

Synthesis of plate-like alumina *via* synergistic activation from the co-combustion ash of coal gangue and corn stalk

MIAO Hengyang¹, WANG Zhiqing^{2,*}, LIU Zheyu², LU Jun², FANG Yitian²

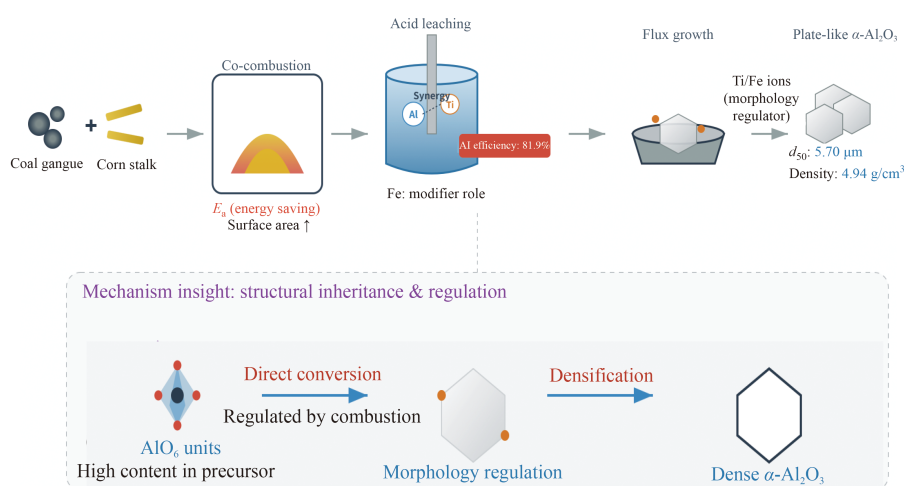
¹Shandong University, Qingdao 266237, China;

²Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

Abstract: This study reports a streamlined route for synthesizing plate-like α - Al_2O_3 *via* co-combustion activation of coal gangue and corn stalk, enabling the high-value utilization of solid wastes. The results demonstrate that the introduction of corn stalk significantly reduces the apparent activation energy of coal gangue combustion and increases

the acid leaching yield of aluminum to 81.9%. Mechanism analysis reveals that titanium and iron ions in the co-combustion ash leachate act as natural morphology regulators, facilitating the formation of a plate-like structure in the alumina product, with titanium exhibiting leaching behavior consistent with that of aluminum. Furthermore, it is found that a high content of AlO_6 structural units in the precursor effectively promotes the direct conversion into dense α - Al_2O_3 crystals during thermal treatment, thereby enhancing the product density. Under optimized conditions (800 °C, 1 h), the as-prepared α - Al_2O_3 exhibits a plate-like morphology, with a median particle size (d_{50}) of 5.70 μm and a density of 4.94 g/cm^3 . This work provides a new approach for the synergistic resource utilization of coal gangue and biomass waste.

Key words: coal gangue; co-combustion; alumina; ion leaching yield; activation energy



Coal gangue is a typical solid waste generated during coal mining and coal washing processes, with an output generally accounting for 10%–20% of raw coal production^[1]. In China, the historical stockpiling of coal gangue has reached approximately 4.5 billion tons^[2–3]. Long-term accumulation not only occupies large areas of land, but also poses significant threats to regional air quality and ecosystems due to spontaneous combustion and the

release of gaseous pollutants such as NO_x and SO_x ^[4]. At present, the utilization of coal gangue can be broadly classified into two categories: bulk utilization and high-value utilization^[5–6]. High-value utilization mainly includes the preparation of adsorbent materials and molecular sieves, recovery of valuable metals, and application in the production of vegetation substrates and soil remediation materials^[7–8]. Although substantial progress has been made

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* Corresponding author. Tel: +86 351 2021137-801, Fax: +86 351 2021137-802, E-mail: qcumt@sxicc.ac.cn.

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in these high-value pathways, most studies still focus on the treatment of a single solid waste or the preparation of a single product. The economic extraction of valuable components from coal gangue, coupled with the direct regulation and fabrication of high-performance materials with tailored morphologies, remains a significant challenge.

Meanwhile, with the continuous advancement of industrialization, the shortage of aluminum resources has increasingly become a critical factor constraining industrial development in China^[9]. Coal gangue contains 15%–40% Al_2O_3 ^[10], indicating its potential as an aluminum resource. Consequently, the efficient extraction of aluminum from coal gangue has become a key research focus in its high-value utilization^[11–14]. The mainstream process is the roasting-acid leaching method^[15–16], in which thermal activation is employed to disrupt the mineral structure, followed by leaching of aluminum ions using inorganic acids. To enhance aluminum dissolution, alkali metal salts such as NaCl and K_2CO_3 have been introduced as roasting additives to form intermediate phases (e.g., nepheline or feldspar-type minerals), thereby promoting aluminum solubilization^[10,17]. However, conventional acid leaching suffers from limited extraction yield and generates large amounts of acid leaching residues. Although alkali metal salt activation can significantly improve aluminum conversion, the subsequent recycling of alkali metals is challenging, leading to poor process economics. In addition, existing studies predominantly focus on the aluminum leaching stage^[18–20], while insufficient attention has been paid to the separation of multiple metal ions (e.g., Fe, Ca, Mg) in the leachate and the subsequent directed transformation of aluminum. These separation steps are usually complex, lengthy and difficult to control.

