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Regeneration dynamics of potassium-based sediment sorbents for CO_2 capture

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Abstract−Simulating regeneration tests of Potassium-Based sorbents that supported by Suzhou River Channel Sediment were carried out in order to obtain parameters of regeneration reaction. Potassium-based sediment sorbents have a better morphology with the surface area of $156.73\ m^2\cdot g^{-1}$, the pore volume of $357.5\times10^{-3}\ cm^3\cdot g^{-1}$ and the distribution of pore diameters about 2-20 nm. As a comparison, those of hexagonal potassium-based sorbents are only $2.83\ m^2g^{-1}$, $7.45\times10^{-3}\ cm^3g^{-1}$ and 1.72-5.4 nm, respectively. TGA analysis shows that the optimum final temperature of regeneration is 200 and the optimum loading is about 40%, with the best heating rate of $10\ ^\circ C\cdot min^{-1}$. By the modified Coats-Redfern integral method, the activation energy of 40% $KHCO_3$ sorbents is $102.43\ kJ\cdot mol^{-1}$. The results obtained can be used as basic data for designing and operating CO_2 capture process.

Key words: CO_2 Capture, Potassium-based Sediment Sorbents, Regeneration, Dynamics Analysis, Mechanism

INTRODUCTION

With the global warming, the greenhouse effect is more and more of a concern during the 21st century. The global average temperature will continue to rise by 1.4-5.8 °C from now to 2100 if we don't take active measures to reduce emissions of greenhouse gases [1]. Carbon dioxide produced from fossil fuel-fired power plants is a major greenhouse gas, so the development of CO_2 capture technologies for these large point sources is of critical importance. Carbon dioxide capture technique using dry alkali metal-based sorbents has been developed as a retrofit technology for existing power plants. The process is based on the reversible reaction between potassium carbonate, CO_2 and water vapor to form potassium bicarbonate. The dry technique for CO_2 capture has the following advantages: circulating utilization efficiency, low energy consumption of reaction, low cost of raw materials, no corrosion to the equipment, and no secondary pollution. Currently, the technology has become a hot research topic at home and abroad. American researchers have studied carbon dioxide capture using alkali-based dry sorbents and its economic evaluation [2-5], displaying that hexagonal K_2CO_3 had better absorption efficiency. Field testing of a prototype dry carbonate process has been completed with a total of 235 h of operation using natural gas and coal-derived flue gases.

The dry carbonate demonstrated high CO_2 capture and minimal adverse effects of exposure to SO_2 [2]. Korean researchers have studied CO_2 capture performance for different supports of potassium-based sorbents and the effect of vapor, SO_x and NO_x, for CO_2 capture through the fixed-bed, the bubbled-bed, the fluidized-bed and the fast transport-bed [6-12]. Korea Institute of Energy Research and Korea Electric Power Research Institute have developed the carbon dioxide capture system using dry regenerable sorbents since 2002. They developed a bench scale unit (BSU) which treated 100 Nm^3/h of flue gas in 2006. Carbonation was effective at the lower temperature over the 50-70 °C temperature range, while regeneration was more effective at the higher temperature over the 135-300 °C temperature range [6]. The CO_2 removal rate increased as gas velocity decreased and solid circulation rate increased [7]. CO_2 removal was effective with water vapor pretreatment and without proper water vapor pretreatment CO_2 removal abruptly decreased from the beginning [6]. The relative experimental results revealed that the removal of heat sorption in the carbonation reactor was important to increase CO_2 removal [8]. A 0.5 MWe pilot plant which could handle 2,000 Nm^3/h of flue gas treatment was successfully constructed at the Hadong Coal-Fired Power Plant, Korea Southern Power Company. As a result, the maximum CO_2 removal reached almost 85% and the CO_2 removal range varied from 50% to 80% according to the operating variables [9]. Six potassium-based dry regenerable sorbents were tested to evaluate their applicability to a fluidized-bed or fast transport-bed CO_2 capture process, and sorb KT-5 and KZ-5 sorbents satisfied most of the physical requirements for a commercial fluidized-bed reactor process along with good chemical reactivity [10]. The Institute of Thermal Engineering, Chinese Southeast University has analyzed carbonation and regeneration reaction mechanism of sodium and potassium-based different support sorbents by TGA, XRD, SEM and N_2 adsorption test [13-17]. The difference of the crystal structure characteristics of the sorbents was investigated with XRD and Inorganic Crystal Structure Database searching, and causes the difference of carbonation reactivity [13]. The reaction temperature and pressure are the key factors for this technique. The conversion rate decreased with the increases in the reaction temperature and pressure, and the effects of CO_2 and H_2O concentration were reduced [14]. Potassium carbonate, which is loaded in a variety of supports, is an innovative research; those supports are activated carbon, TiO_2, MgO, SiO_2, and Al_2O_3 etc. K_2CO_3/TiO_2 is better than others for CO_2 capture, but TiO_2 is so expensive that it cannot be applied cosmically. Therefore, selecting a suitable support has become the key point. However, little research has been done on regenera-

