



Inorganic composite sorbents for water vapor sorption: A research progress

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ABSTRACT

The inorganic composite sorbent provides one of the feasible solutions for water vapor sorption due to large water uptake, high sorption/desorption rate, excellent thermal stability and cycle performance. Additionally, it is also an ideal material for the desiccant air conditioning. This paper reviews inorganic composite sorbents researched in the past two decades, including silica gel-based sorbents, activated carbon-based sorbents and zeolite molecular sieve-based sorbents. Based on a comparative study of such composite sorbents, the paper unrolls a comprehensive picture of the progress thereof, in which the advantages and disadvantages of each sorbent are briefly depicted.

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1. Introduction

On the Earth, fresh water only accounts for 2.53% of the total water reserves, and a majority of fresh water (68.7%), existing in the two poles and high mountain regions, can hardly be used directly. At present, most of the fresh water comes from underground, lake and river water. However, it has been exhausting rapidly due to gradual natural environmental degradation. In contrast, human requires a growing amount of fresh water with social and economic development, which emergently calls for the collection of renewable freshwater resources [1].

The atmosphere stores approximately 14,000 km³ fresh water, more than 10 times the surface fresh water on the Earth [2]. Therefore, renewable technologies of fresh water production have become one of the important solutions to solve the fresh water crisis. At present, frequently-used methods are mechanical compression/condensation [3–5] and sorption [6–9]. The former is not desirable for large-scale commercial implication because of high energy consumption and low efficiency. Comparatively, the sorption method has attracted considerable attention of many researchers due to high efficiency, low energy consumption, high cycling stability, and eco-friendly and renewable sorption technologies.

Physical sorbent displays high specific surface area, low sorption heat, and high sorption/desorption rate. It is widely used in dehumidification and air purification, such as silica gel [10,11], activated carbon [12,13] and zeolite molecular sieves [14,15]. However, limited by low specific water sorption capacity, it can hardly satisfy the requirements of atmospheric water extraction. Chemical sorbent with large water uptake, including halogen salts [8,16] and metallic oxides [17], has to distressfully face the problems of large volume expansion and serious agglomeration which reduce mass and heat transfer and cycle performance. To solve the problems of physical and chemical sorbents, porous media are used to produce inorganic composite sorbents [18–20] with the outstanding water sorption performance. When chemical sorbent is distributed in porous medium, its surface area contacted with the air is increased, and the volume expansion and agglomeration are slowed down. As a result, the water sorption rate is improved. Compared with inorganic sorbent, organic sorbent can hardly be practically applied in the field of water vapor sorption for low water sorption capacity/rate, poor thermal stability and high costs. Therefore, organic sorbent is not a focus of this paper.

This paper summarizes the research and development of inorganic composite sorbent in the field of water vapor sorption, particularly silica gel-based, activated carbon-based and zeolite molecular sieve-based composite sorbents.

2. Principles of sorption

The sorption process is closely related to intermolecular forces, as well as the surface properties of sorbent. According to the

interaction between sorbent and adsorbate molecules, the sorption process can be divided into physisorption and chemisorption.

2.1. Physisorption

Physisorption [21,22] is caused by the van der Waals force existing between sorbent and adsorbate molecules without any chemical bond rupture or formation. Physical sorbent has a lot of outstanding advantages, such as low sorption heat, low activation energy, high sorption/desorption rates and excellent reversibility. Therefore, they have been widely employed in dehumidification and purification. At present, silica gel, activated carbon and zeolite molecular sieves are the most popular physical sorbents.

Physical sorbent supports multilayer sorption, and its sorption capacity is closely related to specific surface areas and surface properties. To increase the specific surface area, physical sorbent is always prepared in special morphology and structure, such as the 1D acicular structure [23], 2D planar porous structure and 3D porous structure [24,25]. Synthesis methods include sol-gel method [26], solvothermal synthesis method [27], micro-emulsion method [28], spray drying method [29], molecular self-assembly method [30] and so on.

2.2. Chemisorption

Chemisorption [31,17] is caused by the reaction between adsorbates and surface active centers of sorbents. Electron transfer, atomic rearrangement and bond rupture or formation always occurs in the process of chemical adsorption. Therefore, chemisorption features high sorption heat and activation energy, and selective sorption. Commonly used chemical sorbents include halogen salts, metal hydrides and metallic oxides. Chemisorption layers are always monomolecular when compared with physisorption with poly-molecular layer sorption, but chemical sorbents are superior to physical sorbents in water sorption capacity. The reason is that chemical sorbents participate in sorption completely, while physical sorbents partly (the surface only). During the process of chemisorption, a new phase forms on the surface of the sorbent, separating the two phases of the sorbent and adsorbate. Driven by concentration gradients and chemical potential, the adsorbate diffuses in the solid phase of the sorbent through the lattice vibration, defect motion and valence state change. The adsorbate cannot stop passing through the new phase until sorbent has been reacted. Limited by the diffusion process of the adsorbate, chemisorption shows a low sorption rate.

In addition, due to large volume expansion and serious agglomeration, chemical sorbent performs poorly in mass and heat transfer Table. 1.

2.3. Composite sorption

In the 1990s, Levitskii and Aristov [32,33] reported a series of SWS materials for the first time which are different from pure

Table 1
The comparisons of sorption principles.

	Physisorption	Chemisorption	Composite sorption
Sorption force	Intermolecular force	Chemical force	Intermolecular and chemical force
Sorption layer	Multilayer	Monomolecular	Multilayer
Water uptake	Low	High	Moderate
Sorption rate	High	Low	Moderate
Sorption heat	Low	High	Moderate
Cycle performance	Good	Poor	Good

physical and chemical sorbents. SWS materials [34–36] are composite sorbents prepared with chemical sorbents and porous matrixes. When chemical sorbent is injected into the porous medium, its surface area contacting with the air is increased, which greatly enhances its sorption rate. Besides, the volume expansion and agglomeration of the chemical sorbent can be prevented effectively because it is segregated by the porous medium. The physicochemical properties of SWS composite sorbents always refer to the water vapor sorption properties, including the equilibrium sorption capacity, energy storage, sorption/desorption rate and thermal conductivity [37,38].

Composite sorbents are studied for primarily two purposes:

1. To improve the heat and mass transfer properties of chemical sorbents [18]. First, chemical sorbent is injected into microporous matrix to increase heat and mass transfer rates. Second, metal or activated carbon with high thermal conductivity is mixed with the composite sorbent to enhance the thermal conductivity of the matrix.
2. To improve the equilibrium sorption capacity of composite sorbents [19]. Increasing the content of the chemical sorbent is the most effective way to improve the equilibrium sorption capacity. The content of the chemical sorbent depends on the pore volume of the matrix adjusted by the specific surface area, pore size and pore distribution.

Chemical sorbents can be mixed with or injected into the media to prepare composite sorbents. To increase the thermal conductivities of the media, the mixtures of composite sorbents and the high heat transfer phases are compacted. However, its diffusion coefficient cannot avoid decreasing. For SWS composite sorbents prepared with porous media and hygroscopic salts, their water sorption properties can be controlled by the following aspects:

1. Adjust the pore structure of the matrix, including the pore size and distribution;
2. Adjust the components of the chemical salt injected;
3. Adjust the content and state of the salt in the pores of the matrix;
4. Adjust the aggregation state (e.g. compaction density) of the porous media; and
5. Add materials with high thermal conductivity into composite sorbents.

3. Inorganic composite sorbents

3.1. Silica gel-based composite sorbents

3.1.1. Silica gel matrix

Porous silica gel is a type of amorphous synthetic silica. It is widely used as a desiccant, due to large sorption rate, and low regeneration temperature (150 °C). The hydroxyls (silanol groups

or $\alpha(\text{OH})$) on the surface determine its surface physical/chemical properties, which can adsorb water or polar organics. Research results indicate that the first layer of water molecules is adsorbed on the surface of silica gel due to the hydrogen bonds between water molecules and silanol groups; and when multi-layers are adsorbed, hydrogen bond clusters form on the surface. That is, the water molecules in the gas phase and those fixed on the surface of silica gel are also combined by hydrogen bonds. The sorption heat of silica gel is approximately 10.5 kcal/mol, equaling the condensation heat of water vapor [35].

According to sorption characteristics of silica gel, its water sorption capacity depends on the density of $\alpha(\text{OH})$. For conventional amorphous silica gel, the density of silanol groups falls within a narrow range of 4.3–5.8 OH/nm² [39,40]. When the temperature exceeds 200 °C, silanol groups will come off from the silica surface [39]. Therefore, attention shall be given to controlling the drying temperature.

Limited by some intrinsic defects, silica gel alone fails to play an important role in water vapor sorption. Such as, silica gel displays a very low sorption capacity (40% at most) and poor thermal stability in contrast with chemical sorbents. Besides, microporous silica gel shows a low sorption rate at low ambient humidity and can hardly be desorbed; macroporous silica gel, with high desorption rate, adsorbs limited amount of water [41]. Doping silica gel with metal ions is an effective method to improve its sorption characteristics because the bonds between metal ions and the surface silicon atoms can reduce the sorption energy of the active centers on the surface. Okada [42] and Li et al. [43] prepared silica gel doped with titanium ion by using the sol–gel method. One of the obvious defects is that the organic silicon and metal used therein are costly and non-environmentally friendly. Chung et al. [44] reported the technology of preparing boron doped silica gel using the neutron radiation method. However, since the neutron radiation requires high experimental equipment and environment, the synthesized way cannot be applied on a large scale. Fang et al. [45] synthesized a series of modified silica gel sorbents by using doping with Al, Ti, and Co ions. Metal ions replaced silicon atoms to enter into silica tetrahedron skeletons, strengthening thermal stability of silica gel. Moreover, the doped silica gel increased specific surface area, pore diameter, volume and saturated sorption capacity. Aluminum (5.53% by mass) doped silica gel had a high saturated sorption capacity of 148.8 g/m², 68.72% higher than that of pure silica gel. But there was still an intractable issue: the participation of metal ions changed the electronic structure of the silanol groups, leading to irreversible chemisorption. As a result, the desorption activation energy increased, which reduces the recycle performance.

