

## Research Article

# Producing Effective and Clean Coke for Household Combustion Activities to Reduce Gaseous Pollutant Emissions

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Received 11 May 2019; Revised 23 October 2019; Accepted 30 October 2019; Published 13 November 2019

Academic Editor: Rita Rosa Plá

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Nowadays, the gaseous pollutant emissions, including particulate matter (PM), sulfur dioxide (SO<sub>2</sub>), and nitrogen oxide (NO<sub>x</sub>) from household coal combustion, cause great threat to environment and public health by contributing to severe haze in China. Particularly, a clean coke free of the major pollutants precursors (sulfur and nitrogen compounds) by sulfur fixation and denitrification has been deemed as an effective strategy to reducing pollutants. In this paper, a preprocessed coke was prepared by co-pyrolysis of high-sulfur coal with the assistance of calcium-based and iron-based complexes at high temperature. The results show that high-temperature co-pyrolysis could remove the volatile compounds that are major precursors for the formation of gaseous pollutants from the raw coal. During the coking process, the sulfur can be removed by being fixed in the form of CaS in presence of a Ca-based complex, which could be beneficial for the CaSO<sub>4</sub> during the coke combustion. The volatile nitrogen is transferred to the gas phase with the addition of Fe-based complexes, which effectively reduce the residual nitrogen in coke. As a result, Ca-based additives captured the released SO<sub>2</sub> and formed CaSO<sub>4</sub> during the combustion process. In addition, in the presence of Fe-based complexes, both char and CO react with NO<sub>x</sub> to form N<sub>2</sub>, which leads to a reduction in NO<sub>x</sub> emissions during combustion. Additionally, the replacement of current residential coal with a new type of clean coke is a facile method for reducing gaseous pollutant emissions from household activities to protect the atmospheric environment. The average emission factors (EFs) of PM, SO<sub>2</sub>, and NO<sub>x</sub> for the prepared clean coke were small during combustion and were much lower than the EFs of the tested raw coal, semicoke, and briquettes.

## 1. Introduction

Coal acts as the main fuel and energy resource in China and will continue to be used because of its abundant reserves and low cost. Nonetheless, the direct utilizations of coal are always associated with the sulfur dioxide (SO<sub>2</sub>), nitrogen oxide (NO<sub>x</sub>), particulate matter (PM), organic compounds, and heavy metals. These pollutants into the atmosphere have led to the greenhouse effect, acid deposition, and formation of photochemical fog and heavy haze, resulting in aggravating environmental and public health concerns [1]. The particles that form haze can be classified as primary and

secondary particles. The particles that are emitted directly from flue gas that result from burning fossil fuels are called primary particles, and the particles formed from the reactions of ammonia (NH<sub>3</sub>) and volatile organic compounds (VOC) in moist air with the SO<sub>2</sub>, NO<sub>x</sub>, and VOCs emitted directly from the flue gas resulting from coal combustion are called secondary particles [2]. Haze pollution is closely related to the PM<sub>2.5</sub> (PM with aerodynamic diameters equal to or less than 2.5 μm) emissions [3]. Over the past decade, 14 million tons of PM<sub>2.5</sub> has been emitted to the atmosphere each year due to anthropogenic activities in China [4]. Hence, techniques involving reducing the PM, SO<sub>2</sub>, NO<sub>x</sub>,

and VOC emissions from direct household coal combustion have been receiving more and more attention [5–9]. In particular, significant haze reduction can be achievable by disrupting the sulfate formation process and potentially by controlling the  $\text{NO}_2$  emissions [10].

The classical types of household fuel used in China include bituminous coal and anthracite coal. However, because coal contains toxic elements that have not been destroyed by combustion, technical limitations make it difficult to burn coal cleanly in households. The World Health Organization has recommended that semicoke, briquette, and formed coke be used as clean alternatives to coal to reduce emissions from coal-burning households in China [11–13]. Semicoke is produced from bituminous coal by subjecting the coal to an industrial carbonization treatment process at low temperature, which removes the volatile compounds from the raw coal that are major precursors for PM formation and carbon emissions. A study conducted by the Institute of Earth Environment of Chinese Academy of Sciences notes that the emission factors (EFs) of primary PM<sub>2.5</sub> and polycyclic aromatic hydrocarbons are reduced by 75% and 80%, respectively, when using semicoke and by 90% and 97%, respectively, when using upgraded semicoke compared with lump coal [14]. Based on the current coal consumption data from China, switching to semicoke briquettes can reduce the average EFs of primary PM<sub>2.5</sub>, elemental carbon, OC, and carbon monoxide by approximately 92%, 98%, 91%, and 34%, respectively [15]. Coal briquettes are made from bituminous coal and clay as a binding material [16, 17]. Because the formulation of raw coal can enhance coal combustion efficiency and reduce air pollution emissions, burning formulated coal is recommended over burning raw coal [18]. Coal briquettes are different from other residential coal combustion emission sources in that the PM in the emissions contains lower amounts of carbonaceous material but is similar in chemical composition to the PM emitted by other types of coal during combustion [19]. To reduce the  $\text{SO}_2$  emissions that result from burning briquettes, 15%  $\text{Ca}(\text{OH})_2$  was added to the briquettes as a sulfur fixation agent to capture the  $\text{SO}_2$  emitted during coal combustion at high temperature (950–1100°C). The results showed that the emission rate and mass-based EF of  $\text{SO}_2$  from the prepared coal briquette were approximately half of the values observed for untreated coal.

As described above, clean coal-based fuels are prepared from raw coal by using physical and thermal methods, such as carbonization treatment at low temperature and the formation of briquettes at normal temperatures, to reduce the pollutant emissions that result from burning fuel. Coal with a low maturity level usually results in emissions with higher volatile contents, which are precursors for the formation of PM during coal combustion. Therefore, EFs are expected to increase as the volatile content of coal increases [20]. Carbonization removes the volatile compounds that are the major precursors for PM and carbon emissions from raw coal, and the EFs of  $\text{SO}_2$  and  $\text{NO}_x$  are also affected by the carbonization process; however, these trends are not clear when data from many samples are considered [11, 15]. Coal generally has relatively high-sulfur contents, and sulfur is a

precursor material for the formation of  $\text{SO}_2$  during combustion. The creation of coal briquettes by adding a sulfur fixation agent can result in the fixation of sulfur in the combustion slag and ash [16]. In addition, adding bentonite or MGO to semicoke can decrease the primary EF of PM<sub>2.5</sub>. Because most PM originates from the incomplete combustion of volatile compounds in coal, the addition of a combustion-promoting agent can improve the combustion of volatile compounds. Semicoke and briquettes play important roles in reducing the PM and  $\text{SO}_2$  emissions from household activities but have some disadvantages, such as large amounts of  $\text{SO}_2$  and  $\text{NO}_x$  emissions for semicoke due to the presence of large amounts of specific types of volatile matter, the absence of existing additives available for semicoke, and large PM and  $\text{NO}_x$  emissions from briquettes due to the presence of large amounts of volatile matter.

