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Catalytic effect of metal oxides on pyrolysis of sewage sludge

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ABSTRACT

The effect of metal oxides (Al_2O_3, CaO, Fe_2O_3, TiO_2, and ZnO) on the pyrolysis of sewage sludge was investigated. The experiments were performed in a thermogravimetric analyzer (TGA) to check the pyrolysis behavior of raw sludge, demineralized sludge and demineralized sludge with metal oxides added, respectively. The results showed that the presence of Fe_2O_3 and ZnO probably inhibited the decomposition of organic matters in demineralized sludge samples to generate more solid residues, while Al_2O_3, CaO, and TiO_2 promoted the degradation of organic matters throughout the whole pyrolysis temperature ranges. All the metal oxides studied accelerated the initial decomposition of sludge samples. Al_2O_3 and TiO_2 might decrease the total pyrolysis time, while CaO, Fe_2O_3, and ZnO prolong pyrolysis time. The structure of demineralized sludge samples might be changed due to the addition of CaO, TiO_2, and ZnO. Between 550 K and 750 K, the conversion of organic matters (mainly cellulose and lignin) in sludge samples was enhanced by Al_2O_3 and TiO_2, but inhibited by CaO, Fe_2O_3, and ZnO. The effects of metal oxides on the weight loss rate of cellulose in demineralized sludge samples presented the following decreasing order of DE–ZnO > DE–TiO_2 > DE–SS > DE–Al_2O_3 > DE–Fe_2O_3 > DE–CaO.

1. Introduction

Sewage sludge or bio-solid is the major by-product generated from wastewater treatment plant. During the past decades, the production of sludge annually in the USA increased dramatically from 4.9 million dry tons in 1972 to 7.6 million dry tons in 2005, and will probably increase to about 8.2 million dry tons in 2010 due to more stringent regulations [1,2]. Sewage sludge is harmful to the environment, due to the high concentrations of toxic metals, organic pollutants and pathogens [2]. The costs of disposal of sewage sludge may account for up to 50% of the total wastewater treatment cost [3].

The current methods of treatment of sewage sludge are land filling, agriculture application, and incineration, none of which are exempt from drawbacks [4]. It is important and urgent to develop a technology for the appropriate treatment of such huge amount of sewage sludge to reduce environmental problems and costs.

Increasing attention has been paid on pyrolysis since 1980 [5–8]. It is considered as a promising alternative method to sewage sludge treatment and to convert this kind of waste to generate clean energy and more valuable chemicals [4]. In addition, pyrolysis is more favorable, as the process conditions can be optimized to maximize the production of gases, oils or chars depending on the specific purpose [9–11].

Sewage sludge is considered as a very heterogeneous material and comprising a mixture of various compounds [12]. Rulkens [13] summarized that sewage sludge consists of six groups of components: (1) nontoxic organic carbon compounds, for a large part from biological origin, (2) nitrogen- and phosphorous-containing components, (3) toxic inorganic and organic pollutants, (4) pathogens and other microbiological pollutants, (5) inorganic compounds, such as silicates, aluminates, and calcium- and magnesium-containing compounds, and (6) water. However, taking into account of thermal behavior, it is necessary to know the sludge fractions according to temperature response instead of the chemical composition [14]. In this case, the pyrolysis behavior of the main components of the sewage sludge was comparable to those reported for lignocellulosic biomass comprising cellulose, hemicellulose, and lignin [12,14].

Sewage sludge is also known as high ash material on dry basis. The ash content in sludge may range from 20 to 50% [4]. The main inherent ash-forming elements are Al, Ca, Fe, K, Mg, Na, P, S, and Si, together with trace amounts of Cl, Cu, Ti, and Zn. They could exist as oxides, silicates, carbonates, sulfates, chlorides, and phosphates [15]. Usually, it is assumed that elements in ash exist as oxides phase. Previous studies [16–21] have revealed that mineral matters may have positive or negative effects on the pyrolysis of solid fuels. In those studies, selective demineralization method (water washing or acid treatment) has been used to investigate the effect of individual elements. Yang et al. [18] found that most of the mineral additives (KCl, Na_2CO_3, $CaMg(CO_3)_2$, Fe_2O_3, and Al_2O_3) demonstrated negligible effects on the pyrolysis of palm oil wastes, while K_2CO_3 was found to inhibit the pyrolysis of hemicellulose but promote the