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tion dynamics. In this paper Suzhou river sediment in Shanghai of China was selected as the support particle. This paper focuses on morphology and regeneration dynamics of hexagonal potassium-based sediment sorbents. There are two advantages of using sediment as the support. One is reducing the cost of support for CO_2 capture, and the other is effective management of the river sediment and to realize the reuse of waste. Suzhou river sediment can be harmlessly handled.

EXPERIMENTAL

Experimental reagents: Analytical reagent $KHCO_3$ was provided by Shanghai Chemical Reagent Co., Ltd. $KHCO_3$ was 99.5% pure, and the average particle size was 300 μm. Suzhou Creek river sediment was chosen as the support of dry sorbents, and the average particle size was 10 μm.

Preparation of the sorbents: The potassium hydrogen carbonate, sodium silicate and sediment were evenly mixed according to the proportion. Through adding some amount of water, the mixture was stirred for over 12 h. The mixture was put into the electric heating vacuum dryer for drying at the temperature of 100 °C. The diameters of 100-500 μm were selected for testing from the dried particles.

Measurements of the sorbents: S-4800 - HITACHI SEM made by Japan was used to analyze the shape of sorbents. The JW-BK Static nitrogen adsorption analyzer made by Beijing Gaobo Science and Technology Co., Ltd. was used for N_2 adsorption tests of hexagonal K_2CO_3 (pc#2) and the sorbents (pc#1). Chemical reactivity of Suzhou Creek river sediment and $KHCO_3$-based Sediment regenerative agent were measured using the TG-209-F1 TGA made by the German NETZSCH Instruments Co., Ltd. The thermogravimetric tests were processed in the gas composition of N_2 at a flow of 80 ml/min. The simulating regeneration tests were processed at regenerated final temperature of 150 °C, 175 °C, 200 °C, 225 °C, 250 °C and 300 °C and at heating rate of 1, 5, 10, 15 and 20 °C/min, respectively. The hexagonal K_2CO_3 (pc#2) and the sorbents (pc#1) were obtained from calcination of $KHCO_3$ and $KHCO_3$-based Sediment in the thermo gravimetric tests.

RESULTS AND DISCUSSION

1. Analysis of Sorbents

1-1. Analysis of Hexagonal K_2CO_3

SEM pictures show that the sample pc#2 has small pores and cracks on the particle surface. N_2 adsorption test shows the BET surface areas and pore volumes of pc#2 are 2.83 $m^2 \cdot g^{-1}$ and 7.45×10^{-3} $cm^3 \cdot g^{-1}$, and the pore diameter of pc#2 is mainly distributed from 1.72 to 5.4 nm.

