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Theoretical insight of adsorption cooling

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This letter proposes and presents a thermodynamic formulation to calculate the energetic performances of an adsorption cooler as a function of pore widths and volumes of solid adsorbents. The simulated results in terms of the coefficient of performance are validated with experimental data. It is found from the present analysis that the performance of an adsorption cooling device is influenced mainly by the physical characteristics of solid adsorbents, and the characteristics energy between the adsorbent-adsorbate systems. The present study confirms that there exists a special type of silica gel having optimal physical characteristics that allows us to obtain the best performance.

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The adsorption of water or other adsorbates on highly porous solid surface is well suited for low-temperature-heat-transformation applications like thermally driven heat pumps, adsorption cooling, and desalination.¹⁻⁵ In recent years, a considerable progress has been made in the development of novel porous materials with controlled architectures and surface treatment.^{6,7} The structural features such as pore width (d), pore volume (v_p), and specific surface area of solid adsorbents are obtained by pore size distribution (PSD) approaches.^{8,9} The macro- and mesopore sizes are calculated by pore filling and Barrett-Joyner-Halenda models.¹⁰ However, these methods fail to describe the pore filling of micropores and narrow mesopores. The Dubinin-Radushkevich and Horvath and Kawazoe models are dedicated to describe micropore filling.^{11,12} The density functional theory (DFT) and molecular simulations provide not only a microscopic model of adsorption but also a more realistic description of the thermodynamic properties of the pore fluid.¹³ The PSDs

are essential to select suitable adsorbents. The choice of adsorbent-adsorbate pair is determined by (i) the amount of heat that can be extracted from the evaporator and (ii) the difference between the adsorbate uptake and offtake per adsorption cycle. The heat of adsorption¹⁴ is of secondary importance since it is simply rejected to the environment. The adsorption cooling system (ADC) utilizes the adsorbent-adsorbate characteristics and produces useful cooling effects at the evaporator¹⁵⁻¹⁷ by the union of “evaporation-activated-adsorption” and “condensation-through-desorption” and this is shown in Fig. 1. The energy flow for each sorption component of ADC is plotted in a pressure-enthalpy-uptake (P - h - c) coordinate system as shown in Fig. 1. Due to the cooling load (Q_{evap}), the enthalpy of evaporation (line G-H) occurs at the evaporator and the evaporated adsorbate is adsorbed onto adsorbent surfaces of sorption bed (H-A). During the regeneration phase (lines A-B-C), the pressure in the

FIG. 1. (Color online) Silica gel water based adsorption cooling system in a pressure-enthalpy-uptake (P - h - c) coordinate system: Q_{ads} is the adsorption heat which is released at the environment. Q_{des} is the driving heat source, and Q_{cond} is the heat released from the heat sink (condenser). Here the amount of adsorbate uptakes varies from 0.01 to 0.4. Here “o” indicates experimental data of type RD silica gel + water system.

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FIG. 2. (Color online) The isosteric heat of adsorption at zero surface coverage and the characteristics energy as a function of pore width, d (for micropore $d < 2$ nm, for mesopore $2 \text{ nm} < d < 50$ nm, and for macropore $d > 50$ nm). Q_{st}^* and E against the average pore width of type “RD” and type “A” silica gels are shown here.

adsorber rises from evaporator pressure to condenser pressure and desorption of adsorbate from highly porous adsorbent occurs by connecting the adsorption bed with the condenser. At the heat sink (condenser), the desorbed adsorbate is condensed and heat is released to the environment (lines C-E-F). Finally, the condensed refrigerant goes to the evaporator and completes the cycle H-A-B-C-E-F-G. During the adsorption phase (lines C-D-A), the sorption bed is cooled and the pressure falls from condenser pressure to evaporator pressure. Based on adsorption isotherms and adsorbent-adsorbate interaction potential data, we have established a thermodynamic approach to calculate the energetic performances (η) of ADC for various pore widths and volumes of adsorbents, and thus providing a useful evaluation as to their trends for surface development of silica gel adsorbents.

