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Investigation of the pyrolysis of Zichang˚Coal using different˚Catalysts in terms of mechanism and reactivity

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Abstract. In this study, the pyrolysis of Zichang˚Coal (ZC) was investigated by thermogravimetry (TG) using three˚Catalysts, and the yields of the products obtained from pyrolysis, as well as gas˚Composition, were investigated by gas˚Chromatography (GC) using a fixed-bed reactor. The˚Catalytic mechanism was discussed from the kinetic analysis and gas˚Composition. The˚Coats–Redfern integral approach was employed for investigating the reaction kinetics of the˚Coal–catalyst mixture. The general effect of the additive on the pyrolysis reactivity of˚Coal was˚Compared by DTG analysis and TG. The results indicated that KCl,˚CaO, and Fe_2O_3 exhibit a˚Catalytic effect on the pyrolysis of ZC. With the addition of˚Catalysts, gas production and˚Char productivity increased, while the tar yield first increased and then decreased.˚Coal pyrolysis˚Can be divided into two areas: With the addition of activation energy, pre-exponential factor and˚Catalysts decreased. Experiments were˚Conducted with three˚Catalysts, and the˚Catalyst reactivities for the pyrolysis of˚Coal followed the order of KCl >˚CaO > Fe_2O_3.

Introduction

In recent years,˚China has suffered serious oil shortage and severe environmental pollution. Furthermore,˚China significantly depends on˚Coal resources.˚Coal accounts for 50% of the total primary energy˚Consumption in˚China [1]. Nevertheless, the direct˚Combustion of˚Coal exhibits a relatively low thermal efficiency, resulting in high pollutant emissions. For these reasons,˚Coal gasification has been˚Considered as one of the most promising˚Clean˚Coal technologies, which˚Can˚Convert a dirty solid fuel into a˚Clean gaseous fuel [2]; it is the˚Core of the integrated gasification˚Combined˚Cycle (IGCC) technology, which˚Can achieve high efficiency and near-zero emissions of greenhouse gases and other pollutants.˚Currently,˚Catalytic gasification is always an attractive topic, with advantages of low operating temperature, high energy˚Conversion efficiency, low˚Capital˚Cost, as well as various reaction pathways for the production of desired gases. Thus, the˚Catalytic steam gasification of low-rank˚Coal should be intensively studied and successfully˚Commercialized in the next several years. Yu Fu et al[3].have reported that KCl,˚CaO, and Fe_2O_3 exhibited a˚Catalytic effect on the pyrolysis of HL. Wang et al[4]. have˚Concluded that K_2CO_3 in raw˚Coal exhibits a high reaction rate and a high distribution of H_2/CO and˚CO_2/CO gaseous products. Ting-yu Zhu et al[5]. have demonstrated that alkaline earth˚CaO decreases reaction energy and promotes the pyrolysis of˚Coal. Matsuoka K et al[6].have˚Concluded that alkali and alkaline earth metals promote the pyrolysis of˚Coal and increase the yield of˚Char. Most of the reported studies have˚Concentrated the use of one or two of the three metal accelerators; on the other hand,˚Careful investigation of three metal˚Catalysts simultaneously for the pyrolysis of

low-rank˚Coal, the addition of the most appropriate amount of˚Catalysts, and˚Comparison among three˚Catalysts have been reported rarely in northern Shaanxi.

Recently, we have been˚Continuously investigating the pyrolysis of Zichang˚Coal (ZC) by the addition of alkali, alkaline earth metals, and transition metals via temperature-programed pyrolysis in a thermogravimetric (TG) system and the˚Conditions most expeditious for˚Catalysis. The output of the pyrolysis products were examined in a fixed-bed reactor, and the gas˚Composition was examined by gas˚Chromatography (GC). The˚Catalytic mechanism was discussed. Furthermore, a dynamic model of pyrolysis was˚Constructed for˚Calculating A and E for a˚Certain˚Composition. The˚Catalytic properties of the three˚Catalysts were˚Compared and analyzed.

Experimental section

Sample Preparation

In this study, ZC with particle sizes between 120 and 160 m was used herein. Before˚Conducting the experiment, the samples were˚Crushed, ground, dried, and preserved. **Table 1** shows the results obtained from the ultimate and proximate analysis and˚Calorific value of the samples. **Table 2** summarizes the ash analysis, BET, and pore diameter of the samples.

Analytical-grade KCl, Fe_2O_3, and˚CaO were used as the additives for the˚Catalysts, with loadings of 0.5%, 1.0%, 1.5%, and 2.0%. The˚Catalysts as (KCl, Fe_2O_3, and˚CaO) were added to raw˚Coal as follows: KCl was added by dipping; the sample and KCl were proportionally mixed up to make up the following˚Compositions of 0.5%, 1.0%, 1.5%, and 2.0%. Second, distilled water was added and stirred for 15 min to ensure that the sample is sufficiently mixed. Finally, the samples were dried at 105°C for 4 h. The˚CaO and˚Coal, Fe_2O_3 esterification with mechanically mixing at the˚Collecting and identical ratio.

