysis reactor were named as YL-HCl-Char, YL-De-Char, YL-HCl-Ca-Char and YL-De-Ca-Char, respectively. The tar composition was analyzed by a two-dimensional gas chromatography-mass spectrometry instrument (GC×CC-MS). Each experiment was repeated at least twice to ensure the accuracy of data. Due to the inevitable mass loss during the experiment, the sum of all the product yield was lower than 100%. A brief process flow of the pyrolysis experiment is shown in Figure 1.

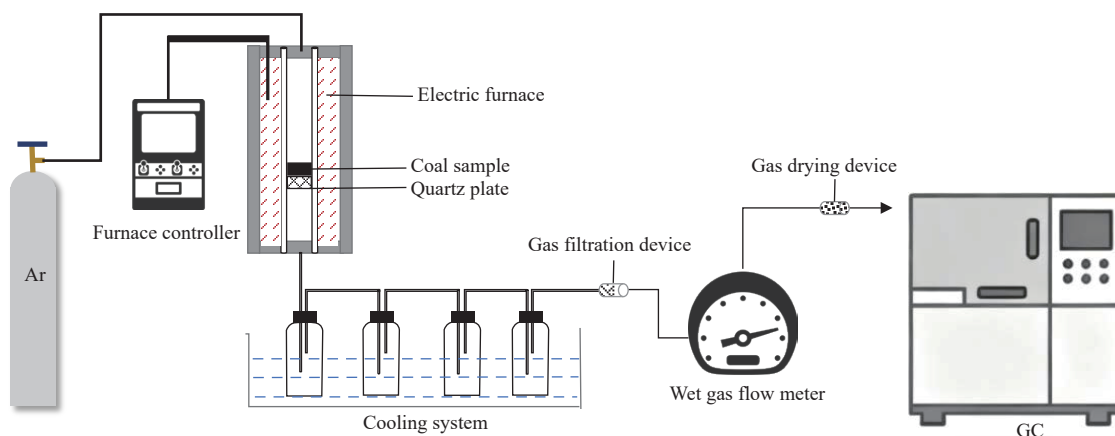


Fig. 1 Schematic diagram of the fixed-bed pyrolysis reaction process

1.3 Characterization

The organic structure and functional groups in coal samples were analyzed using a Fourier Transform Infrared Spectrophotometer (FT-IR, INVENIO-R). After mixing the coal sample with potassium bromide powder and pressing it into a pellet, the sample was scanned in a wavelength range of 400–4000 cm^{-1} . The specific surface area and pore size distribution of the coal samples were measured using a physical adsorption instrument (QUADRASORB evo), from which the total specific surface area and total pore volume were obtained using the BET method. The crystal structure of minerals was analyzed using an X-ray diffraction spectrometer (XRD, Mini Flex 600 type). And a thermal gravimetric analysis (TG, SETARAM) was conducted to get the thermal weight loss curve of the coal sample. About 10 mg sample was placed in a corundum crucible and heated from room temperature to 1050 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$ in an argon gas flow of 100 mL/min.

2 Results and discussion

2.1 Effect of ion exchange on coal basic properties

The basic properties of the coal sample prepared are shown in Table 1. The ash content showed that acid washing effectively removed the mineral components in coal, and the ash content increased again due to the loading of Ca^{2+} by ion exchange, indicating that Ca^{2+} was successfully added to the acid-washed coal sample. After leaching metal minerals with HCl, the volatile matter decreased from 36.46% of YL to 34.99%, while the volatile matter of YL-HCl-Ca increased to 38.01%, indicating that the Ca by ion exchange is positive to the evolution of volatile matter. From the H/C atomic ratio of the coal sample, it can be seen that the acid washing and Ca^{2+} loading processes have a certain impact on the carbon and hydrogen composition of the coal. Some small molecular compounds in coal have been leached out during the process, so the H/C atomic ratio of pretreated coal decreased. In addition, it is worth noting that the S content decreased significantly after acid washing, indicating that most of the sulfur in YL is inorganic sulfur, which was easily leached out during the demineralization process.