Biomass, as a renewable carbon source, has shown great potential for synergistic utilization with aluminum-containing solid wastes^[21–22]. Previous studies have demonstrated that co-combustion of biomass with mineral fuels can not only reduce fossil energy consumption but also improve combustion characteristics^[22]. Although coal gangue is rich in aluminum, its low carbon content and insufficient calorific value limit its direct application in energy utilization. The introduction of biomass can compensate for the calorific deficiency^[23], while the alkali and alkaline earth metals (e.g., K and Na) abundantly present in biomass can participate in solid-state reactions with coal gangue during thermal conversion, disrupting the Si-O-Al network structure and achieving chemical activation of aluminum. Traditional activation approaches often rely on a single feedstock or externally added chemical reagents, resulting in weak resource integration. Moreover, conventional methods, such as the independent combustion of mineral wastes or the addition of chemical activators, generally fail to simultaneously immobilize pollutants during activation. In contrast, “co-combustion activation” leverages chemical synergistic effects between fuels to *in situ* immobilize alkali metals such as Na and K,

thereby reducing the risk of secondary pollution and improving the environmental compatibility of the products. From the perspective of structural regulation, reliance on a single activator often leads to melting and slagging^[24]. Previous studies have shown that the leachate obtained from acid-leached coal gangue ash is enriched in sulfate species, which are commonly used as additives in molten-salt routes for alumina synthesis^[25]. In addition, phosphorus present in biomass and titanium in coal gangue can act as natural crystal phase modifiers for the synthesis of $\alpha\text{-Al}_2\text{O}_3$. Nano-sized Al_2O_3 , as an important high-performance catalyst support and functional ceramic precursor, has been widely applied in electronic materials, pharmaceuticals, and related fields^[26]. The development of green and low-cost preparation routes for nano- Al_2O_3 has therefore become a research hotspot in materials chemistry and engineering^[27].

In this work, we move beyond the traditional aluminum extraction strategy of “separation first, synthesis later” and propose a new approach that directly constructs hydroxide precursors based on the physicochemical characteristics of leachates derived from the co-combustion of coal gangue and biomass. This strategy avoids the process complexity and control challenges associated with multiple pH adjustment steps. The thermochemical behavior of biomass during co-combustion and its mechanistic influence on the leaching kinetics of key metals such as aluminum and titanium from coal gangue are systematically investigated. This study aims to achieve the synergistic high-value conversion of coal gangue and biomass, providing a novel methodological pathway for the resource utilization of solid wastes.

1 Experimental

1.1 Materials

The coal gangue used in this study was collected from the Xiaojingyu Mine in Shuozhou, Shanxi Province, China. The biomass feedstock was corn straw obtained from Jilin Province, China. After preliminary coarse crushing, the samples were ground in a planetary ball mill (YXQM-0.4L) to a particle size of less than 200 mesh. Subsequently, the vertical tubular furnace was heated to 900 °C at a rate of 10 °C/min under a nitrogen atmosphere (flow rate: 300 mL/min). Approximately 10 g of each sample was rapidly placed in a crucible and introduced into the constant-temperature zone for pyrolysis, which was maintained for 30 min. After pyrolysis, the samples were transferred to the low-temperature zone at the furnace outlet and cooled to room temperature under continuous nitrogen protection, yielding coal gangue char (CG) and corn straw char (CS).

Coal gangue and corn straw were then mixed at a mass ratio of 3:1 and mechanically blended in the same ball mill at a rotation speed of 180 r/min for 60 min to ensure

homogeneous mixing. A 2 g portion of the mixed sample was placed in a horizontal tubular furnace and subjected to activation under an air atmosphere (flow rate: 150 mL/min); the resulting sample was denoted as BCA. Acid leaching was performed using a 20% sulfuric acid solution, with reaction times of 30, 60, 90 and 120 min.

Proximate analysis of the raw materials was conducted in accordance with the Chinese national standards GB/T 28731—2012 and GB/T 28732—2012, while ultimate analysis was performed following GB/T 30728—2014. The corresponding ash composition, proximate analysis, and elemental analysis results are summarized in Table 1.

Table 1 Proximate and ultimate analyses of coal gangue char (CG) and corn stalks char (CS)

Sample	Proximate analysis ^a $w_{ad}/\%$				Ultimate analysis ^b $w_{daf}/\%$				
	<i>M</i>	<i>A</i>	<i>V</i>	FC	C	H	O ^c	N	S
CG	0.93	65.00	17.07	17.00	62.46	6.23	30.14	0.88	0.29
CS	8.35	10.57	65.74	15.34	40.99	4.72	35.25	0.93	0.12

^a: air-dried basis; ^b: dry and ash-free basis; ^c: by difference.

1.2 Preparation of nano-alumina

BCA and sulfuric acid solution were added to a conical flask at a liquid-to-solid ratio of 50 mL/g. The flask was placed in a water bath maintained at 80 °C and stirred magnetically. After completion of the reaction, the slurry was cooled to room temperature and filtered through a Büchner funnel. The obtained filtrate was collected for the preparation of an aluminum hydroxide precursor.

The pH of the filtrate was first adjusted to 3 using a mixed solution of sodium hydroxide and potassium hydroxide (denoted as solution A). Sodium phosphate was then added to a saturated sodium carbonate solution (denoted as solution B), and solution B was added dropwise to the filtrate. When the pH of the solution reached 9, the addition of solution B was stopped. At this stage, a large amount of white gel-like precipitate formed in the solution. After standing and aging for 6 h, the gel was filtered and washed thoroughly. The obtained gel was dried in an oven for 12 h, and the resulting precursor was calcined at 1200 °C for 1 h. The calcined product was subsequently washed sequentially with distilled water, alkaline solution, and dilute acid to obtain pure alumina.

1.3 Ion leaching yield

Coal gangue inevitably contains iron, titanium and other metal ions. Previous studies have shown that Fe and Ti ions can significantly affect the morphology of plate-like alumina^[28]. Therefore, their leaching behaviors are expected to influence the quality of the plate-like alumina product. According to the Chinese national standard GB/T 1574—2007, the concentrations of Ti^{3+} and Fe^{3+} in the leachate were determined by spectrophotometric methods using titanium and iron reagents, respectively; detailed procedures are provided in the Supplementary Materials S1. A UV-vis spectrophotometer (UV-2600) was employed, with detection wavelengths of 430 nm for titanium ions and 510 nm for iron ions.

