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The removal of H_2S derived from livestock farm on activated carbon modified by combinatory method of high-pressure hydrothermal method and impregnation method

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Abstract H_2S is considered as the main gas pollutant from livestock farm and activated carbon (AC) is widely used as adsorbent for H_2S. This paper focuses on the influence of modification conditions and operation conditions on the H_2S adsorption performance on AC samples. The H_2S adsorption performance on modified AC (MAC) samples by single and combinatory method has been investigated. It is concluded that the MAC by combinatory method of high-pressure hydrothermal method followed by alkaline solution impregnation method could promote the H_2S adsorption performance remarkably. The H_2S adsorption performance differs with different operation conditions. Meanwhile the samples of fresh AC and exhausted AC have been characterized using BET, FTIR, TPD and Boehm titration method. The experimental results are confirmed that the characteristics of AC have significant influence on the adsorption ability for H_2S.

Keywords Hydrogen sulfide · Livestock farm · Modified activated carbon · High-pressure hydrothermal · Impregnation

1 Introduction

In livestock farms, H_2S has a serious influence on the indoor environment as the main malodorous gas. Currently, the desulfurization is mainly achieved by liquid redox method, biological methods, adsorption or selective catalytic oxidation (Wang 2003; Duan et al. 2007; Seredych and Bandosz 2007; Yasyerli et al. 2004). Adsorption by AC has advantages of simple process, high purification efficiency, good regeneration property and low price (Adib et al. 1999; Bandosz 1999). Owing to the large surface area and well-developed pore volume, AC could be not only used as single adsorbent but also modified to remove pollutants in gas as carrier (Bagreev et al. 2000; Adib et al. 2000; Bagreev et al. 2005; Bandosz et al. 2000). Using impregnation method to modify AC could greatly improve the adsorption ability (Li and Wang 2003; Meljac et al. 2004). Especially AC impregnated with alkaline (KOH or NaOH) is extensively used (Bandosz and Le 1998; Yan et al. 2002) for desulfurization. Besides alkaline, such materials as sodium and potassium carbonate (Wang et al. 2006; Cariaso and Walker 1975) are also used as impregnants. In general, the adsorption process contains both physical adsorption and chemical adsorption owing to combinatory effect of surface groups and pore structure (Rong and Zheng 2001). As the adsorbent of H_2S, AC needs the synergism of surface chemistry and pore structure, and basic environment is beneficial to the creation of sulfur and higher sulfur capacity (Bandosz 2002). The species of AC and modifier plays decisive role in the sulfur capacity of modified AC (Tan et al. 1996). Research has been made on using microwave to modify the surface chemistry of AC (Menendez 1999), the results show that in nitrogen atmosphere, most of the oxygen groups on the surface of AC have been removed and the pH value of AC increases remarkably. AC adsorption is one of the most widely used technologies to treat the malodorous gas from livestock farm (Le Leuch et al. 2003, 2005; Hastie et al. 2011). At present the commonly used physical method to modify AC is HPHM and the popular chemical method is impregnation method. The literature of adsorption

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performance for H_2S by using combinatory method of these two methods above to modify AC is relatively poor (Skubiszewska-Zieba et al. 2011).

In this paper, the adsorption performance for H_2S of modified AC (MAC) by different methods and at different operation conditions has been investigated. The samples also have been characterized by BET, FTIR, TPD and Boehm titration method in order to understand the adsorption mechanism for H_2S.

2 Materials and methods

2.1 Sample preparation

In this experiment, the industrial AC (diameter 3 mm, the ratio of height to diameter 1:1) is selected as raw activated carbon (RAC). The modification method that AC and distilled water are maintained in autoclave according to the volume ratio of 2:3 at constant temperature for 3 h is defined as HPHM in this experiment; the modification method that AC is impregnated with 7 % alkaline solution at 50 °C for 0.5 h is defined as ASIM in this experiment. RAC is modified by HPHM at 150, 250, 270 and 300 °C separately then dried at 105 °C for 3 h to reserve (RAC is referred to as $3^{\#}$, these MAC are separately referred to as G150, G250, G270 and G300); RAC is modified by ASIM with K_2CO_3 solution then dried at 105 °C for 3 h to reserve (this MAC is referred to as KC); G270 is modified by ASIM with K_2CO_3, KOH and NaOH solution separately then dried at 105 °C for 3 h to reserve (these MAC are separately referred to as G270KC, G270KO and G270Na); KC is modified by HPHM at 270 °C then dried at 105 °C for 3 h to reserve (the MAC is referred to as KCG270). In order to simulate the livestock farm atmosphere, the 99.99 % H_2S gas is diluted with N_2 to certain degree to prepare H_2S cylinder gas.