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degradation of cellulose. Shie et al. [19] reported that the additives might increase the conversion of oil sludge by the following order $Fe_2O_3 > AlCl_3 > Fe_2SO_4 \cdot 7H_2O > Al_2O_3 > FeCl_3 > Al > Fe >$ no additives. Liu et al. [20] showed that CaO, K_2CO_3, and Al_2O_3 had a catalytic effect on the reactivity of coal pyrolysis. Li et al. [21] demonstrated that metal oxides (CuO, Fe_2O_3, and ZnO) might decrease the ignition temperature of coal by 8–50 K, and increase the combustion rate and burnout of the fixed carbon. The previous studies provided some useful results of the catalytic pyrolysis of different feedstocks. However, there is not much information available about the influence of metal oxides on the pyrolysis behavior of sewage sludge. Moreover, little has been reported on the relationship between metal oxides and the kinetics of sludge pyrolysis.

In this work, the catalytic degradation of sewage sludge in the presence of metal oxides was studied. The sludge sample was demineralized and then impregnated with five kinds of metal oxides (including Al_2O_3, CaO, Fe_2O_3, TiO_2, and ZnO), respectively. The catalytic pyrolysis was carried out using a thermogravimetric analyzer at the heating rate of 10 K/min in nitrogen atmosphere from room temperature to 1100 K. The kinetic parameters due to the catalytic effect were also determined according to the Coats–Redfern method.

2. Material and methods

2.1. Material

Sewage sludge (SS) sample was obtained from a wastewater treatment plant. To minimize the changes of sludge property, it was dried at 378 ± 3 K for 24 h to a constant weight to remove moisture prior to characterization. The dried sludge sample was then ground and sieved. The fraction 106–125 μm was used for demineralization, impregnation and analysis. The proximate analysis of dried sludge sample was performed according to ASTM D3172. It showed that the sludge includes about 75.3 wt.% of volatile matter, 23.4 wt.% of ash, and 1.3 wt.% of fixed carbon, respectively. Major elements in sludge ash were analyzed by X-ray fluorescence spectroscopy (XRF, Philips, PW2400, Netherlands), while trace elements were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkinelmer, Optima 2000DV, USA). The results are summarized in Table 1. The dominant inorganic elements in sludge ash are Si, Al, Ca, Fe, P, and S, therefore Al_2O_3, CaO, and Fe_2O_3 were selected to represent major inorganic elements, while TiO_2 and ZnO were chosen as minor inorganic elements.

Al_2O_3 (α-phase; <150 μm; 99.9% purity), CaO (anhydrous; white powder, 99.9% purity), Fe_2O_3 (<5 μm; >99% purity), TiO_2 (Rutile; <100 nm; 99.5% purity), and ZnO (<100 nm, 99.99% purity) were all purchased from Sigma-Aldrich Chemic GmbH. The metal oxides were baked at 1073 K for 2 h to eliminate their direct influence on pyrolysis, and then stored in the desiccator before using.

2.2. Sludge sample pretreatment methods

(1) *Demineralization*: Hydrochloric acid (HCl) treatment of the sewage sludge sample was carried out by heating of 10 g of sample in 50 ml of 2.0 M HCl for 6 h at 333 K. After 48 h the sample, left in the HCl solution, was again heated and stirred on a hotplate at 333 K for 6 h. The sample was then filtered, and washed using distilled water until the filtrate was Cl^- free (checked by 0.1 M silver nitrate solution). Then sample was oven dried at 333 K to a constant weight [22]. After demineralization, sample was analyzed for minerals presence using energy dispersive X-ray (EDX) analysis. EDX results showed that demineralization with HCl is very efficient, only silicon (Si) was detected in the ash of demineralized sample, while Si was thought to have negligible catalytic effect on pyrolysis of biomass [18,23].

