

Preparation of composite adsorbent of sawdust and CaCl_2 by carbonization method for creating pore

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Received December 15, 2011; accepted March 12, 2012; published online June 20, 2012

To solve the problem of swelling and agglomeration of CaCl_2 during the process of ammonia adsorption and improve the performance of mass transfer, we present a new method for the preparation of adsorbent. The CaCl_2 is first immersed into sawdust by soaking method, then the composite adsorbent is prepared by carbonizing the mixture of CaCl_2 and sawdust. The SEM image and elements analysis indicated that the new adsorbent has high porosity and uniform distribution of CaCl_2 due to carbonization under temperature of 700°C . The performance testing of ammonia adsorption showed that under the conditions of evaporation temperature of -5°C and condensation temperature of 40°C , the ammonia uptake reaches 0.204, 0.253 and 0.285 kg/kg, the specific cooling power (SCP) is 868.96, 540.02 and 405.16 W/kg, and the average adsorption rate is 6.79×10^{-4} , 4.22×10^{-4} and 3.17×10^{-4} kg/kg/s when the adsorption time is 5, 10 and 15 min, respectively. The problems of swelling and agglomeration of CaCl_2 are solved.

carbonization, creating pore, adsorption refrigeration, composite adsorbent, heat and mass transfer

Citation: Bu X B, Wang L B, Li H S, et al. Preparation of composite adsorbent of sawdust and CaCl_2 by carbonization method for creating pore. *Sci China Tech Sci*, 2012, 55: 2404–2408, doi: 10.1007/s11431-012-4923-5

1 Introduction

Adsorption refrigeration systems have been mostly investigated due to the environmental harmlessness, energy saving and non-moveable elements [1, 2]. However, there are still some problems for the adsorption refrigeration techniques, such as low SCP, low cyclic adsorption capacity and low adsorption rate [3–5]. The key to the above problems is to develop a new working pair with low regeneration temperature and high performance of heat and mass transfer. The core issue on the new working pair is the preparation of a new adsorbent with high performance.

The working pair of silica gel-water has an advantage of low regeneration temperature, however, the adsorption ca-

capacity can hardly exceed 20wt%. The adsorption capacity of metal chloride, such as CaCl_2 , is rather large. However, the problem of swelling and agglomeration always occurs during the process of ammonia adsorption, which results in a poor mass transfer [6, 7]. In view of the above questions, the common solution is to prepare a composite adsorbent. Usually, the composite adsorbent is prepared by impregnating metal chloride (CaCl_2 , BaCl_2 , SrCl_2 , etc.) into the open pores of a porous host matrix (silica gel, zeolite, active carbon, vermiculite and carbon fiber, etc.) with rich micropore and large specific surface area in order to solve the problem of swelling and agglomeration [8, 9]. Presently, the preparation of composite adsorbent by impregnation method is very popular [10–13], and some samples have been successfully prepared, such as SWS-1L and SWS-2L. The impregnation method can successfully solve the problem of swelling and

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agglomeration of metal chloride, however, the content of metal chloride in the composite adsorbent prepared by impregnation method is low due to the limitation of porous host matrix, which limits the adsorption capacity of composite adsorbent [12].

Inspired by the above impregnation method and the carbonization and activation method for the preparation of activated carbon [14–17], this paper presents a new method for the preparation of composite adsorbent with high performance of mass transfer by carbonization method for creating pore. The specific method is shown as follows: the CaCl_2 is first impregnated into sawdust, the mixture of CaCl_2 and sawdust is subsequently dried and carbonized at a high temperature to prepare a new composite adsorbent. A developed pore structure is created by carbonization method and mass transfer is thus improved due to having high porosity. If the conductivity materials, such as graphite and metal powder, are first added into the mixture and then the carbonization measure is taken, the composite adsorbent has not only a developed pore structure but also a high thermal conductivity. In this paper, the composite adsorbent of sawdust and CaCl_2 is first prepared by carbonization method, and then the performance is tested by ammonia adsorption. The addition of conductivity materials will be discussed in the next step.

2 Experimental

2.1 Raw materials

The raw materials for preparing composite adsorbents include fir sawdust with 20–35 meshes, pure calcium chloride powder, deionized water and amyllum; the equipment used includes drier and tube furnace.

