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Studies on Benign Working Pairs for Adsorption Refrigeration

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Abstract: Water and ethanol were selected as refrigerants, 13x molecular sieve, silica gel, activated carbon and adsorbents NA and NB prepared by authors were selected as adsorbents, and the performance of adsorption working pairs in adsorption refrigeration system was studied. The adsorption isotherms of adsorbents (NA and NB) were obtained by high-vacuum gravimetric method. Desorption properties of adsorbents were analyzed and compared by thermal analysis method. The performance parameters of adsorption refrigeration of different adsorption working pairs were studied on experimental device of adsorption refrigeration cycle. The results show: ① The maximum adsorption quantity of water on adsorbent NA arrives at 0.7 kg/kg, and the maximum adsorption quantity of ethanol on adsorbent NB is 0.68 kg/kg, which is 3 times that of ethanol on activated carbon; ② The refrigeration volume of NA-water working pair is 922 kJ/kg, the refrigeration volume of NB-ethanol is 2.4 times that of activated carbon-methanol; ③ As friendly to environment and no public hazard adsorption working pair, NA-water and NB-ethanol can substitute for carbon-methanol in adsorption refrigeration using low-grade thermal energy.

Key words: adsorption refrigeration, working pairs, isotherm, refrigeration volume

Recent studies on ecological impact of traces of halocarbons in the atmosphere have shown that the emission of chlorofluorocarbons (CFCs) affects the ozone layer around the globe and will lead to greenhouse effects. So the CFCs are restricted and prohibited in the world. Thus, on the one hand, there exists a technical interest to develop heat driven refrigerators or heat pumps, and on the other hand, there exists an ecological interest to find other solution than using CFCs as a refrigerant. On this background, adsorption refrigeration systems have received more and more attention and developed very fast as a type of system friendly to environment and a kind of effective means of using low-grade thermal energy. They have many other advantages compared with compression refrigeration, such as simple construction, no moving components, no solution pumps, being able to be driven directly by low-grade thermal energy and no need for electricity. The key of adsorption refrigeration is to develop the adsorption material with excellent performance.

Three known adsorption working pairs have been investigated[1]. The first is 13x molecular sieve-water[2,3]. The adsorption saturates at low aqueous partial pressure, after which the amount adsorbed becomes almost independent of pressure. At ambient temperature, molecular sieve can adsorb large quantities of water vapor even at low partial pressure, corresponding to high condenser temperature. Since water has high latent heat of vaporization and a convenient boiling point, the 13x molecular sieve-water pair is one of the most preferred working pairs. The disadvantage of this working pair is that desorption needs high regenerating temperature. The second is silica gel-water[4,5]. Such a system can operate at a lower temperature (70 – 80 ℃) and is suitable for using low-grade thermal energy and solar energy, but its refrigeration ability is lower than that of 13x molecular sieve. The third is activated carbon-methanol[6]. Methanol has a high boiling point (64.7 ℃) and a low solidifying point (– 98 ℃) and the adsorption system using it as adsorbate can produce a temperature below 0 ℃, but its latent heat of evaporation is only half that of water and it is harmful to the environment.

In this paper, a new kind of adsorption working pairs with two adsorbents NA and NB is presented. Water and ethanol are selected as adsorbates and the performance of adsorption refrigeration of adsorbents NA and NB, 13x molecular sieve, silica gel and activated carbon is investigated.

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1 Experiment

1.1 Main materials and reagents

Main materials and reagents used in the experiments are represented in Tab.1.

Tab.1 Main materials and reagents

Name	Specification	Manufacturing plant
13x molecular sieve Silica gel	Power 100 mesh	Nanjing Inorganic Chemical Plant
γ-Al_2O_3 Concavo-convex stick stone	Power < 100 mesh	Taizhou Chemical Accessory Ingredient Plant
Active carbon	Commercial product	Liyang Activated Carbon Plant
Magnesium chloride Strontium chloride Strontia hydrate	Commercial product	Jinghua Chemical Plant of Shanghai
Water glass	Commercial product	Applied Chemistry Plant of Nanjing University of Technology
Ethanol	A.R	The First Chemical Reagent Plant of Nanjing

1.2 Adsorbent preparation

Mixed method is adopted to prepare for adsorbents in the experiment. A schematic diagram of adsorbent preparation process is shown in Fig.1. First, a certain amount of samples are weighed at selected mixture ratio of materials. Second, the samples mentioned above are abraded to fine particles and mixed uniformly. Third, fine particles are stirred with water and prepared sphericity by hand or bar shape by extruding machine. Then the adsorbent samples (i.e. NA and NB) are gained after drying and calcinations.