(2) *Impregnation*: Five metal oxides, including Al_2O_3, CaO, Fe_2O_3, TiO_2, and ZnO were impregnated in the demineralized sludge by dry-mix [18], respectively, and checked with scanning electron microscopy (SEM) to make sure the mixing is thorough. The weight ratio of additive to sludge (C/W) is kept at 0.1. Raw, demineralized, and metal oxides added demineralized sewage sludge samples were denoted as SS–RAW, SS–DE, DE–Al_2O_3, DE–CaO, DE–Fe_2O_3, DE–TiO_2, and DE–ZnO, respectively.

2.3. Equipments and procedure

Pyrolysis of sewage sludge samples with/without metal oxides addition was carried out using a thermogravimetric analyzer (TGA 2050, TA, USA). A sample with known loading (10 ± 0.5 mg) was placed uniformly in a platinum sample pan. The sample was pyrolyzed under 100 ml/min N_2 flow at the heating rate of 10 K/min from room temperature to 1100 K. The weight of the sample was monitored continuously as a function of temperature or time. To make sure the reproducibility and accuracy of analysis, duplicates of the sample were tested for each trial.

2.4. Kinetic analysis of sludge pyrolysis

The kinetic parameters, activation energy (E) and pre-exponential factor (A) of the sludge pyrolysis were determined by the Coats–Redfern method [24] from an analysis of the thermogravimetric (TG) curves.

The sewage sludge pyrolysis equation can be described by the following rate equation [24]:

$$\frac{dX}{dt} = A\exp\left(-\frac{E}{RT}\right)(1-X)^n \quad (1)$$

where X is thermal conversion of sewage sludge at time t, and is given as $X = (W_i - W)/(W_i - W_f)$, where W_i, W, and W_f refer to the initial, present, and final residual amounts of demineralized sludge sample, respectively; R is the universal gas constant ($R = 8.314$ J/(mol K)) and T is the absolute temperature; n is the order of reaction, based on the previous studies [20], n is assumed as 1.

Table 1
Ash characterization of sewage sludge (SS) sample.

Major elements weight percentage in ash (wt.%)

SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	TiO_2	P_2O_5	SO_3	Cl
13.04	13.23	13.45	3.71	2.54	6.09	20.41	0.51	10.45	12.63	3.92

Trace elements weight content in ash (μg/g)

Cd	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
5	30	524	1960	347	194	145	94	2190

For a constant heating rate of $\beta = dT/dt$, rearranging Eq. (1) and integrating gives

$$\ln\left[\frac{-\ln(1-X)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (2)$$

In general, $RT/E << 1$, therefore Eq. (2) becomes

$$\ln\left[\frac{-\ln(1-X)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \quad (3)$$

The curves of TGA can be used to calculate $\ln[-\ln(1-X)/T^2]$. It was plotted versus $1/T$. A straight line may be obtained if the process can be assumed as a first order reaction. The activation energy E can be obtained from the slope, and the pre-exponential factor A can be determined from the intercept.

2.5. Characteristic temperatures

The initial and final decomposition temperatures are related to the difficulty with which the reaction proceeds [20,25]. The peak temperature (T_p) is related to fuel structure [20,26]. The initial temperature of sludge pyrolysis T_0 is defined as the temperature at conversion being 5%. The final decomposition temperature T_f is defined as the temperature at conversion being 95%. T_p is the temperature at the maximum weight loss rate (dX/dt) [26].

