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Experimental Study on Renewable Porous Carbon Dioxide Adsorbent Materials for Space Shuttles

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Abstract: Porous adsorbent material is promising to be used to regeneratively remove CO_2 from space shuttles. In this work, the amount and isosteric heat of CO_2 adsorption in solid amine are experimentally studied at pressures ranging from 0 to 6 bar and temperatures ranging from 20 °C to 60 °C. The amount and isosteric heat of water adsorption in the solid amine is tested at different humidities (relative humidity 30–80%). The effective thermal conductivity of the solid amine at different atmospheres (air, N_2, CO_2 and water), pressures and temperatures is also investigated. The results show that the best temperature for CO_2 adsorption in the solid amine is 45 °C under dry conditions. The amount of water adsorption increases with enhanced humidity, while the isosteric heat of water adsorption remains a constant value. The effective thermal conductivity of the solid amine increases with an increase in pressure. The adsorbed phase (CO_2 and water) in the solid amine makes a contribution to improving the effective thermal conductivity of solid amine particles. The above findings can help design a better adsorption system in space.

Keywords: space shuttle; porous solid amine adsorbent materials; CO_2 adsorption; effective thermal conductivity

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1. Introduction

Before the 1990s, the method used to remove CO_2 from space shuttles was based on lithium hydroxide (LiOH). Though LiOH has a high CO_2 storage capacity (~30 wt%), this material cannot be regenerated [1]. The long-term service of a space station requires that CO_2 sorbent can be easily regenerated to reduce launch weight and storage volume. Later, 5A zeolite was used in space shuttles [2,3]. In recent years, solid amine, regarded as a promising CO_2 adsorbent for space shuttles, has been investigated due to its low regeneration temperature (~60 °C) at vacuum conditions in two-bed amine solids—which can reduce shuttle weight in space—as well as its high adsorption capacity under different humidities [1,4].