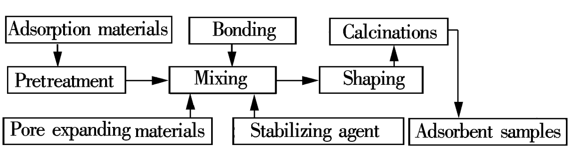

Fig.1 A schematic diagram of adsorbents preparation process

1.3 Adsorption isotherm

The adsorption isotherms of adsorbents NA and NB are determined by using high-vacuum gravimetric method in vacuum adsorption apparatus.

The main steps of the experimental procedure were: the adsorbent sample was activated at 450 ℃ for 2 h in a Muffle furnace, then the adsorbent was put into the basket and the whole apparatus was vacuumized. When the pressure and the temperature were 0.1 Pa and 300 ℃, respectively, such conditions were kept for 3 h. Some samples to be adsorbed were introduced, and the length difference of quartz spring before and after adsorption was measured by cathetometer. The equilibrium adsorption quantities of adsorbent in different pressure were obtained. Accuracy of cathetometer was 0.02 mm, and sensitivity of quartz spring was 37 – 40 cm/g.

1.4 TG-DTA analysis

The desorption performances of adsorption working pairs, such as 13x-water, silicon gel-water, NA-water, activated carbon-alcohol, NB-alcohol etc. are experimentally researched with differential thermal analysis balance of type WCT-1.

1.5 Appratus of adsorption refrigeration cycle

The whole experimental device is made of glass (see Fig.2). It can remain vacuum below 0.1 Pa for about 24 h.

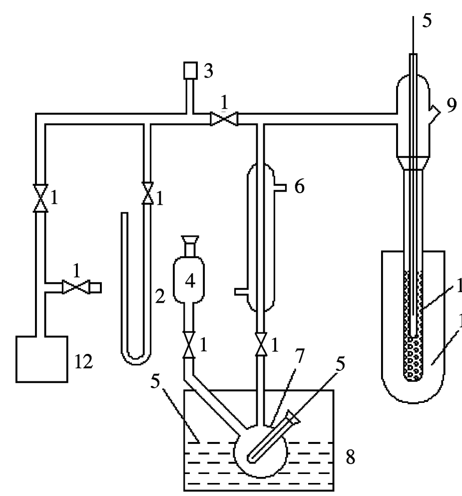

Fig.2 Simulation device of adsorption refrigeration cycle system
1—Valve; 2—Mercury manometer; 3—Vacuum electric couple pipe; 4—Liquid reservoir; 5—Thermocouple; 6—Condenser; 7—Evaporator; 8—Refrigeration room; 9—Feed inlet; 10—Adsorber; 11—Heater; 12—Vacuum system

The adsorption refrigeration experiment includes two processes: adsorption refrigeration process and heating desorption process. System valve was closed when the system vacuum blowed 0.1 Pa before the experiment began.

Turn on the evaporator valve after the adsorbent in adsorber was desorbed and cooled down. Adsorbent adsorbed refrigerant in the evaporator. Liquid refrigerant evaporated and absorbed heat from refrigeration room. Thus the refrigeration occurred. The refrigeration process finished when the adsorbent was saturated. Turn off the evaporator valve and cooling water flowed into the condenser. The adsorber, rich in adsorbed refrigerant, was heated from an initial temperature to regenerating temperature. When the system pressure increased to condensation pressure, the refrigerant vapor condensed in the condenser. Turn on the evaporator valve when adsorber temperature increased to a certain level and no refrigerant gas would condense in the condenser. When the refrigerant condensed in the condenser flowed into the evaporator, turn off the evaporator valve. Then adsorber was cooled down to ambient temperature and the next adsorption refrigeration cycle began.