3.1.2. CaCl_2 /silica gel composite sorbents

CaCl_2 as an important hygroscopic salt, non-toxic, cheap and powerful in water sorption, is widely used as a desiccant. However, since its porous structure is not stable, contact area with the water molecules is limited, and the distance of mass transfer from one bulk phase to another is large. Therefore, low sorption rate is one of the significant drawbacks. In addition, the surface of CaCl_2 powder can form a thin liquid layer after adsorbing water vapor. During drying process, the crystalline grain of CaCl_2 increases. Consequently, the heat and mass transfer from one phase to another is difficult for water molecules. Therefore, its cycle performance is poor. When CaCl_2 is loaded on porous silica gel, the contact area with water vapor is greatly increased. Fig. 1 illustrates the process of extraction water vapor of SWS composite sorbents. Firstly, CaCl_2 distributed in the pores of silica gel adsorbs water vapor and then forms $\text{CaCl}_2 \cdot 0.33\text{H}_2\text{O}$ with stable crystal structure, corresponding a short platform on the sorption isotherm. Secondly, the $\text{CaCl}_2 \cdot 0.33\text{H}_2\text{O}$ crystal phase adsorbs water vapor to

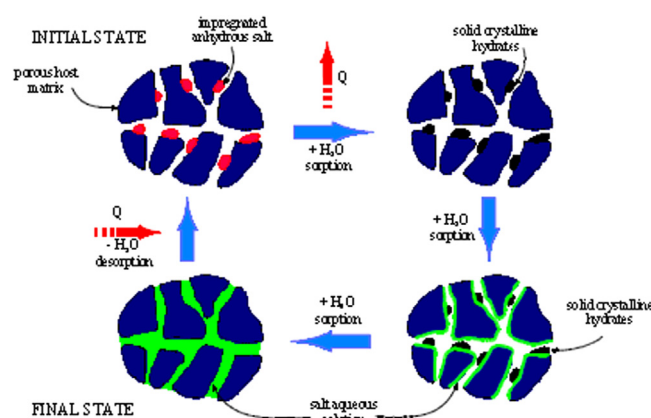


Fig. 1. Scheme of water sorption on SWS-1L [41].

form $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ [46]. Finally, the hygroscopic salt fills the pores of silica gel in the form of liquid.

Apart from water uptake, adsorption rate is also an important indicator to evaluate adsorption performances, which can be estimated based on the slope of the adsorption curve. The formula for calculating the adsorption rate is shown below:

$$r_a = \left(\frac{\partial D_a}{\partial t} \right)_{T, RH}$$

where r_a is the adsorption rate, $\text{g kg}^{-1} \text{min}^{-1}$; D_a and t are adsorption capacity (g g^{-1}) and tested time (s) respectively. It has been proved that the CaCl_2 /silica gel composite sorbent outperforms pure silica gel or CaCl_2 in sorption capacity and rate. For example, Zhu et al. [47] found that the water uptake of the CaCl_2 /silica gel composite sorbent could reach as high as 1.06 g/g at 30 °C. At present, porous silica gel injected into cheap calcium chloride is widely used in sorption refrigeration [49,50], gas desiccation, thermal storage and water vapor sorption [8,51].

Sorption properties of the CaCl_2 /silica gel composite sorbent are adjusted by the ambient temperature and humidity. At a specific temperature, the sorption capacity and rate of the composite sorbent increase as the relative pressure of water vapor rises, which are determined by the diffusion process. When the composite sorbent reaches the sorption equilibrium where the sorption rate equals the desorption rate, macroscopically, sorption saturation is realized. When the relative pressure goes up, the probability of both water molecules and composite sorbent also goes up, thus the sorption rate is higher than the desorption rate. The unbalanced sorption/desorption rates lead to the increase in the sorption capacity. Bu et al. [56] reported that the water uptakes were 10.3, 14.0 and 15.0 g/100 g respectively at the humidity of 20% for the CaCl_2 /silica gel composite sorbent with the CaCl_2 content of 37.75 wt% when the sorption times were 0.5, 1 and 1.5 h, while the values increased to 14, 20 and 23.5 g/100 g respectively at the humidity of 30%. When the relative humidity was adjusted to 50%, the composite displayed 25, 33 and 36 g/100 g at the same sorption time. It is clearly obvious that the sorption rate is also relative with water vapor pressure. During the process of desorption, the environmental humidity also affects the dehumidification performance. Water sorption isobars were tested at different partial water vapor pressures ranging from 8 to 133 mbar [33,54]. All the curves were found to be similar but shifted and partially extended along the temperature axis. Each curve presented a plateau corresponding to $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, the plateaus being longer for low vapor pressures. Cortés et al. [52] reported that desorption temperature was lower at a low relative pressure for the CaCl_2 /silica gel composite sorbent. When the relative pressure is a constant, the environmental temperature rises, causing a sharp drop of the

sorption capacity. When the relative humidity reached a constant state of 0.9, the CaCl_2 /silica gel composite sorbent had a maximum equilibrium sorption capacity of 1.06 g/g at 30 °C but only 0.23 g/g at 70 °C [47]. At constant temperature and humidity, the sorption rate of the composite sorbent decreases gradually with the increase of the amount of water adsorbed. Because the contact area between composite sorbent and water vapor is decreased, the mass transfer distance is lengthened. Kinetics of water sorption in porous media is a subject of numerous studies, and its value is related to diffusion coefficient. The molecular, Knudsen and surface diffusion are considered as main transport mechanisms in pores, thus the overall diffusion coefficient includes these three contributions [48]. For the CaCl_2 /silica gel composite sorbents, the apparent water diffusivity depends on the local slope of their water sorption isotherm. Aristov et al. [51] reported that the pore diffusivity of water in the temperature range 33–69 °C was calculated from experimental data $(0.24 \pm 0.12) \times 10^{-6} \text{ m}^2/\text{s}$, which was approximately 10 times lower than the Knudsen pore diffusivity estimated for silica gel. Dawoud et al. [8] evaluated the kinetic curves of water sorption by measuring the maximum half-time. This time appears to be only slightly dependent on both test temperature and water vapor pressure. The half-time of pure mesoporous silica is only 1.13 min at 50 °C and 60 mbar, however, that of the CaCl_2 /silica gel composite sorbent is about 4 min. The chemical salt impregnated and liquid adsorbed on the outer surface of the composite increase diffusion resistance to water sorption, thus the sorption rate of the host matrix is faster than that of the composite. In addition, the diffusion time is related to the particle size of the composite. Small particles display large sorption rate at the beginning of the sorption process. However, the heat sink to the surrounding medium is not sufficient to dissipate it, causing the increase in the composite temperature. Sorption heat restricts the rise of the sorption rate.

Pore sizes of silica gel also play a role in the sorption performance of the composite sorbent aside from ambient factors as temperature, humidity and air flow intensity. On sorption isotherm, a stable platform can be seen, which reflects the formation of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. According to the change of its position, the sorption properties can be analyzed for the composite sorbent. Fig. 2 shows the sorption isotherms of silica gel-based composite sorbents with three different silica gel pore sizes [53]. As the pore size goes down, the platform corresponding to $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ moves from 1.4–1.7 kPa to 1.0–1.1 kPa. Therefore, the composite with smaller pores can adsorb water vapor at lower pressure. The composite sorbents were synthesized by using Type A and B silica gel with a pore size of 1.8 and 7.5 nm respectively, labeled as SWS-1S and SWS-1L [54]. The water uptake of SWS-1S sorbent is only half of the other because of low loading of CaCl_2 . Interestingly, the desorption curves of the SWS-1S do not have a platform of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and is similar to that of pure Type A silica gel. Bu et al. [55] further studied the D -value of the water uptake for the composite sorbents prepared based on Type A, Type B and Type C silica gel. It is found that both the sorption capacity and rate of the Type A silica gel-based composite sorbent were just a little larger than those of pure silica gel. The Type A matrix with the pore size of between 2 and 3 nm cannot inject into a large amount of CaCl_2 . On the other hand, the CaCl_2 chemical sorbent blocked the mass transfer channels of water molecules. Therefore, the method injected CaCl_2 into the matrix is not suitable for the A silica gel. The equilibrium sorption capacities were similar for the composite sorbents prepared based on Type B and Type C silica gel. However, the sorption rate of the Type C silica gel-based sample was obviously higher than that of the other.

As a powerful chemical sorbent, the loading of the CaCl_2 in porous silica gel greatly determines the sorption performance of the composite sorbent, such as water uptake, sorption/desorption rate and cycle life. Generally, the CaCl_2 /silica gel composite

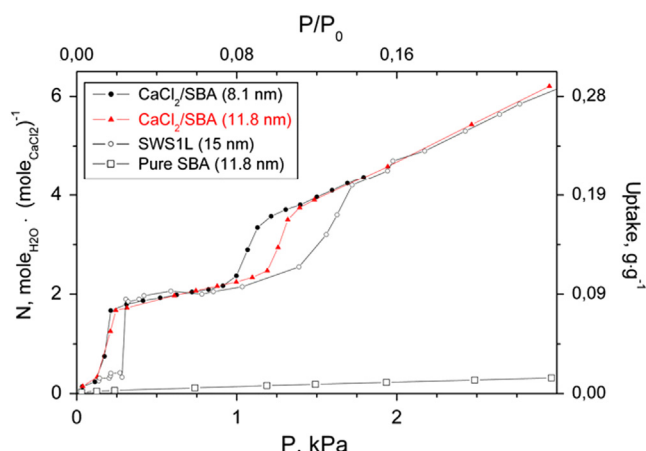


Fig. 2. Isotherms of vapor sorption by the new composites, SWS-1L and pure SBA (11.8 nm) at 50 °C [53].

material is synthesized by impregnating silica gel into CaCl_2 solution with different salt concentrations. Its equilibrium sorption capacity increases obviously as the amounts of CaCl_2 increase [56]. When the CaCl_2 loading is low, the internal surface of the porous silica is adsorbed by a small amount of CaCl_2 . During the sorption process, both the porous matrix and CaCl_2 can adsorb water vapor. When the CaCl_2 contents increase, more internal surface is covered. As the contact area of both silica gel and water vapor reduces, the uptake of silica gel decreases. In addition, the sorption rate is also associated with the content of CaCl_2 . For instance, the water uptakes are 0.18, 0.245 and 0.27 g/g for the composite with the CaCl_2 content of 19.87 wt% at the humidity of 50% when the sorption times are 20, 40 and 60 min. If the CaCl_2 mass ratio is improved to 37.75%, the values are 0.205, 0.29 and 0.33 g/g under the same condition [55].

The CaCl_2 loading also affects the platform of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ on the sorption isotherm. Gordeeva et al. [57] discovered that when the content of CaCl_2 was less than 10–20% in the CaCl_2 /silica gel composite sorbent, the sorption capacity of the sorbent would increase monotonically with the increase of the air humidity. However, the platform reflecting the formation of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ could not be seen on the sorption isotherm. As shown in Fig. 3, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was not found during sorption in XRD pattern for sample 5 with the CaCl_2 weight ratio of 9.2%. When the content of CaCl_2 exceeded 20–30%, the sorption isotherm curve of the composite sorbent was illustrated as steps, corresponding to $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

The composite sorbents of the CaCl_2 and silica gel were developed under different pH values [57]. As the increase of the pH value, crystal defects of the CaCl_2 increase obviously. For the composite sorbents with the CaCl_2 content of 23.3%, the platform of the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ does not appear for the sorbent synthesized under the pH of 8, but can be found on that with the pH of 5.5 [57].