2.2 Preparation procedure

- 1) The fir sawdust with 20–35 meshes is first dried at 120°C for 6 h.
- 2) The CaCl_2 aqueous solution with 50% in mass concentration is prepared.
- 3) The sawdust is soaked into the aqueous solutions of CaCl_2 for 24 h.
- 4) The mixture of sawdust and CaCl_2 is taken out of the solution and dried at 120°C until the mixture weight remains constant.
- 5) A composite is prepared by mixing 200 g mixture of sawdust and CaCl_2 with 20 g amyllum and 50 g deionized water, and then the precursor of adsorbent with diameter of 3 mm is made from the composite. Subsequently, the precursor is dried in a drier at 120°C for 24 h.
- 6) The precursor is placed into a tube furnace and carbonized. The temperature, time and atmosphere of carbonization are respectively 700°C , 1 h and vacuum.

7) The composite adsorbent is then taken out from the tube furnace and put into a drier at 120°C for use.

2.3 Performance testing

The performance testing mainly includes adsorption amounts and adsorption rate of ammonia adsorption on the adsorbent, and is carried out on the self-made experimental equipment of ammonia adsorption. The schematic diagram of the experimental set-up is shown in Figure 1, where valve 5 is used to regulate the pressure in buffer tank 3 and deflate, and valve 8 is connected to the vacuum pump. The experimental set-up mainly consists of buffer tank of NH_3 , adsorber and test equipment. The adsorber is a flange connection that makes the replacement of the sample very convenient. The volumes of the buffer tank and adsorber are 23091.58 and 80.99 cm^3 , respectively.

The experimental procedure is as follows.

- 1) Take out 10 g adsorbent from the drier at 120°C and fill them into the adsorber, and connect the adsorber with the buffer tank (3).
- 2) Vacuumize the adsorber for 1 h at 90°C .
- 3) Adjust the constant temperature water baths (11) and (2) at 40°C and 25°C , respectively.
- 4) Vacuumize the buffer tank (3) and then charge ammonia into it until the pressure reaches 354.76 kPa.
- 5) After the system becomes stable, open valve (7) and start the adsorption experiment.

The pressure of 354.76 kPa in the buffer tank is the pressure corresponding to evaporation temperature of -5°C . The NH_3 uptake on the composite adsorbent is calculated by the following equation:

$$m(t) = m_0 - m_1(t) - m_2(t), \quad (1)$$

where $m(t)$ is the amount of ammonia adsorbed at time t ; m_0 is the initial weight of ammonia in the buffer tank; $m_1(t)$ is the weight of ammonia in the buffer tank at time t ; $m_2(t)$ is the weight of ammonia without being adsorbed in the adsorber at time t . $m_1(t)$ and $m_2(t)$ are calculated according to the ideal gas law.

The sample morphology (SEM image) and elements distribution are observed using a scanning electron microscope (model HITACHI S-4800). The BET surface area and pore

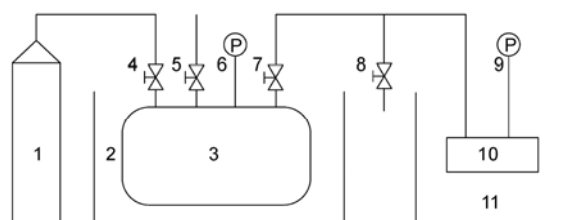


Figure 1 Experimental set-up (1 is a high-pressure container of NH_3 , 2 and 11 are constant temperature water baths, 3 is a buffer tank of NH_3 , 4, 5, 7 and 8 are valves, 6 and 9 are pressure sensors, and 10 is an adsorber).

size are determined by an adsorption apparatus (ASIQMO-002-2). To investigate the degree of scatter and crystallinity of CaCl_2 in the adsorbent, X-ray diffraction analysis is carried out according to an XRD apparatus (PANalytical X'pert Pro MPD).