2 Results and Discussion

2.1 Adsorption quantity

In adsorption refrigeration cycle, the adsorption quantity of adsorbent is used to evaluate the performance of working pairs for given adsorbent. The high-vacuum gravimetric method is used to determine adsorption isotherms of a series of working pairs in this paper. The adsorption isotherms of NA-water and NB-alcohol are shown in Fig.3 and Fig.4.

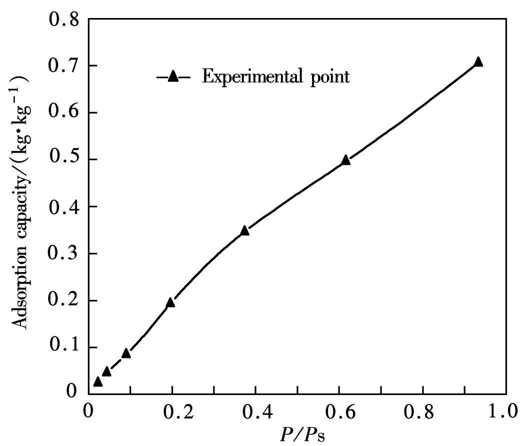

Fig.3 Adsorption isotherm of NA-water (27 ℃)

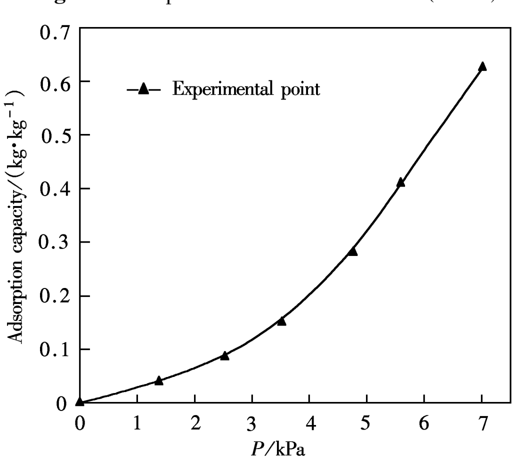

Fig.4 Adsorption isotherm of NB-ethanol (27 ℃)

It is clear in Fig.3 that the shape of NA-water adsorption isotherm is a part of Brunauer type Ⅱ (classification for shape of adsorption isotherms). In adsorption process, it is likely that multilayer adsorption occurs after completing monolayer adsorption. Though the adsorption isotherm does not belong to favorable one, the adsorption quantity that can reach 0.7 kg/kg is very large.

Fig.4 shows that the shape of NB-alcohol adsorption isotherm is a part of Brunauer type Ⅲ. With the increase of partial pressure of the component, the adsorption quantity increases, till the relative saturation value reaches the vicinity of 1. The fovea shape of curve results from interaction in adsorbed molecules, which makes the adsorption heat of first layer less than condensation heat. The maximum adsorption quantity of alcohol on self-prepared adsorbent NB reaches 0.68 kg/kg, which is three times of that of alcohol on activated carbon.

2.2 Desorption performances

In adsorption refrigeration process, it is an important step for adsorbate to desorb from a saturated adsorbent. The desorption temperature and the desorbed level directly influence on the performance of adsorption refrigeration system.

The thermal analysis of adsorption working pairs, such as 13x-water, silica gel-water, NA-water, activated carbon-alcohol, NB-alcohol etc. is carried out and desorption performance of adsorption working pairs measured is shown in Tab.2.

Tab.2 Thermal analysis of adsorption working pairs

Working pairs	Peak temperature /℃	Maximum weight lost/(mg·min^{-1})	Initial desorption temperature/℃	Desorption terminal temperature/℃
13x-water	159	0.26	56	220
NA-water	115	1.32	55	154
13x-ethanol	167	178	55	346
Activated Carbon-ethanol	81	113	59	153
NB-ethanol	104	106	58	149

It can be seen in Tab.2 that the peak temperature of the prepared adsorbent NA is 115 ℃, less than the peak temperature (144 ℃) of adsorbent 13x, and the adsorbent NA has a larger weight lost rate and a desorption terminal temperature of 154 ℃, which is 66 ℃ lower than that of 13x. These indicate that the adsorbent NA has not only larger adsorption quantity, but also lower desorption temperature, which can be used in adsorption refrigeration system with good performance and developing potential.