Apart from sorption property, thermal stability cannot be ignored in engineering practice. CaCl_2 is an excellent refractory material, and its melting point is over 782 °C. Therefore, thermal stability of the composite depends on the silica gel matrix. The main component of the silicone is silicon dioxide, and it cannot burn. However, the silanol groups on the silica gel surface come off at high temperature. The decomposition temperature is related to its aperture and synthesis methods. Ponomarenko et al. [58] tested the TG curve of the CaCl_2 /silica gel composite sorbent. The intensive loss of water starts at about 100 °C and practically finishes at 230 °C. The loss weight does not exceed 2–3% after heating from 230 to 500 °C. Therefore, the composite is thermally stable.

The sorption/desorption heat is also an important factor for practical applications. Aristov et al. [33,54] reported the test

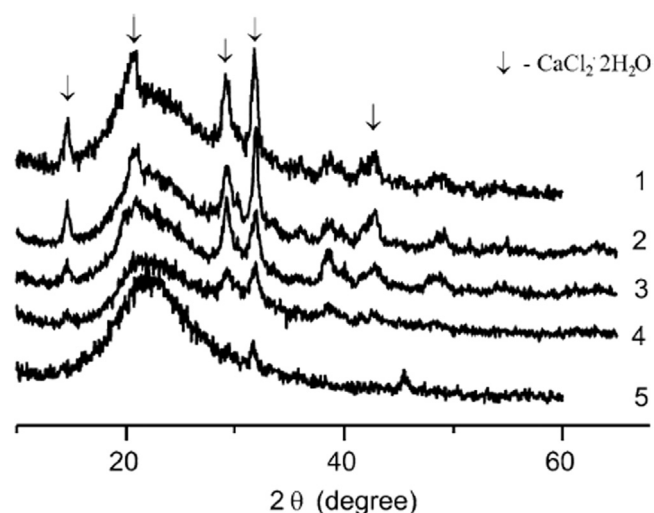


Fig. 3. XRD patterns of composites CaCl_2 (33.7 wt%)/ SiO_2 (1), CaCl_2 (23.3 wt%)/ SiO_2 , prepared at pH of solution 2.0 (2), 5.5 (3), 8.0 (4), and CaCl_2 (9.2 wt%)/ SiO_2 (5) saturated with water up to uptake $N=2$ mol/mol [57].

method of desorption heat. According to isobaric curves, water sorption isosteres were plotted for $w=0.055$ – 0.55 . They appeared to be straight lines $\ln(P)=A(w)+B(w)/T$, with a slope depending on the water content w and water desorption heat $B(w)=\Delta H_{is}(w)/R$, where R was the universal gas constant. For $w > 0.11$, the desorption heat of the CaCl_2 sorbent was 43.9 ± 1.3 kJ/mol, and the value was close to the water evaporation heat from aqueous CaCl_2 solutions [54]. A significant increase of the desorption heat (62–63 kJ/mol) at $w \leq 0.11$ was caused by the formation of the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solid hydrate where the water molecules were bound stronger. By using DSC technique, the average isobaric water sorption heat of the CaCl_2 /silica gel composite displays about 47 kJ/mol. These results indicate that the porous silica gel has little effect on the sorption/desorption heat. According to the experimental sorption data, the differential sorption heat on the composite silica gel supported CaCl_2 sorbent at the temperature T and vapor pressure P could be calculated as $\Delta H_s = \Delta H_{evp} + RT \ln(P_s/P)$, where ΔH_{evp} was the evaporation heat of water, and P_s was the saturated vapor pressure [47]. According to the calculated and fitted results, it is found that the heat of water adsorbed on the composite was noticeably larger than the heat of water evaporation. The heat of sorption decreased slightly with the increase of the water amount adsorbed on the composited sorbent.

The low thermal conductivity of the solid sorbents is one of the major drawbacks of the water extraction, sorption heating/cooling and thermal storage. For the silica gel-based composite sorbents, heat transfer is limited by porosity, bulk density, vapor pressure and water content of the silica gel medium [59,60]. Eun et al. [61] reported that thermal conductivity of composite block mixed expanded graphite was 10 ± 20 W/(m K) depending on the graphite bulk density in the block. It was a much higher value than 0.17 W/(m K) in silica-gel packed bed.

The CaCl_2 /silica gel composite can be efficiently employed in water extraction from atmosphere [51,57,58], sorption heating/cooling [54,56] and thermal storage [47,53] fields. It shows three advantages at last as: (i) both CaCl_2 and silica gel are cut-price, eco-friendly and renewable; (ii) CaCl_2 can adsorb a large amount of water, corresponding to a sorption capacity of up to 0.7–1.5 g/g; (iii) sorption heat of the composite contains condensation heat of water vapor (2443 J/g at room temperature) and the specific enthalpy of the melting of $\text{CaCl}_2 \cdot X\text{H}_2\text{O}$. The melting heat of the $\text{CaCl}_2 \cdot X\text{H}_2\text{O}$ ($X=2, 4$ and 6) is about 87.2 [58], 134 [62] and 198 [62] J/g, respectively.

3.1.3. LiBr/silica gel composite sorbents

LiBr is a hygroscopic salt with excellent thermal stability. The hydrated crystal $\text{LiBr} \cdot \text{H}_2\text{O}$ and $\text{LiBr} \cdot 3\text{H}_2\text{O}$ can form after adsorbing water vapor. During the process of sorption/desorption, two corresponding platforms appear on the sorption isotherm.

The LiBr/silica gel composite sorbent is prepared by impregnating silica gel into LiBr solution. Its sorption capacity was 0.77 g/g, much higher than that of pure silica gel [35,63]. The sorption isotherm indicates that LiBr/silica gel composite sorbent follows the principle of the monovariant type of sorption equilibrium, which is different from the bivariate sorption equilibrium of the composite sorbent prepared based on silica gel, for there is a sorption platform unrelated to temperature on the sorption isobar [64]. On the sorption isobar, the pyrolysis temperatures of the LiBr/silica gel composite sorbent and of the CaCl_2 /silica gel composite sorbent differ a lot, which is closely related to the thermal stability of the crystal water of LiBr and CaCl_2 , excepting ambient factors [65].

Lowering the desorption temperature (110–150 °C) of the LiBr/silica gel composite sorbent is crucial for the application thereof. There are many modified ways to solve the problem, such as decreasing the pore size of silica gel and reducing the loading of LiBr. Essentially, all the methods follow the same principle that destroys the crystallinity of LiBr to lower their activation energy. Gordeeva et al. [66] adopted a new modification method by using LiBr and LiCl as chemical hygroscopic salt. In this way, Cl^- enters into the lattices of LiBr, increasing the number of crystal defects, thus enhancing the activity of the composite sorbent. LiBr–LiBr· H_2O characteristic platform moves towards the low temperature region for 5–10 K, and those of LiCl–LiCl· H_2O and LiCl· H_2O –LiCl· $2\text{H}_2\text{O}$ move for 10–20 K.

3.1.4. $\text{Ca}(\text{NO}_3)_2$ /silica gel composite sorbents

$\text{Ca}(\text{NO}_3)_2$ is an excellent hygroscopic material with a low desorption temperature, but it has a shortage of poor thermal stability. When the environment temperature rises up to 132 °C, $\text{Ca}(\text{NO}_3)_2$ decomposes quickly, producing oxygen and carcinogenic nitrite. To overcome the issue, injecting $\text{Ca}(\text{NO}_3)_2$ into the porous silica gel is an excellent method [67,68], which can reduce regeneration temperature. Its equilibrium sorption capacity is determined by three factors: the heterogeneous sorption of silica gel, the formation of $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and the salt loading in the pores of silica gel. As the loading of $\text{Ca}(\text{NO}_3)_2$, water uptake goes up from 0.04–0.06 to 0.2–0.3 g/g for the composite sorbent [69]. Furthermore, the sorption heat of the $\text{Ca}(\text{NO}_3)_2$ /silica gel composite is related to its sorption capacity in the range of 47–52 kJ/mol. Therefore, the heat transfer of the $\text{Ca}(\text{NO}_3)_2$ /silica gel composite sorbent shall be considered in practical use.

When the pore size of the matrix exceeds 5 nm, the hygroscopic salt in pores exists as crystal phase, and its sorption performance largely rests upon the size distribution. Simonova et al. [69] injected $\text{Ca}(\text{NO}_3)_2$ into silica gel varying in pore size to prepare novel composite sorbents. It can be seen from Fig. 4 that the decomposition temperature of the $\text{Ca}(\text{NO}_3)_2$ drops as the decrease of pore size. For the composite sorbent with the size of 3.5 nm, it can be completely dehydrated at low temperature of about 48 °C. Therefore, the $\text{Ca}(\text{NO}_3)_2$ /silica gel composite sorbent can be well combined with solar energy to realize eco-friendly water vapor sorption.

3.1.5. Others

LiCl is a kind of deliquescent white crystal, and its sorption capacity is twice of those porous silica gel and molecular sieves. However, it also has a number of shortcomings: dissolved LiCl tends to volatile, corroding the water vapor sorption equipment. Besides, Lithium chloride with crystal water produces HCl when the drying temperature is over 98 °C. The LiCl/silica gel composite sorbent kept the high sorption capacity of LiCl while avoiding the

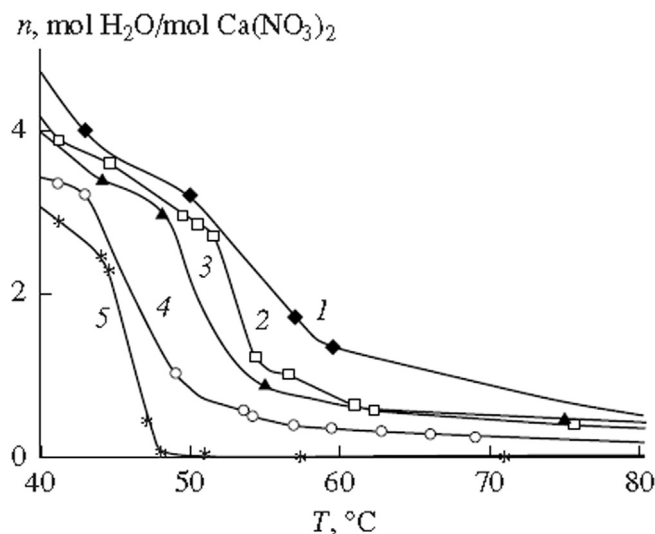


Fig. 4. Isobars of water sorption by (1) bulk $\text{Ca}(\text{NO}_3)_2$ and the $\text{Ca}(\text{NO}_3)_2/\text{SiO}_2$ sorbents with pore sizes $D_{\text{pore}} =$ (2) 12, (3) 9, (4) 6, and (5) 3.5 nm [69].

direct contact of LiCl with the sorbent bed, thus reducing the corrosion on the sorption equipment. When the temperature was 25 °C and relative humidity 80%, the LiCl/silica gel composite sorbent was 3 times the sorption capacity of pure silica gel [64], and could reach 0.702 g/g at 30 °C and a relative humidity of 90% [63]. The SEM images show that the surface structure of the composite sorbent is more complex than that of pure silica gel, which is caused by the LiCl distributed in the pores of silica gel. Due to such a unique physical structure, LiCl solution forming gradually is adsorbed in the pores of silica gel in the sorption process, and thus will not leak. Compared with the CaCl_2 /silica gel composite sorbent, the LiCl/silica gel composite sorbent presents lower activation energy and decomposition temperature. The reason is that the electrostatic interaction between vapor and the sorbent will increase as the increase of the polarization potential of the surface atoms of the sorbent. In the study, since the polarization potential of Ca^{2+} (0.471) is higher than that of Li^+ (0.029), the sorption interaction between water molecules and Ca^{2+} is stronger than that between water molecules and Li^+ . During the process of desorption, water molecules need to overcome stronger sorption forces, which has to improve the desorption temperature of the CaCl_2 /silica gel composite sorbent.