3 Results and discussion

In Table 1, the burn-off is calculated by dividing the weight lost by the carbon content in the sample before carbonization. It can be seen from Table 1 that the weight of sample drops from 25 to 18.89 g after carbonization due to the removal of volatile elements during the carbonization step, resulting in the increase of CaCl_2 content in the sample from 53.64% to 70.99%. In ref. [12], the content of CaCl_2 in sample prepared by confined CaCl_2 into the pore of silica gel is only 34.85%. The porous structure is created in the adsorbent during carbonization process, and the BET surface area and the average pore diameter are respectively $143.6 \text{ m}^2/\text{g}$ and 4.95 nm .

Figure 2 depicts the SEM micrograph of the sample. It is obvious from Figures 2 and 3 that the composite adsorbent after carbonization has a developed pore structure. Furthermore, the elements of C, Cl and Ca disperse uniformly in the sample. This indicates that a developed pore structure in the adsorbent can be created by the carbonization method

Table 1 Performance comparison of sample before and after carbonization

Item	Value
Weight before carbonization (g)	25
Weight after carbonization (g)	18.89
Content of CaCl_2 before carbonization (%)	53.64
Content of CaCl_2 after carbonization (%)	70.99
Burn-off (%)	52.71
BET surface area (m^2/g)	143.6
Crystallinity of CaCl_2 (%)	25.1

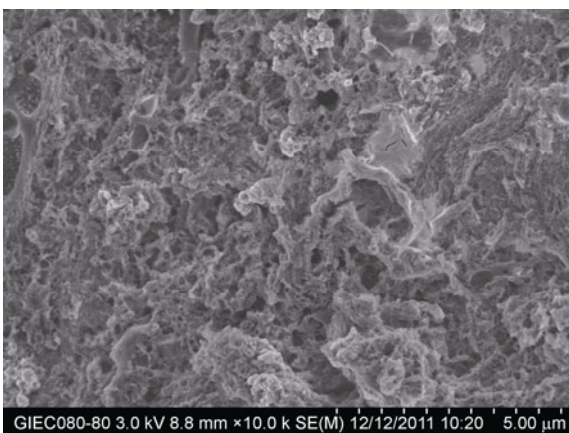


Figure 2 SEM image of sample.

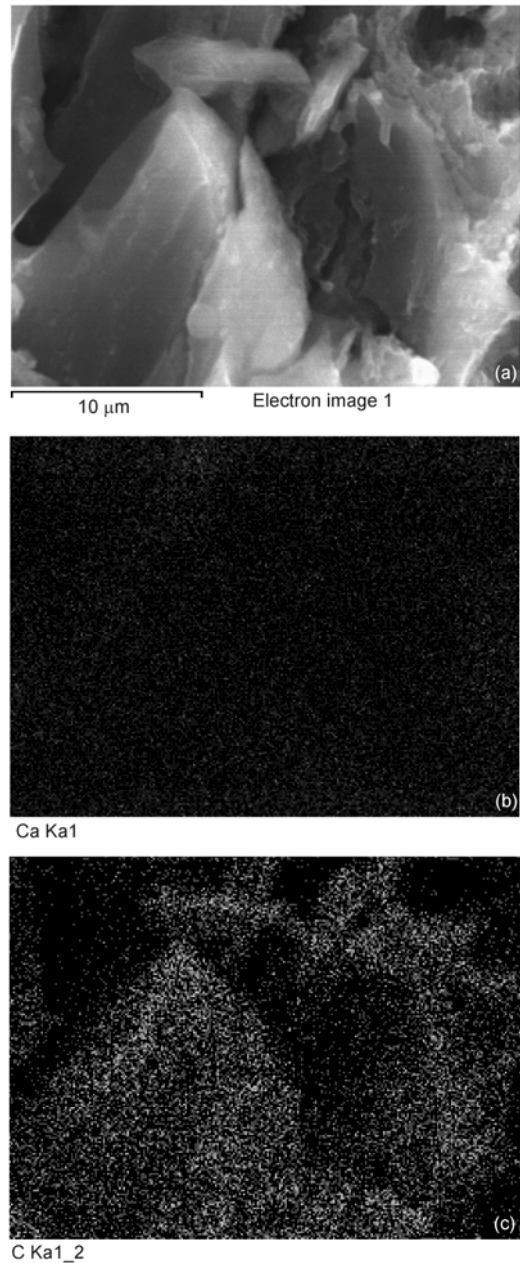


Figure 3 The distributions of elements in sample. (a) Selected sample; (b) distribution of Ca element; (c) distribution of C element.

to improve the mass transfer. Also, rich pore in the adsorbent provides the space for CaCl_2 swelling, even though the swelling occurs, the agglomeration does not take place due to the rich pore and uniform dispersion of CaCl_2 .