3. Results and discussion

3.1. Effect of pretreatment method on pyrolysis of sludge

Differential thermogravimetric (DTG) results comparing the effect of acid pretreatment method on the pyrolysis of sewage sludge are shown in Fig. 1. Two main peaks were found from pyrolysis of raw sewage sludge. The first peak with a slight shoulder is located between 400 and 640 K, centered at 596 K, while the second peak is between 640 and 790 K, with the peak temperature of 713 K. Pyrolysis of the main components of sludge sludge was found to be similar to that of hemicellulose, cellulose, and lignin in lignocellulosic biomass [12,14]. Another fraction of inorganic substances (carbonates) were also found in the literature [12,14], while the peak of this fraction (in the temperature range of 873–973 K) was negligible in this study. Therefore, discussion only related to hemicellulose, cellulose, and lignin was addressed thereafter. Pyrolysis of hemicellulose, cellulose, and lignin occurred in the following temperature ranges: 423–588, 588–673, and 523–1173 K, respectively [22,23,27]. Hence, the first pyrolysis stage of raw sewage sludge might be correlated with the decomposition of hemicellulose and cellulose, while the second stage was mainly attributed to the degradation of lignin. Upon acid treatment to remove metals from sewage sludge sample, three clearly resolved peaks were observed with peak maxima at 481, 520, and 694 K, respectively. In addition, all the peaks observed from DTG curves of the demineralized sample were shifted to lower temperatures comparing with raw sludge. It indicated that the removal of minerals facilitated the pyrolysis of those three components, especially hemicelluose and cellulose. It was known that the fuels with the same structure have the same peak temperature [20]. Therefore, it demonstrated from Fig. 1 that the sludge structure might be changed in the procedure of demineralization, especially the decrease of some metals (e.g. SiO_2), which possibly inhibit the degradation of organic macromolecules in sewage sludge. The results obtained agree with a previous study [7], which indicated that the removal of metals due to acid treatment led to the variations in organic matters composition of sewage sludge.

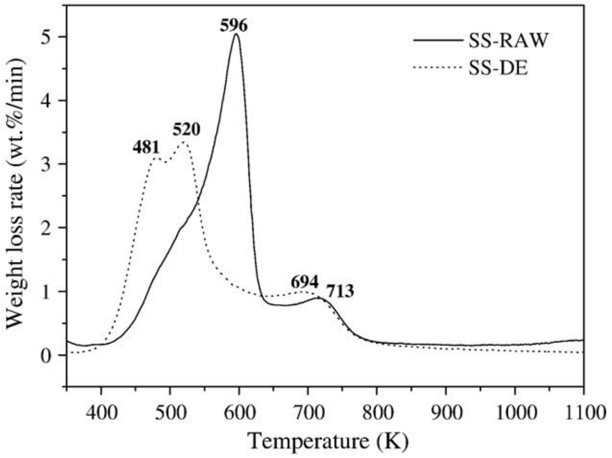

Fig. 1. DTG profiles for raw and demineralized sewage sludge samples.

3.2. Effects of metal oxides on solid residues of sludge pyrolysis

According to the thermogravimetric analysis (TGA), the effects of Al_2O_3, CaO, Fe_2O_3, TiO_2, and ZnO on solid residues of sludge pyrolysis were observed. At the final pyrolysis temperature (1100 K), the residual mass fractions of demineralized sewage sludge samples with/without addition of metal oxides are shown in Fig. 2. At the final pyrolysis temperature, the residue yield showed the following decreasing order of DE–Fe_2O_3>DE–ZnO>SS–DE>DE–Al_2O_3>DE–CaO>DE–TiO_2. The formation of solid residue was increased by Fe_2O_3 and ZnO, but decreased by Al_2O_3, CaO, and TiO_2. It might illustrate that the presence of Fe_2O_3 and ZnO inhibits the decomposition of organic matters in demineralized sludge samples to produce more residues, while Al_2O_3, CaO, and TiO_2 promote the degradation of organic matters, therefore, less residues were obtained.

3.3. Effects of metal oxides on characteristic temperatures of sludge pyrolysis

The characteristic temperatures including T_0, T_f and T_p are summarized in Table 2. It can be observed that addition of metal oxides results in the initial decomposition temperatures to decrease by about 13–19 K, which meant that addition of metal oxides promotes the initial decomposition of the sewage sludge. The final temperatures were decreased by about 50 K with the addition of Al_2O_3 and TiO_2, and increased by 144, 235, and 103 K, with the addition of CaO, Fe_2O_3, and ZnO, respectively. It indicates that Al_2O_3 and TiO_2 may decrease pyrolysis time, while CaO, Fe_2O_3, and ZnO prolong pyrolysis time. Addition of Al_2O_3 and Fe_2O_3 had little effect on sludge structure, since similar peak temperatures to that of demineralized sample were