To effectively reduce the gaseous pollutant emissions resulting from combustion in households, the idea of using two-stage catalytic sulfur fixation and two-stage catalytic nitrogen reduction-denitrification was proposed to obtain a new type of clean coke. The two-stage catalytic sulfur fixation and two-stage catalytic nitrogen reduction and denitrification processes involve catalytic sulfur fixation and nitrogen reduction and have been accomplished by using coal pyrolysis at high temperature (first stage) and catalytic sulfur fixation and denitrification during coke combustion at high temperature (second stage). In this study, clean cokes is prepared through pyrolysis at high temperature (1050°C) to reduce the concentrations of volatile compounds in the coke, and sulfur fixation, pyrolysis-promoting, and catalysis, and combustion-promoting agents are added to reduce the  $\text{SO}_2$ ,  $\text{NO}_x$ , and PM emission resulting from coke combustion. Due to the characteristics of the combustion process and emissions, it is important that policy makers develop policies for household energy use while considering the environmental consequences and the characteristics of clean coke combustion and emissions.

## 2. Experimental Materials and Methods

**2.1. Materials.** The clean coke was prepared as follows. Firstly, raw coal was ground to particles less than 3 mm. Then, 100 g of coal with a certain amount of additives was mixed (physical mixing method) according to a given proportion. About 7%  $\text{CaCO}_3$ , 0.5%  $\text{K}_2\text{SiO}_3$ , and 0.5%  $\text{Fe}_2\text{O}_3$  were added to coal samples, respectively. And, then the mixture was pressed into a cylinder ( $\varphi = 55$  mm,  $h = 95$  mm). The coal cylinders were placed in a corundum tray and pushed into a high-temperature tubular furnace that was then heated to 1050°C at a rate of 10°C/min and then maintained for 1 h to produce cylinders of coke at high temperature. After the temperature was reduced to ambient temperature under an  $\text{N}_2$  atmosphere, the clean coke was prepared.

The additives were listed as follows: sulfur fixation agent ( $\text{CaCO}_3$ , analytical pure reagent), combustion-promoting agent ( $\text{K}_2\text{SiO}_3$ , analytical pure reagent), and denitrifying agent ( $\text{Fe}_2\text{O}_3$ , analytical pure reagent).

*2.2. Instruments and Methods Used for Analyzing the Properties of the Clean Coke.* The clean coke samples were analyzed using a TGA-type industrial analyzer made by ELTRA GmbH (Germany), a Vario MAX CHN type elemental analyzer (Germany), and a Rapid CS Cube sulfur analyzer (Germany).

Based on the standard methods used for detecting Cl contents in wastes and fuel (CEN/TS 15408–2005), the Cl contents in clean coke samples were measured using an ICS-90 ion chromatograph.

The trace heavy metal contents in the clean coke samples were detected using an inductively coupled plasma source mass spectrometer (Thermo iCAP 6300).

The pore structures of the clean coke sample were measured using a Micromeritics ASAP 2020 adsorption instrument that was made in America and nitrogen physisorption at 77 K. The specific surface area, pore volume, and pore diameter were calculated using the Brunauer–Emmett–Teller (BET) and Bopp–Jancso–Heinzinger (BJH) methods.

The volatile components in the clean coke sample were analyzed using the high-temperature pyrolysis apparatus and gas chromatograph-mass spectrometry. The working principles of this analysis system are described as follows: after the solid sample was placed in the high-temperature pyrolysis apparatus, the high-temperature pyrolysis apparatus was immediately heated from ambient temperature to the designated temperature and the solid sample was rapidly pyrolyzed. The gases released from the hydrolysis of the solid sample were subjected to gas chromatograph-mass spectrometry analysis and tested in real time by using online detection. In this experiment, 0.3 mg sample was pyrolyzed at a heating rate of 1000°C/s and using a gas flow rate of 1 ml/min under a high-purity nitrogen atmosphere.

*2.3. Combustion and Emission Characteristics.* The combustion performances of clean coke samples were studied using the thermogravimetric analysis method and a STA 449F3 thermogravimetry analyzer (NETZSCH corporation, Germany). The experimental temperature was increased from ambient temperature to 1000°C at a heating rate of 30°C/min under air atmosphere. The gas flow rate was 100 ml/min, and the sample weight was approximately 5 mg.

The combustion and emission characteristics of the clean coke samples were determined using a horizontal tube furnace consisting of a quartz tube with a length of 1200 mm, internal diameter of 45 mm, and high-temperature resistance of 1300°C. The tube furnace was heated using an electric furnace with a heating power of 3 KW, and the temperature of the electric furnace was controlled by using an XMA5001ZK intelligent universes PID controller. Both ends of the electric furnace were sealed by temperature-sealing rubber plugs. The gas fed into the quartz tube was simulated air containing 79 vol.% N<sub>2</sub> and 21 vol.% O<sub>2</sub>, and the gas flow was controlled by a mass flow meter.

The experimental steps used for measuring the composition of flue gas from the quartz tube are described as follows: (1) the gases were mixed with 79 vol.% N<sub>2</sub> and 21 vol.% O<sub>2</sub> and passed through the horizontal tube furnace

while controlling the flow rate with a mass flow meter, and the furnace was heated to the designed combustion temperature by using the best heating rate before storing at the designed temperature for a period of time. (2) Samples were uniformly layered in a porcelain boat that was then placed 5 mm into an orifice and preheated. (3) The porcelain boat was pushed into the constant temperature zone located in the tube furnace and the composition of the flue gas was determined online by using a hand-held flue gas analyzer and a portable infrared gas analyzer connected to the outlet of the tube. (4) After changing the designed combustion temperature, the next experiment at a given combustion temperature was done according to the above steps. The designed combustion temperatures for these experiments were 800°C, 900°C, and 1000°C, respectively.