The XRD pattern shows that there is a partial crystallization of CaCl_2 in the adsorbent due to the high carbonization temperature of 700°C , and the crystallinity reaches 25.1%, as shown in Figure 4 and Table 1. The crystallinity of CaCl_2 will have a detrimental effect on the adsorption performance, and the crystallinity mainly depends on the carbonization temperature. So, the next work is to determine the relationship between the crystallinity of CaCl_2 and carbonization

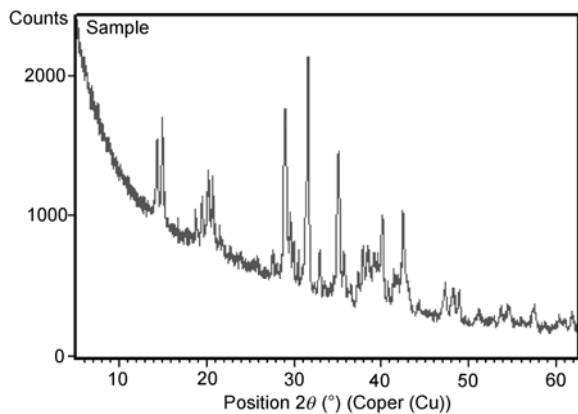


Figure 4 X-ray diffraction patterns of sample.

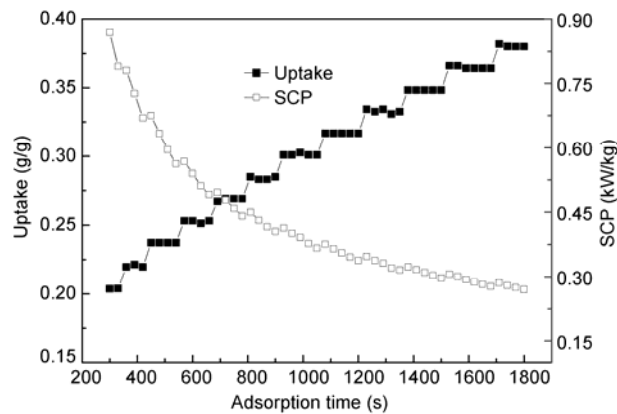


Figure 6 Variations of SCP and adsorption amount with time.

temperature.

Figure 5 describes the adsorption amount as a function of adsorption time. By observing the profiles in Figure 5, it can be noticed that the amount of adsorbed ammonia on the adsorbent increases with time, but the increase rate tends to be reduced. The adsorption amounts are 0.204, 0.253, 0.285 and 0.38 kg/kg at adsorption times of 5, 10, 15 and 30 min, respectively. At adsorption times of 1, 2, 3 and 4 h, the adsorption amounts are respectively 0.511, 0.658, 0.722 and 0.774 kg/kg. The amounts of ammonia adsorbed at 5, 10, 15 and 30 min reach 26.32%, 32.71%, 36.81% and 49.11% of that adsorbed at 4 h, respectively. This indicates that the adsorbent has a high adsorption rate at the start time, which is especially suitable for adsorption refrigeration due to its short running cycle.

Apparently from Figure 6, the specific cooling power has the maximum value at the early stage of adsorption, however, it decreases with time. The adsorption time is generally no less than 5 min for the practical refrigeration operation. Although the SCP is high for short adsorption time, the COP is low. This is due to the fact that the adsorption bed is in the process of cold and heat alternation, if the switch between adsorption operation and desorption operation is too

frequent, the heat loss of the adsorption bed will be large, thus resulting in the low COP. In Figure 6, the SCPs are respectively 868.97, 540.02, 405.16, 337.72, 297.21 and 270.25 W/kg at adsorption times of 5, 10, 15, 20, 25 and 30 min.

Figure 7 describes the average adsorption rate as a function of adsorption time. The average adsorption rate is the greatest at the start time, and decreases gradually with time. The average adsorption rates are 6.79×10^{-4} , 4.22×10^{-4} and 3.17×10^{-4} kg/kg/s at adsorption times of 5, 10 and 15 min, respectively.