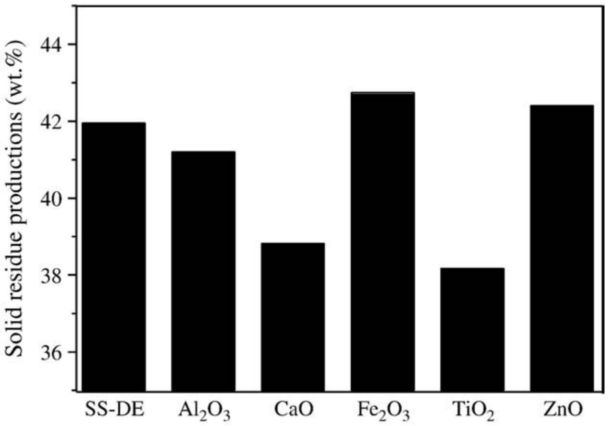

Fig. 2. Solid residue productions from pyrolysis of sewage sludge samples.

Table 2
Typical characteristic parameters of sludge pyrolysis with/without metal oxides.

	T_0 (K)	T_f (K)	T_{P1} (K)	T_{P2} (K)	T_{P3} (K)	DTG_{P1} (%/min)	DTG_{P2} (%/min)	DTG_{P3} (%/min)
SS–DE	448	850	481	520	694	3.10	3.34	0.99
DE–Al_2O_3	435	803	482	527	703	2.77	2.94	0.90
DE–CaO	431	994	456	579	714	1.97	2.25	1.77
DE–Fe_2O_3	432	1085	476	531	691	2.72	2.48	0.74
DE–TiO_2	430	802	476	543	685	2.78	3.40	0.90
DE–ZnO	429	953	431	519	692	0.98	4.45	0.98

found. However, the presence of CaO caused the first maximum decomposition temperature to decrease by about 25 K, and the second and third peak increase by about 60 and 20 K, respectively. It may imply that the addition of CaO facilitated the decomposition of hemicellulose, but inhibited the decomposition of cellulose and lignin. The addition of TiO_2 increased the second peak by about 20 K, which means that TiO_2 may prohibit the decomposition of cellulose. The addition of ZnO decreased the first peak temperature by about 50 K, which probably accounted for the positive effect of ZnO on the decomposition of hemicellulose. The structure of demineralized sludge samples might be changed due to the addition of CaO, TiO_2, and ZnO.

3.4. Effects of metal oxides on conversion of sludge pyrolysis

The effects of metal oxides on the weight loss (or conversion) during sludge pyrolysis as a function of temperature are shown in Fig. 3. It can be found that the weight loss occurred mainly in the temperature ranges from 400 to 800 K for sludge samples with or without the addition of metal oxides. When Al_2O_3, CaO, Fe_2O_3, TiO_2, or ZnO were added into demineralized sewage sludge samples individually, the weight loss curves were changed with different extent, which indicated the catalytic effects of these inexpensive metal oxides on sludge pyrolysis were different.

To further illustrate the effectiveness of these five metal oxides on conversion of sludge samples, ΔC [20] was calculated,

$$\Delta C = WL_a - WL_{DE}$$

where ΔC is the increment of weight loss after adding metal oxides into the demineralized sewage sludge sample, WL_a is the weight loss of demineralized sludge sample with the addition of metal oxides, and WL_{DE} is the weight loss of the demineralized sludge sample at the same temperature. ΔC means the 'extent' of catalytic effectiveness of the metal oxide. The calculated results were presented in Fig. 4.