The concentration of Al^{3+} in the diluted filtrate was

determined in accordance with GB/T 1574—2007 using a fluoride displacement-EDTA (disodium ethylenediaminetetraacetate) complexometric titration method^[29]. The detailed procedure is given in the Supplementary Materials S2.

1.4 Characterization methods

The combustion characteristics of BCA were investigated using a thermogravimetric analyzer (TGA, Setaram, France). Approximately 8 mg of sample was evenly spread in an alumina crucible. The heating rate was set to 10 K/min under an air flow of 50 mL/min. The mineral phases of the samples were identified by X-ray diffraction (XRD) using a MiniFlex 600 diffractometer (Rigaku, Japan). Prior to analysis, the samples were ground to 200 mesh in an agate mortar. The XRD measurements were carried out with Cu $K\alpha$ radiation at a tube voltage of 40 kV and a scanning rate of 10(°)/min.

The specific surface area and pore volume were determined using a physical adsorption analyzer (JW-BK132F) based on the Brunauer-Emmett-Teller (BET) method. Before each measurement, the samples were pretreated at 300 °C for 8 h to remove impurities and adsorbed moisture. Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet IS50 spectrometer. The samples were mixed with KBr at a mass ratio of 1:150, with a resolution of 4 cm^{-1} and 32 scans.

Scanning electron microscopy (SEM) images were obtained using a JSM-7001F field-emission scanning electron microscope equipped with a Bruker spectrometer. Particle size analysis was conducted using an Ambival particle size analyzer.

The apparent density of the alumina powders (ρ_s , g/cm³) was determined based on Archimedes' principle^[30] and calculated according to the following equation:

$$\rho_s = \frac{m_1 \times \rho_{H_2O}}{m_1 + m_2 + m_3} \quad (1)$$

where m_1 is the mass of the sample measured in air (g); m_2

is the mass of the bottle containing water measured in air (g); m_3 is the total mass after adding alumina into the bottle filled with water (g); and $\rho_{\text{H}_2\text{O}}$ is the density of water at 25 °C (0.997 g/cm³).

1.5 Kinetic analysis

The activation energy and pre-exponential factor of solid-state reactions can be determined using differential and integral methods. The integral methods include the Kissinger-Akahira-Sunose (KAS) method and the Flynn-Wall-Ozawa (FWO) method. In this study, the KAS method was employed to evaluate the kinetic characteristics of the co-combustion process of coal gangue and biomass. All kinetic analyses were based on the fundamental rate equations shown in Eqs. (2) and (3)^[31]:

$$\ln(\beta/T^2) = \ln(AR/E_a G(x)) - E_a/RT \quad (2)$$

$$\ln(G(x)/T^2) = \ln(AR/\beta E_a) - E_a/RT \quad (3)$$

In thermal analysis kinetics, the specific forms of the functions $G(x)$ is jointly determined by the reaction mechanism as well as the size and shape of the reacting particles. By plotting $\ln[G(x)/T^2]$ against $1/T$, a straight line with a slope of E_a/R can be obtained, from which the activation energy (E_a) can be calculated. Based on the TG curves, these functions can be used to infer the reaction mechanisms controlling the thermo-oxidative process, including chemical reaction models (first-order, second-order, third-order and nth-order reactions), random nucleation and growth models (two-dimensional and three-dimensional), and phase-boundary-controlled models. Generally, the ($G(x)$) function that yields the best linear correlation (evaluated by the coefficient (R^2)) is considered the optimal kinetic model describing the mass-loss behavior of the combustion process.

2 Results and discussion

2.1 DTG analysis of CG and CS combustion

From Table 1, it can be concluded that CS has a lower ash content, a higher proportion of volatile matter, and higher H and O contents, which are favorable for enhancing thermochemical reactivity^[32]. As shown in Table 2, CS and CG contain similar types of components and both include additives required for the preparation of nano-alumina, such as TiO₂ and phosphorus species. Moreover, as shown in Figure S1, biomass contains a considerable amount of alkali metals, particularly potassium, which can also enhance the combustion reactivity of coal gangue. The DTG results for the co-combustion of CS and CG are shown in Figure 1, illustrating the characteristic mass-loss peaks of the mixture.

CS is mainly composed of cellulose, hemicellulose, and lignin. When the temperature exceeds 200 °C, these components volatilize, leading to the first mass-loss peak of the biomass. During combustion, aluminosilicate gangue undergoes dehydroxylation of kaolinite to form metastable metakaolinite, an endothermic mineral decomposition process that is largely independent of the combustion atmosphere. XRD patterns show that kaolinite is the dominant mineral phase in CG, whereas boehmite is the main mineral component in CS.

When the temperature rises to approximately 400 °C, a distinct mass-loss peak appears due to the dehydroxylation of kaolinite into metakaolinite, which exhibits poor crystallinity and is therefore difficult to detect by XRD. At around 800 °C, metakaolinite decomposes to release SiO₂. Upon biomass addition, the combustion performance of CG is slightly improved, with the mass-loss peak temperature decreasing from 538 to 507 °C. Thus, the two mass-loss peaks of the mixture correspond to the superposition of the combustion behaviors of CS and CG^[33].

2.2 Activation energy analysis of CG and CS combustion

Thermogravimetric analysis provides critical thermodynamic parameters for understanding the thermal conversion behavior of fossil fuels^[34]. Among these parameters, activation energy serves as a key criterion for determining the optimal mixing ratio of coal gangue and biomass, while thermal characteristics at different heating rates form the basis for designing and optimizing co-combustion processes. To eliminate the interference of moisture and volatiles, char samples derived from coal gangue and corn straw were selected for combustion experiments.