2.2 Experimental methods

2.2.1 *Activity tests*

The activity tests are carried out on the fixed bed device (Fig. 1a). The flow chart of adsorption removal of H_2S is shown in Fig. 1b. The influence of modification conditions on H_2S adsorption performance has been investigated at adsorption temperature of 80 °C, gas space velocity of 900 h^{-1} and inlet H_2S concentration of 750–850 mg/m^3; the influence of operation conditions on H_2S adsorption performance also has been investigated on G270KO. About 20 ml AC is loaded into the fixed bed reactor for each H_2S adsorption experiment.

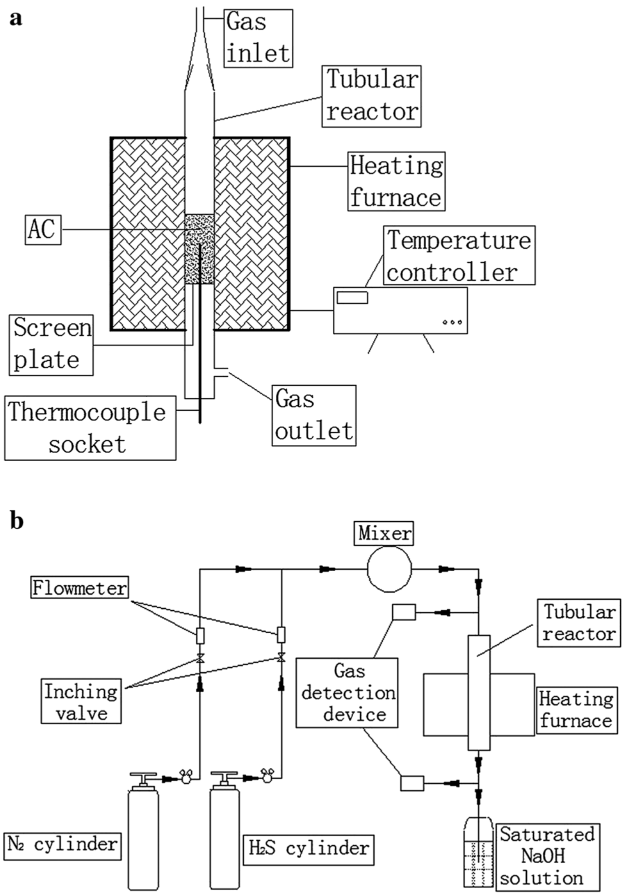

Fig. 1 **a** Equipment of fixed bed device. **b** Flow chart of adsorption removal of H_2S

In this experiment, the inlet and outlet H_2S concentration are measured through Iodometry Method, according to National Standard of the People's Republic of China GB/T11060.1-2010. All the experiments are stopped when the removal rate attains 20 %.

2.2.2 *BET*

The surface area of RAC and MAC has been characterized to investigate the influence of pore structure on H_2S adsorption through N_2 isothermal adsorption in Sorptomatic 1990 adsorption instrument (Italy CE Co.).

2.2.3 *Fourier transform infrared (FTIR)*

The surface groups of the samples have been characterized in VERTEX70 Fourier transform infrared spectrometer (Bruker Co.). The samples are grinded into about 200 meshes and mixed with the samples of potassium bromide. Then the mixture is grinded into powder and pressed to be slice sample. At last the slice samples are put into the spectrometer to be tested. (scanning range 400–4,000 cm^{-1}, scanning speed 0.2 cms^{-1}).