Xu et al. [5] prepared a novel CO_2 "molecular basket" adsorbent by synthesizing and modifying a mesoporous molecular MCM-41-type sieve with polyethylenimine (PEI). The effects of the preparation conditions (PEI loadings, preparation methods, PEI loading procedures, types of solvents, solvent/MCM-41 ratios, addition of additive, and Si/Al ratios of MCM-41) on the CO_2 adsorption/desorption performance of MCM-41-PEI were reported. Su et al. [6] modified commercially available Y-type zeolite with a Si/Al molar ratio of 60 (abbreviated as Y60) with tetraethylenepertamine (TEPA) to study the characterization and adsorption/desorption properties of CO_2 from gas streams. The surface nature of Y60 was changed after TEPA modification, which caused a significant enhancement in CO_2 adsorption capacity. Su et al. [7] built a dual-column temperature/vacuum swing adsorption (TVSA) with zeolite 13X to study cyclic CO_2 capture from a gas stream. The results showed that a dual-column TVSA with solid 13X could be a promising CO_2 capture technology. Liu et al. [8] evaluated the adsorption behavior of CO_2 on solid amine adsorbent in simulated flue gas. The effects of amine, temperature, moisture and other factors on the CO_2 adsorption performance of the adsorbent were investigated. The results showed that amine-functionalized XAD-4 resin is a promising adsorbent for CO_2 adsorption. Sanchez-Zambrano et al. [9] studied CO_2 adsorption on mesoporous silica modified with amines by double functionalization. The adsorption microcalorimetric study suggests a change in active site distribution as the amine density increases. Ravi et al. [10] studied amine-oxide mixed materials for CO_2 separation from the bio-hydrogen model. BET analysis confirmed that due to the low surface area of the adsorbent system, the high amine load contributed to the reduction in CO_2 adsorption. Panda et al. [11] synthesized a new type of composite adsorbent by the amine modification of binder-containing zeolite 4A bodies, and its potential application in post-combustion CO capture was evaluated. Fan et al. [12] developed an amine-modified silica adsorbent with high amine efficiency and fast adsorption speed for CO_2 capture by adding amines, including hydroxyl, into mesoporous silica loaded with polyethylene imine (PEI). The adsorbent had good reversibility and the adsorption capacity was basically stable after two adsorption–desorption cycles. Kuang et al. [13] directly modified polyacrylonitrile (PAN) fibers with amination reagent and prepared a series of amine-containing solid fiber absorbents, including diethylenetriamine (DETA), triethylenetetraamine (TETA), tetraethylenepentamine (TEPA), and polyethylene imine (PEI). The results showed that the chemical modification of PAN fiber with amine compounds could significantly improve the adsorption capacity of amine adsorbent for CO_2. Liu et al. [14] prepared solid amine adsorbents by the suspension polymerization of divinylbenzene (DVB) and acrylonitrile (AN), and then amination with TEPA. The factors affecting the adsorption performance of solid amine adsorbents for CO_2, such as amine type, adsorption temperature and moisture, were investigated. Liu et al. [15] selected commercial porous phenolic resin (XAD-761) as the carrier material to prepare solid amine sorbents. The results showed that the Avrami kinetic model was better than the quasi-first-order and quasi-second-order kinetic models for CO_2 adsorption, indicating that the adsorption process of CO_2 by the prepared adsorbent included both physical adsorption and chemical adsorption. Rezaei et al. [16] reported a breakthrough experiment of packed-bed CO_2 adsorption using amine impregnation and amine-grafted silica adsorption material in the presence of SO_2, NO and NO_2 impurities. The effects of temperature, feeding concentration and amine loading on the dynamic adsorption capacity of the adsorbent were investigated. Yilmaz [17] prepared a novel amine-modified hollow mesoporous silica (HMS)@Mg-Al layered dihydroxide (LDH) composite to evaluate its CO_2 adsorption capacity. The amine-modified adsorbent showed stable adsorption performance in four consecutive adsorption/desorption cycles. He et al. [18] prepared a carbon dioxide-imprinted solid amine adsorbent (IPEIA-R) using polyethylene imide (PEI) as the skeleton and glutaraldehyde crosslinked carbon dioxide as the pre-adsorption of PEI. The adsorption results showed that NaBH4 had an imprinting effect on CO_2 and the reduction in the imine group gave the adsorbent higher CO_2 adsorption capacity. Darunte et al. [19] reviewed the latest progress of solid-loaded amines for carbon dioxide capture, with emphasis on amine-functionalized metal–organic framework (MOF) materials. Diamine-functionalized Mg-DOBPDC MOF has good CO_2 capture performance, a unique adsorption mechanism, and good thermodynamic characteristics. Chang et al. [20] synthesized a solid diamine adsorbent and discussed the effects of temperature, the dosage of mixed amine, the mass ratio of DMAEE to PEHA, and the partial pressure of CO_2 on CO_2 adsorption performance. Keramati et al. [21] functionalized activated carbon with two different amines, chitosan and triethylene tetramine. The results showed that the adsorbent functionalized by amine could significantly improve the adsorption capacity of CO_2. Bae et al. [22] functionalized the synthesized mesoporous hollow silica with amine solid adsorbents for CO_2 capture. The morphological, structural, and textural properties of the amine-functionalized mesoporous hollow silica were characterized. In order to alleviate the phenomenon of amine aggregation in solid amine sorbents and achieve efficient CO_2 capture, Zhang et al. [23] synthesized a new dual-functional adsorbent by grafting 3-aminopropyl triethoxylsilane and impregnating tetraethylenepentamine with the original mesoporous silica molecular sieve as the carrier. The effects of organic amine loading, gas flow rate and adsorption temperature on the adsorption performance of CO_2 were studied. Later, Wang et al. [24–27] studied gas adsorption in metal–organic frameworks and found that they were promising as adsorbents which could be coated by the amine.

As reviewed above, the amount and heat of CO_2 adsorption in solid amines are key parameters in space shuttles. In fact, the case of a high amount and a low heat of CO_2 adsorption in a solid amine is the best option for space shuttles. In addition, the vapour existing in space shuttles affects CO_2 capture. During the CO_2 capture process, the adsorption heat will release which increases the temperature in the adsorption bed to lower the CO_2 adsorption amount. The degree of heat accumulation is controlled by the specific thermal conductivity of the solid amine. Therefore, water sorption and thermodynamical parameter measurements are necessary for space shuttle applications. In the present work, the CO_2 adsorption in a solid amine (chemical adsorption) is investigated systematically and the water adsorption in a solid amine is studied, as is the effective thermal conductivity at different pressures, temperatures, and atmospheres (air, N_2, CO_2 and water).

2. Experimental Section

2.1. Material Characterization

Solid amine particles, namely, amine-functionalized porous polyacrylonitrile resin particles, were supplied from the National Key Laboratory of Human Factors Engineering (China). The characteristics of the solid amine, which had a polyethylene polyamine level of ~20 wt%, are shown in Table 1.

Table 1. The details of the adsorbent.

Adsorbent	Solid Amine
Type	Sphere
Particle size (cm)	0.02
Particle density ($g{\cdot}cm^{-3}$)	0.728
BET ($m^2.g^{-1}$)	30.37
Pore diameter (nm)	2.5–40
Micropore volume ($cc{\cdot}g^{-1}$)	0.167

Thermal gravimetric analysis (TGA, Eltra, Germany) and differential scanning calorimetry (DSC, NETZSCH, Germany) were performed. The solid amine particle was heated and weighted from 30 to 500 °C at the rate of 2 °C/min under a N_2 (99.999%) atmosphere.