The release characteristics of the pollution emissions from the combustion of the clean coke in three different stoves were tested. The compositions of gaseous pollutants in the flue gas from the combustion of carbon-based fuel were analyzed as follows: the SO<sub>2</sub> concentrations were determined by using the stationary source-fixed potential electrolysis method (HJ/T57-2000), the NO<sub>x</sub> concentrations and fixation potential were determined by using stationary source emission-determination of NO<sub>x</sub> and the electrolysis method (HJ 693–2014), and PM was sampled using the sampling methods for gaseous pollutants from the exhaust gas of stationary sources (GB/T16157-1996).

### 3. Results and Discussion

#### 3.1. Properties of Clean Coke

*3.1.1. Industrial and Elemental Analyses.* Clean coke was prepared by the high-temperature co-pyrolysis of coal (1050°C) in the absence of air and was obtained using a mixture of raw coal and composite additives obtained by mechanical mixing. The clean coke, de-coal (demineralized coal), and raw coal were characterized, and the characterization results are shown in Table 1.

As shown in Table 1, the ash and volatile contents of the coal used for coking were larger than the ash and volatile contents of the raw coal; however, the fixed carbon content was lower in the raw coal than in the coal used for coking. Simultaneously, the N and S contents in the coal used for coking were lower than the N and S contents in the raw coal because the composite additive agent is inorganic and because adding the composite additives only changes the composition of the coal used for coking. Consequently, adding the composite additives increased the relative ash content and decreased the relative N and S contents but did not change the absolute amounts of these materials or elements.

When comparing the information obtained from the clean coke and coal used for coking shown in Table 1, large amounts of volatile compounds were observed in the coal used for coking due to the high-temperature pyrolysis process, i.e., the volatile matter content (by dry weight) was reduced from 30.85 wt.% in the coal used for coking to 2.76 wt.% in the clean coke. These volatile compounds are major

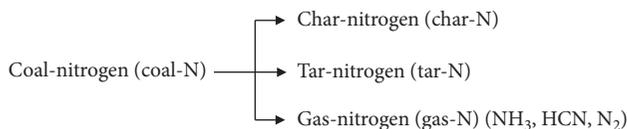
TABLE 1: Proximate and ultimate analysis of the samples used.

Name	Proximate analysis (wt.%)					Ultimate analysis (wt.%)		
	$M_{ad}$	$A_{ad}$	$V_{ad}$	$FC_{ad}$	$N_{ad}$	$C_{ad}$	$H_{ad}$	$S_{ad}$
Raw coal	1.26	8.07	15.66	72.61	1.72	89.08	4.63	2.45
De-coal	0.16	0.86	10.47	88.51	1.83	91.14	3.86	1.55
Clean coke	0.24	16.50	2.30	76.78	0.59	78.89	0.52	0.52

M, moisture; V, volatile; A, ash; FC, fixed carbon; ad, air-dried basis.

precursors for the formation of pollutants such as PM, SO<sub>2</sub>, and NO<sub>x</sub>. Consequently, the low amounts of volatile compounds in the clean coke will result in lower PM, SO<sub>2</sub>, and NO<sub>x</sub> emissions during combustion.

Simultaneously, the N content was reduced from 1.00 wt.% in the coal used for coking to 0.59 wt.% in the clean coke. Based on a coke yield of 70%, the ratio of N removed from the coal used for coking by high-temperature co-pyrolysis was approximately 56%, which reduced the NO<sub>x</sub> emissions during the combustion of the clean coke. The distribution of nitrogen in the coal during high-temperature co-pyrolysis is illustrated as follows.

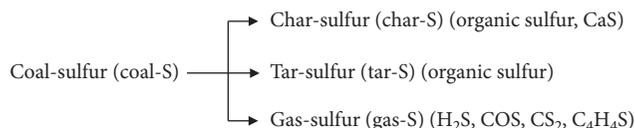


During high-temperature co-pyrolysis, the nitrogen in the coal is released as volatile nitrogen (volatile-N, including tar-N), gaseous N (gas-N, including NH<sub>3</sub>), HCN, and N<sub>2</sub>. The remaining nitrogen is retained in the residual solids as char-N. Some of the char-N is converted to NO<sub>x</sub> during the combustion process. To reduce and restrain the formation of NO<sub>x</sub> during combustion, it is important that char-N is transformed into volatile-N during coal pyrolysis. Devolatilization played an important role in reducing char-N, in which char-N was partially transformed into NH<sub>3</sub>, HCN, and N<sub>2</sub> emitted from pyrolysis. The formation of volatile-N from coal-N was influenced by the type of coal, pyrolysis temperature, residence time, atmosphere, and additives. The minerals inherently present in the coal, and the externally added iron-containing compounds have important influences on the formation and release of HCN, which is one of the main precursors of NO<sub>x</sub> during coal pyrolysis [21]. The interactions between iron and char promote more efficient solid reactions between metallic iron and char-N to form N<sub>2</sub> [22]. The existing state of the Fe-containing minerals and added Fe catalyst are important for catalytic N<sub>2</sub> formation during coal pyrolysis [23]. The highly dispersed CaO in coal catalyses the efficient conversion of char-N to N<sub>2</sub> in the process of carbon crystallization [24].

In conclusion, our objective is to change the composition of coke by using additives and catalytic reduction to reduce the amount of char-nitrogen that is generated during the pyrolysis process. The low nitrogen content of clean coke proves that the objective of reducing the generation of char-N by using first-stage catalytic reduction was achieved.

In comparison with the change of the N content in the clean coke, the S content in both clean coke and coal as coking was not significant, which indicated the effects of

catalytic sulfur fixation promoted by the addition of a sulfur fixation agent. The distribution of coal-sulfur during co-pyrolysis at high-temperature is shown as follows.