Table1 Proximate and ultimate analysis and˚Calorific value of ZC˚Coal sample

	Proximate (wt%,)				Ultimate (wt%)					High˚Calorific value
	M	A	V	FC	C	H	O	N	S	MJ/kg
Coal	4.28	25.80	61.44	12.76	65.30	2.24	28.06	3.26	0.14	22.62

Table 2 Ash analysis, BET, and pore diameter of the samples

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	BET m^2/g	Pore diameter A°
Sample	45.32	26.42	5.83	12.49	3.28	2.17	1.65	1.08	64.96	136.4

Apparatus and Procedure

The˚Combustion˚Characteristics of˚Coal with or without˚Composite˚Catalysts were investigated using a Netzsch STA 449 F3 TGA. Under a nitrogen flux of 30 mL/min, a˚Coal sample (5 mg) was placed in an Al_2O_3˚Ceramic˚Crucible and burned under a simulative air atmosphere at a heating rate of 10 K/min from ambient temperature to 800C. The weight of sample was˚Continuously monitored as a function of temperature.

Pyrolysis experiments were˚Conducted using a fixed bed reactor. First, a desired amount of the sample was placed in a stainless steel tube reactor (15 mm width., 220 mm length), and the reactor was flushed using high-purity nitrogen for evacuating the air from the system before the pyrolysis

experiment. Second, the reactor was placed into a preheated furnace (500, 550, 600, 650, and 700°C) and maintained at the desired temperature for 10 mins. Third, the pyrolysis products were removed from the reactor under high-purity nitrogen into a˚Cool trap for˚Collecting liquids, whereas gaseous products were˚Collected using a gas bag. Gas˚Composition was analyzed by GC (GC112A). In addition, the weight of the residual˚Char was quantified by weighing the stainless steel tube before and after pyrolysis. After˚Collecting the products, the tube was heated at 750°C under air for 1 h for removing the residual˚Char. Each experiment was repeated at least five times under the same˚Conditions.

Results and discussion

TG and DTG analyses

Pyrolysis˚Characteristics of ZC with Different KCl Ratios

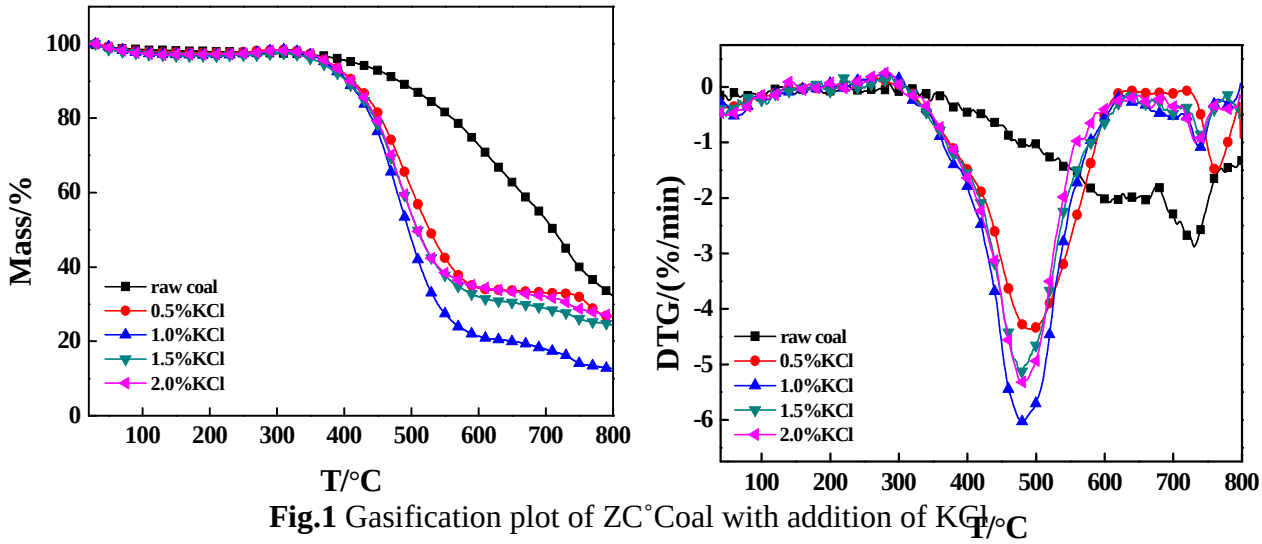


Fig.1 Gasification plot of ZC˚Coal with addition of KCl

Fig. 1 shows the TG˚Curves and derivative data (DTG)˚Curves of ZC with KCl at a heating rate of 10 K/min. As shown in **Fig. 1**, without KCl, the pyrolysis temperature of˚Coal was 722°C, the maximal weight loss rate was 2.75%/min, and weight loss was 66.11%. On the other hand, with the addition of KCl, the weight loss increased, and four weight loss peaks were distinctly observed in the DTG˚Curves. The peak temperature decreased from 722°C to 517.7°C. Furthermore, with increasing amount of KCl, weight loss and the weight loss rate first increased and then decreased. At 1.0% KCl, the pyrolysis rate and maximal weight loss rate were observed, indicating that with the addition of 1.0% KCl, the best˚Catalytic effect is observed. This observation was related to the addition of alkali metals, making the˚Coal surface˚Charged via the migration of the˚Carbon atoms from the frame, leading to modification in the electron density of˚Carbon atoms and weakening of˚Carbon-carbon bond strength; this weakening in turn increased the bonding force between oxygen and˚Carbon, thereby making the˚Coal surface more reactive and facilitating pyrolysis; in the presence of excessive K salt, however, the pores of the˚Coal particles are blocked, affecting the heat transfer of the reaction for mass transfer; as a˚Consequence, the response rate decreases with increasing KCl amount[3,6,7,8,9,10,11,12].