1-2. Analysis of Suzhou Creek River Sediment

Suzhou Creek river sediment could be roughly divided into three layers in gravity, the top and middle layers of which were chosen as the support of dry sorbents for CO_2 capture. The results of TGA experiments of the top and middle sediment are shown in Fig. 1 and chemical compositions of the top and middle sediment are in Table 1.

Fig. 1 shows the three temperature stages of pyrolysis in Suzhou river sediment, including the dehydration stage range of 0 °C to 180 °C, the organic carbon pyrolysis stage range of 180 °C to 600 °C and the calcination stage of over 600 °C. Since sediment was pretreated at the temperature of 600 °C to 1,000 °C, it therefore had no effect on absorption and regeneration reactions.

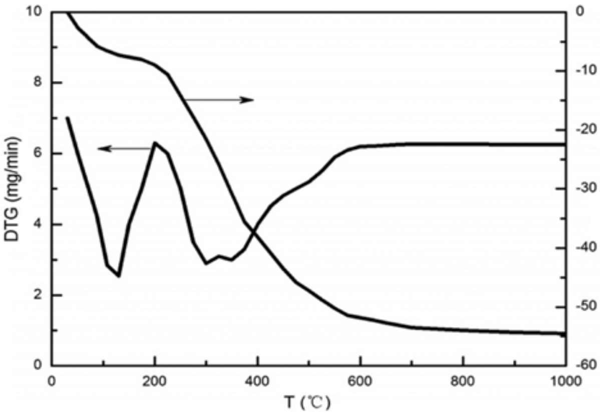


Fig. 1. DTG/TG curves of Suzhou river sedimen.

Table 1. Chemical compositions of Suzhou Creek river sediment (%)

Composition	SiO_2	Fe_2O_3	Al_2O_3	CaO
Content	62.5	3.99	9.7	5.37
Composition	MgO	K_2O	Na_2O	
Concentration	2.31	2.04	1.6	

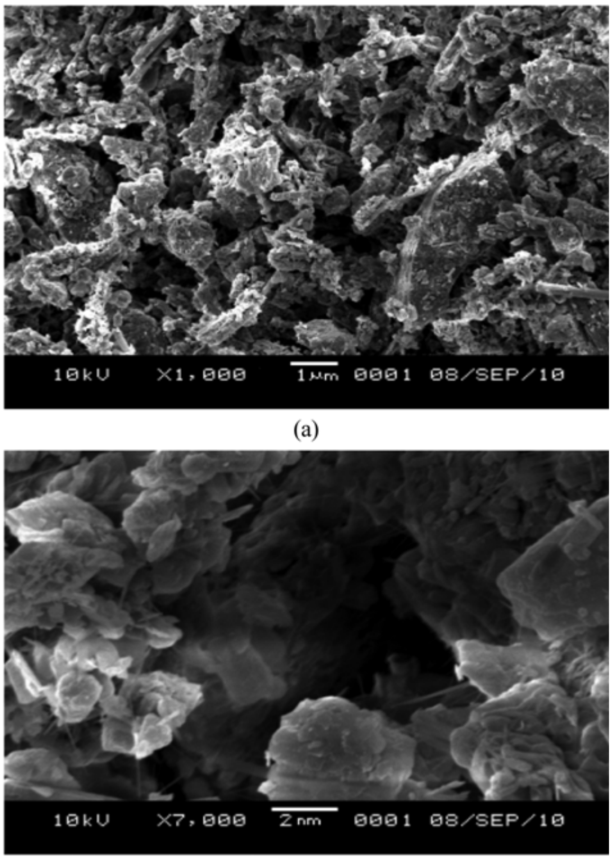
Table 2. Material components of Regenerated sorbents (%)

Active component	Support		Binder
$KHCO_3$	Suzhou sediment	Guangxi plaster	Na_2SiO_4
20	56	14	
30	48	12	10
35	44	11	10
40	40	10	10
50	32	8	
100	0	0	0

Table 1 shows that the total content of SiO_2 and Al_2O_3 arrive at 70%. Meanwhile, K_2O, Na_2O, MgO, CaO and FeO etc. can reduce energy of calcining sediment, because they are helpful oxide for melting. So Suzhou Creek river sediment was chosen as the support of dry sorbents for CO_2 capture.