To investigate the effect of ion exchange on the chemical structure of the coal, an infrared spectroscopy analysis was performed on the acid-washed coal and the sample with Ca^{2+} loading, and the results are shown in Figure 2. The characteristic position of $-\text{COOH}$ is at 1700 cm^{-1} , and it can be seen that the peak intensity here decreased significantly after ion exchange, proving that the ion exchange reaction converted the structural $M-\text{COOH}$ (where M represents the organic structure of coal) into $M-\text{COO}-\text{Ca}$. However, the structures such as aliphatic $-\text{CH}_3$, $-\text{CH}_2-$ and aromatic $\text{C}=\text{C}$ did not exhibit obvious change, proving that the ion exchange did not destroy the main structure of the coal.

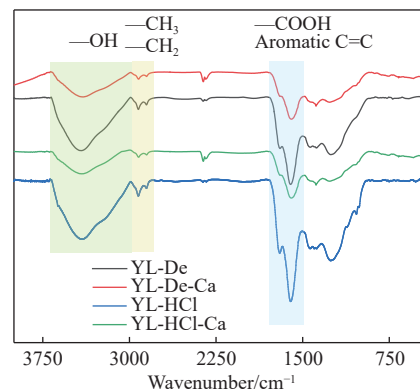


Fig. 2 Infrared spectra of acid-washed coal and coal samples loaded with Ca^{2+}

2.2 Effect of Ca^{2+} and acidic mineral components on the thermal reactivity of coal

To investigate the thermal reactivity of coal samples, the TG and DTG (differential thermal gravity) curves of coal were obtained. Because the ash content of coal could interfere the results, the data were converted to the dry ash-free basis (daf) in this section. The results are shown in Figure 3. Coal samples not only underwent changes in the content of minerals but also lost low molecular weight compounds during the acid washing and ion exchange reaction^[15,23]. The content of hydrogen in low molecular weight compounds is relatively high, so the loss of organic substances would lead to a decrease in the hydrogen content of coal^[24]. Meanwhile, the loss of minerals and low molecular weight compounds would cause changes in the physical structure, with an increase in specific surface area (Table 3). The developed pore structure is conducive to the diffusion of volatile matter produced during pyrolysis. Therefore, the thermal weight loss behavior of coal is the result of the combined effects of multiple factors. The TG curves show that there is little difference in the weight loss of coal samples below 450 $^{\circ}\text{C}$. With the temperature rising, the differences gradually become more obvious, and the order of final weight loss is: YL-De < YL-HCl < YL-HCl-Ca < YL-De-Ca. The DTG curves show that the maximum weight loss rates of the coal samples are very close, but the weight loss rates between 500 and 550 $^{\circ}\text{C}$ are significantly different. The peak temperature of the weight loss rate of the coal samples loaded with Ca is approximately 514 $^{\circ}\text{C}$, which is 16 $^{\circ}\text{C}$ lower than that of the corresponding coal samples without ion exchange. Moreover, the weight loss rates of YL-De-Ca and YL-HCl-Ca are also higher at the peak temperature, indicating that the thermal reactivity of coal is higher and the cracking ability is enhanced after loading Ca^{2+} . It has also been observed that the trend or difference in the reactivity of coal or biomass before and after adding Ca varies with temperature in other research^[7,22,25], indicating that the thermal reactivity behavior with Ca is related to the temperature.