Pyrolysis˚Characteristics of ZC Different˚CaO Ratios

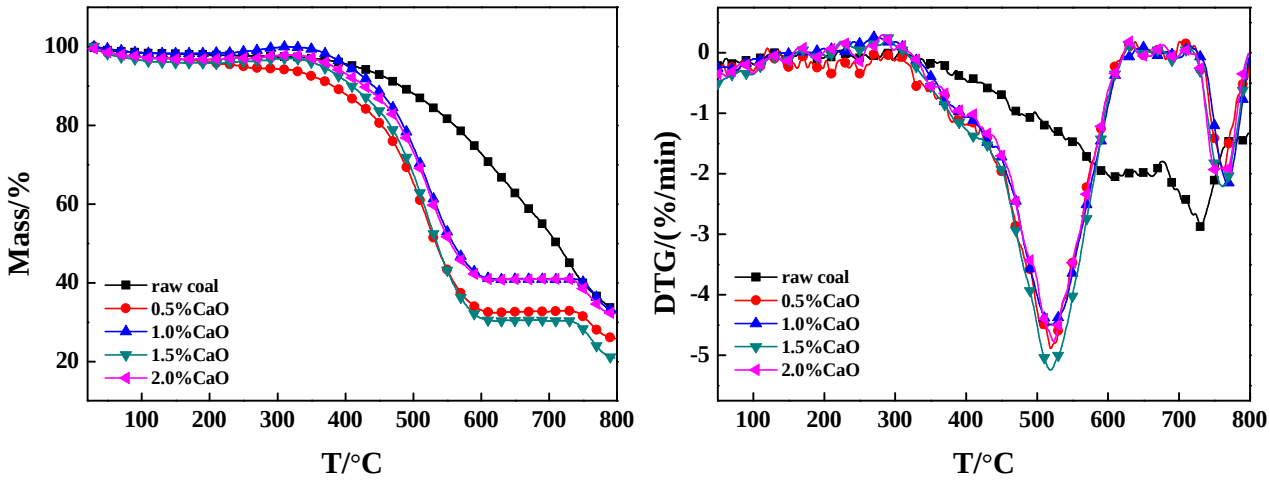


Fig.2 Gasification plot of ZC˚Coal with the addition of˚CaO

Fig. 2 shows the DTG˚Curves and TG of alkaline earth metal˚CaO under non-isothermal˚Conditions and ZC. As shown in **Fig. 2**, alkali earth metals, such as˚CaO, exhibited˚Catalysis similar to that of KCl. The experiment indicated that in the absence of additives, ZC did not exhibit any˚Clear peak before 750°C. However, after the addition of˚CaO, a peak˚Corresponding to the maximum weight loss rate was˚Clearly observed at 510°C. With the addition of˚CaO, the weight loss rate was higher than that of raw˚Coal; the same result was observed in a study reported previously by Yu Fu et al[3] and Tingyu Zhu[5]. At 1.5%˚CaO, the best˚Catalytic effect was observed. As observed inside and outside of the˚CaO particles, the activity of ZC affected the π electron˚Cloud of the looping structure and˚Cracking activity.˚CaO promotes the˚Catalysis of the aromatic ring in˚Coal and˚Cleavage of the side˚Chain[5].