In Figure 2, two distinct mass-loss stages of the sample can be observed, which confirms that for char samples, the combustion process consists of volatile combustion and fixed carbon combustion. The activation energies required for the combustion of mixtures with different CS contents at various heating rates are listed in Table 3 and Table 4.

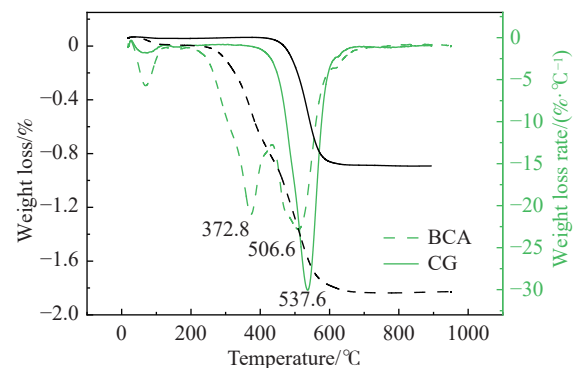
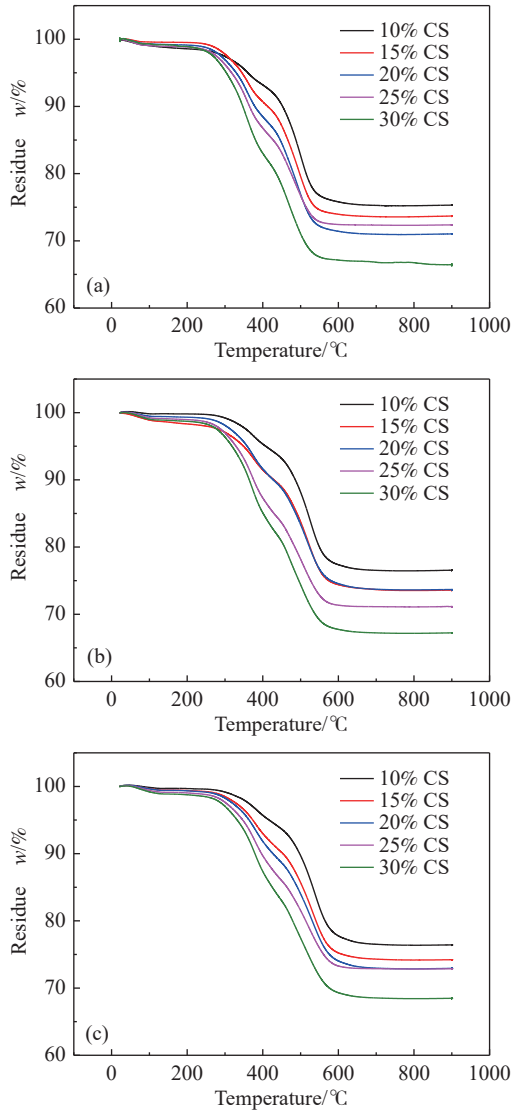


Fig. 1 TG and DTG curves of CG and BCA

Table 2 Chemical compositions of ash of (coal gangue) CG and corn stalks (CS)

Sample	Chemical compositions w/%									
	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
CG	52.51	44.96	0.32	0.20	0.21	1.02	0.00	0.13	0.00	0.42
CS	54.51	5.66	2.78	9.16	5.73	0.35	0.34	18.31	1.63	1.53



(a): 5°C/min; (b): 10°C/min; (c): 15°C/min.

Fig. 2 The TG curves of sample at different heating rates

By fitting the kinetic data using different solid-state reaction models, it was found that the first-stage combustion process is best described by the random nucleation and growth model, with correlation coefficients exceeding 98%. The second-stage combustion process is more consistent with a first-order reaction model, with correlation coefficients above 97%, indicating good model applicability.

The activation energy of the first combustion stage does not vary monotonically with increasing CS content; instead, it reaches a minimum at a CS addition of 25%. In contrast, the activation energy of the second stage (fixed carbon combustion, approximately 450–570 °C) decreases significantly with increasing CS content. When the CS content increases from 10% to 30%, the activation energy decreases from 38.04 to 17.78 kJ/mol (at a heating rate of 5 °C/min). Although increasing the heating rate has a limited effect on reducing activation energy, the lowest activation energy is achieved at a CS content of 25% and a heating rate of 10 °C/min, indicating the highest reactivity of the mixed sample under these conditions and identifying them as optimal activation parameters.

2.3 Structural analysis of co-combustion ash

The pore size distributions of CG before and after CS addition are shown in Figure 3(a) and (b). As illustrated, combustion temperature has a significant influence on pore structure. The specific surface area of CG increases markedly after CS addition. Without CS, CG exhibits a specific surface area of only 5.31 m²/g at 800 °C, whereas co-combustion significantly enhances this value.