Activated carbon has the lowest peak temperature, which suggests that activated carbon-ethanol can be desorbed at lower temperature. The adsorbent NB's peak temperature, desorption terminal temperature and the temperature to maximal weight lost rate are lower than 13x's, and its desorption terminal temperature and initial desorption temperature are equivalent to activated carbon's. The peak temperature of NB-ethanol is slightly higher than that of the activated carbon-ethanol, while activated carbonethanol is superior to NB-ethanol, except that desorption condition of NB-ethanol is similar to activated carbon-ethanol.

In addition, the thermal analysis experiment shows that at temperature of 313 ℃ there is an evident heat liberation peak in thermal analysis figure of 13x molecular sieve. This probably results from a catalytic reaction occurring on ethanol and releasing reaction heat that has an effect on the molecular sieve at this temperature. Therefore, the working pair of 13x molecular sieve-ethanol has a poor heat-steady performance.

2.3 Characteristic curve of adsorption refrigeration

The adsorber temperature rises rapidly in adsorption process because of the emission of adsorption heat at the beginning of adsorption refrigeration. Then it gradually drops to ambient temperature. The evaporator temperature drops rapidly when the refrigeration process begins. Then the temperature increases because evaporator exchanges heat with the fluid in refrigeration room. The refrigeration room temperature drops gradually. When the evaporator temperature and refrigeration room temperature are almost the same and both have the increasing tendency, the adsorbent saturates and adsorption refrigeration finishes. From Fig.5 – Fig.9, we can see that the refrigeration time of molecular sieve-water is the shortest, the midst is prepared NA-water, and the longest is silica gel-water.

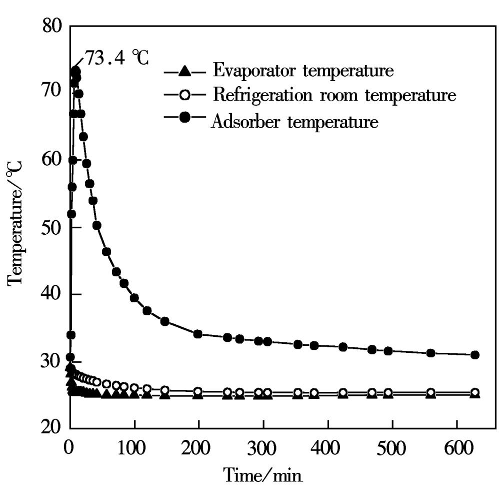

Fig.5 Characteristic curve of adsorption refrigeration for silica gel-water (30.5 ℃)

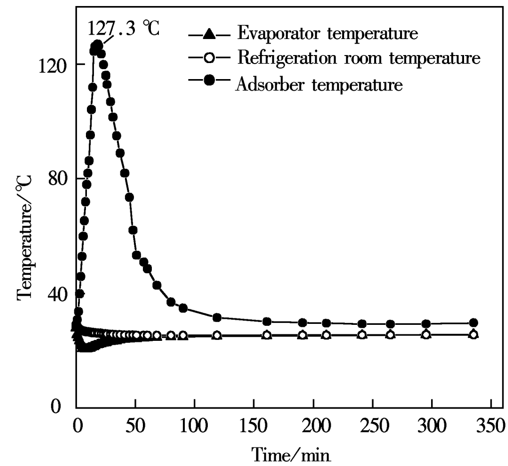

Fig.6 Characteristic curve of adsorption refrigeration for 13x-water (29.5 ℃)

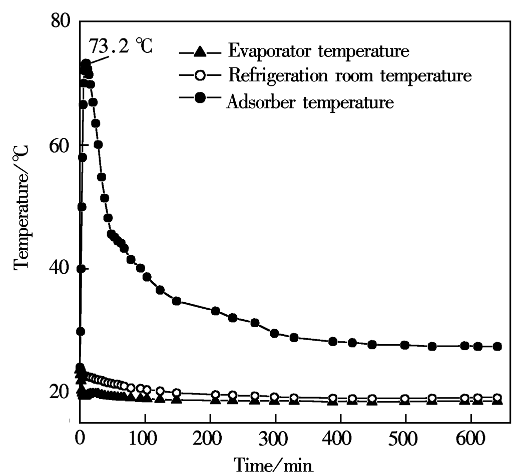

Fig.7 Characteristic curve of adsorption refrigeration for NA-water (29.5 ℃)