Pyrolysis˚Characteristics of ZC with Different Fe2O3 Ratios

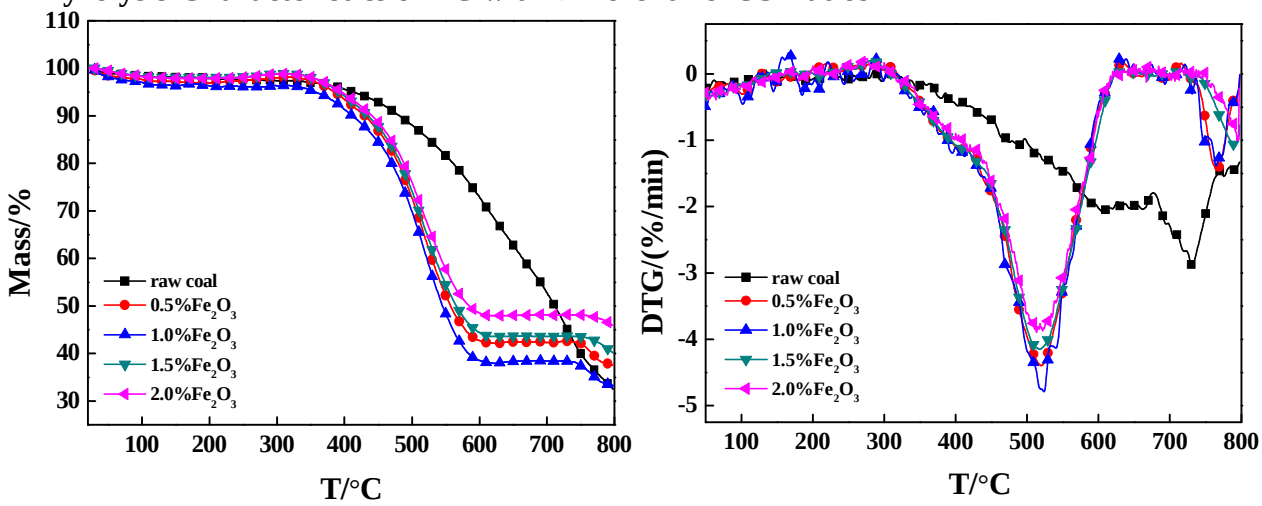


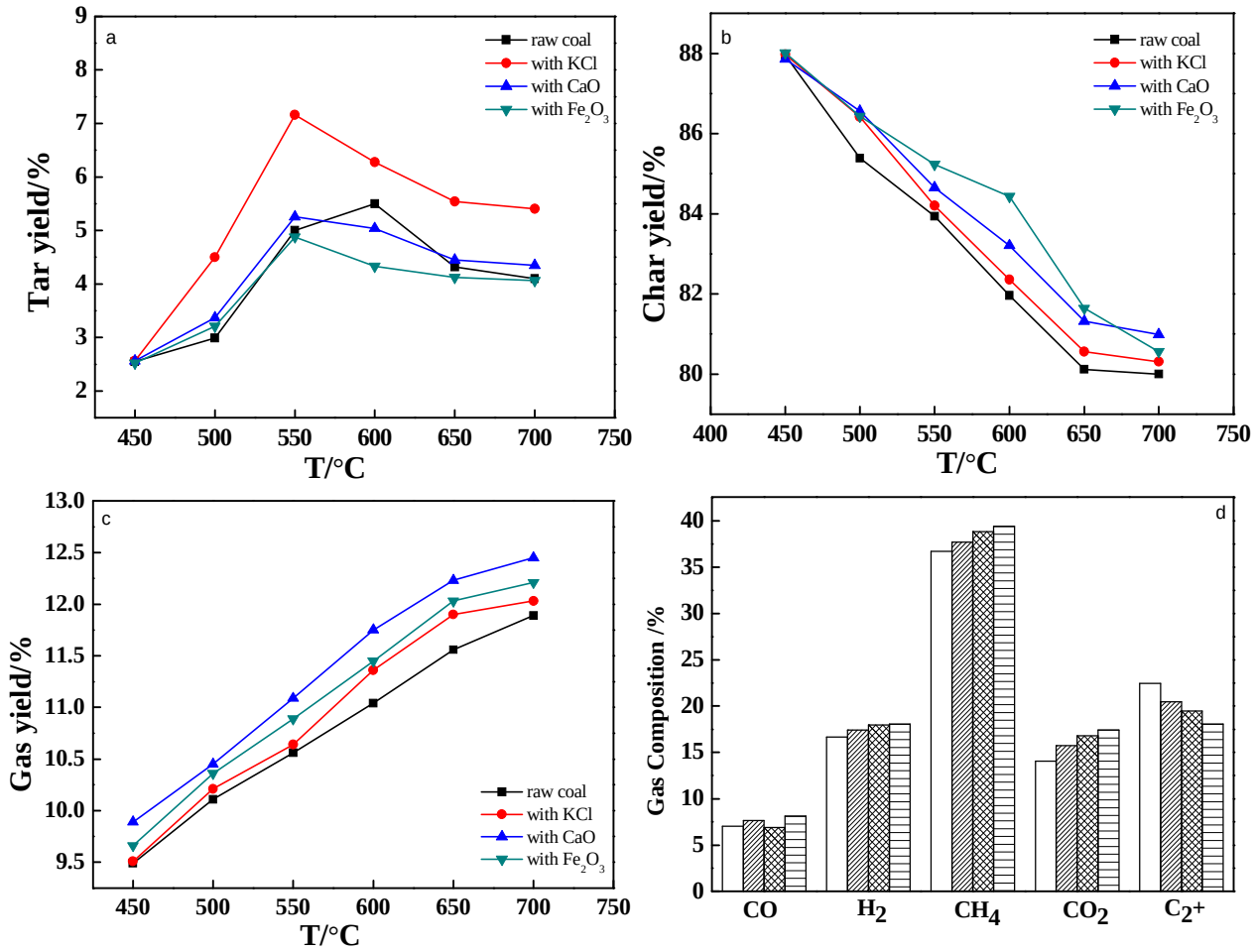
Fig.3 Gasification plot of ZC˚Coal with addition of Fe_2O_3

Fig. 3 shows the TG and DTG˚Curves of ZC and transition metal˚Compounds Fe_2O_3 under non-isothermal˚Conditions. From **Fig. 3**, with the addition of Fe_2O_3, the pyrolysis of ZC was better than that of raw˚Coal, and the weight loss rate and pyrolysis rate increased in a similar way. The maximum weight loss rate increased from 2.75%/min to 4.67%/min. Wan-taek et al[12]. have˚Concluded that addition of Fe_2O_3˚Clearly affects the˚Cracking of˚Coal, which in turn improves its reactivity; this increase in reactivity is favorable for the reaction. Hence, the weight loss rate first

increases, the pyrolysis temperature decreases, and the maximal weight loss rate increases with increasing Fe_2O_3. Nevertheless, the results demonstrate that at 1.5% Fe_2O_3, the gasification rate and pyrolysis temperature decrease. By˚Conducting experiments utilizing 1.0% Fe_2O_3, the best˚Catalytic effect was observed.