2.2. Experimental Method

2.2.1. CO_2 Adsorption in the Solid Amine

The adsorption calorimeter system used the PCT Proe and E and Calvet calorimeter device (PCT and C80, French) [28], and the accuracy of the adsorption calorimeter system was validated in refs. [29,30]. The solid amine particles in the C80 battery were heated by a vacuum C80 at 50 °C for 20 h to remove the water and gas adsorbed by the solid amine particles in the air, serving as a pretreatment. The gas supply system was connected to the adsorption system which had three high-purity gas supply lines: carbon dioxide (CO_2), nitrogen (N_2), and helium (He). Nitrogen was used to drive the pneumatic valve in the PCT, and the sample cell in the C80 was volumetrically calibrated with helium. CO_2 was then fed into the sample cell as an adsorbent gas to meet the set pressure. Different target temperatures were controlled by C80. During the adsorption process, PCT and C80 were used to measure the adsorption capacity and heat synchronously. The test signal was recorded by the data acquisition system. Then, the isosteric heat of CO_2 adsorption in the solid amine could be measured directly by the software in C80.

2.2.2. Water Adsorption of the Solid Amine

The water adsorption in the solid amine was tested by using thermogravimetric combined differential scanning calorimetry analysis (TGA-DSC, French). The solid amine particles in the cell were pretreated at 50 °C and heated by TGA under vacuum for 20 h. Then, nitrogen gas under different humidities was set to the cell at the temperature of 30 °C. The TGA tested the mass change and the DSC recorded the heat of the water adsorption during the process of water adsorption.

2.2.3. Effective Thermal Conductivity of the Solid Amine

The effective thermal conductivity of the solid amine in different environments was measured by a Hot Disk 2500S thermal constant analyzer based on a transient plane source method. The 1.5% accuracy of this instrument was validated by NIST1453 (0.032 W/m·K) at 25 °C. The detailed process has been described elsewhere [31].

In the different pressure conditions in the N_2 atmosphere, the solid amine was put into the container kept at 50 °C under vacuum for 5 h as the pretreatment. Then, the different pressures were set through the gas manometer; the accuracy of gas manometer was 1.0%. In a N_2 atmosphere under atmospheric pressure, different temperatures were also set. The accuracy of the temperature was ±0.5 °C. The effective thermal conductivity of the solid amine was recorded three times at every fixed pressure and temperature to obtain accurate results.

In the condition of different temperatures with controllable constant temperatures, two solid amine cases with no and saturated CO_2 adsorption were tested, respectively. The controllable constant temperature environment was provided by a hygrothermostat with uncertainties of ±0.5 °C for temperature. Different temperatures were set. The effective thermal conductivity of solid amine was also recorded three times at every fixed temperature.

In the condition of different humidities, the controllable constant temperature and humidity environment was provided by a hygrothermostat with uncertainties of ±0.5 °C for temperature of 25 °C and ±3% for the relative humidity. The water uptake of the materials was measured by an electronic balance with an accuracy of ±0.1 mg.

Adsorbing the water vapour with the solid amine was completed as follows: firstly, the solid amine was placed in the hygrothermostat and dried at 50 °C under 1.0 bar for 48 h. Then, the dried sample was wrapped in a plastic bag to keep it away from the room air. Secondly, when the temperature and humidity of the hygrothermostat reached the pre-set values, the dried samples were put into the hygrothermostat to absorb water vapor. The weight of the sample was recorded at a series of time steps unless the weight did not increase any more when the saturated adsorption was reached. Finally, the effective thermal conductivity of the solid amine was measured more than three times after the adsorption balance was obtained. The adsorption and thermal conductivity measurement were conducted from low humidity to high humidity and dried once.

3. Results and Discussion

3.1. The Basic Properties of Adsorbent

Figure 1 shows the structural stability of the solid amine at different temperatures. The solid amine lost only ~10 wt% of its original mass at a temperature of ~200 °C. The slope of the mass loss curve changed from a gradual slope to a steep slope at 250 °C. The amine completely disintegrated around 400 °C. This means that the solid amine had good thermal stability.

Figure 2 shows the heat capacity of the solid amine at the temperature range of 35 to 80 °C, tested by microcalorimetry (C80, French). The heat capacity of the solid amine increased slowly with an increase in temperature, and the heat capacity of the solid amine decreased slightly from 70 to 80 °C, which means that the solid amine could store more energy.