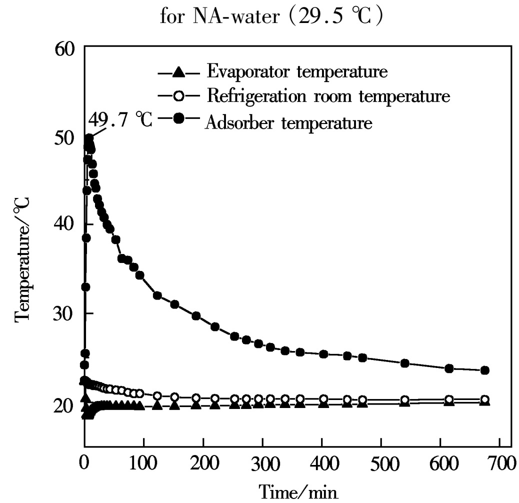

Fig.8 Characteristic curve of adsorption refrigeration for NB-ethanol (24.1 ℃)

2.4 The effect of regenerating temperature on desorption volume

In refrigeration cycle, the more the refrigerant volume gives out during the process for heat and

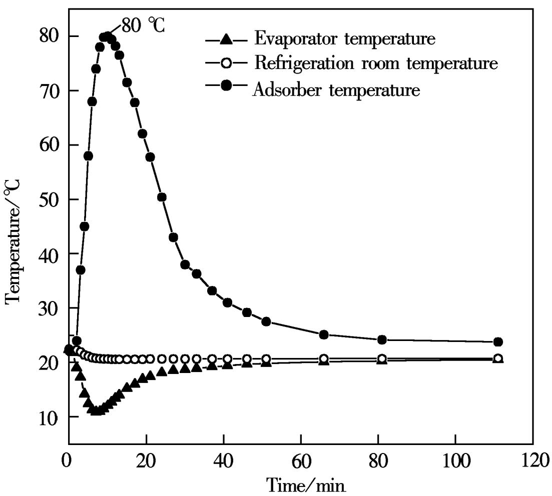

Fig.9 Characteristic curve of adsorption refrigeration for activated carbon-ethanol (29.5 ℃)

desorption, the more capability of the refrigerant's re-desorption is and the better effect of cooling is. Generally, one hopes that not only desorption process can run under the low regeneration temperature, but also larger desorption quantity can be obtained; so that the efficiency of energy use and the coefficient of performance (COP) of adsorption refrigeration system can be enhanced. The value of COP is influenced by many factors, such as round-robin mode of system, refrigeration volume and performance of heat and mass transfer of system, from the simple simulation device mentioned above, and the value of COP can be estimated.

Tab.3 gives desorption and refrigeration volume of desorption working pairs on refrigeration cycles at different regeneration temperatures. It can be seen that desorption volume of self-prepared adsorbent is larger than that of 13x molecular sieve at each regeneration temperature, especially at lower regeneration temperature.

When the regeneration temperature is over 200 ℃, the desorption volume of NA adsorbent increasing is little, which suggests that self-prepared adsorbent NA can work at low temperature and its capability is superior to 13x molecular sieve.

That the 13x molecular sieve's desorption to ethanol is relatively little suggests that it's hard to desorb and regenerate; activated carbon whose adsorption quantity is much larger than that of 13x molecular sieve is easy to adsorb; the self-prepared adsorbent NB has the largest adsorption quantity which can get to 0.572 kg/kg at 150 ℃. All these suggest that self-prepared adsorbent NB has larger adsorption refrigeration volume and there is so good potential that it can substitute for active carbon-ethanol working pair.