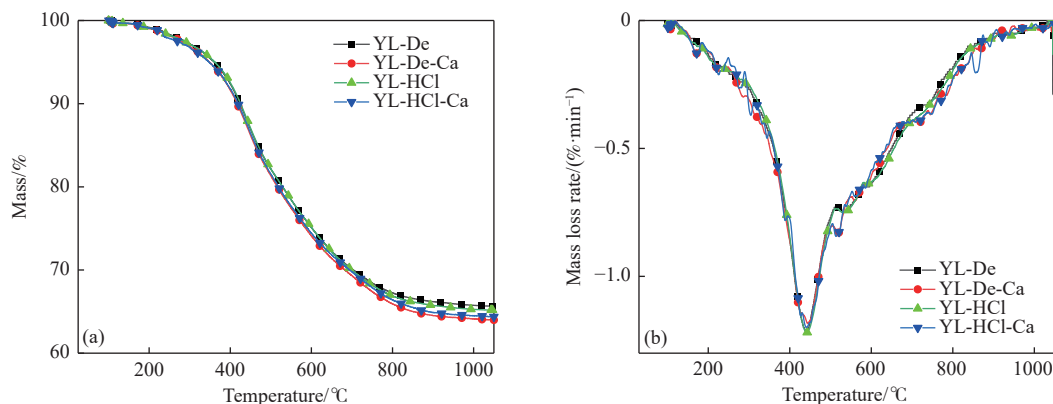


Fig. 3 TG-DTG curves of acid washed coal and coal samples loaded with Ca^{2+}

Table 3 Surface area and parameters of pore structure of acid washed sample

Sample	BET surface area/($\text{m}^2 \cdot \text{g}^{-1}$)	Total pore volume /($\text{cm}^3 \cdot \text{g}^{-1}$)	Average pore diameter/nm
YL-HCl	3.5258	0.0081	9.2441
YL-De	4.1204	0.0092	8.9309

2.3 Distribution of products obtained from fixed-bed reactor pyrolysis

The yields of products obtained from coal pyrolysis in the fixed-bed reactor are shown in Figure 4. During the acid washing process, the loss of minerals and small molecular compounds increased the pore volume and specific surface area, while the hydrogen content decreased. During the process of loading Ca, the hydrogen of carboxyl groups decreases due to the ion exchangeable reaction and more small molecular compounds are dissolved in the solution, resulting in a decrease in the H/C atomic ratio of coal loaded with Ca^{2+} . The distribution of the pyrolysis products is also affected by these factors. The tar yield of YL-HCl is 10.03%, significantly lower than that of other coal samples. YL-HCl was just undergone one step acid washing. Although YL-HCl had a high H/C atomic ratio, its specific surface area was smaller, and the diffusion of volatile matter was the

most unfavorable among the coal samples, resulting in a low yield of tar. However, the tar yields of YL-De, YL-De-Ca and YL-HCl-Ca did not show a significant difference. The reason is that the physical structure, the organic matter type changes and the loading of ionic exchangeable Ca^{2+} all have an impact on the pyrolysis process, and the tar yield is related to the combined effect of multiple factors.

The composition of the tar fractions is shown in Figure 5. The proportions of aliphatic hydrocarbons in coal tar obtained by YL-HCl and YL-De pyrolysis were 29.74% and 21.36%, respectively, while the contents of aromatic compounds were 47.37% and 54.25%, respectively.

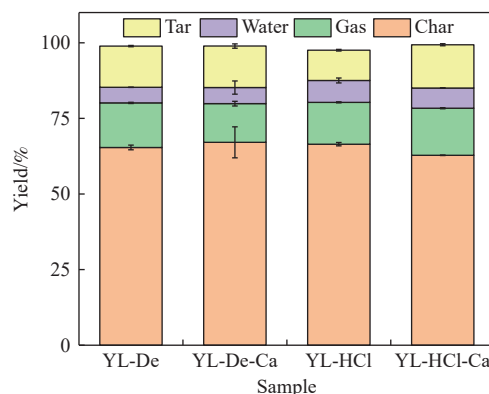
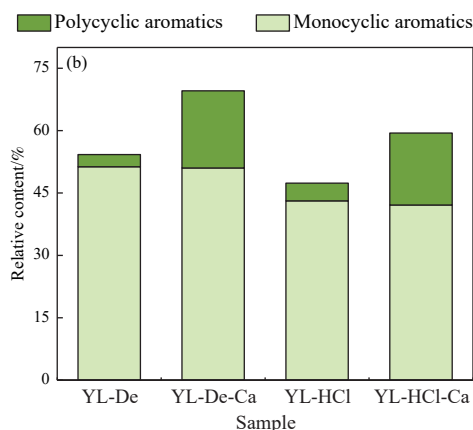
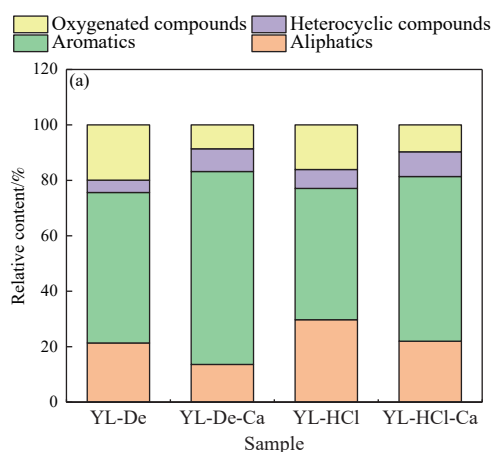


Fig. 4 Product distribution of coal pyrolysis in the fixed-bed reactor



(a): Group composition of tar; (b): Distribution of aromatics.