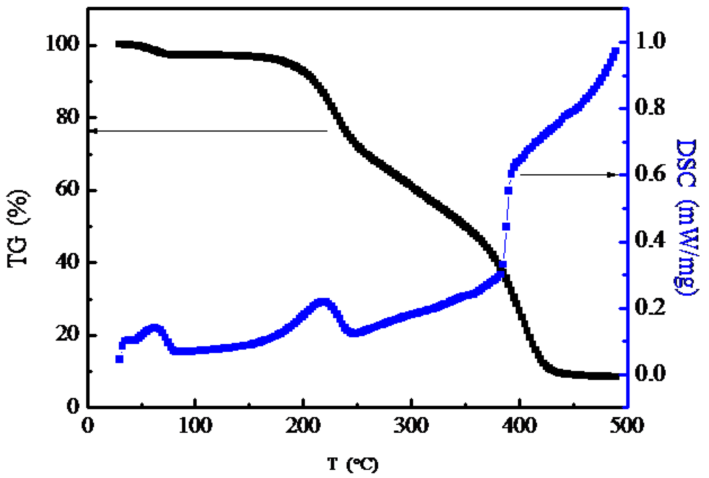


Figure 1. Thermogravimetric (TGA) and differential scanning calorimetry (DSC) analysis of the solid amine.

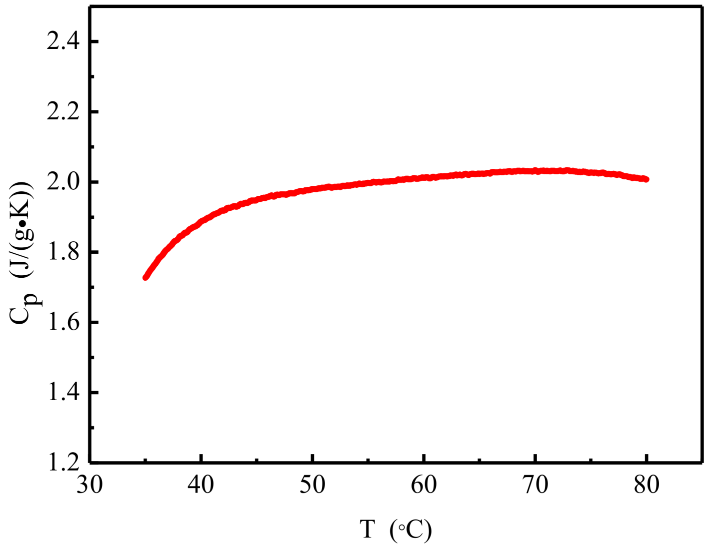


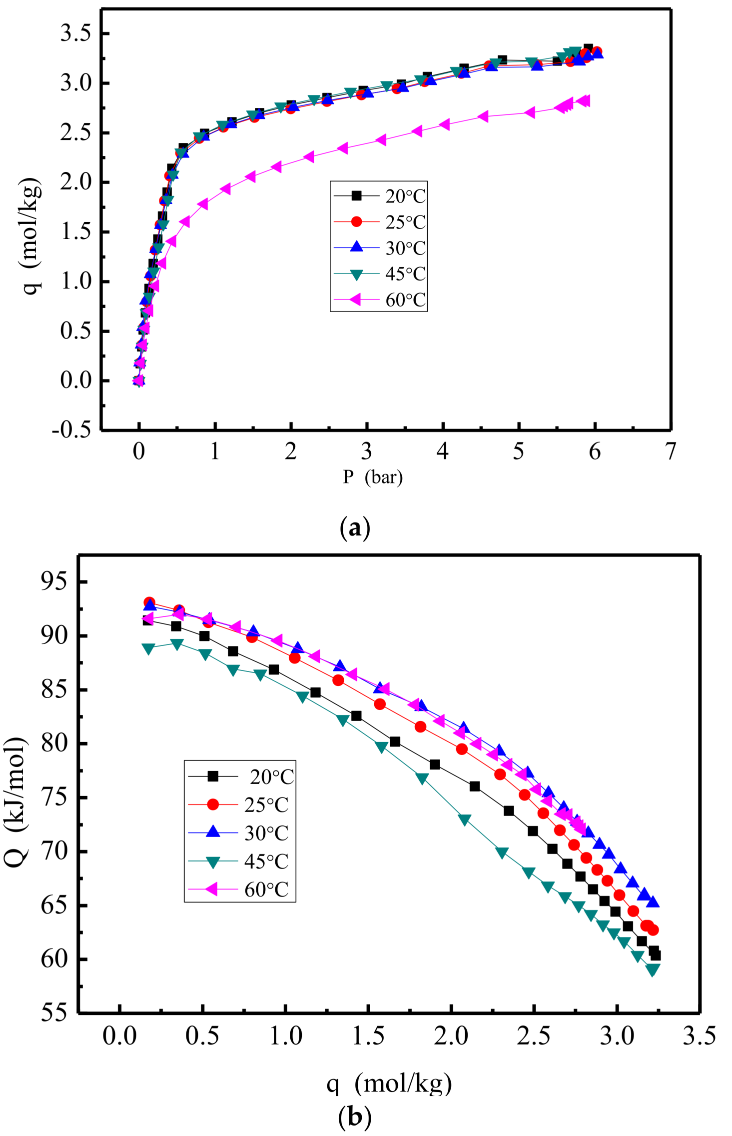
Figure 2. Heat capacity of the solid amine at different temperatures.