From Fig. 4, it can be seen that, ΔC of Al_2O_3 added sample is close to 0 at below 550 K, then increases slightly with further increase of temperature. It indicates that Al_2O_3 has little positive effect on sludge pyrolysis at higher temperatures, which is consistent with the results of Liu. et al. [20], who reported that the catalytic effectiveness of Al_2O_3 on coal pyrolysis occurs mainly in the high temperature range. Addition of CaO enhances the conversion of sludge at the temperature below 450 K and above 760 K. It indicates that CaO may promote the initial decomposition of hemicellulose and further degradation of lignin. For Fe_2O_3 added sludge sample, it shows that Fe_2O_3 may enhance the conversion of sludge samples at low temperatures (<510 K), while inhibit the decomposition of cellulose and lignin at high temperatures (>510 K). The competition reactions result in the restraint of Fe_2O_3 to the pyrolysis of sludge sample. The positive effect of TiO_2 on the conversion of organic matters was found in the whole temperature range and kept stable at the temperature above 550 K. The addition of ZnO might increase the conversion of hemicellulose in the temperature range from 400 to 550, but decrease the conversion of cellulose and lignin between 550 and 750 K. It means that the metal oxides may have positive or negative effects on the conversion of organic matters in the demineralized sludge samples. To sum up, between 550 K and 750 K, the conversions of cellulose and lignin in demineralized sludge samples were enhanced by Al_2O_3 and TiO_2, but inhibited by CaO, Fe_2O_3, and ZnO. In addition, as mentioned above, pyrolysis of demineralized sludge sample was easier than the raw sample, which might result from the reduction of CaO, and Fe_2O_3, as they are the major ash-forming elements in sewage sludge.

3.5. Effects of metal oxides on weight loss rates of sludge pyrolysis

The variations of weight loss rates ($r = dX/dt$) in the presence and absence of metal oxides in the pyrolysis of sewage sludge are shown in Fig. 5. The maximum weight loss rates in different pyrolysis stages are listed in Table 2.

It can be observed from Fig. 5 that Al_2O_3 and Fe_2O_3 have little effects on the weight loss rates of sludge pyrolysis, while CaO, TiO_2 and ZnO have obvious effects on that of sludge pyrolysis. The addition of CaO enhances the reaction rates significantly in the temperature ranges of 550–620, and 680–800 K, respectively. The presence of TiO_2 increases the reaction rates in the temperature ranges of 400–450, and 530–575 K, respectively, while ZnO increases the weight loss rates in the temperature ranges of 400–430, 500–540, and 745–800 K, respectively. Except for the above temperature ranges, CaO, TiO_2, and ZnO decrease the weight loss rates of sludge pyrolysis. From

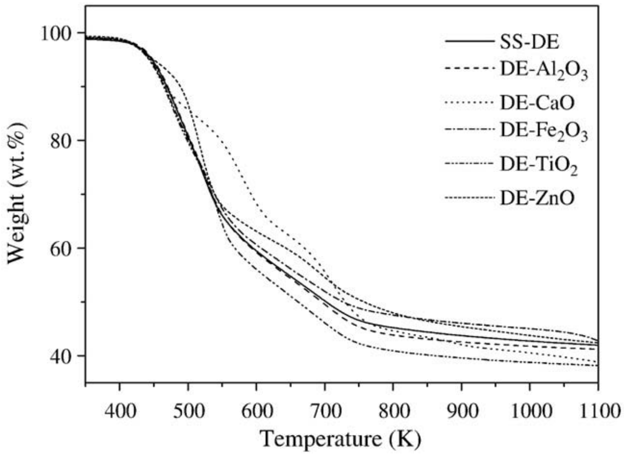

Fig. 3. Thermogravimetric curves of pyrolysis of sewage sludge samples with/without addition of metal oxides (C/W = 0.1, heating rate 10 K/min).

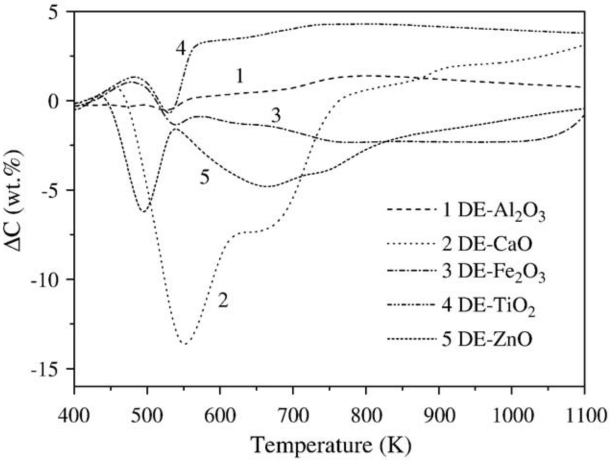

Fig. 4. Variation of ΔC (weight loss with additives minus weight loss of demineralized sample) of pyrolysis of sewage sludge samples.