During high-temperature co-pyrolysis, the sulfur in coal is released as volatile-sulfur (volatile-S), such as tar-S and gas-S (including H<sub>2</sub>S, COS, CS<sub>2</sub> and C<sub>4</sub>H<sub>4</sub>S), and the remaining sulfur is retained in the residual solid fraction as char-S, which includes organic sulfur and CaS. After the high-temperature hydrolysis process, the char-S formed mainly includes the original organic sulfur and the CaS produced during co-pyrolysis. During co-pyrolysis, the Ca-based agent in the composite additive agent reacts with the sulfide in the coal to form calcium sulfide fixed in the coke through two reaction pathways. In the first reaction pathway, the CaS formed by the reaction of FeS<sub>2</sub> in the coal used for coking with CaO is fixed in the clean coke. In the second pathway, the CaS formed by the reaction of the H<sub>2</sub>S produced from the pyrolysis of organic sulfur in the coal used for coking with CaO is fixed in the clean coke [25]. The fixation of sulfur during coal pyrolysis at high temperatures was influenced by the pyrolysis atmosphere, temperature, type of coal, and presence of different minerals. The FeCl<sub>3</sub> loaded by mechanical mixing inhibits the formation of sulfur-containing gases [26]. The CaS formed in the clean coke will be transformed to CaSO<sub>4</sub> and fixed in the combustion slag and ash during the clean coke burning process at high temperature (950~1100°C). Compared with the thermodynamics and kinetics of the capture of SO<sub>2</sub> emissions by CaO to form CaSO<sub>4</sub> at high temperatures, the transformation of CaS into CaSO<sub>4</sub> has more potential for significantly reducing SO<sub>2</sub> emission during the combustion of clean coke. Thus, our objective was to reduce SO<sub>2</sub> emissions from combustion by using first-stage catalytic sulfur fixation.

For comparison, the ranges of the compositions of the other Chinese coal-based fuel and anthracite coal were also analyzed and are summarized in Table 2.

As shown in Tables 1 and 2, the N content of the clean coke was the lowest among the investigated coal-based fuel samples, which indicates that the clean coke resulted in significantly lower NO<sub>x</sub> emissions during combustion. This finding is confirmed from the results of the following combustion experiment.

**3.1.2. Toxic Trace Metal and Volatile Matter Analysis.** The toxic trace metals in PM can be damaging to human health. The chlorine (Cl) and heavy metals that exist in the

TABLE 2: Proximate and ultimate analysis of other samples.

Name	Proximate analysis (wt.%)				Ultimate analysis (wt.%)			
	M <sub>ad</sub>	A <sub>d</sub>	V <sub>ad</sub>	FC <sub>ad</sub>	N <sub>ad</sub>	C <sub>ad</sub>	H <sub>ad</sub>	S <sub>ad</sub>
Anthracite coal	1.26	10.02	4.22	83.96	0.98	82.12	2.74	0.32
Briquette coal	2.02	11.52	8.20	76.98	0.74	77.55	1.54	0.29
Semicoke	3.64	16.86	9.86	67.10	0.72	70.34	0.99	0.27

M, moisture; V, volatile; A, ash; FC, fixed carbon; ad, air-dried basis; d, dried basis.

PM<sub>2.5</sub> emitted into the atmosphere during combustion processes are related to the contents of Cl and heavy metals that exist in coal-based fuel. The contents of Cl and heavy metal for several typical coal-based fuel samples were analyzed and are shown in Table 3.

As shown in Table 3, the concentrations of Cl and most heavy metals in the clean coke were low, especially the Cl, Cd, and Hg contents. The concentrations of Cl and most heavy metals were also affected by the high-temperature pyrolysis process. Pyrolysis may result in the release of volatile matter, such as Cl and Hg, which exists in the coal to reduce the emissions of trace toxic matter during combustion.

The high indoor concentrations of airborne polycyclic aromatic hydrocarbons that result from household coal combustion are associated with elevated incidences of lung cancer in some regions of China [27]. Consequently, the contents of volatile matter produced by the pyrolysis of clean coke are listed in Table 4.

As shown in Table 4, the volatile components produced by the pyrolysis of clean coke were alkanes, olefins, aromatic hydrocarbons, and acids, esters, and aldehydes. Alkanes and olefins accounted for 80~90% of all volatile matter, and the macromolecular organic compounds were relatively small. By comparison, the contents of aromatic hydrocarbons and macromolecular organic compounds were the lowest. Based on the concentrations of the different volatile components in the various coal-based fuels, the release of polycyclic aromatic hydrocarbons was the lowest.

### 3.2. Combustion Characteristics of Clean Coke

**3.2.1. Ignition and Ash Fusion Temperature.** With the rapid development of the coking industry and the decreasing demands for metallurgical coke, the commercialized production of clean coke is feasible because China's industrial capacity for coking will meet and exceed the consumption demands in the next few years. The production of household fuel consisting of metallurgical coke rather than raw coal is a feasible method for reducing pollution emissions from household activities. However, the following problems are encountered that limit the applicability of metallurgical coke as a household fuel: high ignition temperature and difficult ignition, poor reactivity and low combustion rates, and the presence of low volatile matter and a short flame. To overcome these shortcomings, we altered the composition of the coal used for coking in the existing coking industry by adding combustion and structure promoting agents to produce a household fuel. The combustion characteristics of the clean coke samples prepared by the coking industry were

TABLE 3: The contents of Cl and heavy metals in several typical coal-based fuel samples.

Name	Cl (wt.%)	Heavy metal ( $\mu\text{g/g}$ )						
		Ni	Cu	Cr	As	Cd	Hg	Pb
Anthracite coal	0.17	1.73	0.21	0.50	0.03	0.0014	0.0908	0.35
Briquette coal	0.16	1.44	0.14	0.92	0.02	0.0011	0.0084	0.11
Semi-coke	0.19	3.55	0.15	2.48	0.02	0.0003	0.0061	0.14
Clean coke	0.08	1.31	0.11	0.28	0.01	ND	0.0045	0.11

tested using thermogravimeter. The combustion TG, DTG, and DSC curves of the clean coke samples are shown in Figure 1.

As shown in Figure 1, as the combustion temperature increased, the amount of mass lost by the clean coke sample was small according to the TG curve, and a small endothermic peak was observed on the corresponding DSC curve at the initial stage that corresponded to the evaporation of trace water at low temperature. This result shows that the clean coke sample contained trace amounts of water and hydroxide. When the combustion temperature increased up to 475°C, the mass lost by the clean coke sample began to decrease sharply, and a large endothermic peak was observed on the corresponding DSC curve that belonged to the combustion of the clean coke. These results indicated that the combustion of the clean coke sample occurred once the combustion temperature was reached and then the mass decreased rapidly. The combustion temperature for clean coke was approximately 475°C. When the combustion temperature continued to increase and approached 775°C, the mass loss indicated by the curve did not decrease and remained stable, which indicated that the clean coke sample burned out and that the surplus ash was an incombustible substance. Thus, the burnout temperature for the clean coke was approximately 775°C. Ignition temperature and burnout temperature are the leading indicators used to estimate the ignition characteristics of coal-based fuel and reflect the difficulty level of coal-based combustion. According to the ignition temperature determined by using the thermogravimetry method, the ignition temperature and burnout temperature of the clean coke sample and other coal-based fuels were determined and are listed in Table 5.