3.2. CO_2 Adsorption in the Solid Amine

Figure 3a shows the CO_2 adsorption in the solid amine at the temperature range of 20 °C to 60 °C and pressure ranging from 0 to 6 bar. The amount of adsorption increased rapidly at low pressure (0–1 bar), then increased slowly at high pressure (1–6 bar) because the CO_2 adsorption in the solid amine was mainly chemical adsorption, as shown in Equation (1).

$$2R_xNH_y + CO_2 = \left(R_xNH_y\right)_2CO_3 + \Delta H \quad (1)$$

At low pressure, the chemisorption of CO_2 in the amine-based adsorbent was more dominant over physisorption; the CO_2 molecules interacted with CO_2 to form ammonium carbamate in the dry condition [32,33]. With an increase in pressure, the amine–CO_2 occupied the CO_2 molecule completely. Little physical adsorption occurred at the micropore. The effect of temperature on the amount of adsorption was inconspicuous at the study temperature range because the chemical adsorption needed a suitable activation energy at a certain temperature. The CO_2 adsorption decreased with increased temperature; at a high temperature, the amine may have been volatile and the adsorption amount at the micropore absorbed by the physical adsorption desorbed, which may be different from refs. [6,9].



(**a**)

(**b**)

Figure 3. Amount and isosteric heat of CO_2 adsorption in the solid amine. (**a**) Isotherm adsorption in the solid amine. (**b**) Isosteric heat of adsorption in the solid amine.

The isosteric heat of the adsorption decreased with an increase in the adsorption amount, which indicates that the interaction between the adsorbed molecules will become weak with an increase in the adsorption molecule. The shape of the decrease in the isosteric heat of adsorption in the solid amine was convex. Figure 3b shows that the isosteric heat of CO_2 adsorption in the solid amine decreased with an increase in temperature, then decreased and increased again. The minimum value was at 45 °C under dry conditions, which means that the heat release was at a minimum at this fixed temperature.

Parasitic energy is an index to consider desorption condition optimization in the separation process design. This indicator is a measure of power loss caused by the increased carbon capture and storage (CCS) process [34]. For this work, the material with the least parasitic energy was the best material. The total amount of energy required for CCS was the amount of heat required for separation [35]. This consists of two components: (1) the energy required to heat the adsorbent to achieve the desorption conditions (sensible heat); (2) the energy required to remove the adsorption process. For the endothermic process of CO_2 desorption, we need to provide an energy equivalent to adsorption heat Q in atmospheric pressure. The total thermal energy $Q_{thermal}$ per kilogram of captured CO_2 (m_{CO_2}) is given by:

$$Q_{thermal} = \frac{C_p m_{adsorbent} \Delta T}{m_{CO_2}} + \frac{Qq}{m_{CO_2}} \quad (2)$$

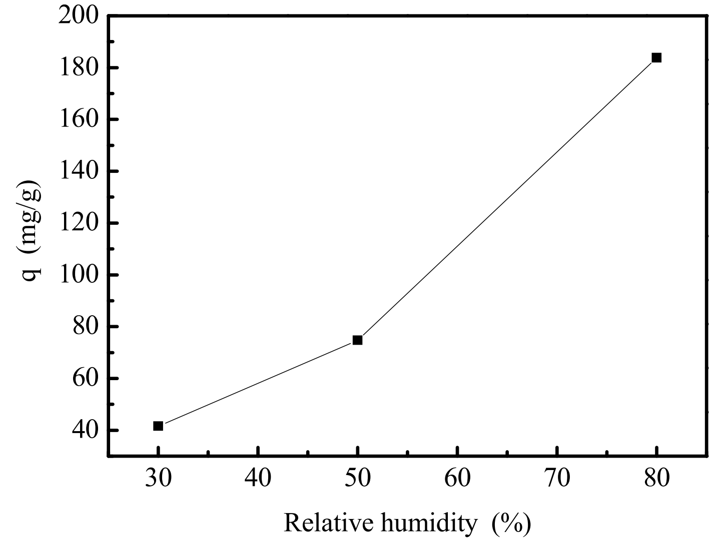
The parameters in the equation are illustrated in Table 2. The first term corresponds to the sensible heat requirement to drive the process by heating the bed. C_p is the specific heat capacity of the adsorbent. $m_{adsorbent}$ is the total mass of the adsorbent. ΔT is the temperature difference between the adsorption and desorption conditions. The second part of heat energy is the energy required for CO_2 desorption, which is composed of working capacity and adsorption heat. Working capacity is defined as the difference between the amount adsorbed under gas conditions (1 bar, 25 °C) and the remaining amount in the material under desorption conditions. The final parasitic energy for the solid amine was 2286.3 kJ/kg_{CO_2}, the sensible heat was 604.5 kJ/kg_{CO_2}, and the energy needed to regenerate was 1681.8 kJ/kg_{CO_2}.