1-3. Analysis of Potassium-based River Channel Sediment Regenerated Sorbents

Figs. 2 shows images of pc#1 were obtained from calcination of $KHCO_3$-based sorbents when the load was 40%. Fig. 2(a) shows the image magnified for 1,000 times. Numerous pores and cracks on the particle surface of dry sorbents can be seen in Fig. 2(a). Many pores and cracks blend together and form a mesh structure. This structure can increase the contact area between the gas and solid, and it is good at gas adsorption and can increase the adsorption efficiency. In the regenerated process, the structure promotes the diffusion of gas molecules and improves regeneration efficiency. As Fig. 2(b) shows, the sample was magnified for 7,000 times; the pores



(a)

(b)

Fig. 2. Images of dry sorbents SEM.

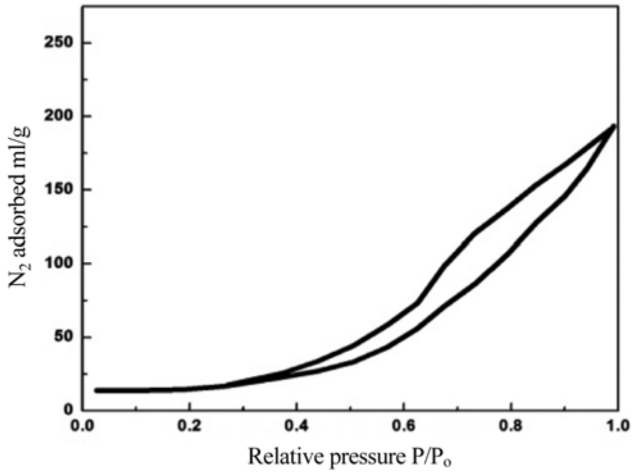


Fig. 3. Images of N_2 adsorption test.

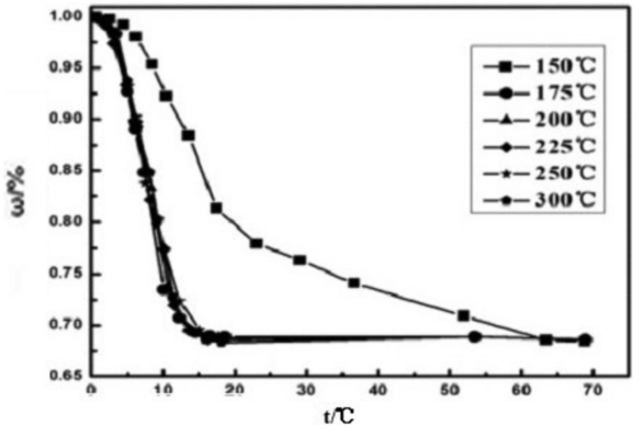


Fig. 4. TG curves of pure $KHCO_3$ at different regenerated final temperature.

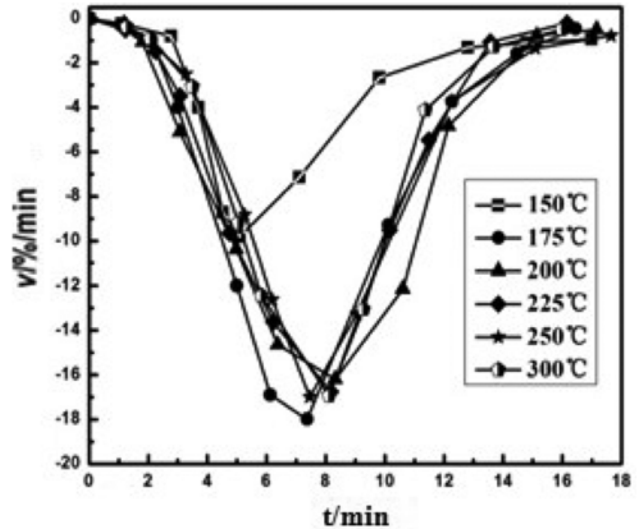


Fig. 5. DTG curves of pure $KHCO_3$ at different regenerated final temperature.

are irregular and the diameter of that is distributed from 10 to 20 nm. There are many pores in pc#1.