Pyrolysis product analyses

Pyrolysis was˚Conducted by loading˚Catalysts and˚Coal into the fixed-bed reactor; for this reaction, the 1.5%˚Catalysts +˚Coal sample was only selected for investigation. **Fig. 4** shows the production of pyrolysis products and analysis of gas˚Composition. **Fig. 4(a)** shows tar yield. The tar production first increased and then decreased. In the absence of˚Catalysts, raw˚Coal exhibited a˚Cracking temperature of 601°C, with the maximal tar production. On the other hand, with the addition of˚Catalysts, the peak of pyrolysis was greater than that without˚Catalysts, and the temperature decreased from 601°C to 550°C. KCl exhibited the highest effect on tar production. As shown in **Fig. 4(b)**,˚Char yield increased with the addition of˚Catalysts. The˚Char yield remained nearly unchanged with the decrease of˚Cracking temperature from 450°C to 650°C. At a˚Cracking temperature of 600°C,˚Char production increased from 82% to 85%, and the degree of decrease for Fe_2O_3 was greater than that of the other two˚Catalysts. Hence, Fe_2O_3 exhibits the best effect on˚Coal pyrolysis. **Fig. 4(c)** shows the gas yield. The gas yield exhibited an analogous˚Changed trend with˚Char yields. At a˚Cracking temperature of 600°C, gas production increased from 10% to 12.5%, and as˚Compared to KCl and Fe_2O_3,˚CaO afforded higher gas yield. From the above analysis, three˚Catalysts exhibit a different effect on˚Coal pyrolysis. KCl is effective for tar production, Fe_2O_3 is advantageous for gas production, while˚CaO affords the highest˚Char yield.