Table 2. The parameters of the parasitic energy model.

Parameters	Solid Amine
C_p [kJ·(kg K)$^{-1}$]	1.90
ΔT(K)	35
${m_{CO_2}}/{m_{adsorbent}}$ (kg·kg^{-1})	0.11
Q (kJ·mol^{-1})	74
${m_{CO_2}}/{q}$ (g·mol^{-1})	44

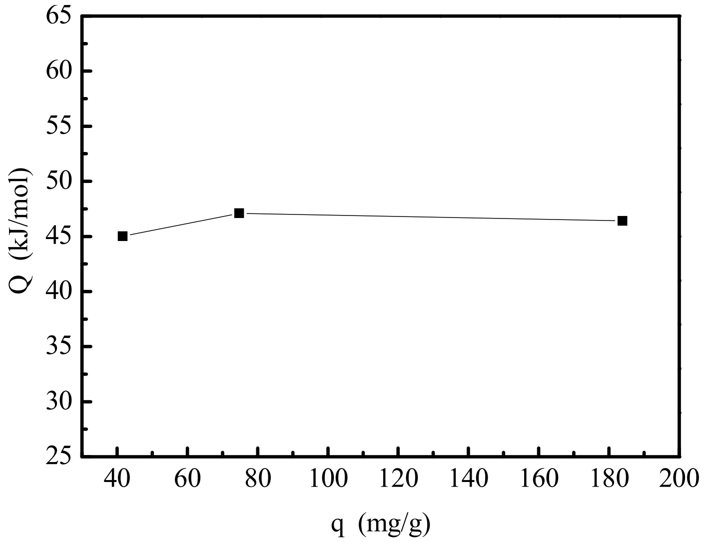
3.3. Water Adsorption in the Solid Amine

Figure 4a,b show the amounts and the isosteric heat of the water adsorption at different humidities at an atmosphere of 30 °C. Figure 4a shows that the amount of water adsorption increases exponentially with an increase in humidity, which means the water can be easily adsorbed in the cavity of the solid amine. The solid amine has a rich hydrogen bond, and thus the water molecule and solid amine form the hydrogen bond easily. Figure 4b shows that the isosteric heat of the water adsorption keeps at a constant value with an increase in water adsorption amount. Perhaps at low coverage the heat of the water adsorption would be high.



(**a**)

Figure 4. *Cont.*



(**b**)

Figure 4. Amount and isosteric heat of water adsorption in the solid amine. (**a**) Isotherm adsorption in the solid amine. (**b**) Heat of water adsorption of the solid amine at 30 °C.

3.4. Effective Thermal Conductivity of the Solid Amine

3.4.1. The Effect of Pressure

Figure 5 shows the effective thermal conductivity of the solid amine at different pressures (0–10 bar) and ambient temperatures. The effective thermal conductivity of the solid amine in the N_2 atmosphere increased in an 'S' shape, which is consistent with ref. [3]. The effective thermal conductivity of the solid amine included gaseous thermal conductivity, adsorbed thermal conductivity, and solid thermal conductivity at low temperature [3].

$$\lambda_{eff} = \frac{\lambda_{wvo}}{1+2\beta Kn} + \frac{\lambda_{c0}(1+a_{\lambda c}(T-T_0))\sqrt[3]{(1-\varphi)}}{\mu} + \frac{\lambda_{w0}(1+a_{\lambda w}(T-T_0))\sqrt[3]{q(1-\varphi)\frac{\rho_z}{\rho_w}}}{\mu} \tag{3}$$