As shown in Table 5, the clean coke is an inflammable and long-burning coal-based fuel that has beneficial characteristics for household activities.

The ratio of mass loss of 68.8% corresponding to the latter mass loss showed that the ash content of the clean coke

TABLE 4: Analysis of the components in volatile matter.

Sample name	Alkane (wt.%)	Olefin (wt.%)	Aromatic hydrocarbon (wt.%)	Acid, ester, aldehyde (wt.%)
Anthracite coal	19.95	68.69	6.21	5.15
Briquette coal	21.18	51.72	15.67	11.43
Semicoke	21.58	66.39	8.80	3.23
Clean coke	21.53	70.63	6.47	1.37

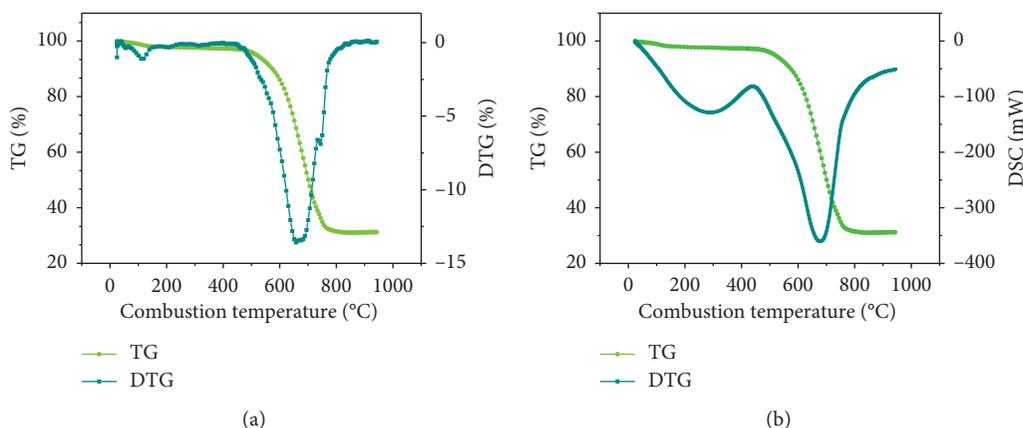


FIGURE 1: Thermogravimetric curve of the clean coke sample. (a) TG-DTG curve. (b) TG-DSC curve.

TABLE 5: Ignition temperatures and burnout temperatures of coal-based fuel.

Sample	Anthracite coal	Briquette coal	Semicoke	Clean coke
Ignition temperature (°C)	550	500	524	510
Burnout temperature (°C)	720	800	760	770

determined by combustion was 31.2%. Compared to the proximate analysis of the clean coke sample, the ash content of the clean coke sample determined at 1000°C was high. This result likely occurred because the sulfur fixation agent resulted in the formation of  $\text{CaSO}_4$  in the combustion slag and ash and reduced the  $\text{SO}_2$  emissions during combustion. The  $\text{CaSO}_4$  in the ash increased the amount of ash that was obtained after complete combustion.

**3.2.2. Coke Reactivity Index.** According to the international standards of using coke for metallurgy, the reactivity indexes of primary and secondary coke for metallurgy (CRI) are less than or equal to 30% and 35%, respectively. The reactivity index of coke reflects the ability of the coke to react with carbon dioxide at high temperature. Although high CRI values result in lower coke strength and are unfavourable for the melting process, high CRI values are beneficial for household combustion because of the flammability of CO produced by the reaction of coke with carbon dioxide. According to the national standards used to determine coke reactivity and strength after reaction (GB/T4000-2008), the CRI of the clean coke sample was 48~58%. The results indicated that the clean coke sample has good flammability, which is useful for solving the problems of a high ignition temperature, difficult ignition, poor reactivity, low combustion rate, low volatile matter

content, and short flame that are involved with using coke for metallurgy.

The thermal performance of coke is related to its porosity and pore structure. Adequate control of porosity and pore structure would be helpful for improving the thermal intensity of coke, and the “anomalously” favourable combustion performance of semicoke is due to the developed pore structure [28]. The specific surface area, pore volume, and pore diameter of both the clean coke and coke from the metallurgy samples were measured using a Micromeritics ASAP 2020 adsorption instrument. The differences between the clean coke and the coke from the metallurgy samples was that a composite agent was added to the coal used for coking to produce clean coke. The results are shown in Table 6.

As shown in Table 6, compared with coke, the specific surface area and pore volume of clean coke are obviously changed, in which the specific surface area is  $25.55 \text{ m}^2/\text{g}$ , which is 2.5 times higher than coke. And the pore volume of clean coke is  $0.084 \text{ m}^3/\text{g}$ , which is 3.4 times higher than coke, and the pore diameter of clean coke is 12.75 nm, which increases the 2.03 nm. The pore structure of clean coke is more abundant than that of coke, which provides the necessary conditions for adequate gas-solid contact surface for high-temperature coke combustion, and at the same time, the rate of gas diffusion is increased to accelerate the reaction rate of the coke. These results indicate that the pore

TABLE 6: Comparison of the surface area and porosity of the clean coke and the coke from the metallurgy samples.

Sample	Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (nm)
Clean coke	25.55	0.084	12.75
Coke	7.28	0.019	10.72

structure of the clean coke was more developed than that of the coke obtained from metallurgy samples, which increased the contact area between the coke and air during the combustion process and improved the rate of the combustion reaction. Ignition of clean coke sample was easy.

### 3.3. Environmental Benefits of Clean Coke

**3.3.1. SO<sub>2</sub> Emissions.** SO<sub>2</sub> is a major air pollutant in China and is significantly associated with increased morbidity and the population risks of cardiovascular and respiratory mortality [29]. Reducing SO<sub>2</sub> emissions from household combustion is important. The profile of SO<sub>2</sub> emissions that occur during clean coke combustion when a fire is started until the fire is extinguished at three different burning temperatures of 800°C, 900°C, and 1000°C is shown in Figure 2.