Fig. 5 Group composition of tar derived from fixed bed pyrolysis

It is indicated that the existence of silicon-aluminum minerals in coal can promote the formation of aliphatic hydrocarbons. Compared with the corresponding ion exchangeable coal samples YL-De-Ca and YL-HCl-Ca, the contents of aliphatic hydrocarbons in coal tar produced by YL-De and YL-HCl pyrolysis were higher. This suggests that after loading Ca^{2+} , the aliphatic compounds produced by the pyrolysis of coal underwent an aromatization reaction, especially the formation of polycyclic aromatic compounds was enhanced. The proportions of aromatic and aliphatic compounds obtained from the pyrolysis process of YL-HCl-Ca were 59.41% and 21.98%, respectively, which are between those of the tar fractions obtained from YL-HCl and YL-De-Ca pyrolysis. The oxygen-containing compounds in the tar produced from ion exchangeable coal sample became lower than that from coal without Ca. The type of oxygen-containing functional groups in coal had changed during the ion-exchange process. With the breaking and forming of bonds between Ca and organic matter, the migration path of oxygen in the system is also affected^[14].

2.4 Structural analyses of coal and the char

2.4.1 XRD analysis

Figure 6 shows the XRD spectra of different coal samples and the char obtained from fixed-bed coal pyrolysis. It can be seen that the HCl insoluble crystalline minerals in YL used mainly consist of SiO_2 , kaolinite and pyrite. Pyrite is insoluble in HF, therefore, it still exists in YL-De. There is a difference in affecting the coal pyrolysis between SiO_2 and kaolinite. SiO_2 did not change during coal pyrolysis because SiO_2 is stable at 600 °C and cannot participate in the chemical reactions. It dispersed as an impurity in the organic structure of the coal during pyrolysis and mainly affects the contact of organic matter. As a result, the influence on the production of pyrolysis tar is little^[16]. Comparing the XRD spectra of YL-HCl and its pyrolysis char YL-HCl-Char, it was found that kaolinite crystals disappeared after pyrolysis, indicating that the kaolinite structure transformed during pyrolysis.

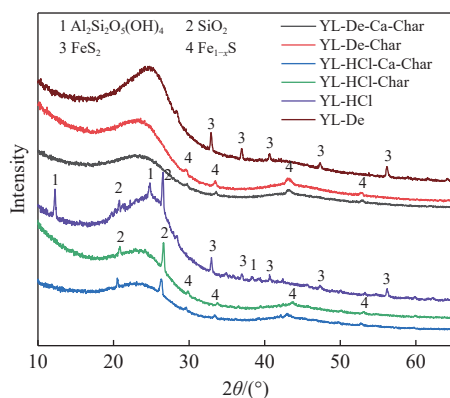


Fig. 6 XRD patterns of coal and char

The studies by Fabbri et al.^[26] have confirmed that the hydroxyl groups in kaolinite gradually decompose under thermal condition, and the aluminum-oxygen octahedral framework is destroyed, leading to a transition of kaolinite from a crystalline to an amorphous structure. The dehydroxylation effect is the strongest at 525 °C. As the pyrolysis temperature was 600 °C in this work, the dehydroxylation was complete. As a result, the characteristic diffraction peaks of kaolinite disappeared and metakaolin was formed. Although pyrolysis changed the coordination structure of Al from Al^{VI} to Al^{V} and Al^{IV} , in the case of only calcination, metakaolin did not have acidic centers and would not catalyze the volatile matter cracking^[17]. However, if the dehydroxylation reaction of kaolinite is accompanied by coal pyrolysis, hydroxyl groups may participate in the reactions among coal volatile matter. Hydroxyl groups can lower the energy barrier for aromatic ring cracking^[27] and induce the aromatic ring deformation and ring opening. When tar precursor in the coal macromolecular structure cross-linking with Ca undergoes aromatization reaction, the hydroxyl groups can attack the aromatic compounds and lead to the subsequent cracking, generating more aliphatic hydrocarbons. This can also explain the results of tar composition obtained from YL-HCl and YL-De pyrolysis. In addition, SiO_2 and kaolinite dispersed in the coal organic matter and can generate a spatial steric hindrance, which inhibits the cross-linking of coal molecules to some extent.