In the chlorate family, aside from CaCl_2 and LiCl, MgCl_2 can also act as a sorbent. Cortés et al. [52] impregnated silica gel with MgCl_2 solution to prepare a MgCl_2 /silica (17: 83 by mass) gel composite sorbent. The sorption capacity of the composite sorbent was 0.2 g/g, 3 times that of pure silica gel. Comparatively, the CaCl_2 /silica gel composite sorbent prepared with the same mass ratio had a higher sorption capacity of about 0.33 g/g. Poor thermal stability is also an obvious shortcoming of MgCl_2 in practical application. When the temperature was higher than 110 °C, MgCl_2 can react with vapor, forming highly corrosive HCl. For this reason, MgCl_2 is seldom used as a sorbent.

Aristov et al. [26] studied the sorption properties of six hygroscopic salts: LiBr, CaCl_2 , MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, Na_2HPO_4 and Na_2SO_4 . It can be seen from Fig. 5 that $\text{Ca}(\text{NO}_3)_2$, Na_2HPO_4 and Na_2SO_4 have higher equilibrium sorption capacities, but show very low sorption capacities at low ambient humidity. For example, Na_2SO_4 can hardly adsorb water vapor even when the relative humidity is over 80%. However, LiBr, CaCl_2 and MgSO_4 present excellent sorption performance; when the relative humidity is only 30%, their sorption capacities all exceed 5 mol/mol. Gordeeva et al. [57] tried to use CuSO_4 , MgSO_4 and Na_2SO_4 as hygroscopic salts to prepare composite sorbents. After silica gel was

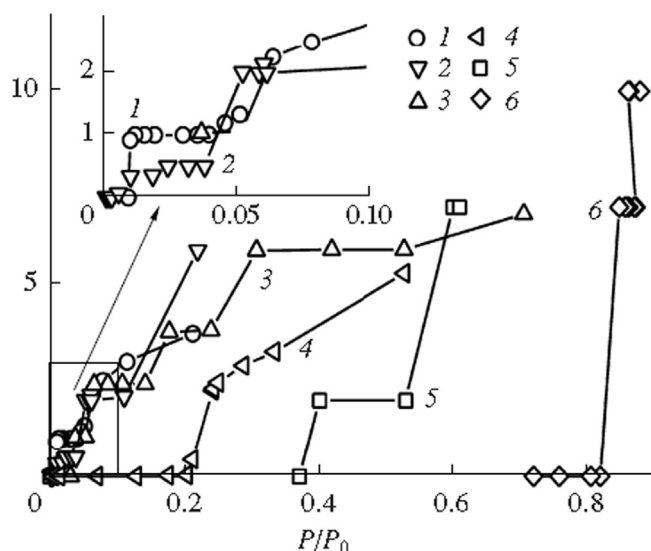


Fig. 5. Regions of occurrence and mutual transitions of the crystal hydrates of bulk salts: (1) LiBr, (2) CaCl_2 , (3) MgSO_4 , (4) $\text{Ca}(\text{NO}_3)_2$, (5) Na_2HPO_4 , and (6) Na_2SO_4 [70].

placed in the solution of these salts, its surface interacted with the solution. Due to the cation interaction, crystal and amorphous phases of salts can co-exist on the surface of silica gel, and their contents were determined by the concentrations and pH values of the salt solution. Gordeeva et al. [70] injected MgSO_4 into porous silica gel to prepare a novel composite sorbent. As the sorption isotherms show, the sorption platform of MgSO_4 becomes more and more obvious with the increase of MgSO_4 . Similar with other composites, the water uptake of MgSO_4 chemical salt shows an upward trend when the content of MgSO_4 increases. The equilibrium sorption capacity of the prepared MgSO_4 /silica gel composite sorbent (MgSO_4 content: 38% by mass) reached over 0.4 g/g, about 8 times that of pure silica gel. Sukhyy et al. [71] synthesized a Na_2SO_4 /silica gel composite sorbent using the sol-gel method. Its equilibrium sorption capacity reached as high as 0.85 g/g, higher than that (0.66 g/g) of the Na_2SO_4 /silica gel composite sorbent prepared through the mechanical mixing of Na_2SO_4 and silica gel of the same amount. The non-linear superposition of the sorption capacity of the composite sorbent proves the increase of the sorption reaction rate of the vapor in the pores of silica gel with the aquo-complex.

3.2. Activated carbon-based sorbents

3.2.1. Activated carbon matrixes

Since the 19th century, activated carbon has been widely used as sorbent for large porosity and specific surface area (300–4000 m^2/g). The active carbon is synthesized by using materials such as wood, coal, petroleum coke, bones and pits. Among raw materials, coal is the most popular one.

Activated carbon has a net structure formed by irregular hexagon carbon layers which are cross-linked by aliphatic bridging groups [72,73]. Some heteroatoms enter into the pores of activated carbon or adhere to the edges of carbon layers, and those atoms adhering to the surface determine the properties of the functional groups. In surface chemistry, such as the fields of aqueous solution sorption and surface catalysis, functional groups always play the main role. The surface functional groups of activated carbon are primarily acid groups, like the carboxyl, quinone, hydroxyl, carbonyl, carboxylic acid group and lactone. There are also some basic functional groups, such as the pyrone and benzopyran. The difference between activated carbon and other types of sorbent is the surface feature. The whole surface of activated carbon is covered by an oxide matrix and by some inorganic materials, and therefore,

it is non-polar or has a weak polarity. But for polar molecules (such as water, ethanol, amine, ammonium hydroxide and sulfur dioxide) which have permanent dipole moments, there is a strong interaction between the electric field and the dipole. Therefore, the groups with small amounts of charge can strongly adsorb polar molecules. For example, when water vapor is adsorbed by activated carbon, it hydrogen bonds with activated carbon surface, and the amount of water adsorbed largely depends on the number of the oxygen-containing functional groups on activated carbon surface. Kaneko et al. [74] found that there are also water molecule clusters which exist in the form of $(\text{H}_2\text{O})_5$ in the pores of activated carbon. Do et al. [75] proved that water molecule clusters are adsorbed by the functional groups on activated carbon surface. As expected, after the functional groups were removed on activated carbon surface, the sorption capacity dropped sharply. Therefore, the surface properties of activated carbon play a crucial role in water vapor sorption.

3.2.2. CaCl_2 /activated carbon composite sorbents

Activated carbon has an excellent sorption performance due to large porosity and outstanding heat transfer property. The composite sorbent composed of CaCl_2 and activated carbon has been widely employed in the field of sorption refrigeration, as such the ammonia sorption refrigeration system [76], methanol sorption refrigeration system [77], and water sorption refrigeration system [78]. Spiridon et al. [79] studied that the content of CaCl_2 affected the morphology of the CaCl_2 /activated carbon composite sorbent. It can be seen from Table 2 that the micropore volume of pure activated carbon is 0.2736 cm^3/g , and those of the composite sorbents (MCC1 and MCC1*) prepared with 15% and 30% CaCl_2 solution respectively are 0.2685 and 0.1846 cm^3/g respectively. With the increase of the amount of CaCl_2 , the specific surface area also decreases obviously for the composite sorbent. The equilibrium water uptake of the MCC1 is less than 0.15 kg/kg, but that of the MCC1* with the CaCl_2 content of 29.01% is 0.2 kg/kg. Their initial sorption rates are 0.027 and 0.033 $\text{kg}/\text{m}^3/\text{s}$. When the sorption times are 50, 100 and 200 min, sorption rates decrease to 0.016, 0.008 and 0.001 $\text{kg}/\text{m}^3/\text{s}$ respectively for the MCC1 with the CaCl_2 weight ratio of 13.03 wt%, respectively. At the same measured environment, these of the MCC1* are 0.025, 0.015 and 0.005 $\text{kg}/\text{m}^3/\text{s}$ respectively. It can be noticed that the sorption capacity and rate of the MCC1* sample is higher than that of the MCC1. Okada et al. [80] prepared activated carbon by chemical activation of tissue paper using K_2CO_3 under various experimental conditions to optimize the value of specific surface area and porosity. The optimal results are 1820 m^2/g and 1.30 ml/g by adjusting K_2CO_3 /tissue paper, activation temperature, activation time and N_2 flow. Optimized activated carbon was impregnated with CaCl_2 solution to prepare CaCl_2 /activated carbon sorbent. As the solution concentration of CaCl_2 rose, the loading of CaCl_2 increased evidently. When the relative pressure ranges from 0.1 to 0.3, the sorption capacities of the composites with the mass ratio of 0%, 30%, 40%, 50% and 70% are 0.04, 0.15, 0.2, 0.28 and 0.52 g/g respectively.

Table 2

Micropore volumes, average pore diameters, BET surface areas and micropore surfaces of AC, MCC1 and MCC1* [79].