As shown in Figure 2, most of the SO<sub>2</sub> was emitted, and the SO<sub>2</sub> concentration quickly reached a maximum concentration during the initial burning period of the clean coke. The SO<sub>2</sub> content gradually decreased to 0 when the clean coke was burned. Simultaneously, as the combustion temperature of the clean coke increased, the peak concentrations and the amount of emitted SO<sub>2</sub> gradually increased. A sharp peak of SO<sub>2</sub> was observed, and the SO<sub>2</sub> concentration corresponding to a peak at 1000°C was less than 100 mg/m<sup>3</sup>. In addition, the maximum and total SO<sub>2</sub> emitted from clean coke combustion were lower than the maximum and total SO<sub>2</sub> concentrations emitted from household coal combustion and from power plant coal boilers with air pollution control devices meeting the SO<sub>2</sub> emission requirements for protecting the atmospheric environment. A comparison of SO<sub>2</sub> emission between clean coke and clean coal is shown in Figure 3.

As shown in Figure 3, the SO<sub>2</sub> emissions of clean coke during combustion were lower than those of clean coal under the same combustion conditions.

Most of the organic sulfur and CaS in clean coke is oxidized and converted to SO<sub>2</sub> gas during combustion, and the formed SO<sub>2</sub> may be retained as a solid compound by CaO. The added CaO and Ca(OH)<sub>2</sub> had better sulfur retention effects and higher reactivity than the added CaCO<sub>3</sub> [30]. In addition, the desulfurization properties of CaO during combustion were mainly affected by the flame temperature, residence time, initial molar ratio of Ca/S, and reaction activity of the alkaline components [31]. The combustion atmosphere is an important factor that influences the products resulting from desulfurization. For a fixed-bed furnace ignited at the bottom, the coal bed can be divided into four layers from bottom to top, the ash layer, oxidizing layer, reducing layer, and fresh fuel layer. The CaS phase produced in the reducing layer and the CaSO<sub>4</sub> phase

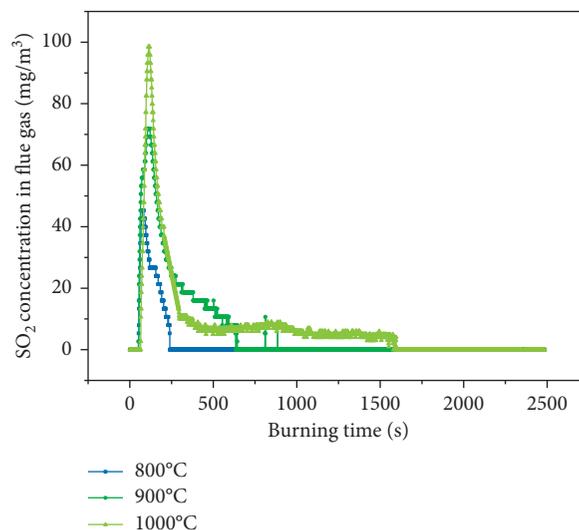


FIGURE 2: SO<sub>2</sub> emissions during combustion at different temperatures.

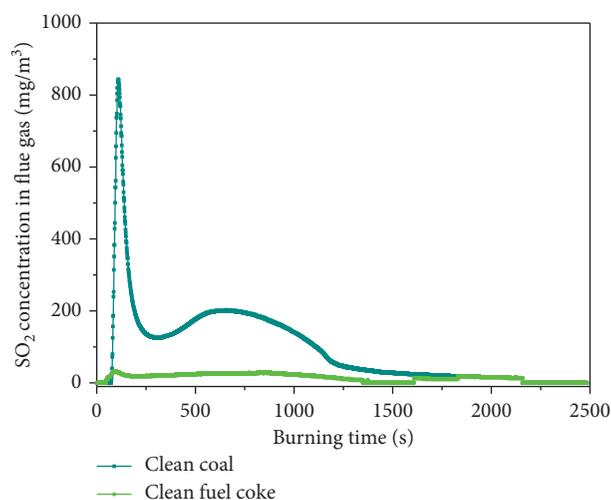
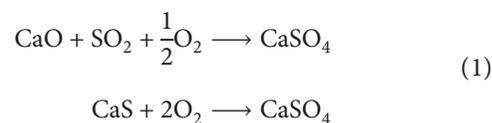


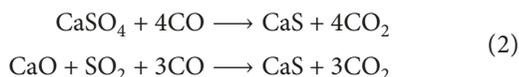
FIGURE 3: SO<sub>2</sub> emissions during combustion for clean coal and clean coke.

produced in the oxidizing layer had been identified in desulfurization residues derived from coal briquette combustion [32]. The product resulting from sulfur fixation during clean coke combustion was calcium sulfate (CaSO<sub>4</sub>) under oxidizing condition, which was formed as shown in the following reactions:



The SO<sub>2</sub> emitted from organic sulfur during combustion was captured by CaO in the clean coke and oxidized by O<sub>2</sub> in the air to form CaSO<sub>4</sub>, which hardly decomposes below 1050°C. On the other hand, the CaS formed during coal pyrolysis at high temperatures was further converted to CaSO<sub>4</sub> in an oxidizing atmosphere.

The product of sulfur fixation during the combustion of clean coke was calcium sulfide (CaS) under reducing condition, which was formed as shown in the following reactions:



The rate of CaS oxidation is slower than the oxidation rates of most coal chars [33]. However, the CaS formed during coal pyrolysis at high temperature was not oxidized, and the SO<sub>2</sub> formed during coal pyrolysis was captured by CaO in the reducing atmosphere to form CaS. CaS is thermally stable at high temperature (up to 2400°C) under reducing atmospheric conditions [34].

Alkali and transitional metal compounds such as NaCl, FeCl<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> can act as catalysts, accelerating CaO sulfation reactions during combustion at temperatures below 1200°C [35–37].

Generally, the low SO<sub>2</sub> emissions that were observed when burning the clean coke occurred because the sulfur compounds (mainly in the form of organic sulfur and calcium sulfide) in the clean coke were fixed in ash by promoting the fixation of sulfur through the addition of additives as catalysts. The low SO<sub>2</sub> emissions that were observed when burning the clean coke indicated that the objective of reducing the SO<sub>2</sub> emissions through the second-stage fixation of sulfur was achieved.