For researching characteristics of dry sorbents, N_2 adsorption test was performed, and the results are shown in Fig. 3. Isotherm is anti-"s" type, so it is a typical class adsorption isotherm. The adsorption and desorption curves are separated when the relative pressure is medium-sized. So it can be considered as a class "A" adsorption curve. The curve shows the pore is a tubular pore opening at both ends, and it accords with the result of SEM. N_2 adsorption test shows the BET surface area and micropore volume of pc#1 are 156.73 $m^2\cdot g^{-1}$ and (1.7-300 nm) 357.5×10^{-3} $cm^3\cdot g^{-1}$, the pore diameter ranges of pc#1 are mainly distributed from 2 to 20 nm. And the literature [17] shows the surface area and micropore volume of K_2CO_3/Al_2O_3 are 138.96 $m^2\cdot g^{-1}$ and (1.7-300 nm) 334.5×10^{-3} $cm^3\cdot g^{-1}$.

In summary, compared with pc#2, the surface area, pore volume and pore diameter of pc#1 were better for CO_2 capture.

2. Analysis of Final Temperature of Regeneration

The temperature rises from 0 °C to final temperature at the heating rate of 10 °C/min. When the temperature was 100 °C, we began to record the time. Figs. 4-5 show TG and DTG data of pure $KHCO_3$ at different regenerated final temperature.

The results are shown in Figs. 4-5. When the final temperature was over 175 °C, the reaction was finished after about 18 min. The conversion rate reached 50% and the maximum reaction rate reached 17% in 8 min. $KHCO_3$ can be completely decomposed when the final temperature is 150 °C, but the process required a long time, close to 70 min. In conclusion, the conversion rate was above 85% at the end of the reaction; average rate of which was around 5%

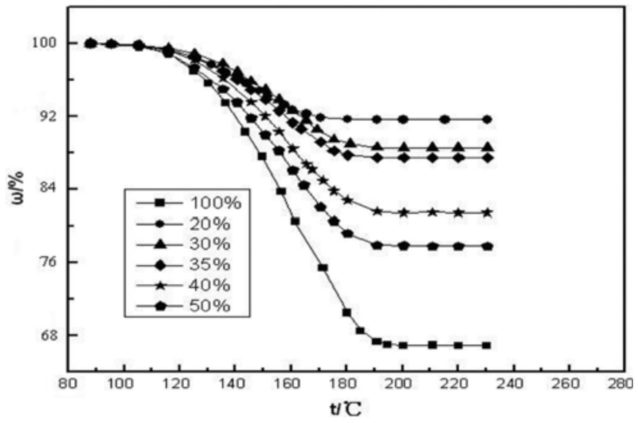


Fig. 6. TG curves of different load of $KHCO_3$ regeneration.

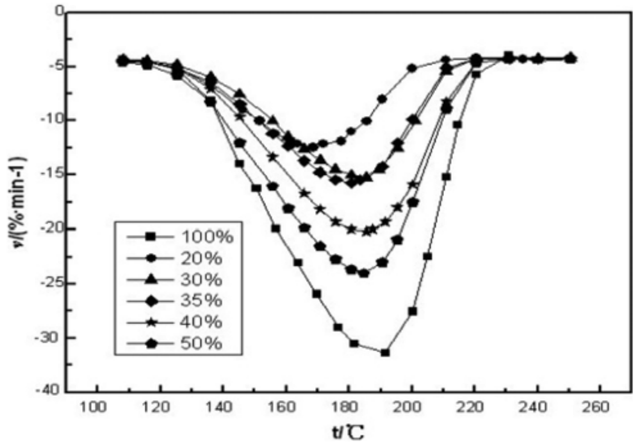


Fig. 7. DTG curves of different load of $KHCO_3$ regeneration.

when the final temperature was over 175 °C. Besides, the average rate was only 1.24% with the final temperature of 150 °C.