2.4.2 Analysis of char by Raman spectroscopy

Raman spectra of the char obtained from fixed-bed coal pyrolysis is shown in Figure 7(a). The spectra within the range of 800–1800 cm^{-1} were fitted using the ten-peak method^[13,28], which is shown in Figure 7(b). The specific location and attributions are as follows. The G peak at 1590 cm^{-1} corresponds to the E_{2g} vibration of the aromatic ring plane; the G_L peak at 1700 cm^{-1} corresponds to the carbonyl structure; the G_R peak at 1540 cm^{-1} corresponds to the aromatic ring of 3–5 rings; the V_L peak at 1465 cm^{-1} corresponds to the vibration of methyl, methylene functional groups or semi-circular aromatic rings; the V_R peak at 1380 cm^{-1} corresponds to the vibration of methyl functional groups or semi-circular aromatic rings; the D peak at 1300 cm^{-1} corresponds to the highly ordered carbon materials with a large aromatic ring system of no less than six rings; the S peak at 1185 cm^{-1} corresponds to C–C and C–H bonds between the aromatic group and alkyl group; the S_L peak at 1230 cm^{-1} corresponds to the aromatic alkyl ether with a bridge bond structure; the S_R peak at 1060 cm^{-1} corresponds to C–H bond of the aromatic ring; the R peak at 960–800 cm^{-1} corresponds to C–C bond of alkanes and cyclic alkanes. A_D/A_{all} represents the proportion of large aromatic structures of ≥ 6 rings, and $A_{(G_R+V_R+V_L)}/A_D$ represents the ratio of the small aromatic ring structures (≤ 5 rings) to the large aromatic ring structures. As shown in

Table 4, YL-De-Ca-Char had a higher A_D/A_{all} value and a lower value of $A_{(G_R+V_R+V_L)}/A_D$ than YL-De-Char. The results indicated that small aromatic rings transformed into large aromatic ring structures during the pyrolysis process with addition of Ca^{2+} , and the content of large aromatic ring structures in the char increased. However, the A_D/A_{all} values of YL-HCl-Char and YL-HCl-Ca-Char were similar, indicating that the retaining quartz and kaolinite to some extent suppresses the thermal decomposition and condensation reaction caused by ion exchange. The A_D/A_{all} value of the char obtained from the pyrolysis of the coal sample with quartz and kaolinite was higher than the corresponding value of the char obtained from the coal

sample treated by HCl-HF, whereas the corresponding $A_{(G_R+V_R+V_L)}/A_D$ value was lower, indicating that the aromaticity of char with clay mineral is higher and the hydrogen content is lower. However, as shown in the elemental analysis in Table 1, the H/C atomic ratio of coal sample with mineral acid components was higher. The proportion of aliphatic compounds in the pyrolysis tar of the coal sample with mineral acid components was higher than that of the corresponding coal washed by HCl-HF, indicating that the acidic mineral components can act on the hydrogen transfer reaction in the pyrolysis process, promoting the transfer of hydrogen to the volatile matter.

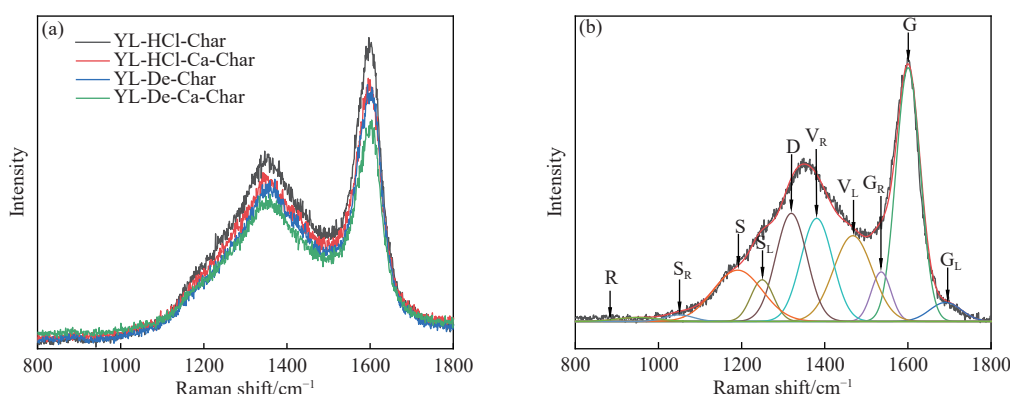


Fig. 7 Raman spectra of pyrolysis char and the example of fitting curves

Table 4 Fitting parameters of raman spectra

Sample	$A_{(G_R+V_R+V_L)}/A_D$	A_D/A_{all}
YL-De-Char	2.3101	0.1514
YL-De-Ca-Char	2.0832	0.1665
YL-HCl-Char	1.8482	0.1751
YL-HCl-Ca-Char	1.7714	0.1706