Material	AC	MCC1	MCC1*
V_{micro} (cm^3/g)	0.2736	0.2685	0.1846
D (nm)	19.08	18.09	17.46
S_{BET} (m^2/g)	869.49	680.66	422.54
S_{micro} (m^2/g)	595.63	601.65	396.37

The wettability of activated carbon is related to the acid functional groups on the surface. However, a part of functional groups is decomposed under the high temperature, lowering the hydrophilia of activated carbon. To overcome the problem, Huang et al. [81] reported the modified method which deposited a small amount of silica gel into the pores of activated carbon. According to SEM images, silica gel particles are homogenously distributed in the pores of the activated carbon. Tso et al. [78] found that the specific surface area and pore volume of the matrix kept decreasing until its pores were filled with CaCl_2 crystal. After the

maximum loading of CaCl_2 was reached, the infiltration time had no effect on the morphology of the composite matrix, but the equilibrium sorption capacity kept increasing.

In-situ synthesis method is proposed to obtain the composite with high CaCl_2 loading. Specifically, CaCl_2 is injected into sawdust with a loose structure, and then the mixture is carbonized at high temperature. The composite sorbent shows high porous structure, and CaCl_2 is homogenously distributed in the activated carbon. Bu et al. [82] prepared CaCl_2 /activated carbon composite sorbents with sawdust at 400, 500, 600 and 700 °C. As the carbonization

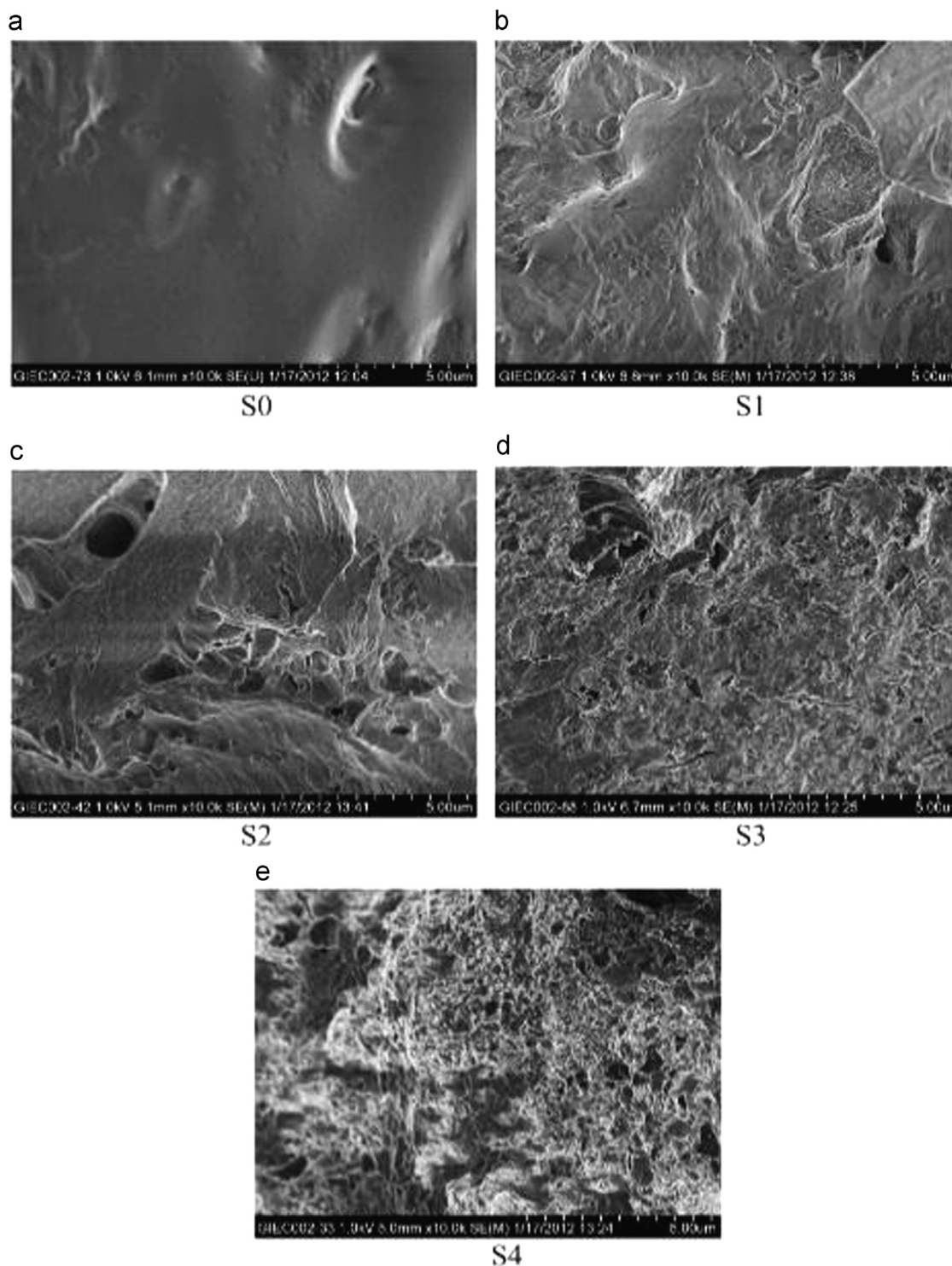


Fig. 6. The SEM images of the sawdust (a) and activated carbon sintered at 400 (b), 500 (c), 600 (d), 700 °C (e) [82].

temperature rises, the losses on ignition, porosities and carbonization rates all go up in Fig. 6. When the activation temperature is equal to 700 °C, the loss on ignition reaches 56.8%. Besides, the content and crystallinity of CaCl_2 increases with the increase of carbonization temperature. The CaCl_2 loading of CaCl_2 /activated carbon is bigger than 0.7, but the content can hardly exceed 0.5 through injected method. The pore size of activated carbon is smaller than 2 nm, which makes it hard for CaCl_2 to fully impregnate activated carbon. On the other hand, the hydrophobic composite further decreases the contact area of aqueous solution and activated carbon.

Graphite, with a layered and planar structure, is an allotrope of carbon element. Each carbon atom is joined to the other three carbon atoms by covalent bonding. Since each carbon atom provides an electron that can move freely in the layer, graphite is greatly superior to other carbon materials in thermal conductivity. Therefore, graphite is an ideal matrix to prepare composite sorbents. Tian et al. [83] found that the thermal conductivity of the CaCl_2 /graphite composite sorbent is closely related to the content of graphite and the density of the composite sorbent. For a compact CaCl_2 /graphite composite sorbent with a graphite content of 16.7%, even the compaction density is only 550 kg/m³, its thermal conductivity can still reach a high level of 1.08 W/(m K), 6 times that of the thermal conductivity of pure CaCl_2 particles.

Aside from graphite, the carbon fiber is also a desirable carbon matrix. Ye et al. [84] synthesized composite sorbents with CaCl_2 and carbon fiber sheets. When the content of CaCl_2 is lower than 38.2%, all the CaCl_2 is located inside the pores of carbon fiber sheets. The composites exhibit a greater amount of adsorbed water than the equivalent pure CaCl_2 , indicating that the carbon fiber sheets contribute to the amount of water uptake. Besides, CaCl_2 distributed in the pores of carbon fibers exhibits a lower hydration pressure than bulk CaCl_2 . Water sorption of the composite can reach as high as 90% of the equilibrium water sorption amount within only 2 min. Compared with CaCl_2 /silica gel composites sorbents, CaCl_2 /carbon fiber composite sorbents can greatly shorten the cycle of sorption.

We have reported CaCl_2 /MWNT composite obtained by using multi-wall carbon nanotube (MWNT) as matrix, in which the CaCl_2 hygroscopic salt is adsorbed on the surface of the MWNT matrix [85]. The excellent surface structure makes CaCl_2 contact fully with water vapor, thence both sorption capacity and rate are enhanced obviously in comparison with the conventional composite sorbent prepared by using impregnation method. For instance, the CaCl_2 /MWNT composite with the CaCl_2 content of 50 wt% shows a large water uptake of 1.41 g/g, and it takes less than 10 h for one sorption process. Besides, the microstructure and sorption performance of the hydrophilic/hydrophobic composites are discussed. The stable porous architecture is obtained for the hydrophilic CaCl_2 /MWNT sample, and it shows a large water uptake of 0.76 g/g and initial sorption rate of 6.7 g/kg/min at the low relative humidity of 50%. For the hydrophobic sample with the same CaCl_2 content, the first rate is only 3.7 g/kg/min, reducing down to 45%. Finally, the CaCl_2 /MWNT sample modified by using the PVP has also been reported, and it displays many outstanding physical/chemical performances. During sorption process, the PVP powder improves water-retaining ability of the CaCl_2 /MWNT which enhances the MWNT adsorptive power for the CaCl_2 solution. During regeneration process, the PVP water-based adhesive makes sorbent particles macroscopically agglomerate with the same microcosmic structure. Therefore, PVP can avoid raising dust problem under the unchanged sorption performance. Interestingly, sorption rate of the modified sample is obviously improved at low humidity environment. For example, the reversible sorption capacity of the modified sorbent is 0.75 g/g for the initial 6 h, increasing to 25% in contrast with the unchanged sample.

Thermal stability of the activated carbon-based sorbent depends on the porous matrix. The thermal conductivities of expanded graphite are 0.09, 0.095, 0.081 and 0.074 W/m/K at 500, 600, 700 and 800 °C respectively [83]. The expansion time between 5 and 50 min has no effect on the value of thermal conductivity at 600 °C. It is clear that the expanded graphite has excellent thermal stability. For carbon nanotube, the decomposition temperature is above 180 °C at air condition [85]. In terms of the CaCl_2 /activated carbon, water begins to evaporate about 100 °C. When temperature reaches 200 °C, water is completely removed and the carbon matrix begins to be oxidized [79]. Therefore, drying temperature of carbon-based sorbents shall be less than 120–150 °C.

The activated carbon-based sorbents are widely used in sorption cooling system due to excellent thermal conductivity of the carbon matrix. The dimension stability of CaCl_2 and expanded graphite was studied by the research group of Mauran, and results showed that the volume expansion rate was null if the density of graphite block used to produce composite sorbent was 156 kg/m³ [86, 87]. Wang et al. [88] develops a composite sorbent of CaCl_2 and activated carbon, which compromises the mass transfer of the refrigerant in the sorbent bed. The heat transfer performance can be improved for the type of sorbent when it is consolidated. In the condition of heat sink of 28 °C and evaporation temperature of –10 °C, the volumetric cooling density of the composite sorbent with activated carbon as additive is 40% higher than that of the single chemical sorbent [89].