The TG curve became plane smooth after 200 °C in Fig. 6 and the largest weightlessness rate appeared between 160 and 200 °C in Fig. 7. In summary, the optimum final temperature of regeneration was over 200 °C.

3. Regeneration Dynamics Analysis

As the modified Coats-Redfern integral method is simple and accurate, the dry sorbent regeneration of non-isothermal chemical dynamics parameters is solved by the method in this paper.

The thermal decomposition mechanism of dry sorbents is as follows:

$$2KHCO_3=K_2CO_3+H_2O+CO_2\uparrow$$

The function of thermal decomposition reaction of $KHCO_3$ is $f(\alpha)=(1-\alpha)$.The modified Coats-Redfern integral method by mathematical transformation is approximate as:

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

Supposing:

$$a=\ln\left(\frac{AR}{\beta E}\right), \tag{2}$$

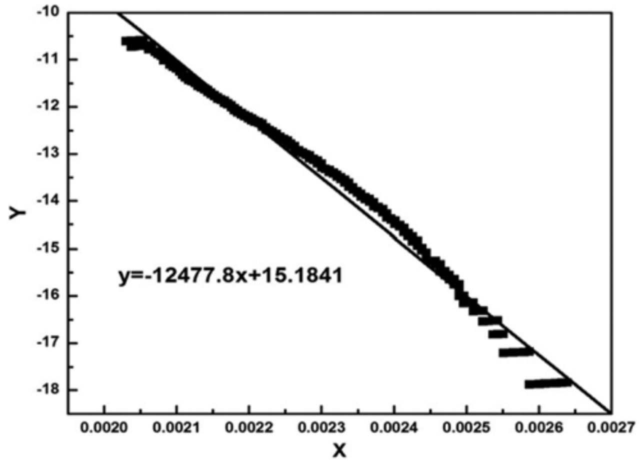


Fig. 8. Regeneration dynamics parameters fitting curve of 40% $KHCO_3$ sorbents.

Table 3. Regeneration dynamics of different loading of $KHCO_3$-based sorbents

Loading of $KHCO_3$ %	E $kJ\cdot mol^{-1}$	A 10^9 s^{-1}	R
20	103.45	8.04	0.99456
30	105.64	8.04	0.99568
35	109.54	5.47	0.98962
40	102.43	4.04	0.99307
50	104.06	5.11	0.98937
100	109.91	19.28	0.98839

$$b=-\left(\frac{E}{R}\right), \tag{3}$$

$$x=1/T, \tag{4}$$

$$y=\ln[-(\ln(1-a)/T^2)], \tag{5}$$

then has y=a+bx. According to the above equations, experimental data are fitted into synthetic curves. Thus, we can obtain the pre-exponential factor and activation energy.

3-1. Regeneration Dynamics Analysis of Different Loading of Dry Sorbents

Different loading of $KHCO_3$-based regenerated sorbents was tested with a pressurized thermogravimetric apparatus in the gas composition of N_2 at heating rate of 10 °C/min. The temperature rose to 300 °C and maintained constant.

Fig. 8 shows regeneration dynamics parameters fitting curve of 40% $KHCO_3$ sorbents. Through the curve, we can calculate activation energy to be 102.43 $kJ\cdot mol^{-1}$ and pre-exponential factor to be 4.04×10^9 s^{-1}. Regeneration dynamics parameters of different loading of $KHCO_3$-based sorbents are shown in Table 3.