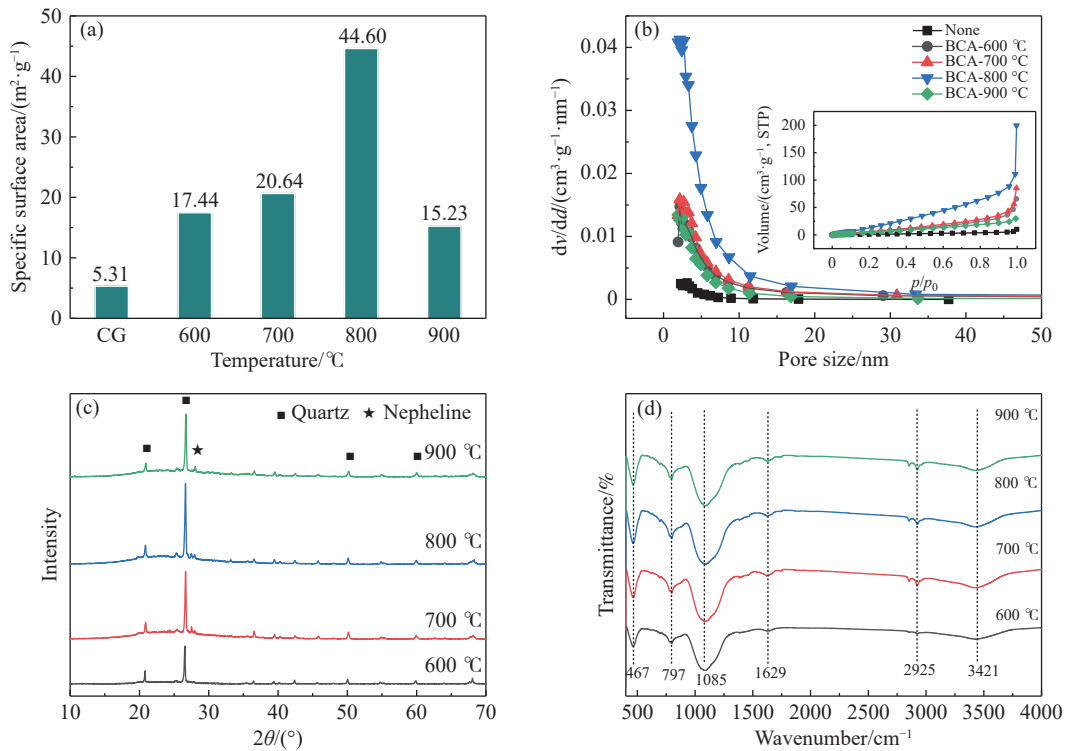
For BCA produced at co-combustion temperatures of 600, 700 and 900 °C, the differences in specific surface area are relatively small. However, at 800 °C, the proportion of micropores (<2 nm) increases sharply, accompanied by a rapid increase in specific surface area. This phenomenon is likely caused by phase transformations in BCA at 800 °C, which alter the pore structure.

Table 3 Kinetic properties of BCA in the first stage at different heating rates

CS/%	5 °C/min			10 °C/min			15 °C/min		
	range/°C	E/(kJ·mol ⁻¹)	R ² /%	range/°C	E/(kJ·mol ⁻¹)	R ² /%	range/°C	E/(kJ·mol ⁻¹)	R ² /%
10	297–384	9.96	98.28	379–427	15.57	98.48	355–436	15.33	98.90
15	277–377	16.66	99.49	328–391	13.58	98.76	291–412	15.74	98.87
20	297–366	16.35	98.91	317–392	17.25	99.23	321–398	17.31	98.83
25	283–352	14.84	99.01	296–365	16.18	98.98	306–366	15.20	98.95
30	280–347	15.08	99.25	294–363	16.10	98.99	303–375	16.05	98.42

Table 4 Kinetic properties of BCA in the second stage at different heating rates

CS/%	5 °C/min			10 °C/min			15 °C/min		
	range/°C	$E/(\text{kJ}\cdot\text{mol}^{-1})$	$R^2/\%$	range/°C	$E/(\text{kJ}\cdot\text{mol}^{-1})$	$R^2/\%$	range/°C	$E/(\text{kJ}\cdot\text{mol}^{-1})$	$R^2/\%$
10	487–533	38.04	99.92	480–561	36.58	98.97	491–579	35.23	99.62
15	453–523	28.40	98.18	476–555	27.81	98.14	488–568	26.71	98.40
20	464–522	26.78	99.05	493–555	28.49	99.56	477–567	24.09	97.80
25	447–514	21.11	97.44	460–537	19.41	97.18	479–555	21.07	97.41
30	436–512	17.78	97.87	455–534	18.29	98.67	470–552	18.67	98.61



(a): specific surface area; (b): pore size distribution at different activation temperatures; (c): XRD patterns; (d): FT-IR spectra.

Fig. 3 Physicochemical characterization of BCA

Selective separation of silicon and aluminum from coal gangue relies on generating acid-soluble active aluminosilicate phases through thermal activation. XRD results (Figure 3(c)) show that no fully developed crystalline active phase is present in the ash at 600 °C. When the temperature reaches 700 °C, characteristic diffraction peaks of nepheline begin to appear. FT-IR spectra further reveal the temperature-dependent structural evolution of the ash: the absorption band at 3421 cm^{-1} corresponds to the stretching vibration of structural hydroxyl groups^[26]; bands at 2927–2924 cm^{-1} originate from aliphatic groups in residual organic matter^[27]; and the peaks at 1085 and 467 cm^{-1} correspond to asymmetric stretching vibrations of Si–O–Al bonds^[28].

Notably, the intensity of the Si–O–Al vibration reaches its maximum at 800 °C, indicating the most pronounced reorganization of the aluminosilicate network and the formation of the largest amount of amorphous or

microcrystalline active aluminosilicate intermediates. This structural evolution is consistent with the sharp increase in specific surface area measured by BET at 800 °C.

These processes follow the reaction pathway whereby kaolinite in coal gangue first undergoes dehydroxylation to form amorphous metakaolinite^[30]. Subsequently, under the catalytic effect of alkali metals (K and Na) introduced by biomass, metakaolinite reacts with free SiO_2 and Al_2O_3 to reconstruct crystalline phases such as nepheline. When the temperature further increases to 900 °C under silica-rich conditions, nepheline and related aluminosilicates become unstable and decompose into metasilicates and metaaluminates^[31–32]. During subsequent acid leaching, aluminum enters the solution in ionic form, while soluble metasilicates hydrolyze to form amorphous SiO_2 precipitates, thereby achieving efficient separation of silicon and aluminum.