**3.3.2. NO<sub>x</sub> Emissions.** NO<sub>x</sub> emissions are responsible for numerous environmental problems, including photochemical smog, acid rain, water quality deterioration, global warming, and visibility impairment (U.S. EPA, 2003). Particularly, the role of NO<sub>x</sub> in the formation of haze has been determined and considered. Reducing NO<sub>x</sub> emissions is important in household combustion. The NO<sub>x</sub> emission profiles during the combustion of clean coke combustion (from fire initiation to fire extinction) at three different burning temperatures of 800°C, 900°C, and 1000°C are presented in Figure 4.

As shown in Figure 4, at the beginning of clean coke combustion, NO<sub>x</sub> was emitted and the maximum NO<sub>x</sub> concentration was achieved quickly. Then, the NO<sub>x</sub> concentration fluctuated at relatively high concentrations for a period of time before sharply decreasing to 0 when combustion was complete. Simultaneously, as the combustion temperature of the clean coke increased, the maximum NO<sub>x</sub> emitted significantly decreased, in contrast with the trend observed for SO<sub>2</sub> emissions. A broad emission peak was observed for NO<sub>x</sub>, and the NO<sub>x</sub> concentrations corresponding to the peak at 800°C were less than 90 mg/m<sup>3</sup>. Similar to the SO<sub>2</sub> emissions, the maximum NO<sub>x</sub> and total concentrations of NO<sub>x</sub> emitted from clean coke combustion

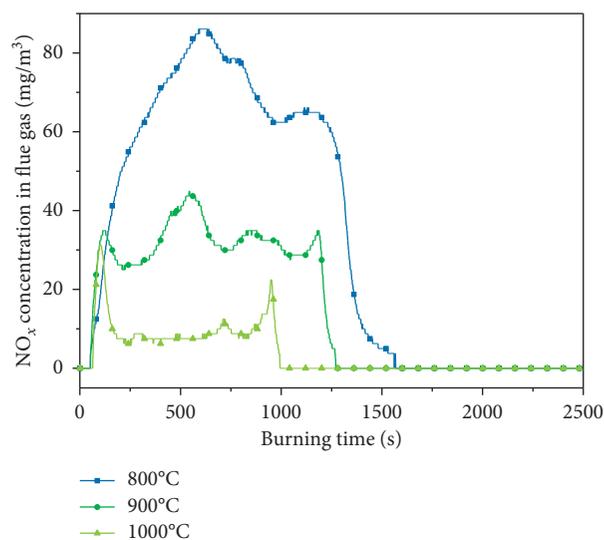


FIGURE 4: NO<sub>x</sub> emissions during combustion at different temperatures.

were lower than the maximum and total concentrations of NO<sub>x</sub> emitted from household coal combustion and power plant coal boilers with air pollution control devices, which meet the requirements of NO<sub>x</sub> emissions to protect the atmospheric environment. A comparison of NO<sub>x</sub> emissions between clean coke and clean coal is shown in Figure 5.

As shown in Figure 5, the NO<sub>x</sub> emissions from clean coke during combustion were lower than the emissions of NO<sub>x</sub> from clean coal under the same combustion conditions.

The emissions of NO<sub>x</sub> during combustion were very dependent on several operating conditions, and many homogeneous and heterogeneous reactions are important for the formation and destruction of NO<sub>x</sub> [38]. Three well-known reactions result in the formation of NO<sub>x</sub> when burning coal; thermal NO<sub>x</sub> forms from the reaction of N<sub>2</sub> in the atmosphere with O<sub>2</sub> at temperatures greater than 1600°C. The NO<sub>x</sub> formed from this reaction then reacts with carbon or hydrogen groups in the atmosphere. In addition, NO<sub>x</sub> is formed from the thermal-decomposition and oxidation of fuel nitrogen with O<sub>2</sub>. Due to the low combustion temperatures that occur in household coal combustion, no thermal formation of NO<sub>x</sub> occurs. Thus, for household coal combustion, only the formation of NO<sub>x</sub> from fuel nitrogen (fuel-N) will be considered. During combustion, the char-N (as fuel-N) is oxidized to NO and N<sub>2</sub>O and reduced to N<sub>2</sub>. A simplified scheme for the conversion of char-N is shown in Figure 6.

As shown in Figure 6, the key to decreasing NO<sub>x</sub> emissions is that NO<sub>x</sub> is further reduced to N<sub>2</sub> by CO and char. NO<sub>x</sub> formed is further reduced to N<sub>2</sub> by char in route 1. Char is an active reactant for NO and N<sub>2</sub>O reduction, and less NO<sub>x</sub> is formed within the pore system of char when the NO<sub>x</sub> diffuses to the char surface. The porosity and specific surface area of char significantly affect the reduction of NO<sub>x</sub> by char, and the mineral material in coal is another important factor that affects reduction reactions. The specific surface area determines the amount of NO<sub>x</sub> reduction by char [38]. The NO<sub>x</sub> reduction reaction is influenced by

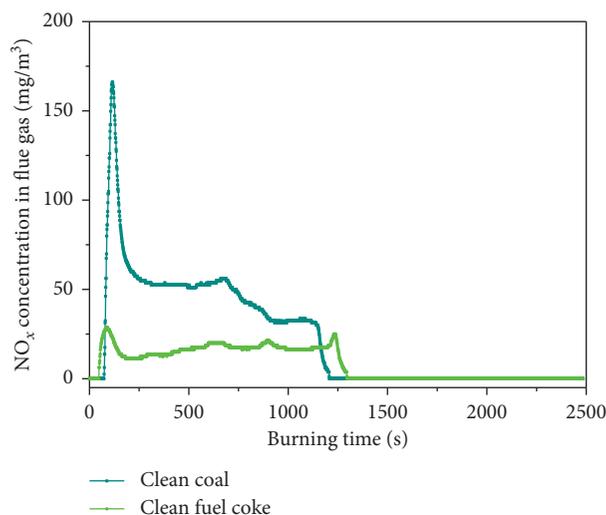


FIGURE 5:  $\text{NO}_x$  emissions during combustion for clean coal and clean coke.