3.2.3. LiBr/activated carbon composite sorbents

LiBr [36,90] with excellent thermal stability is a deliquescent hygroscopic salt. Anhydrous LiBr can be obtained at a relatively low temperature of 160 °C, while anhydrous CaCl_2 is 260 °C. Therefore, LiBr is an excellent sorbent. However, a few dozens times more expensive than CaCl_2 , LiBr has to face high costs in application. As one method to solve the problem, LiBr is injected into graphite to prepare high-powered LiBr/graphite composite sorbents. Research results show that the equilibrium sorption capacity of the LiBr/graphite composite sorbent could reach 1.85 g/g [36], twice as high as the that of the LiBr/silica gel composite sorbent. However, an obvious defect of this kind of composite sorbent can hardly be distributed homogeneously between the layers of graphite due to the narrow interlayer spacing of graphite (averagely 0.335 nm). Usually, LiBr is distributed on the surface of graphite. Therefore, it will be agglomerated after repeated use, which lowers its sorption capacity.

Activated carbon has a very high external specific surface area relative to graphite. The LiBr/activated carbon composite sorbent can be prepared by injecting LiBr into porous carbon. Its equilibrium sorption capacity could reach 0.6 g/g [36], twice as high as that of pure silica gel. As shown in Fig. 7b, there is no any sorption platform for the composite sorbent in the temperature and pressure ranges, which indicates that no $\text{LiBr} \cdot \text{H}_2\text{O}$ crystal is formed in the pores of activated carbon [91].

The amount of sorption heat is also an important index to judge the performance of a composite sorbent. As shown in Fig. 7, when the atmospheric pressure is low, the water content of the LiBr/activated carbon composite sorbent can be decreased to 1 mol/mol at only 80–90 °C, while for the LiBr/graphite composite sorbent, above 110 °C. This fully demonstrates how the crystalline state of LiBr hygroscopic salt affects the process of desorption. Gordeeva et al. [91] proved it again. The LiBr/activated composite sorbent consumed 1.1 kJ to adsorb 1 g water vapor, 40% of the energy needed by the LiBr/expanded graphite. It can be said that the LiBr/activated carbon composite sorbent is an efficient sorbent with low energy consumption and a long cycle life.

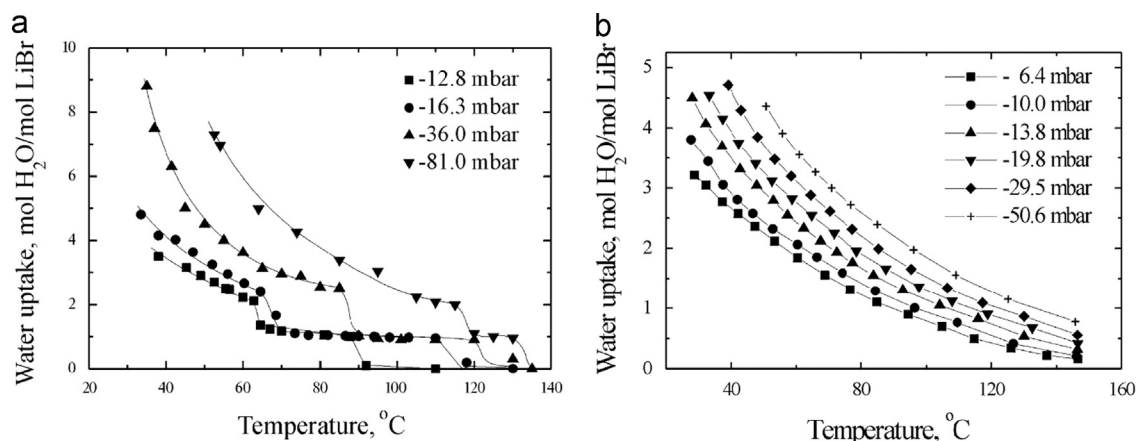


Fig. 7. Isobars of water sorption on LiBr/expanded graphite (a) and LiBr/activated carbon composite sorbents (b) [91].

3.2.4. Others

Kim et al. [92] mixed activated carbon, silica gel and zeolites to obtain a composite sorbent. The equilibrium sorption capacity of the composite sorbent exceeds 11 mol/kg (0.2 g/g) at 20 °C and 2.3 kPa. Like other physical sorbents such as molecular sieve and Al₂O₃, the composite sorbent drops sharply in equilibrium sorption capacity as the temperature rises.

Oliveira et al. [93] injected LiCl into activated carbon to prepare LiCl/activated carbon composite sorbents (LiCl content: 14% and 21% respectively by mass). The equilibrium sorption capacity of the composite sorbent is much higher than that of pure activated carbon at the same atmospheric pressure and temperature. This indicates that the LiCl/activated carbon composite sorbent is promising in the fields of water vapor sorption and sorption refrigeration.

A high temperature greatly disables the hydrophilic functional groups on the surface of porous activated carbon by lowering the wettability. Actually, how to increase the wettability of carbon-based materials is a bottleneck of their application in water vapor sorption. If the issue is overcome, more hygroscopic salts can be used to prepare cheap and eco-friendly hygroscopic salt/activated carbon composite sorbents like CuSO₄, MgSO₄, and Na₂SO₄. There are many ways to modify activated carbon. For example, Mahajan et al. [83] found that treating activated carbon with nitric acid can increase the vapor sorption of activated carbon by 100 times at a low partial pressure.

3.3. Zeolite-based composite sorbents

3.3.1. Zeolite matrixes

The zeolite, expressed as $M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot zH_2O$, is an aluminosilicate mineral of alkali or alkaline earth metal which contains crystal water. There are many polyhedron units for zeolite, including cube, hexagonal prism, and octahedron. These structure units compose of silica tetrahedron and alumina tetrahedron. Every two silica tetrahedra are connected by a point, that is, they share a bridging oxygen atom. However, alumina tetrahedra cannot be connected by the bridging oxygen. For silica tetrahedron, silicon atom can be replaced by aluminum atom to form alumina tetrahedron. Aluminum atom only provides 3 electrons, thereby obtaining alumina tetrahedron which lacks a negative charge. Alkali metal and alkaline earth can neutralize electrons for the alumina tetrahedron. By replacing the aluminum/silicon atoms, many types of molecular sieves can be obtained. Commercial zeolite molecular sieves fall into three types: Type A, Type X and Type Y [72]. Water can be removed by heating. The porosity of the aluminosilicate skeletal is between 0.2 and 0.5. The aluminosilicate skeleton has a

cage format, and it is usually connected by six casement sections, which can adsorb a large amount of extra molecules [73].

When the relative humidity is lower than 30%, both the sorption capacity and rate of the molecular sieve are obviously higher than those of silica gel and activated Al₂O₃ [94]. The molecular sieve is the only usable high temperature sorbent. Even at 100 °C and the relative humidity of 1.3%, its sorption capacity can reach 15%, 10 times higher than that of activated Al₂O₃, and over 20 times higher than that of silica gel. Cortés et al. [15] studied the sorption curve of the zeolite molecular sieve through thermogravimetric analysis and mass spectrometry. Its equilibrium sorption capacity is greatly affected by the ambient temperature and humidity. When the temperature rises, the physisorption is sharply dropped for the zeolite molecular sieve. In contrast, the saturated vapor pressure increases fast with the increase of the environment temperature, thereby water uptake is improved obviously. In general, with the increase of environment temperature, its equilibrium sorption capacity enhances and then decreases. Unfortunately, the regeneration temperature of the zeolite molecular sieve reaches a very high level of about 300 °C. Natural solar energy can hardly desorb the water of the pores of molecular sieve. Fang et al. [95] modified the zeolite molecular sieve with rare earth elements of lanthanum and rubidium. The desorption activation energy decreased obviously for the modified molecular sieve. Its desorption temperature dropped from 269 °C to 165–157 °C, but there was no evident drop in water uptake. Jänchen et al. [14] prepared a series of zeolite molecular sieves, including NaX, MgNaX and CaMaA-60. When Na⁺ were partly replaced by Mg²⁺, the modified molecular sieve exhibits improvement in equilibrium sorption capacity, heat of sorption and energy density. Chan et al. [96] modified the 13X molecular sieve using calcium ions. The water uptake is as high as 0.27 g/g for the sorbent, increasing by 17.8%.

Low thermal conductivity is another obvious defect for zeolite molecular sieve. The equivalent thermal conductivity is only 0.07–0.16 W/m K for the packed bed of zeolite particles. Michael et al. [97] reported that the particle diameter of the NaY/zeolite molecular sieve had a significant effect on its thermal conductivity. NaY/zeolite molecular sieves with particle diameters of 2 and 0.8 μm respectively had thermal conductivities of 0.16 and 0.08 W/m K. At present, modified methods consist of adding high thermal conductivity materials and compressing the zeolite molecular sieve. Adding powered expanded graphite can greatly increase the thermal conductivity, but the synthesis technology is very complex [61]. Guillemot et al. [98] prepared a foamed aluminum/zeolite molecular sieve composite sorbent. The thermal conductivity is much higher than that of the zeolite particles.

3.3.2. CaCl_2 /zeolite molecular sieve composite sorbents

Compared with that of the zeolite molecular sieve, the sorption isotherm moves towards the region of high vapor pressure for 2 orders of magnitude for the CaCl_2 /zeolite composite sorbent. It means that the composite molecular sieve has a lower desorption temperature than the zeolite molecular sieve. Fig. 8 illustrates the desorption curves of activated carbon, silica gel, the zeolite molecular sieve and the CaCl_2 /zeolite composite sorbent. Chan et al. [99] found that the equilibrium sorption capacity of zeolite 13X was 0.3 g/g, twice as high as that of porous silica gel. On the other hand, the desorption temperature of zeolite 13X was very high that its water content reached more than 0.1 g/g even at 125 °C. The CaCl_2 /zeolite composite sorbent performed well. Its sorption capacity reached 0.46 g/g at 25 °C, and the reversible capacity was 0.404 g/g in the temperature range of 25–100 °C. The value was 295% and 320% of those of zeolite 13X and silica gel respectively.

The content of CaCl_2 hygroscopic salt is the crucial factor affecting the sorption performance of the CaCl_2 /13X. It can be seen from Table 3 that the quantity of the CaCl_2 entering zeolite 13X increases as CaCl_2 solution concentration increases. Li et al. [100] reported that the equilibrium sorption capacities of the composites with the CaCl_2 contents of 12.8%, 20.5%, 27.4%, 33.2% and 37.7% are 0.34, 0.38, 0.47, 0.52 and 0.55 g/g, respectively. In addition, the sorption rate of the composite sorbent was faster than those of silica gel and zeolite 13X, and increased as the increase of CaCl_2 content. Just one hour after the sorption started, the sorption capacity reached 0.223 g/g, higher than the equilibrium sorption capacities of silica gel (0.34 g/g) and zeolite 13X (0.221 g/g). However, when the loading of CaCl_2 in the molecular sieve was too low, the sorption capacity of the composite sorbent did not fall obviously. Cortés [53] prepared a CaCl_2 /zeolite molecular sieve composite sorbent with a CaCl_2 content of 17%, and found that its sorption capacity was less than 5% higher than that of zeolite 13X.