Table 1 Experimental conditions of TPD

Item	Experimental condition
Carrier gas	He
Adsorption gas	CO_2
Particle size	60 mesh (0.25 mm)
Bridge current	80 mA
Pretreatment temperature	500 °C
Adsorption temperature	50 °C
Desorption temperature	25 °C
Total volume of gas	25 ml/min

2.2.4 Temperature-programmed desorption (TPD)

The samples have been characterized through CO_2-TPD method in FINESORB-3010 temperature programmed adsorption instrument (Finetec Instruments Co.). The samples are placed in the sample holder, and heated at the heating rate of 15 °C/min from room temperature up to 500 °C with a helium flow rate of 10 ml/min. The experimental conditions of TPD are shown in Table 1.

2.2.5 Boehm titration

The acidic and basic surface groups are determined according to Boehm titration method. 1 g AC sample is placed in 20 mL, 0.05 N HCl or NaOH solutions. The flasks are sealed and shaken for 48 h and then 10 mL each filter liquid is pipetted and the excess of basic or acid is titrated with HCl or NaOH, as required.

3 Results and discussion

3.1 Influence of different modification methods on H_2S adsorption performance

Figure 2a shows the H_2S adsorption performance on MAC by HPHM at different modification temperature. The sulfur capacity of $3^{\#}$, G150, G250, G270 and G300 is 8.08, 10.83, 11.54, 12.22 and 10.56 mg/g separately. From Fig. 2a and the sulfur capacity results, it is concluded that in temperature range of 150–270 °C, the H_2S adsorption performance increases with the rise of modification temperature. HPHM produces pressure difference between the inside and outside of the originally blocked pores and makes these pores open up. But at 300 °C, the sulfur capacity is close to that of RAC. Perhaps in this high temperature, the collapse of the interior structure makes some of the pores blocked. In this experimental condition, 270 °C is the best modification temperature for HPHM.