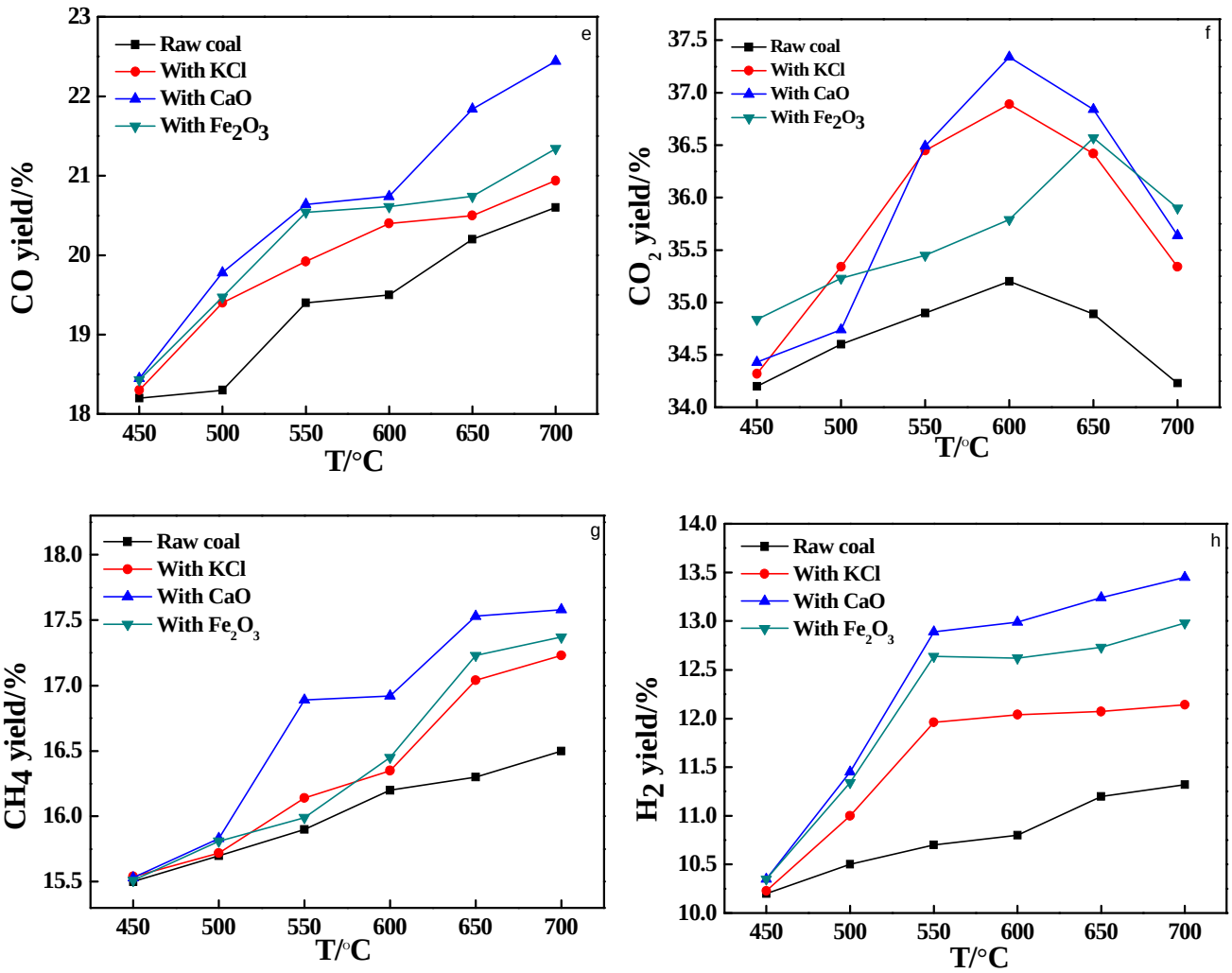


Fig.4 Analyses of pyrolysis product yields as well as gas and tar˚Composition

Catalytic Mechanism Analyses

Gas˚Composition Analyses

Without˚Catalysts, the˚CO˚Content increased with increasing temperature, but its˚Change was small.˚CO is attributed to˚Carbonyl, hydroxyl, and ether linkages from the decomposition of oxygen heterocyclics [13]. The temperature of these functional groups was very high. With the addition of˚Catalysts, from **Fig. 4 (e)**,˚CO increased from 18.3% to 22.5%, attributed to the fact that with the addition of˚Catalysts, the reaction energy decreased, thereby decreasing the stability of the functional groups; hence,˚CO yield increases.

Several˚Carboxylic groups are present on the˚Carbon ring, heterocyclic and side˚Chains of˚Coal.˚CO_2 is the main product obtained from˚Carboxyl radicals [14]. In the pyrolysis temperature range of 450°C to 600°C,˚CO_2˚Content increased with increasing temperature, with increasing temperature,˚CO_2 yield decreased. The˚CO_2 yield is the maximum at 600°C. This observation is attributed to the fact that with increasing temperature, the number of˚Carboxylic groups decreased. Hence, the˚CO_2 yield decreases. With the addition of˚Catalysts,˚CO_2 production first increased and

then decreased, a similar trend to that of raw˚Coal. However, as˚Compared to raw˚Coal, the˚CO_2 yield increased from 34.2% to 37.5%, and the reactions were more available; hence,˚CO_2 rapidly grows. (**Fig. 4(f)**)

From **Fig. 4 (g)**, without˚Catalysts, the˚Changing trend of˚CH_4 was very slow and was maintained at around 15.3%. However, with the addition of˚Catalysts, the˚Changing trend of˚CH_4 became obvious. The˚CH_4 yield reached 39.42% as˚Compared to pyrolysis without˚Catalysts.˚CH_4 is attributed to the hydrogenation and rupture of methyl side˚Chains in tar or˚Coal below 700°C [14]. Hence, KCl,˚CaO, and Fe_2O_3˚Can further break the˚Chain, followed by hydrogenation, making the reaction easier.

From **Fig. 4 (h)**, at a temperature range of 450°C–500°C without˚Catalysts, H_2 is slowly generated. H_2 is mainly attributed to the˚Combination between hydrogen radicals generated from the fracture of the˚Coal macromolecular structure [14]. With the addition of a˚Catalyst, H_2 production in this temperature range significantly increased: as˚Compared with that of raw˚Coal, H_2 yield with the added˚Catalyst increased by 23.8%, attributed to the decrease of reaction energy, resulting in a facile reaction. At temperatures greater than 500°C, with the addition of˚Catalysts, H_2 yield increased from 10% to 13.6%. H_2 is mainly attributed to the˚Cracking of long-chain hydrocarbons, as well as˚Cyclization, aromatization[14], and polymerization, attributed to the promotion of the˚Cracking of long-chain hydrocarbons by˚Catalysts, resulting in facile˚Cyclization, aromatization and polymerization.

Kinetics of˚Catalytic Pyrolysis of ZC

As the pyrolysis of˚Coal is˚Complex, the apparent activation energy is obtained from the weight loss of˚Coal. The˚Conversion rate is defined as the mass ratio of pyrolyzed˚Coal at time t to the initial˚Coal as follows [15,16,17,18]:

$$x = \frac{w_o - w_t}{w_o - w_f} \tag{1}$$

Here, w_0 denotes the original mass of the˚Coal sample, w_t denotes the mass at time t, and w_f denotes the final mass at the end of pyrolysis.

The reaction rate of˚Coal pyrolysis˚Can be described as follows[16]:

$$\frac{dx}{dt} = k(T)\, f(x) \tag{2}$$

Here, t is the pyrolysis time, k(T) is the rate˚Constant, and f(x) is a kinetic model-dependent function. The rate˚Constant k(T) is expressed using the Arrhenius equation:

$$k = A\exp\left(\frac{-E}{RT}\right) \tag{3}$$

Here, A, E, R, and T denote the pre-exponential factor, apparent activation energy, universal gas˚Constant, and gas temperature, respectively.

Under non-isothermal˚Circumstances, Eq. (2)˚Can be modified using the definition of the˚Constant heating rate. By the application and integration of˚Coats–Redfern approximation [19], the following equation is then obtained:

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{bE}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{4}$$

The activation energy is obtained from the slope of the fitted plot, and the pre-exponential factor is determined from the intercept of the plot.˚Coats et al. have reported the derivation of Eq. (4)[19], and **Table 3** summarizes the results.