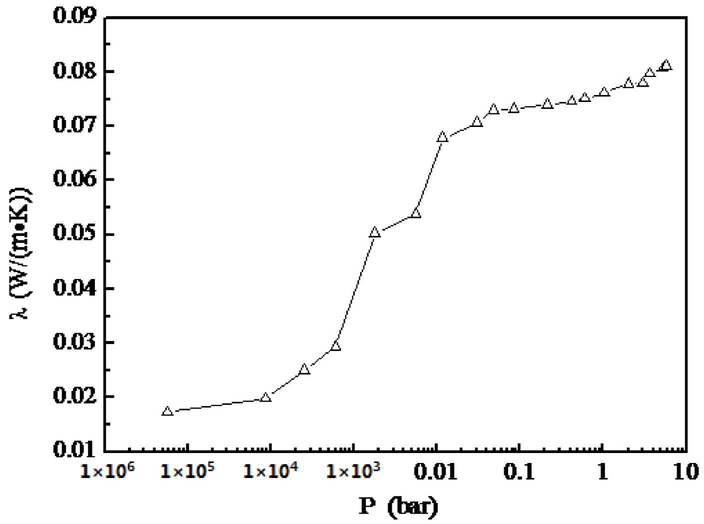
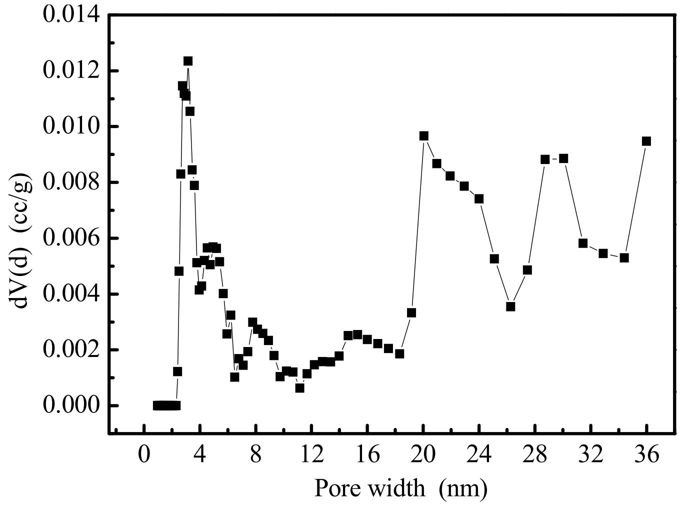


Figure 5. Effective thermal conductivity at different pressures.

From Equation (3), it can be noted that filling gas can greatly influence the effective thermal conductivity of a solid amine. This can be explained by the Knudsen number (*Kn*), which is defined by the mean free path of the gas molecules divided by the pore size and adsorbed N_2. The pore size of the solid amine is calculated by nonlocal density functional theory (DFT) in combination with Barrett–Joyner–Halenda (BJH) provided by the manufacturer, as shown in Figure 6. It can be noted that the solid amine contains wide mesopores of 4 nm (check from fitting, especially for BJH). At low pressure (0–0.0001 bar), the variation mainly comes from the gaseous thermal conductivity because, at this region, $Kn > 0.01$, the collision between gas molecules increases with increasing gas pressure, and the exchange of energy between gas molecules is directly proportional to the number of gas molecules. At medium pressure (0.0001–0.01 bar), the increase in effective thermal conductivity comes from the gaseous thermal conductivity and adsorbed N_2. At this region, the adsorbed N_2 increases fast with the increase in pressure, which makes a contribution to the effective thermal conductivity of the solid amine. At high pressure (0.01–5 bar), adsorbed N_2 reaches saturation and the stagnant gas can be considered as a continuum with a thermal conductivity independent of gas pressure, which results in the saturation trend of the effective thermal conductivity.



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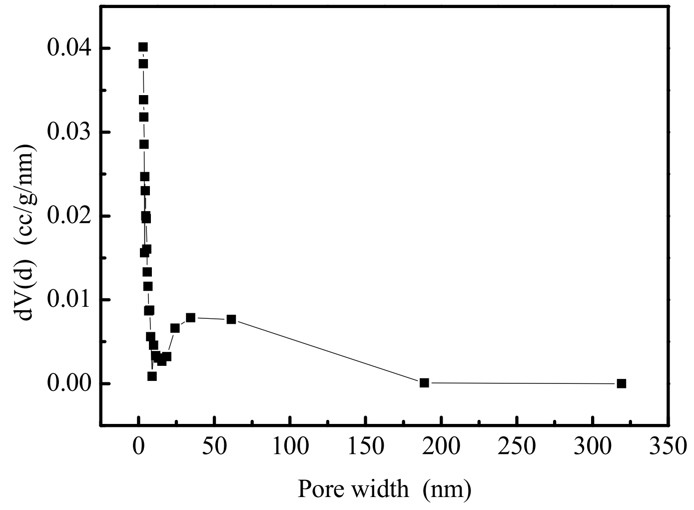

(**b**)

Figure 6. Distribution of the pore width of the solid amine. (**a**) Pore size distribution calculated using the DFT method. (**b**) Pore size distribution calculated using the BJH method.