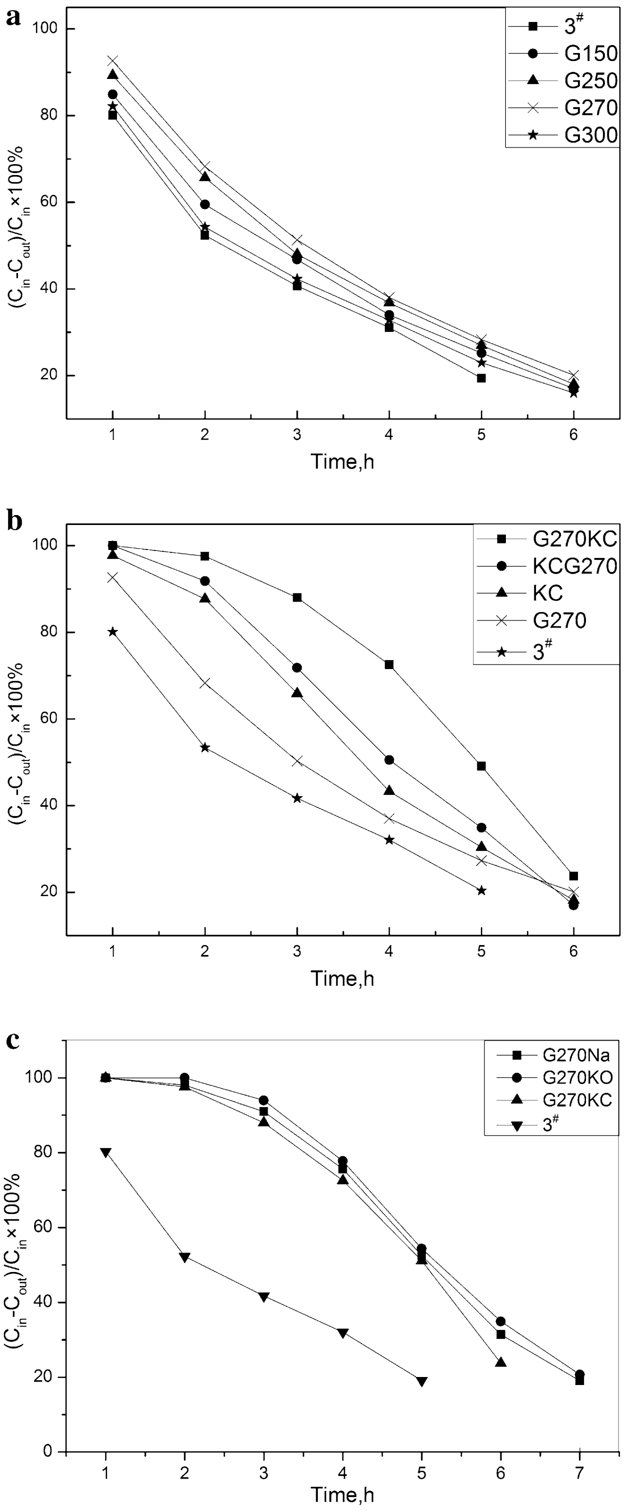

Fig. 2 **a** H_2S adsorption curves of MAC by HPHM at different temperatures. **b** H_2S adsorption curves of MAC by single and combinatory method. **c** H_2S adsorption curves of MAC by combinatory method in different alkaline solutions

Figure 2b shows the H_2S adsorption performance on MAC by single and combinatory method. The sulfur capacity of $3^{\#}$, G270, KC, G270KC and KCG270 is 8.08, 12.22, 13.91, 19.11 and 15.00 mg/g separately. The sulfur capacity of G270KC is twice as much as that of RAC. Fig. 2b and the sulfur capacity demonstrate that the modification effect of combinatory method is better than that of single method; the modification effect of HPHM followed by ASIM is much better than that of ASIM followed by HPHM. The pore structure becomes much more well-developed after modified by HPHM, so modifying AC by ASIM on the basis of HPHM could improve the load quantity of modifier.

Figure 2c shows the H_2S adsorption performance on MAC by combinatory method in different alkaline solutions. These sulfur capacity of $3^{\#}$, G270KC, G270KO and G270Na is 8.08, 19.11, 23.21 and 22.34 mg/g separately. The sulfur capacity of G270KO is almost 3 times as much as that of RAC. Figure 2c and the sulfur capacity illustrate that, in these three MAC, the H_2S adsorption performance on G270KO is the best. Because the basicity of OH^- is stronger than those of CO_3^{2-}, and the atomic radius of K^+ is smaller than Na^+. KOH is easier to be loaded on AC. So AC modified by HPHM at 270 °C firstly then by ASIM with KOH solution has good H_2S adsorption performance.

3.2 Influence of different operation conditions on H_2S adsorption performance

Figure 3a shows the H_2S adsorption performance on MAC at different adsorption temperature. The sulfur capacity of 30, 50, 70, 80 and 90 °C is 18.38, 20.88, 21.91, 23.21 and 19.83 mg/g separately. From Fig. 3a and the sulfur capacity, the adsorption performance increases with the rise of adsorption temperature and the sulfur capacity reaches maximum value at 80 °C. At low temperature, the physical adsorption plays the main role in adsorption process. With the rise of temperature, chemical adsorption ability increases and physical adsorption decreases. At 80 °C, the coaction of them reaches maximum. These results support the mechanism proposed previously (Tian et al. 2009; Choi et al. 2008) and emphasize the importance of adsorption temperature.

Figure 3b shows the H_2S adsorption performance on MAC at different gas space velocity. The sulfur capacity of 300, 600, 900 and 1,200 h^{-1} is 25.09, 24.09, 23.21 and 15.69 mg/g separately. At 1,200 h^{-1}, H_2S begins to overflow at 2 h and the breakthrough time is 6 h; at 300 h^{-1}, H_2S begins to overflow at 8 h and the breakthrough time is 11 h. The sulfur capacity of 300 h^{-1} is 1.5 times as much as that of 1,200 h^{-1}. Figure 3b and the sulfur capacity show that, high gas space velocity makes retention time not enough for H_2S to be adsorbed before it overflows. Also because of external diffusion, the sulfur capacity will not increase remarkably with the decrease of gas space velocity.