Table 3 shows that the correlation coefficient is above 0.985, and activation energy is between 100 and 110 kJ/mol. The activation energy of 40% $KHCO_3$ sorbents is the smallest, so their renewable performance is good. It has been reported that when the active component ranges from 30% to 40%, carbon dioxide capture efficiency is the best [18,19]. The current experimental data support the above conclusions.

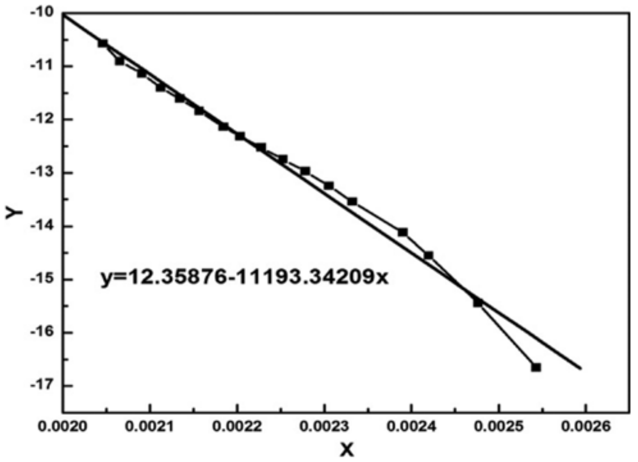


Fig. 9. Regeneration dynamics parameters fitting curve at heating rate of 10 °C/min.

Table 4. Regeneration dynamics of 40% $KHCO_3$ sorbents at different heating rate

β °C·min^{-1}	E kJ·mol^{-1}	A 10^8 s^{-1}	R
1	92.59	1.61	0.98683
5	98.04	8.58	0.99654
10	93.06	2.17	0.99321
15	96.05	4.91	0.99367
20	102.24	3.25	0.98547

3-2. Regeneration Dynamics Analysis of Dry Sorbents at Different Heating Rate

Regenerated sorbents of 40% $KHCO_3$ were tested with a pressurized thermogravimetric apparatus in the gas composition of N_2 at different heating rate. The temperature rose to 300 °C and maintained constant.

Fig. 9 shows regeneration dynamics parameters fitting curve of 40% $KHCO_3$ sorbents at heating rate of 10 °C/min. Through the curve we can calculate activation energy of 93.06 kJ·mol^{-1} and pre-exponential factor of 2.17×10^8 s^{-1}. Regeneration dynamics parameters of 40% $KHCO_3$ sorbents at different heating rate are shown in Table 4.

Table 4 shows the correlation coefficient is above 0.985 and the activation energy is between 90 and 105 kJ/mol. The activation energy is relatively small at a heating rate of 1 and 10 °C·min^{-1}; they are 92.59 and 93.06 kJ·mol^{-1}, respectively. According to the experimental results, when the heating rate was higher than 5 °C·min^{-1}, the conversion rate of 40% $KHCO_3$ renewable sorbents exceeded 90%. According to the experimental data the optimum heating rate is 10 °C·min^{-1} in this study.

CONCLUSIONS

The particle morphology and the regeneration dynamics of hexagonal K_2CO_3-based Suzhou River Channel Sediment dry sorbents (pc#1) have been studied by SEM, N_2 adsorption tests and TGA. The main conclusions are as follows. The particle morphology of pc#1 is better than that of K_2CO_3 in hexagonal crystal structure. The optimum renewable technology condition is that the final temperature was 200 °C, the loading is about 40% and the heating rate is 10 °C·min^{-1} by simulative experiment of regeneration and modified Coats-Redfern integral method. The activation energy of 40% $KHCO_3$ sorbents is 102.43 kJ·mol^{-1} and becomes 93.06 kJ·mol^{-1} at heating rate of 10 °C·min^{-1}. The activation energy of the renewable technology conditions is relatively low.

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NOTATION

A : pre-exponential factor [s^{-1}]
E : activation energy [kJ·mol^{-1}]
R : correlation coefficient
T : temperature [°C or K]
α : the conversion rate of samples [%]
β : heating rate [°C·min^{-1}]

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