3.4.2. The Effect of Temperature at Different Atmospheres

Figure 7 shows the effective thermal conductivity of the solid amine at different temperatures and different atmospheres: N_2, air, and adsorbed CO_2. The effective thermal conductivity of the solid amine in the N_2 atmosphere was lowest, while the highest was the condition of adsorbed CO_2. However, the gaseous thermal conductivity was that N_2 > air > CO_2. The main difference came from the adsorption phase. There was a little CO_2 in the air which was adsorbed by the solid amine. The adsorbed CO_2 made the effective thermal conductivity higher than that in the nitrogen atmosphere. The effective thermal conductivity decreased with increasing temperature because the amount of adsorption decreased, especially for the adsorbed CO_2, which meant that the kind of adsorbed gases affected the effective thermal conductivity of the adsorbent.

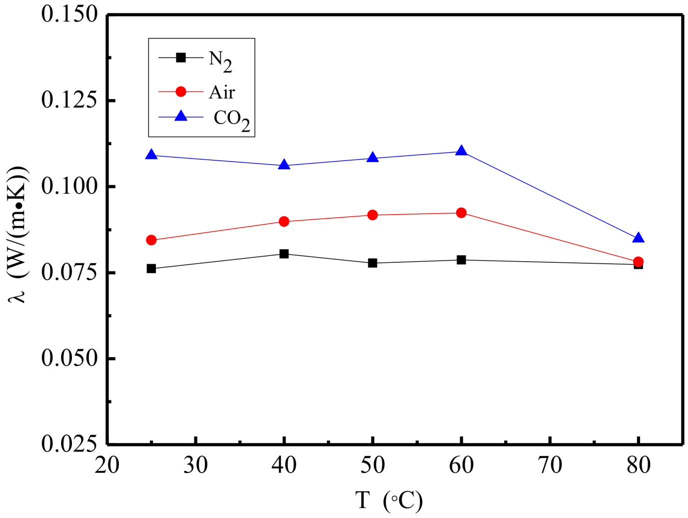

Figure 7. The effective thermal conductivity of the solid amine at different temperatures and different atmospheres.

3.4.3. The Effect of Humidity on the Effective Thermal Conductivity

Figure 8 shows the effective thermal conductivity of the solid amine at different humidities at an air atmosphere of 25 °C. The water uptake increased slightly with the increment of humidity when the humidity was less than 50%, then increased rapidly with increases in humidity over 50%, which was similar to water vapor sorption in silica nanoporous materials [36]. This implies that the surface of the solid amine was firstly covered by the monolayer water molecules and then the multilayer adsorption occurred. The effective thermal conductivity of solid amine increased with an increase in humidity. The key factor is that the increase in the thermal conductivity of the absorbed water was significant with the increase in gaseous thermal conductivity.

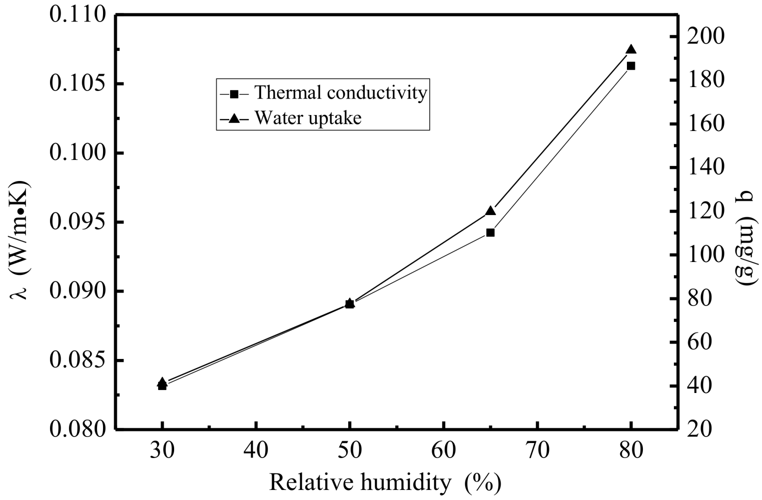

Figure 8. Effective thermal conductivity and water uptake of the solid amine at different humidities.

4. Conclusions

The solid amine, which is a promising option to regeneratively remove CO_2 from space shuttles, was studied systematically. The amount and heat of CO_2 adsorption in the solid amine was tested experimentally. The water adsorption at different humidities was investigated, and increasing the humidity increased the amount of water adsorption in the solid amine. The effective thermal conductivity of the solid amine was also studied at different pressures in a N_2 atmosphere. The results showed that the effective thermal conductivity increased in the shape of an 'S'. At different atmospheres, such as air, N_2, and adsorbed CO_2 at different temperatures, the amount of adsorption played an important role in the effective thermal conductivity. The effective thermal conductivity of the solid amine increased with an increase in humidity. In fact, the effect of water vapour should be considered during CO_2 adsorption. In future, we can test the carbon dioxide adsorption capacity in solid amines under different humidity conditions.

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