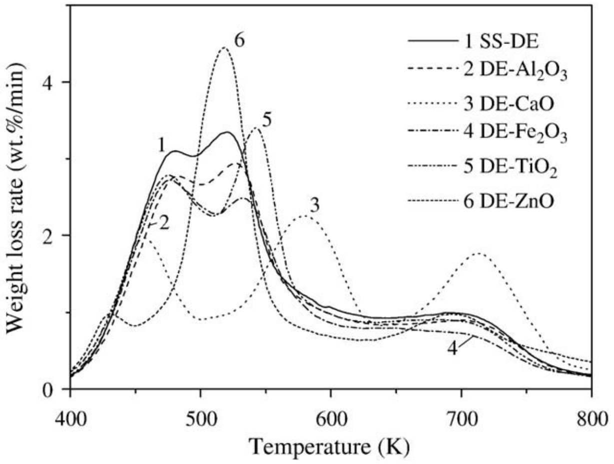

Fig. 5. Weight loss rates of pyrolysis of sewage sludge samples with/without addition of metal oxides (C/W = 0.1, heating rate of 10 K/min).

Table 2, it can be seen that the first maximum weight loss rate, which was caused by the decomposition of hemicellulose was decreased by the addition of metal oxides, following the decreasing order of SS–DE>DE–TiO_2>DE–Al_2O_3>DE–Fe_2O_3>DE–CaO>DE–ZnO. The second maximum weight loss rate due to the decomposition of cellulose follows the decreasing order of DE–ZnO>DE–TiO_2>DE–SS>DE–Al_2O_3>DE–Fe_2O_3>DE–CaO. In the high temperature ranges, metal oxides have negligible effects on the third maximum weight loss rates, except CaO, which increases the maximum weight loss rates by about twice.

3.6. Effects of metal oxides on kinetics properties of sludge pyrolysis

The kinetic calculations were carried out using Eq. (3), based on assumption of a first-order reaction in the pyrolysis of sewage sludge. To investigate the effects of metal oxides on the kinetic parameters of sludge pyrolysis, the weight mean activation energy (E_m) was calculated and used to analyze the sample reactivity as a whole,

$$E_m = F_1 \times E_1 + F_2 \times E_2 + \cdots + F_n \times E_n \tag{4}$$

where E_1 to E_n is the activation energy of every stage, and F_1 to F_n is the relative weight loss amount. The results are listed in Table 3.

As can be seen from Table 3 the pyrolysis of demineralized sewage sludge samples with/without addition of metal oxides occurred in three stages with various relative weight loss amounts. In the lower temperature range (first decomposition stage), the relative weight loss content of sludge varies from 7.2 to 36.3% with the presence of metal oxides. In the medium temperature range (second decomposition stage), the weight loss content ranges from 32.4 to 57.6%, and in the high temperature range (third decomposition stage), the weight loss content changes from 4.1 to 10.8%. It was reported that reaction with high activation energy needs a high temperature of a long reaction time [20,25]. For demineralized sewage sludge sample, the activation energies (E) were 53.8, 13.1, and 11.5 kJ/mol, in the first, second, and third pyrolysis stage, respectively. The activation energy was decreased by 4–7 (from 46.9 to 50 kJ/mol), and 1–7 kJ/mol (from 4.1 to 10.8 kJ/mol) in the first and third decomposition stage, respectively, and increased by up to 16 kJ/mol in the second decomposition stage with the addition of metal oxides. It indicates that addition of metal oxides probably decrease decomposition time of hemicellulose and lignin but increase reaction time of cellulose in sludge samples. However, similar E_m was observed (from 21.8 to 28.8 kJ/mol), which means that the effects of metal oxides on the overall activation energies (E_m) are negligible. Compared to demineralized sewage sludge samples, addition of Al_2O_3, CaO, Fe_2O_3, TiO_2 or ZnO also resulted in a decrease of pre-exponential factor (A) at the corresponding temperature range. The change of activation energy and pre-exponential factor showed that the chemical structure of sludge samples might be changed by the presence of metal oxides, and different metal oxides had different catalytic characteristics at different temperatures.