Zhao et al. [101] studied the morphology of CaCl_2 /zeolite composite. The surface of the zeolite particle is covered by microcrystalline CaCl_2 , indicating that the microstructure of the CaCl_2 /zeolite composite is different from that of silica gel-based composite. Although most of the CaCl_2 deposit on the surface of zeolite 13X grains, the sorption capacity is still much higher than that of pure zeolite 13X. When the sorbent temperature is 35 °C, the composite sorbent with a CaCl_2 content of 46.2% shows a big sorption capacity of 0.557 g/g, 2.2 times that of pure zeolite 13X.

Work temperature of Zeolite 13X with the aperture size of 1 nm is over 350 °C, and it has an excellent thermal stability. Therefore, it should be safe for engineering application of the CaCl_2 /13X composite sorbent during regeneration process. However, the low value of the equivalent thermal conductivity cannot meet commercial application due to porous characteristic and low contact area of the particles. For example, the thermal conductivity of the NaX anhydrous grain is 0.18 W/m/K. So far, various strategies have been proposed to resolve the issue of poor thermal conductivity, which include reducing the grain size and intergranular porosity [102], enhancing the packing density, mixing/coating with excellent thermal conductivity materials (carbon nanotube, graphite and metal materials) [98,103]. Guillemot et al. [98] reported that an improvement in the thermal conductivity by 85% was tested for non-consolidated mixture containing zeolite and copper metallic foam. However, the increase in density and thickness due to the powder compaction caused decrease in the water vapor permeability, so that, mass transfer becomes the new limiting issue. To overcome the heat and mass transfer limitations, a copper foam, on purpose prepared, was used as support to grow a multilayer Zeolite coating [104]. The water sorption uptake measured on the coated copper foam resulted to be comparable with that of

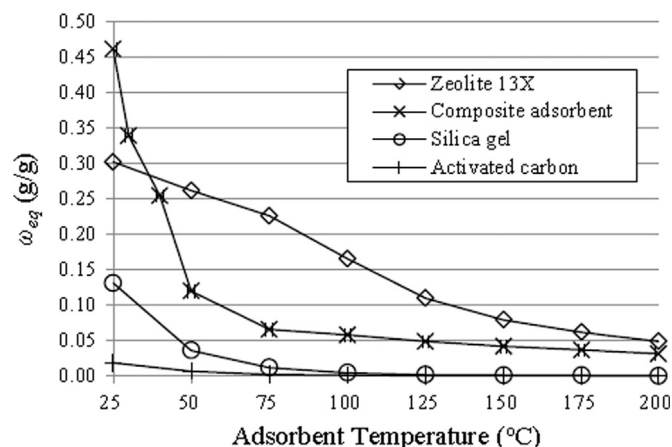


Fig. 8. Equilibrium water uptake of zeolite 13X/ CaCl_2 composite sorbent, zeolite 13X, silica gel and activated carbon. All data obtained at 870 Pa [99].

Table 3

Results of adsorbance [101].

Composite sorbent	Salt solution concentration (mol/L)	Sorption capacity (%)
CaCl_2 /13X	0	18.5
	1.5	27.6
	3.0	32.8
	4.5	46.9
	Saturated solution	30.4

unmodified zeolite in the whole range of temperatures and pressures investigated.

Compared with silica gel and activated carbon, zeolite has two unique advantages. (i) Adjusting the pore size of zeolites can selectively adsorb adsorbates. For example, Kuznicki et al. [105] synthesized a titanosilicate molecular sieve with adjustable pores. The cage structure of the nanopore allows removal of N_2 from natural gas with water vapor contents of 80–150 ppm, reducing an initial N_2 content of 18% to less than 5% with a methane recovery of at least 90%. (ii) Zeolites shows large water uptake at high temperature and low humidity. Therefore, zeolite-based composite sorbents are widely used in removal of metallic ions/phosphine from contaminated water [106,107], sorption CO_2 [108], and water extraction from atmosphere under extreme conditions [109,110].

3.3.3. LiCl /zeolite molecular sieve composite sorbents

At present, LiCl is widely used to prepare sorbents together with silica gel, due to high water sorption capacity. The zeolite molecular sieve has a strong selectivity for the sorbent. It can be used to prepare composite sorbents together with LiCl . Zou et al. [111] synthesized a LiCl /zeolite molecular sieve composite sorbent by homogeneously dispersing LiCl in the zeolite molecular sieve using the thermal dispersion method. The chemical bond mobility test results show that LiCl deposited in the pores of zeolites, and the Li^+ provided by LiCl balanced the charge of zeolites. Lexa et al. [112] also proved the ion exchange interaction between Li^+ in pores and zeolite. Therefore, the sorption between LiCl in the pores and zeolites is stronger than that on the surface of zeolite. One obvious advantage of the LiCl /zeolite molecular sieve composite sorbent is that, unlike silica gel based composite sorbents, LiCl does not leak during the process of sorption. Besides, the LiCl /zeolite molecular sieve composite sorbent is very sensitive to humidity [113], and has a high sorption capacity. Given the above, the LiCl /zeolite molecular sieve composite sorbent is expected to be widely used as a sorbent.

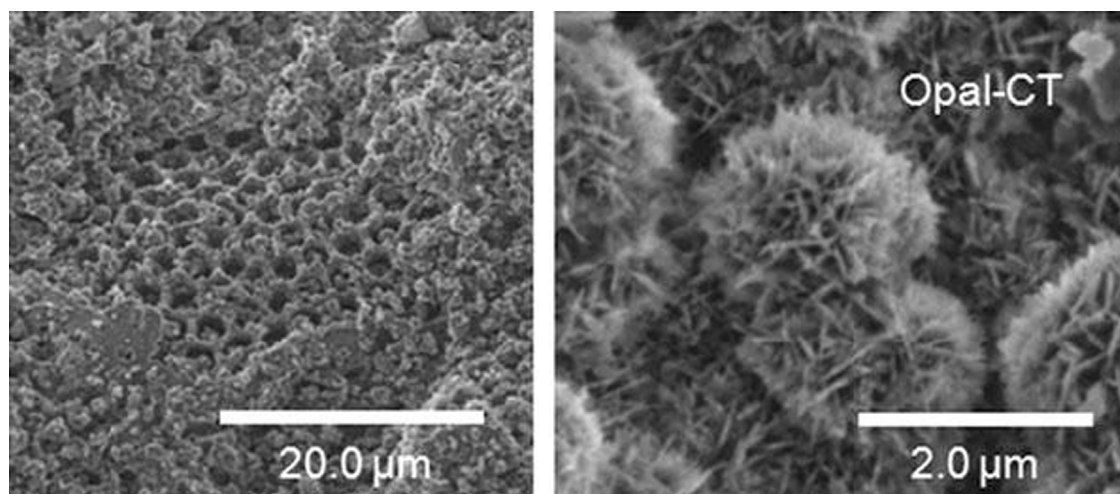


Fig. 9. The SEM images of WSS material [118].

As mentioned in many researches concerning silica gel based composite sorbents [46,56,57], the loading of LiCl affects the equilibrium sorption capacity and sorption/desorption rate of the composite sorbent. The higher the loading of LiCl is, the higher the equilibrium sorption capacity of the composite sorbent will be. However, if the loading is too high, LiCl will be agglomerated in the pore of the molecular sieve. As a result, the sorption/desorption rate and stability of the composite sorbent decrease. Li et al. [114] prepared a LiCl/NaY composite sorbent. Experimental results proved that LiCl is agglomerated at high ambient temperature and humidity, and its loading has a significant effect upon the porosity of NaY. Even when the loading of LiCl is 10%, the porosity of NaY also drops by 70%; and when the loading rises to 50%, the porosity is only 17% of the original [114]. The sharp attenuation of the porosity of the composite sorbent narrows or even completely blocks the mass transfer path of water molecules, greatly weakening the diffusion force. This is the primary reason for the decrease of the sorption rate of the composite sorbent. Therefore, in the application of the LiCl/zeolite molecular sieve composite sorbent, its equilibrium sorption capacity and sorption rate shall be considered to find the optimal loading of LiCl.

3.3.4. Others

Molecular sieves perform well in water vapor sorption at a low ambient humidity. Jiang et al. [115] prepared a silica gel/molecular sieve composite sorbent by taking silica solution as an adhesive and ceramic fibers as the matrix. This composite sorbent integrated the high sorption capacity of molecular sieves at a low humidity and of silica gel at a high humidity, thus had a high equilibrium sorption capacity in a wide range of ambient humidity. When the ambient humidity was 35%, the sorption capacity of the composite sorbent was 30% higher than that of silica gel; and the sorption capacity was 1.38 times that of the molecular sieve at the relative humidity of 75%. Besides, when the ambient humidity was 23%, the sorption capacity of the composite sorbent was 1.66 and 2.1 times that of silica gel in the 5 and 10 min after the sorption started, and the sorption capacity was 57% and 34% higher than that of the molecular sieve at the relative humidity of 72%. The above figures show that the sorption rate of the composite sorbent was greatly increased.

Cui et al. [116] tried to synthesize a composite sorbent with 13X molecular sieve, attapulgite clay, and metal chloride. Its desorption performance was superior to those of 13X and activated carbon, but the sorption capacity was obviously lower than those of pure sorbents.

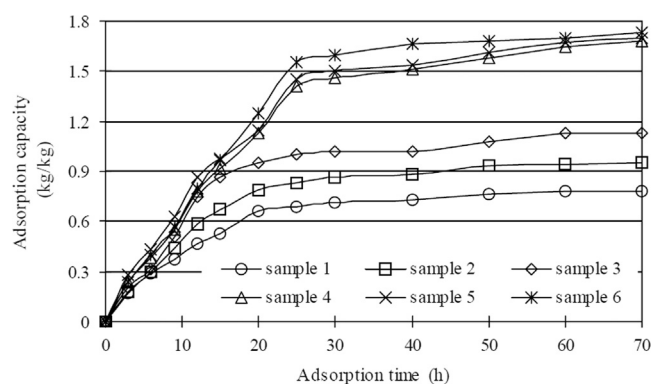


Fig. 10. Sorption characteristics for the 30 (sample 1), 50 (sample 2), 53 (sample 3), 58 (sample 4) mass % $\text{CaCl}_2/\text{MCM-41}$ and 17 (sample 5), 28 (sample 6) mass % $\text{CaCl}_2/\text{silica gel}$ composite sorbents [120].