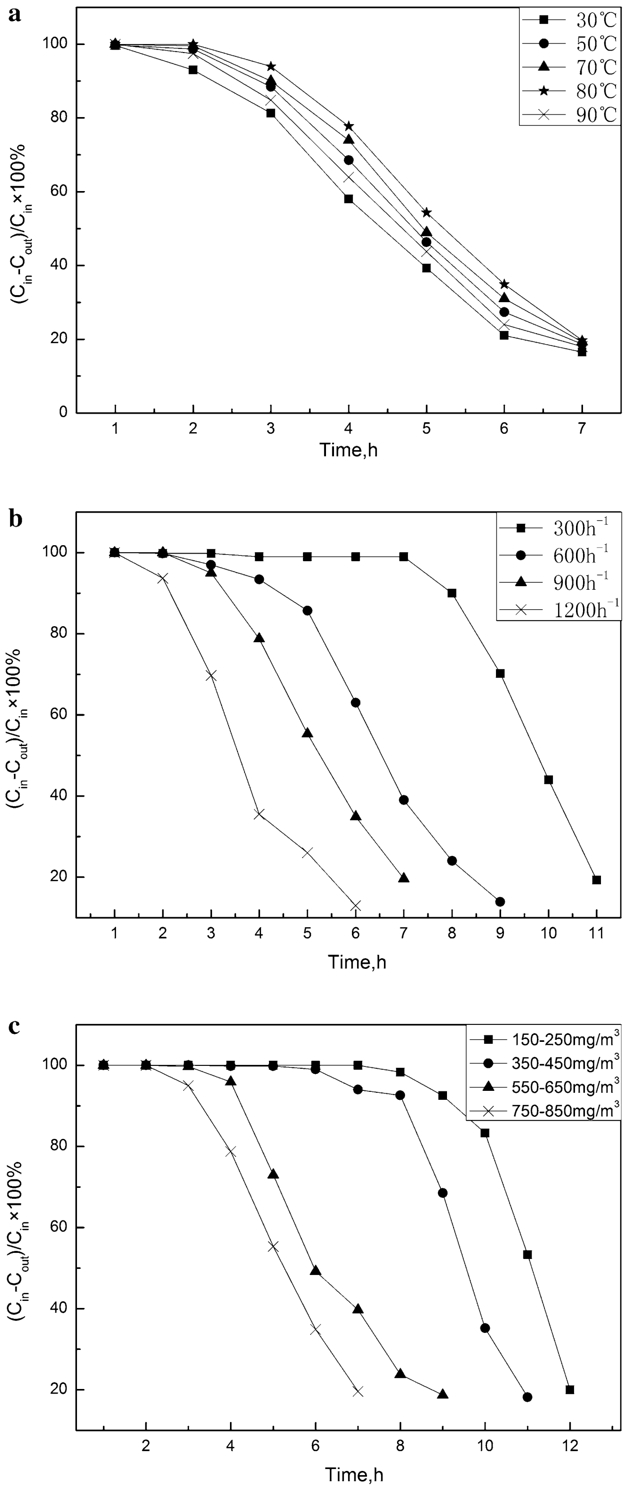

Fig. 3 **a** H_2S adsorption curves of MAC at different adsorption temperatures. **b** H_2S adsorption curves of MAC at different gas space velocity. **c** H_2S adsorption curves of MAC at different inlet H_2S concentration

Figure 3c shows the H_2S adsorption performance on MAC at different inlet H_2S concentration. The sulfur capacity of 150–250, 350–450, 550–650 and 750–850 mg/m^3 is 27.34,

Table 2 BET characterization for AC

Type of AC	Surface area (m^2/g)	Micropore area (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)	Total pore volume (cm^3/g)	Average pore size (nm)
$3^{\#}$	196.3352	169.3630	0.078160	0.053322	0.131482	2.6787
G270	281.2198	242.3899	0.111626	0.152934	0.264560	3.7630

49.21, 71.08 and 23.21 mg/g separately. The sulfur capacity of 550–650 mg/m^3 is 3 times as much as that of 750–850 mg/m^3. Figure 3c and the sulfur capacity show that, at the inlet H_2S concentration of 150–650 mg/m^3, with the increase of inlet concentration, the adsorption performance increases gradually. And the inlet concentration of 750–850 mg/m^3 is too high for H_2S adsorption on MAC.