2.4 Ion extraction yield

After calcination of coal gangue char (CG) at 900 °C followed by acid leaching, the extraction yields of Al, Ti, and Fe ions are shown in Figure 4. The dominant mineral phase in CG is kaolinite (as shown in Figure S2 of the Supplementary Materials). When the activation temperature increases from 600 to 700 °C, the extraction yield of aluminum increases significantly from 32.8% to 43.1%. Combined with the mass-loss behavior shown in Figure 1, the stabilization of mass loss at 700 °C indicates that mineral phase transformation is essentially complete.

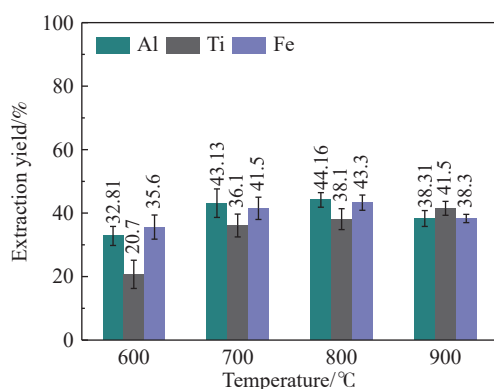


Fig. 4 Acid leaching extraction yields of Al, Ti and Fe ions from coal gangue char (CG)

With further temperature increases, the extraction behavior of Ti is similar to that of Al: its extraction yield increases from 20.7% at 600 °C to 36.1% at 700 °C and then stabilizes at approximately 38%. In contrast, the extraction yield of Fe shows little dependence on temperature over the range of 600–900 °C.

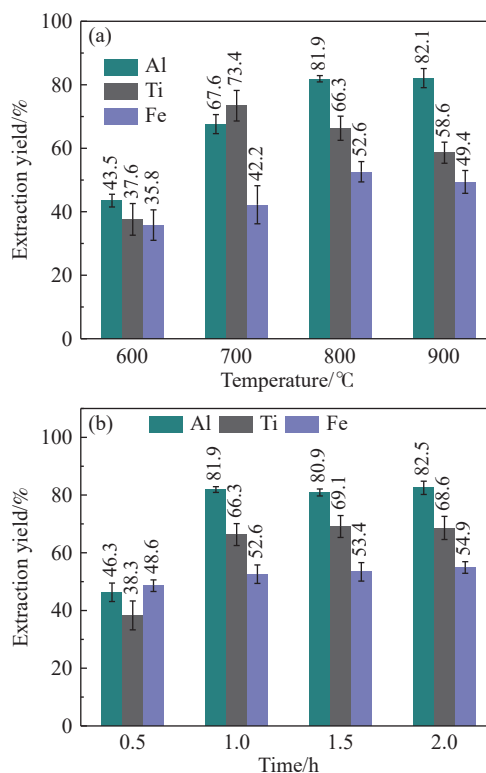
Upon CS addition, as shown in Figure 5, the extraction efficiencies of all ions increase, with particularly pronounced enhancements for Al and Ti. The extraction yield of Al increases by approximately 40%, while that of Ti increases by about 30%. According to acid-base theory, coal ash components can be classified into network formers, modifiers, and neutral components.

Network formers typically form tetrahedral units and constitute the basic framework of the network; modifiers disrupt the network structure; and neutral components can switch between these roles^[35–36]. Fe^{3+} is generally classified as a modifier, Ti^{4+} as a network former and Al^{3+} as a neutral component.

Thermal activation of CG and disruption of its dense network structure can enhance aluminum extraction, with temperature and alkali metals acting as key activation factors. The similar leaching behaviors of Al^{3+} and Ti^{4+} indicate that both participate in the network structure, whereas the leaching behavior of Fe^{3+} is relatively insensitive to CS addition, suggesting that most Fe acts merely as a modifier rather than a network former.

In addition to activation temperature, acid leaching time

is also a critical factor affecting extraction yield. Under conditions of 800 °C activation and 25% CS addition, the extraction yield of Al^{3+} stabilizes above 80% after 1 h of leaching, while the extraction yield of Ti^{4+} stabilizes at approximately 68%. In contrast, the extraction yield of Fe^{3+} reaches 48.6% after only 0.5 h. With further increases in leaching time, Fe^{3+} extraction increases slightly, likely due to increased contact area between the solid and acid solution after Al^{3+} dissolution. Overall, under the investigated conditions, an aluminum extraction yield of up to 81.9% can be achieved, and 1 h of acid leaching is sufficient for efficient extraction.



(a): activation temperature; (b): acid leaching time.

Fig. 5 Effect of different process conditions on ion extraction yields from coal gangue char after CS addition

2.5 Structural analysis of the precursor

The absorption band at 618 cm^{-1} is attributed to Al–O bonds in AlO_6 octahedra^[37–38]. As shown in Figure 6, the precursor obtained at an activation temperature of 700 °C (denoted as 700-pre; similarly for 600, 800 and 900 °C) exhibits the most pronounced band at 618 cm^{-1} , indicating the highest content of AlO_6 units. The absorption band at 1130 cm^{-1} corresponds to sulfate species and is noticeably broader than other bands, suggesting the presence of a substantial amount of sulfate molten salts in the precursor.

No characteristic absorption band is observed near 3710 cm^{-1} , indicating that water does not exist in a free state

but rather as adsorbed or structural water. The band at 1644 cm^{-1} corresponds to hydroxyl stretching vibrations, confirming the presence of structural water in the precursor^[39]. The peak at 1054 cm^{-1} is assigned to the symmetric bending vibration of Al–O–Al bonds, and additional Al–O stretching vibration are observed in the range of $500\text{--}900\text{ cm}^{-1}$ ^[40].

