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Performance predictions for a new zeolite 13X/$CaCl_2$ composite adsorbent for adsorption cooling systems

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ABSTRACT

Composite adsorbents synthesized from zeolite 13X and $CaCl_2$ were investigated for applications in solar adsorption cooling systems. The effects of Ca ion exchange on the adsorption properties of zeolite 13X were studied. Ca ion exchange was found to decrease the specific surface area of the zeolite while increasing the total pore volume. Soaking zeolite 13X in 46 wt.% $CaCl_2$ solution for 24 h gave the optimum Ca ion exchange. The increase in the total pore volume facilitated further impregnating the zeolite with $CaCl_2$. In all, 41.5 mol% of $CaCl_2$ was impregnated in the Ca-ion-exchanged zeolite from a 40 wt.% $CaCl_2$ solution to form the zeolite 13X/$CaCl_2$ composite adsorbent. A 0.4 g/g difference in equilibrium water uptake between 25 and 75 °C at 870 Pa was recorded for the composite adsorbent. This was 420% of that of zeolite 13X under the same conditions. Numerical simulation predicts that an adsorption cooling system using the composite adsorbent could be powered by a low grade thermal energy source using the temperature range 75–100 °C. Greatly improved efficiency is predicted compared to a system using pure zeolite 13X or impregnated silica gel.

1. Introduction

In many places, air-conditioning is a daily necessity but it also contributes significantly to electricity consumption - 183 billion kWh, or 16% of electricity consumption by US households, for example [1]. In 1997, 72.5% of homes in the US were equipped with air conditioning, and the figure has doubtless increased since 1978 [2]. Air conditioning systems play an even more important role in regions with higher average ambient temperatures. For example, it contributes 40–50% to total building electricity consumption in Hong Kong [3]. This significant amount of electricity is mostly consumed by the compressors in cooling systems utilizing vapor compression (VC). Traditional VC systems use HCFCs or HFCs as refrigerants, which have strong ozone depletion potential [4–6] and global warming power [7,8]. To ease the problems of energy shortage, ozone depletion and global warming, adsorption cooling systems can be a good alternative. Adsorption cooling offers a number of distinctive advantages, as it are an environmental thermal system where solar energy can be used as the energy source. It utilizes the temperature dependence of the equilibrium adsorbate uptake of adsorbents which can adsorb more adsorbate at lower temperatures. The working principle of adsorption cooling system was described in many literatures [9–14].

An adsorption system offers energy efficient cooling, but some difficulties need to be overcome. Currently, the coefficient of performance (COP) and specific cooling power (SCP) of adsorption cooling systems are rather low – COP of 0.15–0.6 and 10–1000 for the SCP [10,13,19]. The difference in the equilibrium adsorbate uptake between the adsorption and desorption phases, $\Delta\omega$, and the adsorption rate are positively related to the COP and SCP of the system [15]. The $\Delta\omega$ of different adsorbent-adsorbate pairs varies and is a function of the adsorbate's vapor pressure and the operating temperature [16]. Thus, improving the adsorption properties of the adsorbent can increase both the COP and the SCP of the cooling system.

Apart from developing new adsorbents with completely different compositions, another way to improve adsorbent performance is to impregnate the adsorbent with hygroscopic salt to form a composite adsorbent [17–19]. Calcium chloride ($CaCl_2$) is often chosen and water is used as the adsorbate because $CaCl_2$ has high affinity for water and water has a high latent heat with no pollution implications. Mobile Crystalline Material 41 (MCM-41) impregnated with $CaCl_2$ has achieved a reported COP of 0.7 [17]. Silica gel impregnated with $CaCl_2$, called selective water sorbent (SWS), shows an adsorption capacity of 0.7 grams of water per gram of adsorbent. Systems using SWS have reported a COP of 0.6 and an SCP of 20 W kg^{-1} [18]. However, silica gel may not be

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Nomenclature

c_p	specific heat capacity (J/kg K)
d_p	average adsorbent particle (m)
D_{s0}	pre-exponential constant of surface diffusivity (m^2/s)
E_a	activation energy of surface diffusion (J/mol)
h_{ad}	heat of adsorption (J/mol)
Δha	isosteric enthalpy of adsorption (J/mol)
$h_{fg,\mathrm{water}}$	latent heat of vaporization of water (kJ/kg)
k	thermal conductivity (W/m K)
K	adsorption rate coefficient (1/s)
k_1	empirical constant used in Eq. (3) (1/s)
k_2	empirical constant used in Eq. (3) (1/K)
m	total mass of the tested sample (g)
$\dot{m}_{ad}$	adsorption rate (g/g s)
P	pressure (Pa)
R	universal gas constant (J/mol K)
R_p	average radius of the adsorbent particles (m)
T	temperature (K)
u_g	flow velocity of the adsorbate vapor in the z direction (m/s)
U_m	mean velocity of the HTF flow (m/s)
v_g	flow velocity of the adsorbate vapor in the r direction (m/s)
α	thermal diffusivity (m^2/s)
ε	adsorbent bed's porosity
μ	dynamic viscosity (kg/m s)
ρ	density (kg/m^3)
ω	water uptake (g/g)