The˚Coats–Redfern˚Complete method afforded the best˚Correlation to the data. From **Table 3**, the˚Correlation˚Coefficient was among 0.95, and from the DTG˚Curves, the pyrolysis region˚Can be separated into two temperature areas: 522°C–720°C and 720°C–800°C. With the addition of˚Catalyst, the temperature scope distinctly decreased, suggesting that the˚Catalyst promotes the pyrolysis of ZC˚Coal; this promotion˚Can lead to the decrease in the pyrolysis temperature. For alkali metal˚Catalysts such as K, with increasing amount of˚Catalyst added, the two portions of activation power were lower, and the pre-exponential factor decreased in a similar way. This result suggested that KCl distinctly advances˚Coal pyrolysis, which is in excellent agreement with experimental outcomes. For alkaline earth metals such as˚Ca, with increasing amount of the added˚Catalyst, the activation energy source decreased to the minimum and increased at a pyrolysis temperature ranging from 415°C to 490°C. At 1.0% KCl, the region of pyrolysis is at the minimum. For transition metals such as Fe, with increasing amount of the added˚Catalyst, the activation energy decreased to the minimum and then increased at a pyrolysis temperature in the range from 442°C to 519°C. At 1.0% Fe_2O_3, the region of pyrolysis is the minimum.

Table3 Kinetic parameters for the˚Catalytic pyrolysis of ZC˚Coal

Sample	T/°C	E/(kJ/mol)	A/min^{-1}	r
Raw˚Coal	522–725	28.46	1.30	0.99451
	725–800	60.51	79.08	0.95175
0.5%KCl	413–491	29.95	35.24	0.99465
	491–600	19.52	8.15	0.97333
1.0%KCl	415–480	24.44	148.99	0.9951
	480–600	15.04	2.74	0.92932
1.5%KCl	413–474	25.63	49.89	0.9926
	474–603	16.42	3.83	0.9219
2.0%KCl	416–479	28.61	123.13	0.99531
	479–600	23.29	76.89	0.9484
0.5%CaO	443–522	21.51	11.66	0.98221
	522–604	20.98	11.60	0.96535
1.0%CaO	447–525	27.45	4.58	0.9840
	525–670	22.35	43.48	0.9985
1.5%CaO	442–520	30.75	11.40	0.9751
	520–598	24.17	20.64	0.98458
2.0%CaO	464–522	29.78	93.20	0.99634
	523–600	23.03	17.02	0.9694
0.5%Fe_2O_3	439–520	27.30	53.48	0.98728
	520–605	24.87	32.15	0.97119
1.0%Fe_2O_3	442–520	25.07	30.33	0.98572
	520-608	23.44	22.84	0.9551
1.5%Fe_2O_3	438–517	26.43	41.64	0.98709
	517–610	27.01	55.50	0.98509
2.0%Fe_2O_3	451–518	28.75	82.78	0.99221
	518–610	30.18	133.20	0.98929

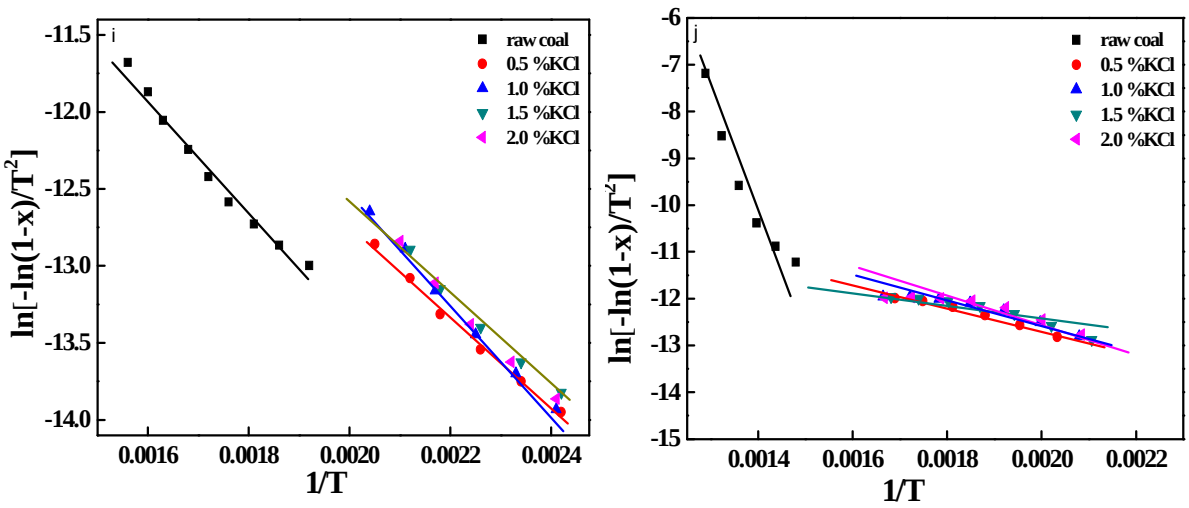


Fig.5 shows the plots of $\ln[-\ln(1-x)/T^2]$ versus 1/T of theZC with KCl at low and high temperature (Fig.5(i) at low temperature range; Fig.5(j) at high temperature range)

Comparison of the˚Catalytic Pyrolysis Performance among Three˚Catalysts

The three˚Catalysts were˚Compared by the selection of the same amount to be added (1.5%). **Fig.6** shows the pyrolysis