The attenuation performance experiments of ammonia adsorption were carried out according to the operation procedure in section 1.3, and the experimental results are shown in Table 2. From Table 2, the amounts of ammonia adsorbed at the second, third and fourth experiments respectively took up 93.5%, 90.9% and 89.6% of that at the first experiment. The adsorption performance would almost no longer decay after three times of experiments, and the agglomeration of CaCl_2 during the process of ammonia adsorption did not occur.

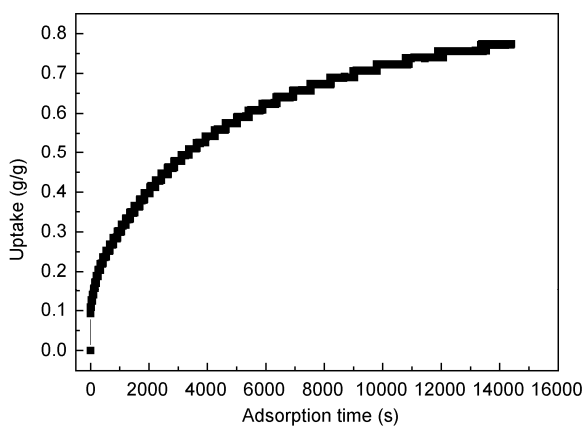


Figure 5 Variation of adsorption amount with time.

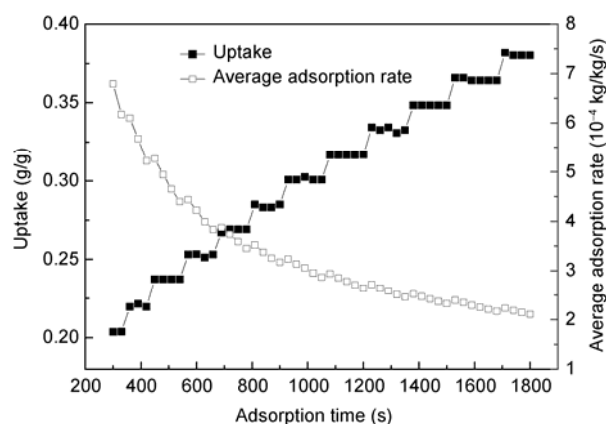


Figure 7 Average adsorption rate.

Table 2 Attenuation performance of ammonia adsorption at adsorption time of 4 h

Number of times	Uptake (g/g)
1	0.77
2	0.72
3	0.7
4	0.69
5	0.69
6	0.69
7	0.69
8	0.69

4 Conclusion

A new method and technology for the preparation of composite adsorbent of CaCl_2 and sawdust is developed. The following conclusions can be drawn from the performance testing.

1) SEM image and elements analysis shows that the adsorbent prepared by carbonization method under vacuum condition has a developed pore structure, and CaCl_2 disperses uniformly in the adsorbent.

2) The performance testing of ammonia adsorption on the composite adsorbent shows that under the conditions of evaporation temperature of -5°C and condensation temperature of 40°C , the adsorption amounts are 0.204, 0.253 and 0.285 kg/kg, and the SCPs are 868.96, 540.02 and 405.16 W/kg, at the adsorption times of 5, 10 and 15 min, respectively.

3) This paper presents a new technology for the preparation of composite adsorbent by carbonizing the mixture of CaCl_2 and sawdust, and this technology can conduct a comprehensive promotion. Not only sawdust but also agricultural and forestry wastes, such as coconut shell and straw, can be used for the preparation of composite adsorbent, which indicates that the raw materials are cheap and have a wide range of sources.

The developing direction in the future consists of two aspects: one is the improvement of the thermal conductivity by adding graphite or metal powder into the adsorbent; the other is the integration of adsorbent with heat exchanger and the development of adsorption chiller or ice making using composite adsorbent in order to verify its practical performance.

This work was supported by the Chinese Academy of Sciences and Foreign Experts Bureau of Guangdong under the Adsorption Refrigeration Pro-

gram (Grant nos. y007y51001 and 2010004). The structure and preparation process of the new adsorbent has a patent (China Patent 20111015-1114.2).

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