Subscripts

ad	adsorbed water vapor
eq	equilibrium for ω, equivalent for k
f	heat transfer fluid (HTF)
g	water vapor
m	copper tube
z	zeolite

the most suitable host material for synthesizing composite adsorbents. The low equilibrium uptake at low pressure limits the $\Delta\omega$ between the low pressure adsorption and high pressure desorption states, and thus the COP of the system. This raises energy consumption and installation costs. Moreover, equilibrium water uptake in silica gel decreases sharply above about 30 °C [20]. More adsorbent is needed, which increases the system's size and reduces the SCP.

The adsorption capacity of zeolite 13X remains high at low pressure and its $\Delta\omega$ is high [21]. The equilibrium water uptake of zeolite 13X remains high up to 100 °C. Thus, zeolite 13X is quite suitable for adsorption cooling systems. Impregnating zeolite 13X with $CaCl_2$ should raise its adsorption capacity and increase the difference in equilibrium water uptake between the adsorption and desorption states. However, zeolite 13X has Na^+ ions in its structure. When the zeolite is placed in an aqueous solution of $CaCl_2$, ion exchange takes place between the Na^+ ions in the zeolite and Ca^{2+} ions in the solution. Ca-ion-exchanged zeolite is formed, and this may change the properties of the composite adsorbent and affect its performance in a cooling system. It has been reported that the ion exchange process has a beneficial effect in NO_x conversion as a catalyst because the ion exchange can affect the surface functionality of the zeolite [22]. A molecular simulation of water adsorption in silicalite also showed that different cations can affect the equilibrium water uptake of the silicalite [23].

This study was designed to investigate the changes in the zeolite's crystalline structure and its adsorption properties caused by the ion exchange process. A 13X/$CaCl_2$ composite adsorbent was then prepared and its performance under the operation conditions of a typical adsorption cooling system was assessed. The measured adsorption properties were used to construct a numerical simulation of the adsorber, and this was used to predict the performance of an adsorption cooling system utilizing the zeolite 13X/$CaCl_2$ composite adsorbent. The result was compared with that of a system using conventional zeolite 13X.

2. Material preparation and characterization

2.1. Calcium ion exchange

The raw materials used were zeolite 13X powder with an average particle size of 2 μm (Sigma–Aldrich) and anhydrous $CaCl_2$ powder (Sigma–Aldrich, 96.0 wt.%). After drying the zeolite 13X at 200 °C for 12 h, ion exchange and calcination were carried out. The dried zeolite 13X was mixed with aqueous $CaCl_2$ solution in the mass ratio of 1:9 at different concentrations with stirring at room temperature. Calcium ions diffused into the micropores of the zeolite 13X and ion exchange took place. Since diffusion is generally a slow process, the soaking process was carried out for at least 12 h. The $CaCl_2$ solution was then filtered and the ion-exchanged zeolite was washed with deionized water. The zeolite was then dried at 110 °C for 12 h before calcination. During calcination the zeolite was held at a fixed high temperature for a predetermined period of time.

The concentration of the $CaCl_2$ solution and the soaking time have previously been shown to significantly influence the adsorption capacity [24]. The high temperature calcination process should also affect the structure of the zeolite. Thus, there were four variable parameters to be studied: the concentration of the $CaCl_2$ solution, the ion exchange time, the calcination temperature and time. Table 1 shows the different values of the four parameters tested. It was assumed that these four parameters have little coupling effect so their effects on the properties of the ion-exchanged zeolite 13X can be studied separately. The base condition was chosen arbitrarily to be soaking in 40 wt.% $CaCl_2$ solution for 24 h and calcining at 400 °C for 4 h. The four parameters were varied in turn to elucidate the effect of each individual parameter on the properties of the ion-exchanged zeolite.

2.2. $CaCl_2$ re-impregnation

Aristov et al. reported that $CaCl_2$ confined to a mesoporous silica gel has improved adsorption capacity [25], and this effect should also apply to zeolite. After finding the most suitable conditions for

Table 1
Sample preparation conditions.

Parameter	Value					Unit
$CaCl_2$ solution concentration	10	20	30	40	46 (saturated)	wt.%
Soaking time	12	24	36	48	72	h
Calcination temperature	300	400	500	600		°C
Calcination time	2	4	8	12	24	h