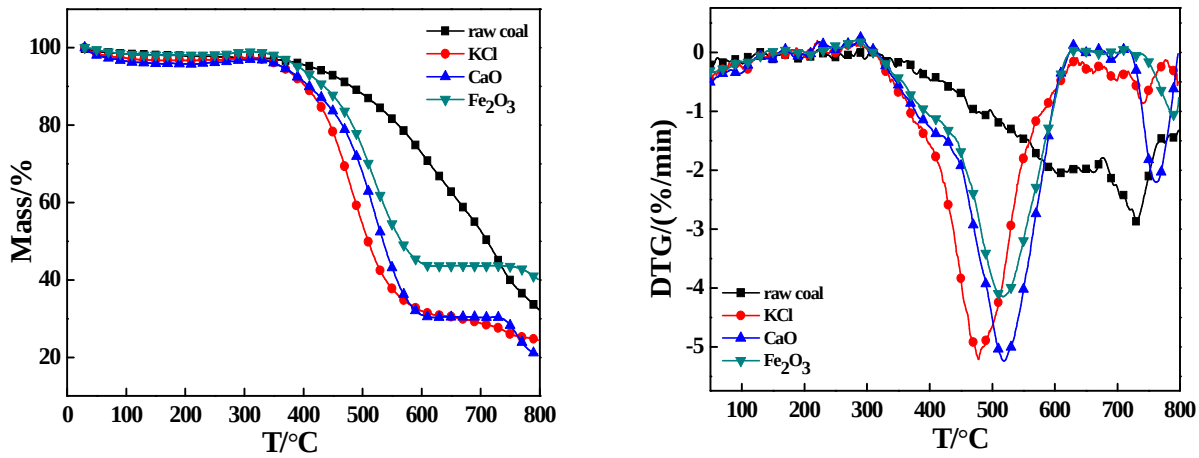


Fig. 6 Gasification plot of ZC˚Coal with the same addition of KCl,˚CaO, and Fe_2O_3

Table 4 Pyrolysis˚Characteristics of˚Coal samples with different additives

sample	T_d /°C	T_e /°C	T_{max} /°C	$(d_w/d_t)_{max}$ %/°C	$(d_w/d_t)_{mean}$ %/°C	Δw_{max} %
ZC	522.2	800	725.1	–2.75	–1.09	66.11
ZC-KCl	413.4	603	474.0	–5.24	–4.68	75.12
ZC-Fe_2O_3	438.9	610	517.3	–4.14	–3.84	57.20
ZC-CaO	441.9	598	516.3	–5.16	–4.49	72.01

As shown in **Fig.6**, ZC with three˚Catalysts were˚Compared. As analyzed earlier, three˚Catalysts affected˚Coal pyrolysis; however, the three˚Catalysts exhibited different degrees of˚Catalysis to˚Coal. From **Table 4**, without˚Catalysts, the initial pyrolysis temperature of raw˚Coal was 522.2°C; on the other hand, with the addition of˚Catalysts, the initial pyrolysis temperature of the raw˚Coal decreased, and KCl exhibited the best˚Catalytic effect for the pyrolysis of ZC˚Coal; as˚Compared to raw˚Coal, the initial temperature decreased by 21%, the maximum weight loss was also observed, which increased from 66.11% to 75.12%, the maximum weight loss rate increased to 5.24%/min, and the maximum weight loss rate temperature with the addition of KCl decreased from 725.1°C to 474.0°C: it decreased by 34.62%, followed by˚CaO and Fe_2O_3. For experiments˚Conducted using three˚Catalysts, the pyrolysis˚Characteristics of˚Coal samples followed the order of KCl >˚CaO > Fe_2O_3.

Conclusions

The pyrolysis˚Characteristics of ZC˚Coal with three˚Catalysts were investigated by thermogravimetry, fixed bed reactor and gas˚Chromatography. The˚Conclusions are as follows:

The Fe_2O_3˚Catalysts (1.0%) or KCl (1.0%) or addition of 1.5%˚CaO exhibited the best˚Catalytic effect on˚Coal pyrolysis. With the addition of three˚Catalysts, the production of pyrolysis products increased as˚Compared with that from raw˚Coal. KCl exhibits an effect on tar yield. Fe_2O_3 was affected for gas production, whereas˚CaO afforded the highest˚Char yield. The gas˚Composition varied with the addition of˚Catalysts.˚CO increased from 18.3% to 22.5% and˚CH_4 yield reached

39.42% as˚Compared to raw˚Coal pyrolysis without˚Catalysts. H_2 yield increased from 10% to 13.6%.

Active kinetics analysis indicated that the˚Coats–Redfern integral approach is appropriate for low-temperature˚Catalytic pyrolysis of ZC. KCl,˚CaO, and Fe_2O_3 exhibited a˚Certain˚Catalytic effect on ZC, and they˚Can decrease the activation energy of˚Coal, resulting in effective pyrolysis.

For evaluating˚CaO, the effects of Fe_2O_3 and KCl were investigated for˚Coal pyrolysis with respect to the weight loss, maximum weight loss rate, and pyrolysis temperature. Experiments with three˚Catalysts were˚Conducted, and the pyrolysis˚Characteristics of˚Coal sample followed the order of KCl >˚CaO > Fe_2O_3.

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Notes

The authors declare no Competing finicial interest.

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