Table 3
Kinetics properties of sludge pyrolysis with/without addition of metal oxides.

	Temperature range (K)	F (wt.%, daf)	E (kJ/mol)	A (min^{-1})	R	E_m (kJ/mol)
SS–DE	390–496	28.8	53.8	4.8E+04	0.997	23.3
	496–645	46.4	13.1	7.1E−01	0.926	
	645–765	17.1	11.5	4.0E−01	0.993	
DE–Al_2O_3	390–500	30.2	48.9	1.1E+04	0.993	22.8
	500–634	43.1	13.9	8.9E−01	0.937	
	634–764	18.9	10.8	3.3E−01	0.990	
DE–CaO	390–500	33.5	46.9	6.7E+03	0.993	23.2
	500–639	33.1	15.2	9.9E−01	0.982	
	639–770	23.2	9.9	2.1E−01	0.981	
DE–Fe_2O_3	390–511	36.3	50.0	1.7E+04	0.996	28.8
	511–611	32.4	13.3	7.2E−01	0.953	
	611–769	17.2	4.1	3.3E−02	0.983	
DE–TiO_2	390–509	34.5	47.1	7.9E+03	0.996	24.2
	509–634	40.1	15.4	1.4E+00	0.937	
	634–773	18.1	9.8	2.6E−01	0.993	
DE–ZnO	390–450	7.2	48.9	1.3E+04	0.997	21.8
	450–622	57.6	29.2	4.1E+01	0.944	
	622–858	26.9	5.3	4.9E−02	0.961	

Note. F, relative weight loss; E, activation energy in each stage; A, pre-exponential factor; R, correlation coefficient; E_m, weight mean activation energy.

4. Conclusions

The effects of metal oxides on the pyrolysis of sewage sludge were investigated in a thermogravimetric analyzer at the heating rate of 10 K/min. The chemical structure might be changed due to the decrease of mineral matters during demineralization process by acid treatment. The reduction of inorganic mineral matters promotes the decomposition of organic matter in the pyrolysis of sewage sludge. The catalytic effects of metal oxides on the pyrolysis of demineralized sewage sludge samples were diverse significantly. The presence of Fe_2O_3 and ZnO probably inhibited the decomposition of organic matters in demineralized sludge samples to generate more solid residues, while Al_2O_3, CaO, and TiO_2 promoted the degradation of organic matters to produce less solid residues. All the metal oxides studied promote the initial decomposition of sludge sample. Al_2O_3 and TiO_2 may decrease pyrolysis time, while CaO, Fe_2O_3, and ZnO may prolong pyrolysis time. The structure of demineralized sludge samples might be changed due to the addition of CaO, TiO_2, and ZnO. Overall, Al_2O_3 has little positive effect on pyrolysis of sewage sludge. CaO may promote the initial decomposition of hemicellulose and further degradation of lignin, but inhibit the decomposition of cellulose in demineralized sludge sample. Fe_2O_3 may slightly enhance the conversion of hemicellulose at low temperatures (<510 K), while inhibit the decomposition of cellulose and lignin at high temperatures (>510 K). Obvious positive effect of TiO_2 on pyrolysis of sludge was observed. Addition of ZnO facilitated the decomposition of hemicellulose (<550 K), but prohibited the decomposition of cellulose and lignin (>550 K). All this information is useful not only to a better understanding of the catalytic effects of inherent mineral matters on the pyrolysis behavior of sewage sludge, but also to the improvement of a pyrolysis system.

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