Tab.3 Desorption and refrigeration volume of adsorption working pairs on refrigeration cycles at different regeneration temperatures

Sorption working pairs	Desorption temperature /℃	Desorption volume /($kg \cdot kg^{-1}$)	Refrigeration volume /($kJ \cdot kg^{-1}$)
13x-ethanol	100	0.033 1	28
	200	0.086 7	72
Activated carbon-ethanol	80	0.140	118
	120	0.189	159
NB-ethanol	90	0.325	274
	120	0.454	383
13x-water	150	0.572	452
	100	0.078	190
	150	0.118	302
	200	0.158	385
	250	0.186	454
	300	0.21	512
NA-water	100	0.21	522
	150	0.31	756
	200	0.36	883
	250	0.37	903
	300	0.38	922

2.5 Refrigeration volume

Refrigeration volume is an important factor to affect adsorption refrigeration.

Usually, simplified method is adopted to calculate refrigeration volume. The difference of sensible heat is ignored and desorption volume of adsorbent in adsorption refrigeration cycle is used to calculate desorption refrigeration volume. The following is the equation:

Refrigeration volume (Q_{ref}) = (desorption volume) × (gasification latent heat of adsorbent at corresponding temperature)

Tab.3 shows refrigeration volume of different working pairs on refrigeration cycles. It can be found that NA-water has large refrigeration volume of 922 kJ/kg. The refrigeration volume of NA is 1.8 ~ 2.7 times that of 13x at the same condition and the refrigeration volume's reducing of NA following with the reducing of regeneration temperature is slower than other adsorbents. At temperature of 100 ℃, the refrigeration volume after desorption is 522 kJ/kg, which is higher than 13x's (512 kJ/kg). These suggest that self-prepared adsorbent NA not only has large refrigeration volume but also has a wide working temperature using range, and can be used at middle and low temperature. At temperature of 120 ℃, the refrigeration volume of NB-ethanol is 2.4 times that of activated carbon-ethanol; after adsorbent NB is desorbed at 90 ℃, and its refrigeration volume is 1.7

times that of activated carbon's, which is desorbed at 120 ℃. This shows that NB is adsorbent with good capability and development prospect and can be driven by low-temperature heat source such as solar energy etc.

3 Conclusions

1) The maximum adsorption quantity of water on prepared NA arrives at 0.7 kg/kg, which is 2.3 times that of water on 13x. The maximum adsorption quantity of ethanol on prepared NB is 0.68 kg/kg, which is three times that of ethanol on activated carbon.

2) In the view of adsorption refrigeration cycle time, the prepared NA is superior to silica gel but molecular sieve is the best. From the point of utilizing low-temperature waste heat, the prepared NA is a promising adsorbent to substitute for molecular sieve.

3) The refrigeration volume of NA-water is 922 kJ/kg. The refrigeration volume reaches 522 kJ/kg at the regeneration temperature of 100 ℃, which is higher than that of 13x-water at 300 ℃ regeneration temperature (512 kJ/kg). This working pair is suitable for adsorption refrigeration, which uses middle or low temperature heat source.

4) Working pair NB-ethanol has a large refrigeration volume and low regeneration temperature. Its refrigeration volume is 2.4 times that of activated carbon-methanol. It can be well applied in such a situation where large refrigeration volume and low regeneration temperature are required. As a friendly to environment and no public hazard adsorption working pair, the prepared NB-ethanol can substitute for activated carbon-methanol in adsorption refrigeration using low-temperature heat source.

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优良吸附制冷工质对的研究

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摘 要 对水、乙醇和13x分子筛、硅胶、活性炭以及自制吸附剂NA、NB组成的吸附工质对的制冷性能进行了研究.用高真空重量法测取了自制吸附剂NA和NB的吸附等温线;用热分析法对吸附剂的脱附性能进行了分析;在吸附制冷循环实验装置上研究了吸附工质对的制冷性能参数.结果表明:①自制吸附剂NA对水的最大吸附量高达0.7 kg/kg;自制吸附剂NB对乙醇的最大吸附量达0.68 kg/kg,是活性炭对乙醇吸附量的3倍;② NA-水工质对的制冷量是922 kJ/kg,NB-乙醇工质对的制冷量是活性炭-甲醇的2.4倍;③ NA-水和NB-乙醇是环境友好型、无公害的吸附工质对,可替代活性炭-甲醇工质对用于以低温热源驱动的吸附制冷系统.

关键词 吸附制冷,工质对,等温线,制冷量

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