3.3 Characterization and analysis for MAC

3.3.1 BET characterization and analysis

Table 2 is the BET characterization for AC. From Table 2, it is concluded that the surface area, micropore area, micropore volume and average pore size increase by 84.8846 m^2/g (43.2 %), 73.0269 m^2/g (43.1 %), 0.033466 cm^3/g (42.8 %) and 1.0843 nm (40.5 %) separately after modification. The total pore volume and mesopore volume increase by 100 and 80 % separately. The similar results were demonstrated by Bagreev and Bandosz (2001). In the modification process, the quantity and volume of mesopore and micropore all increase. In addition, the amplification of mesopore volume is larger than that of micropore volume. That makes the surface area increase by 43.2 %; HPHM not only gets through the originally blocked micropore but makes the surface area and micropore volume increase. It also makes micropore turn into mesopore in high pressure. These two causes lead to the increase of average pore size.

3.3.2 FTIR characterization and analysis

Figure 4 shows the FTIR spectra graphs of MAC. According to literature (Gregg and Sing 1982), peaks at 1102, 1417, 1627, 2877, 2925 and 3444 cm^{-1} are specified as the stretching vibration characteristic peak of ether group (–C–O), carboxylate group (symmetric and asymmetric), carbonyl group (–C=O), aliphatic group (–CH_3), aliphatic group (–CH_2) and hydroxyl group (intermolecular association). As Fig. 4a shows, HPHM makes the peaks of MAC above weaker than those of RAC. As Fig. 4b shows, peaks of ether group (–C–O), aliphatic group (–CH_3) and aliphatic group (–CH_2) of MAC are weaker than those of RAC. But peaks of carboxylate group (symmetric and asymmetric), carbonyl group (–C=O) and hydroxyl group (intermolecular association) are stronger than those of RAC. It claims that modification doesn't change the types of functional group but changes the quantity of group. It is consistent with Dmitrii et al. (2007) and Feng et al.'s (2005) results. So ether group (–C–O), aliphatic group (–CH_3) and aliphatic group (–CH_2) are not conducive to the removal of H_2S and carboxylate group (symmetric and asymmetric), carbonyl group (–C=O) and hydroxyl group (intermolecular association) help promoting the adsorption for H_2S. At the same time, this phenomenon is more remarkable among MAC by combinatory methods. That is one of the main reasons why combinatory method is better

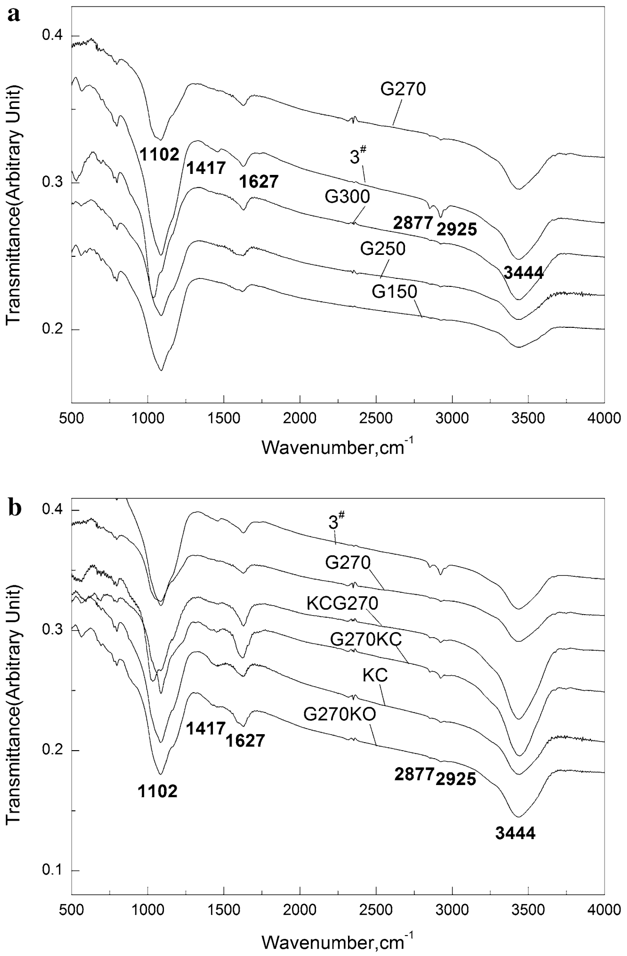

Fig. 4 **a** FTIR spectra graphs of MAC by HPHM at different temperature. **b** FTIR spectra graphs of MAC by different methods