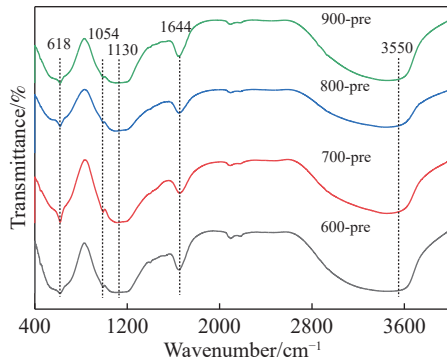


Fig. 6 FT-IR spectra of the precursor

2.6 Characterization of alumina products

Figure 7 presents the XRD patterns and FT-IR of $\alpha\text{-Al}_2\text{O}_3$ powders prepared from BCA activated for 1 h at different temperatures. The characteristic absorption bands in the FT-IR spectra within the range of $400\text{--}1000\text{ cm}^{-1}$ are assigned to $\alpha\text{-Al}_2\text{O}_3$ and the XRD patterns further confirm that $\alpha\text{-Al}_2\text{O}_3$ is the dominant crystalline phase, accompanied by a small amount of Fe_2O_3 doping. The density and particle size distribution of the products are summarized in Table 5.

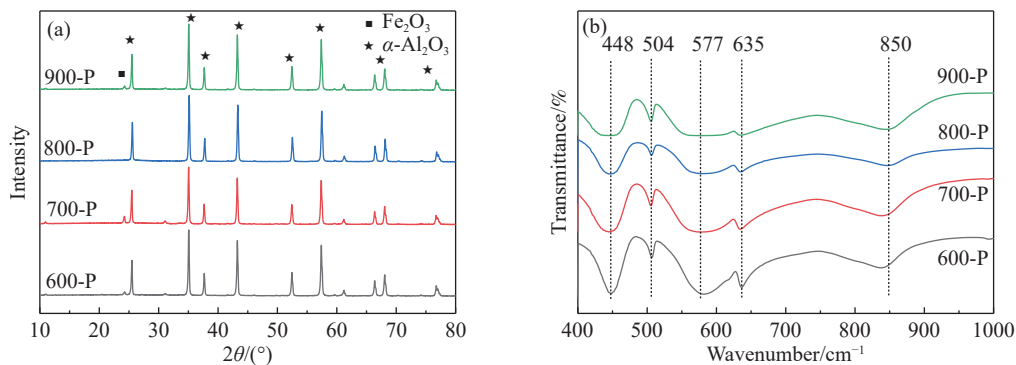


Fig. 7 (a): The XRD patterns of products; (b): The FT-IR spectra of products

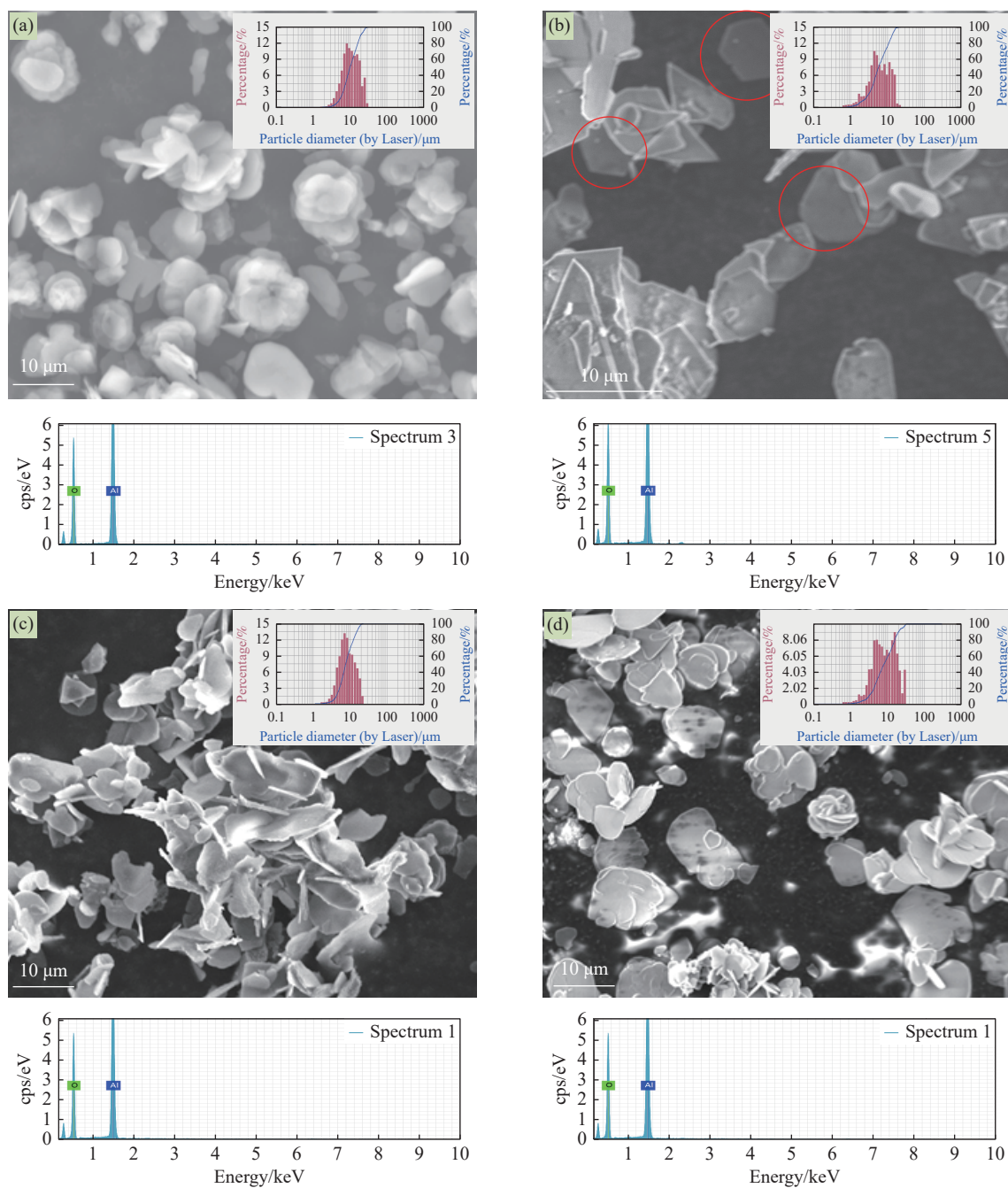
Table 5 The density and size distribution of products