3.4. Composite sorbents prepared based on other matrixes

3.4.1. Attapulgite clay-based composite sorbents

Attapulgite clay is a natural porous sorbent, and widely used in a lot of fields due to low price, high specific surface area, fast sorption/desorption, and eco-friendly. Chen et al. [117] prepared a LiCl/attapulgite clay composite sorbent. It can be seen that when the vapor pressure is less than 500 Pa, the sorption capacity of the composite sorbent is closely related to the content of LiCl; when the vapor pressure reaches 750 Pa, the equilibrium sorption capacity of the composite sorbent (LiCl content: 30%) is 0.31 g/g; and when the vapor pressure reaches 1500 Pa, the sorption capacity of the composite sorbent rises to 0.44 g/g. However, the desorption temperature is as high as 170–190 °C for the composite, which means very high desorption energy consumption.

3.4.2. Wakkanai siliceous shale based composite sorbents

Wakkanai siliceous shale (WSS), with silica content more than 85%, has a microporous structure as Type B silica as shown in Fig. 9. Nakabayashi et al. [118] prepared a novel composite sorbent using natural WSS as a porous medium and NaCl as a hygroscopic salt. Although NaCl is not an excellent sorbent, the sorption capacity of composite material is increased by 5–7 times at a relative humidity of 50–70%. After adsorbing full water vapor, the volume of the composite expands by 5%. When the regeneration temperature is adjusted to 40 °C, the obtained water from the composite sorbent is 60 g/h (2.4 g/m³, 90 mg/g), while those of silica gel and zeolites are only 10 g/h (0.4 g/m³, 16 mg/g) and

Table 4
Sorption/desorption performances of SWSs materials.

Matrix	Component	Synthesis method	Water uptake (g/g)	Sorption time (h)	Sorption heat (kJ/g)	Drying temperature (°C)
Silica gel	CaCl ₂ /Silica gel	Impregnation	0.75	> 6	2.41–2.62	95
			1.5	> 30		
	CaCl ₂ /Silica gel		0.75		2.4–4.3	95
	CaCl ₂ /Silica gel		0.45	2		95
	CaCl ₂ /Silica gel		0.73	> 6	2.41–2.62	
	LiBr/Silica gel		0.35			125
	Ca(NO ₃) ₂ /Silica gel		0.3		2.6–2.9	65
	LiCl/Silica gel		0.66			
	MgSO ₄ /Silica gel		0.65			
	CuSO ₄ /Silica gel		0.58			
	Na ₂ SO ₄ /Silica gel		0.62			
Carbon	CaCl ₂ /Carbon nanotubes	Mixture	1.4	< 10		115
	CaCl ₂ /carbon fiber	Impregnation	0.9	< 1	2.8	
	LiBr/Activated carbon	Impregnation	0.6		1.1	150
	LiBr/Graphite	Impregnation	1.85		2.8	115
Zeolite	CaCl ₂ /Zeolite	Impregnation	0.55	> 10	0.8	> 120
				6	1.4	
MCM-41	CaCl ₂ /MCM-41	Impregnation	1.75	> 30		80
Attapulgit clay	LiCl/Attapulgit clay	Impregnation	0.44		2.3–2.8	> 170
Wakkanai siliceous shale	NaCl/Wakkanai siliceous shale	Impregnation	0.09			
Al	CaCl ₂ /Al	Impregnation	0.14–0.175			
Al ₂ O ₃	CaCl ₂ /Al ₂ O ₃	Impregnation	0.52			

25 g/h (1.0 g/m³, 28 mg/g) respectively. The NaCl/WSS composite sorbent shall be one of the promising sorbents in the field of water vapor sorption.

3.4.3. Phosphoric acid/silica composite sorbents

Molecular sieves, especially zeolite molecular sieves, are widely employed in sorption and heat exchange. Since their sorption performance can be adjusted by changing the ratio of Si to Al, it is a desirable sorbent in commercial application. AIPO-18 and SAPO-34, with unique component and microstructure, also present extraordinarily excellent sorption performances. Van et al. [119] prepared AIPO-18 porous membranes. When the thickness of the sample was less than 200 μm, its thermal and mass transfer performance reached the optimum. Besides, the AIPO-18 microporous molecular sieve can adsorb water when the ambient humidity was only 25 wt%.

3.4.4. MCM-41-based composite sorbents

The MCM-41 molecular sieve is an ordered mesoporous material with arranged hexagon pores. Its pore diameter is uniform and can be adjusted continuously in the range of 2–10 nm. Some researchers prepared a CaCl₂/MCM-41 composite sorbent using MCM-41 as a porous medium [120]. It can be seen from Fig. 10 that the equilibrium sorption capacity of the composite sorbent is 1.75 g/g, higher than that of the CaCl₂/silica gel composite sorbent. At a relatively low temperature of 80 °C, its desorption capacity can still reach over 90%. Working with the solar thermal collector, its water yield can reach 1.2 kg/m²/day, which makes it an ideal sorbent. However, the sorption cycle of the composite sorbent lasts for a whole day. Such an extremely low sorption rate is a great barrier for its application.

3.4.5. Al-based composite sorbents

Aluminum is the third abundant element in the crust of the Earth after oxygen and silica. It is a wise choice to use aluminum as a porous matrix to prepare composite sorbents. Dawoud et al. [8] synthesized a CaCl₂/Al composite sorbent by injecting CaCl₂ into porous aluminum. When the vapor pressure was 40 mbar and sorption temperature 50 °C, its equilibrium sorption capacity was as high as 0.14 g/g, about 1.6 times that of pure porous aluminum. When the sorption temperature dropped to 35 °C, the sorption

capacity rose to 0.175 g/g, 0.065 g/g higher than that of pure aluminum-based material.

Al₂O₃, which is more likely to form the porous structure than aluminum, can also be used to prepare composite sorbents. Research results show that the equilibrium sorption capacity of activated Al₂O₃ particles is greatly affected by vapor pressure. The sorption capacity was 0.2 g/g at 2 kPa, 2.5 times that of Al₂O₃ at 0.5 kPa [92]. For composite sorbent, the equilibrium sorption capacities of the CaCl₂/Al₂O₃ [121,122] and LiBr/Al₂O₃ [31] were 0.52 and 0.55 g/g respectively. Besides, the passive film forming on the surface of the Al-based composite sorbent can prolong its service life as a protector. At present, Al-based composite sorbents have held a share of the sorbent market due to its relatively high equilibrium sorption capacity, low prices and long cycle life.

4. Conclusions

4.1. Adsorbate

Composite sorbents prepared with hygroscopic materials and porous media are superior to pure hygroscopic materials in sorption performance. Among hygroscopic materials, CaCl₂ is the most popular one for cheap, non-toxic and powerful in water vapor sorption, and thus composite sorbents using CaCl₂ are still a hot research area.

4.2. Heat transfer characteristic

The heat transfer characteristics of hygroscopic materials affect both the sorption and desorption processes. On the one hand, during the sorption process, they affect the transfer of sorption heat from material to environment, thus affecting the sorption rate; while in the desorption process, they affect thermal sorption of composite material, thus affecting the desorption rate. On the other hand, heat and mass transfer are closely related: the former directly affects the latter. Therefore, future researches should also pay much attention to the heat transfer characteristics of hygroscopic materials as well as the effect of the enhancement of heat transfer on mass transfer.

Table 5
Practical application of the silica gel, activated carbon and zeolite composites.

	Matrix performance		Sorption performance		Practical application
	Advantages	Disadvantages	Advantages	Disadvantages	
Silica gel-based composite	Suitable pore size, large porosity, good hydrophilic	Poor thermal stability, and low thermal conductivity	Large water uptake, low drying temperature and good cycle life	Long sorption/desorption time	Water extraction, sorption heating/cooling and thermal storage
Activated carbon-based composite	Excellent thermal stability and conductivity, and large porosity	Poor hydrophilic	Moderate water uptake, short sorption/desorption time	Poor cycle life	Sorption heating/cooling system
Zeolite-based composite	High selective sorption, abundant natural resources, and outstanding thermal stability	Small pore size, poor low thermal conductivity	High selective sorption, large water uptake at high temperature and low humidity	Poor cycle life, low water uptake, high drying temperature and long sorption/desorption time	Removal of metallic ions/phosphine from contaminated water, sorption CO ₂ and water extraction at harsh environment

4.3. Research sorption and desorption process

Present researches primarily focus on the sorption capacity of composite sorbents, but the factors associated with the sorption rate are unclear. The internal sorption theory shall be researched for the chemical/composite sorbents. In engineering practice, desorption process is also important. Therefore, in the next step, more efforts should be paid to studying the desorption process, and comprehensively analyzing the sorption and desorption characteristics of hygroscopic materials.

4.4. Comparisons of sorption/desorption performances

Table 4 displays sorption/desorption performances of SWS-type materials synthesized by using porous matrices and chemical hygroscopic salt. In terms of matrix, silica gel contains a large number of hydrophilic groups (Si–OH) and stable micropores, providing with enough room to load chemical sorbent when compared with activated carbon and zeolite matrices. Therefore, silica gel-based composite exhibits large water uptake. It can be widely used in water extraction from air, sorption heating/cooling and thermal storage as shown in Table 5. Excellent thermal conductivity is an outstanding advantage of the activated carbon matrix. The sorption time of the activated carbon-based composite is less than that of the others. Therefore, the carbon-based composite is applied in the field of sorption heating/cooling systems. 40 types of natural zeolite have been found on earth, and the types of artificially synthesized zeolites are more than 150. The zeolite-based composite can adsorb water vapor under the abominable environment of high temperature and low humidity. It can be found in the removal of metallic ions/phosphine from contaminated water, sorption CO₂, and water extraction from atmosphere under extreme conditions.

4.5. Modified methods

Sorption performances of composite depend on pore structure of matrix, component of chemical salt, adsorbate loading and thermal conductivity. In order to improve sorption performances, porous media (silica gel, activated carbon, zeolite, attapulgite clay, wakkanai siliceous shale and Al-based material) and chemical sorbents (CaCl₂, LiCl, MgCl₂, NaCl, Ca(NO₃)₂, MgSO₄, CuSO₄ and else) have been widely researched in the past two decades. On the other hand, modified methods have been proposed, which include enhancing mass and heat transfer, and extending cycle life. For mass transfer, the porous matrices of large porosity and specific surface area have been synthesized by using the sol–gel method, solvothermal synthesis method, micro-emulsion method, spray drying method, and molecular self-assembly method. There are many methods for enhancement of thermal conductivity, such as mixing/coating with excellent thermal conductivity materials and increasing packing density. Apart from thermal stability, cycle life is also limited by the sorption stability. For example, the activated carbon-based composite has to face the problem of solid–liquid phase separation during sorption process. Enhancement of water-retaining property of the matrix is a key to extend cycle life, such as improvement of hydrophilicity of matrix and adding PVP water-based adhesive.

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