3 Conclusions

Coal samples with different mineral components were prepared through HCl acid washing or HCl-HF acid washing. The samples were followed to load Ca^{2+} by ion exchangeable reaction. The distribution and composition of coal pyrolysis products in a fixed-bed reactor were investigated, and the conclusions were drawn as follows.

During the acid washing and ion exchangeable reactions, both the physical and chemical structures of coal changed. Some small molecular compounds in the coal samples were dissolved in the solution besides the minerals. The two-step HCl-HF acid washing makes the pore volume and specific surface area of the coal sample larger than that of the HCl washing samples. The H/C atomic ratio values of YL-De, YL-HCl, YL-De-Ca and YL-HCl-Ca were 0.61, 0.64, 0.58 and 0.59, respectively.

The TG-DTG analyses of coal indicates that the thermal reactivity of coal with Ca is high and the cracking ability is enhanced. When the final temperature of coal pyrolysis reaches 600 °C, kaolinite will undergo dehydroxylation

reaction. As a result, the acidic mineral component in coal promotes the transfer of hydrogen to the volatile matter during coal pyrolysis process. The coexistence of ion-exchangeable Ca^{2+} and acidic mineral components can increase the content of aliphatic compounds in coal tar.

Declaration of Competing Interest

The authors declare no conflict of interest.

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矿物质酸性组分对离子交换态 Ca 在煤热解过程中反应行为的影响机制研究

李鸿升^{1,2,3}, 郝盼^{1,3,*}, 闫伦靖^{1,2,3}, 孔娇^{1,2,3}, 王美君^{1,2,3}, 鲍卫仁^{1,2,3}, 常丽萍^{1,2,3}

(1. 太原理工大学 化学与化工学院, 山西 太原 030024;

2. 太原理工大学 省部共建煤基能源清洁高效利用国家重点实验室, 山西 太原 030024;

3. 太原理工大学 煤科学与技术教育部重点实验室, 山西 太原 030024)

摘要: 固有矿物质对煤热转化具有非常重要的影响, 然而矿物质间相互作用对煤热解焦油的生成影响机制尚不清晰。为了研究矿物质酸性组分对 Ca^{2+} 在煤热解过程中反应行为的作用机制, 通过 HCl 一步酸洗和 HCl-HF 两步酸洗得到矿物质酸性组分赋存状态不同的煤样, 进行 Ca^{2+} 离子交换制备得到实验用煤, 并对其热解行为进行考察。结果表明, 酸洗处理使灰分含量有效降低的同时, 煤中的有机元素碳、氢含量也变少; 担载离子交换态 Ca 后, 煤样在 500–550 °C 的热失重速率增大, 对应峰温从未进行离子交换反应煤样的 530 °C 降低至 514 °C; 煤在终温为 600 °C 下进行慢速热解时, 矿物质酸性组分中的高岭石发生脱羟基反应生成偏高岭石, 担载 Ca 煤样的热解半焦中小芳香环(<6 环)含量低于仅酸洗处理煤样的热解半焦; 煤样 YL-HCl-Ca 包含了矿物质酸性组分与离子交换态 Ca, 其热解焦油中脂肪烃含量为 21.98%, 显著高于 YL-De-Ca 热解焦油中对应的 13.60%。从表观结果上看, 保留的矿物质酸性组分抑制了离子交换反应担载 Ca^{2+} 对煤焦油轻质化的不利影响。

关键词: 矿物质; 离子交换态 Ca; 热解; 煤焦油

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作者简介:



李鸿升(1999), 硕士研究生, 研究方向为煤炭清洁高效利用, lhs1312729882@163.com。



郝盼(1989), 博士, 讲师, 硕士生导师, 研究方向为煤炭清洁高效转化, haopan@tyut.edu.cn。