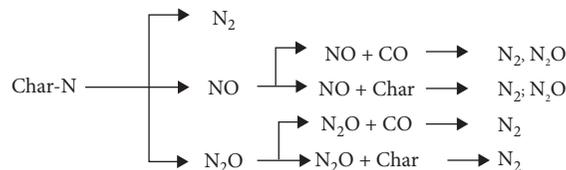


FIGURE 6: Simplified reaction scheme for the formation and reduction of NO and  $\text{N}_2\text{O}$ .

catalysts. Calcium and iron exhibit remarkable catalytic activity and reduce the  $\text{NO}_x$  emissions that occur during char combustion [39, 40]. In the second route,  $\text{NO}_x$  is reduced to  $\text{N}_2$  by CO. During combustion, CO is formed by the reaction of C with  $\text{O}_2$  in air, resulting in the formation of  $\text{CO}_2$ . In addition, CO is an important reductant, and the reaction of  $\text{NO}_x$  with CO is influenced by catalysts. Calcined limestone is an active catalyst for the reduction of NO by CO, and CaS is an even more active catalyst for the reduction of  $\text{NO}_x$  by CO than CaO [41]. As the mineral content increases, the NO emissions decrease for N-5 and N-6 in the model coal.

In conclusion, the factors that influence  $\text{NO}_x$  emissions during burning coke include the porosity and specific surface area of coke, the reduction atmosphere, and the catalysts in the coke. As shown in Table 6, the pore volume and specific surface area of clean coke increased significantly, which was beneficial for the reduction of  $\text{NO}_x$  by char. This reduction process resulted in lower  $\text{NO}_x$  emissions when burning the clean coke. While clean coke was produced by high-temperature pyrolysis, the Ca-based additive became CaS, which is an active catalyst for the reduction of  $\text{NO}_x$  by CO. This process also reduced the amount of  $\text{NO}_x$  emissions that resulted from the combustion of clean coke. Simultaneously, the Fe in the composite additives may catalyze the reduction of  $\text{NO}_x$  by CO. These reactions explain why the clean coke resulted in lower  $\text{NO}_x$  emission during combustion. The low  $\text{NO}_x$  emissions that resulted from burning clean coke indicate that the objective of reducing  $\text{NO}_x$  emissions by second-stage catalytic reduction and denitrification was achieved.

**3.3.3. Particulate matter (PM) Emissions.** The particles directly emitted from the flue gas produced by burning fossil fuels are primary particles, and the particles contribute to the formation of haze. The average concentrations of PM in the flue gas emitted from clean coke, raw coal, semicoke, and briquettes during combustion were monitored and are shown in Table 7.

As shown in Table 7, the average concentrations of particles in the flue gas emitted from clean coke during combustion were the lowest among several types of coal-based fuel. The low amounts of PM in the emissions resulted from devolatilization at high temperature and from the use of the composite additives.

**3.3.4. Emission Characteristics at Different Stoves.** The emission characteristics of clean coke produced by industrial coking were tested in four types of the most popular household coal stoves (NQ-BWM stove used for heating, LSH0.06-0.1/65/45-AIII stove, boiler, domestic stove used for both heating and cooking). The results from detecting the concentrations of  $\text{SO}_2$  and  $\text{NO}_x$  emissions and PM are provided in Table 8.

As shown in Table 8, the concentrations of particulate matter,  $\text{SO}_2$ , and  $\text{NO}_x$  emitted when burning clean coke in several tested stoves were different. Nevertheless, these observed concentrations were lower than those observed for semicoke and briquettes when using the same device and conditions. This finding further demonstrates that the clean coke produced using two-stage catalytic sulfur fixation and

TABLE 7: Concentrations of PM in the flue gas resulting from the combustion of various carbon-based fuels.

Sample name	Clean coke	Raw coal	Semicoke	Coal briquette
Particulate matter (mg/m <sup>3</sup> )	22.0	76.2	126.2	52.5

TABLE 8: The particulate matter, SO<sub>2</sub>, and NO<sub>x</sub> emissions from burning clean coke in several different stoves.

Number	Stove name	Fuel type	Emission concentration (mg/Nm <sup>3</sup> )		
			Particulate matter (PM)	SO <sub>2</sub>	NO <sub>x</sub>
1	Domestic stove	Clean coke	112	247	75
		Semicoke	150	333	57
2	Boiler	Clean coke	257	377	124
		Briquette	1180	1250	384
3	LSH0.06-0.1/65/45-AIII stove	Clean coke	271	256	239
4	NQ-BWM stove	Clean coke	7.0	93	88
		Briquette	64.0	285	271

two-stage catalytic nitrogen reduction and denitrification could be used as a replacement for current residential coal to reduce pollutant emissions from burning coal in households and to protect the environment.

#### 4. Conclusions

The emission characteristics of gaseous pollutants resulting from burning clean coke that was produced using two-stage catalytic sulfur fixation and two-stage catalytic nitrogen reduction and denitrification were studied. High-temperature co-pyrolysis removed volatile compounds from the raw coals which are major precursors for the formation of gaseous pollutants led to the fixation of sulfur compounds as CaS by the calcium-based complex additive and reduced the transfer of char-nitrogen to volatile nitrogen through the addition of a catalyst in the clean coke. The reduced pollutant emissions that resulted from burning clean coke mainly resulted from the effects of the complex additives. The Ca-based additive captured the released SO<sub>2</sub> by forming CaO, and the CaS formed during pyrolysis process was transformed to CaSO<sub>4</sub> and fixed sulfur in the ash that resulted from the reduction of SO<sub>2</sub> emissions during the combustion of the clean coke. Complex additives catalyzed the reduction of NO<sub>x</sub> in the char and CO to N<sub>2</sub> resulted in the reduction of NO<sub>x</sub> emissions during combustion. The replacement of residential coal with the newly developed clean coke is a feasible method for reducing gaseous pollutant emissions and for protecting the atmospheric environment. The production of clean coke embodies the results of our own original research adopting a two-step fixation sulfur mechanism and two-step nitrogen reduction and NO<sub>x</sub> removal process, and the catalytic combustion-promoting technology produced clean coke with the help of coking production in China.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

#### Acknowledgments

This study was supported by the Air Heavy Pollution Cause and Control Project of China (DQGG-0511); Key Laboratory of Coal Science and Technology, Taiyuan University of Technology (MKX201805); Independent Innovation Project of Shanxi Transition Comprehensive Reform Demonstration Zone (2016CXJJ021); and National Natural Science Foundation of China (21878210) and sponsored by Mettler Toledo, Taiyuan Green Coke Energy Co., Ltd. (China).

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