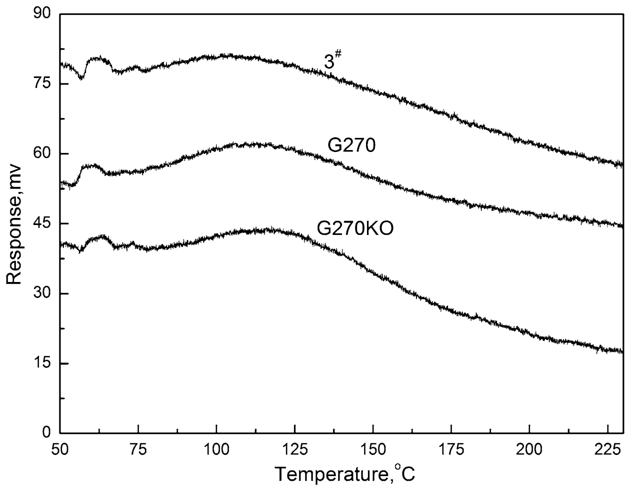

Fig. 5 CO_2-desorption curves of RAC and MAC

than single method. Combinatory method integrates the advantages of two single methods.

3.3.3 TPD characterization and analysis

Figure 5 is the CO_2-desorption curves of RAC and MAC. As it shows that both RAC and MAC have a weaker basic site at 60 °C and a stronger basic site at 110 °C. Similar result was reported by Tsai et al. (2001). On the stronger basic site, the peak intensity of G270KO is stronger than that of RAC and it shows that the increase of the quantity of adsorption center helps promoting the adsorption ability for CO_2 and makes MAC have higher adsorption activity and stability. It also shows that for G270, on the weaker basic site, there is no remarkably difference with the peak temperature and peak intensity of RAC. But on the stronger basic site, the highest peak temperature deflects towards high temperature compared with RAC. This may be the reason why HPHM could promote the activity of AC but the performance is not remarkable.

3.3.4 Boehm titration characterization and analysis

Table 3 Surface acidic and basic groups content on AC by Boehm titration

Type of AC	Content of acidic group (mmol/g)	Content of basic group (mmol/g)
$3^{\#}$	0.0752	0.1856
G270	0.0975	0.4689
KCG270	0.0883	0.5384
G270KC	0.0805	0.6228
G270Na	0.0799	0.6356
G270KO	0.0802	0.7195

Table 3 is the surface acidic and basic groups' content on AC by Boehm titration. From Table 3, the content of basic group increases greatly and the content of acidic group shows little increase after modification. On the one hand, vapor of HPHM makes originally blocked pore open up, creates new pore and expands the original pore; on the other hand, HPHM makes some acidic group break up. The results show that the higher proportion of basic group in total surface groups, the more beneficial to H_2S adsorption. The characterization results are consistent with the literatures (Elsayed et al. 2009; Bagreev et al. 2004). Modification by combinatory method increases the proportion of basic group and decreases the proportion of acidic group. That leads the proportion of basic group to increase to 86–88 %. In the aspect of the combination order of modification method, modification by HPHM firstly increases the surface area and changes the pore structure, and then modification by ASIM secondly increases the load quantity of modifier and the content of basic group greatly.

4 Conclusions

In this paper, at the experimental conditions, 270 °C is the best modification temperature of HPHM for AC. The combination of HPHM and ASIM could combine the advantages of these two modification methods. The H_2S adsorption performance on MAC by combinatory method is better than that of single method and the combinatory method of HPHM followed by ASIM is better than that of combinatory method of ASIM followed by HPHM. The MAC by HPHM at 270 °C firstly then by ASIM with 7 % KOH solution at 50 °C has the best adsorption performance. 80 °C is the best adsorption temperature; at gas space velocity of 300–1200 h^{-1}, with the increase of gas space velocity, the adsorption performance decreases; inlet H_2S concentration of 550–650 mg/m^3 is the best inlet H_2S concentration for adsorption. Moreover, the pore structure, surface groups and basic site of MAC have effects on the removal of H_2S derived from livestock farm.

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