Sample	Density/($\text{g}\cdot\text{cm}^{-3}$)	$d_{10}/\mu\text{m}$	$d_{50}/\mu\text{m}$
600-P	2.91	5.24	10.17
700-P	4.94	2.31	5.70
800-P	2.77	4.16	7.56
900-P	4.39	3.23	8.16

Among these, the sample obtained at $700\text{ }^\circ\text{C}$ (designated as 700-P) possesses the highest density (4.94 g/cm^3) and the smallest d_{10} and d_{50} values.

The microstructures of the products are shown in Figure 8. Well-developed hexagonal plate-like particles with pronounced anisotropy are observed in the 700-P sample (Figure 8(b)). This morphology is consistent with previous reports, which indicate that the size and shape of alumina particles can be significantly regulated by additives such as TiO_2 and Fe_2O_3 ^[41–42]. Combined with the relatively high Ti leaching yield at $700\text{ }^\circ\text{C}$ shown in Figure 5(a) and the stronger Fe_2O_3 diffraction peaks in Figure 7(a), the higher Ti and Fe doping levels in 700-P are inferred to suppress grain growth and promote plate-like morphology. This is consistent with the observed smaller particle size and pronounced lamellar structure. In contrast, activation at $800\text{ }^\circ\text{C}$ results in higher Al leaching but lower Ti leaching, which is unfavorable for the formation of small-sized, highly anisotropic alumina particles.

Furthermore, Figure 6 shows that the precursor corresponding to 700-P (700-pre) contains the highest concentration of AlO_6 structural units. This provides a structural explanation for the high density of the final product: $\alpha\text{-Al}_2\text{O}_3$ crystals are composed of AlO_6 octahedra, and the pre-formed AlO_6 units in the precursor can be regarded as “structural embryos” that match the final crystal structure^[43]. These embryos reduce the energy barrier for transformation from transitional phases to the α phase and minimize volume shrinkage and pore formation during phase transformation, thereby facilitating the formation of a denser microstructure.



(a): 600-P; (b): 700-P; (c): 800-P; (d): 900-P.

Fig. 8 The morphology and particle size distribution of products

3 Conclusion

This study systematically investigates the process routes and underlying mechanisms for the preparation of plate-like α - Al_2O_3 using co-combustion ash derived from coal gangue and corn straw as raw materials. The main conclusions are summarized as follows:

The addition of corn straw significantly improves the combustion characteristics of coal gangue by reducing its apparent combustion activation energy and increasing the specific surface area of the co-combustion ash, thereby

enhancing the aluminum leaching yield to as high as 81.9%. The leaching behaviors of Al and Ti exhibit a synergistic trend, indicating similar modes of occurrence within the aluminosilicate framework, whereas Fe mainly acts as a network-modifying component during combustion, with its leaching yield being only weakly dependent on temperature.

A short-process route integrating “co-combustion activation-acid leaching for aluminum extraction-molten salt synthesis” is proposed and validated, enabling the direct preparation of plate-like α - Al_2O_3 from coal gangue and biomass co-combustion ash. This approach effectively simplifies the conventional separation and purification steps

required for producing high value-added aluminum products from solid wastes, providing a novel pathway for the resource utilization of industrial solid residues.

The relative content of AlO_6 structural units in the precursor plays a critical role in determining the density of the final $\alpha\text{-Al}_2\text{O}_3$ product. By regulating the co-combustion activation conditions, the precursor structure can be directionally tailored, thereby enabling control over the crystal phase and morphology of the alumina product. This finding not only deepens the understanding of alumina crystal growth mechanisms but also offers innovative insights and technical support for the high-value utilization of coal gangue and biomass wastes.

Declaration of Competing Interest

The authors declare no conflict of interest.

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煤矸石与玉米秸秆共燃协同活化制备片状氧化铝的工艺研究

苗恒洋¹, 王志青^{2,*}, 刘哲语², 路 军², 房倚天²

(1. 山东大学, 山东 青岛 266237; 2. 中国科学院山西煤炭化学研究所, 山西 太原 030001)

摘 要: 本研究基于煤矸石与玉米秸秆的共燃活化, 开发了一种短流程制备片状 α - Al_2O_3 的新方法, 实现了固体废弃物的资源化利用。结果表明, 玉米秸秆的引入显著降低了煤矸石燃烧的表现活化能, 并将酸浸提铝率提高至 81.9%。共燃灰酸浸液中的钛、铁离子在氧化铝结晶过程中起形貌调控作用, 促进片状结构的形成, 其中, 钛的溶出动力学行为与铝高度一致。此外, 前驱体中丰富的 AlO_6 结构单元有效促进了热处理过程中致密 α - Al_2O_3 晶相的定向转化, 从而提升产物密度。在优化条件(800 °C、1 h)下, 所得 α - Al_2O_3 呈片状形貌, 中值粒径(d_{50})为 5.70 μm , 密度可达 4.94 g/cm^3 。本工作为煤矸石和生物质废弃物的协同资源化提供了新思路。

关键词: 煤矸石; 共燃烧; 氧化铝; 离子溶出率; 活化能

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作者简介:



苗恒洋(1995), 博士, 实验师, 研究方向为煤基固废资源化利用研究, mhy95@sdu.edu.cn。



王志青(1982), 博士, 研究员, 研究方向为煤基固废资源化及功能材料制备研究, qcumt@sxicc.ac.cn。