The adsorbate uptakes and off-takes at various pressures and temperatures are essential to the understanding of the nature of solid adsorbents and these are measured by volumetric and gravimetric methods^{18,19} and are predicted by adsorption isotherms equations, namely Langmuir, Tóth, and Dubinin–Astakhov (DA). Hence, the experimentally measured adsorption isotherm data (silica gels+water) are fitted well with the DA equation as presented by $c = c^0 \exp[\{RT \ln(P_s/P)/E\}^n]$, where T is the temperature, R defines the gas constant, P_s is the saturation pressure and c^0 indicates the limiting uptake.^{20–22} The heterogeneity coefficient n lies in the range 1 to 3 depending on the types of adsorbents, and the characteristics energy E is linked with the pore widths. Stoeckli and Morel calculated E for a wide range of adsorbates and a variety of activated carbons, and this is given by $Q_{st}^* - Q_{st} = (0.85 \pm 0.07)E$, where Q_{st}^* is the isosteric heat of adsorption at low surface coverage.²³

When any adsorbate comes into contact with an adsorbent surface, the number of adsorbent surface atoms (N_s) with binding energy (Q_s) is related to the number of adsorbate surface atoms (ranging from Henry region, N^* , to condensation phase, N^0) with energy varying from Q_{st}^* to Q^0 , where Q^0 is the least adsorption energy.²⁴ Using the Boltzmann distribution law, we can write $N_s/N^* = \exp\{-(Q_{st}^* - Q^0)/N_A kT\}$ for Henry region, and $N_s/N^0 = \exp\{-(Q_{st}^* - Q^0)/N_A kT\}$ for the condensed phase, where k is the Boltzmann constant and N_A is the Avogadro number. By employing these two equations, it could be written here that $Q_{st}^* - Q^0 = N_A kT \ln(N^0/N^*)$. This means that E approaches to $(Q_{st}^* - Q^0)$. The isosteric heat of adsorption at zero surface coverage is $Q_{st}^* = RT - N_A V$, where V defines the external wall potential as a function of pore width.^{25,26} Employing all these information, the DA model is used to calculate the amount of adsorbate uptake as a function of pore width and pore volume. The equation now becomes $c = v_p \rho_l \exp[-\{\ln(P_s/P)/1 - (N_A V/RT) - (Q^0/RT)\}^n]$, with $V = \int_0^\infty w(y) \exp\{-w(y)/kT\} dy / \int_0^\infty \exp\{-w(y)/kT\} dy$, where v_p is the pore volume, ρ_l defines the density of water at liquid phase, y indicates the direction of pore width, and w represents the external wall potential. The adsorption characteristics energy is given by

FIG. 3. (Color online) PSD of (a) type “RD” and type “A” silica gels and (b) CaCl_2 -in-silica gel (Ref. 29).

$E = RT - N_A \frac{\int_0^\infty w(y) \exp\{-w(y)/kT\} dy}{\int_0^\infty \exp\{-w(y)/kT\} dy} - Q^0$. (1)

The adsorbent wall potential is described by $w(y) = U_{sf} + U_{sf}(H-y)$, where U_{sf} defines the adsorbent-adsorbate interaction potential, H is the distance between the nuclei of the outer adsorbent atoms on opposite walls. The adsorption interaction potential of adsorbate along the pore width direction y of silica gel pore is written as²⁶ $U_{sf} = 2\pi\epsilon_{sf}\rho_s\sigma_{sf}^2\Delta[5/2(\sigma_{sf}/y)^{10} - (\sigma_{sf}/y)^4 - \sigma_{sf}^4/3\Delta(0.61\Delta+y)^3]$, where σ_{sf} and ϵ_{sf} are the solid-fluid collision diameter and the solid-fluid well depth potential, respectively. Δ defines the separation between the adsorbent planes and ρ_s is the density of solid adsorbent.^{25,27} For the silica gel-water system: $\sigma_{sf} = 3.43 \text{ Å}$, $\epsilon_{sf} = 8.119 \times 10^{-21} \text{ J/mol}$, $\Delta = 3.35 \text{ Å}$, and $\rho_s = 0.055$. The amount of water vapor uptake (c_{ads}) and offtake (c_{des}) during adsorption and desorption phases are given as $c_{ads} = v_p \rho_l \exp[-\{\ln(P_s(T_{ads})/P_{evap})/1 - (N_A V_{ads}/RT_{ads}) - (Q^0/RT_{ads})\}^n]$ and $c_{des} = v_p \rho_l \exp[-\{\ln(P_s(T_{des})/P_{cond})/1 - (N_A V_{des}/RT_{des}) - (Q^0/RT_{des})\}^n]$, respectively.

During the desorption stage, the quantity of heat (Q_{des}) added to the sorption bed is calculated from the thermodynamic property surfaces of silica gel-water system,²⁸ and this is given by

FIG. 4. (Color online) Performance of adsorption cooling cycle as a function of total micropore volume and pore size for the regeneration temperature of 80 °C.

$$Q_{\text{des}} = \int_{T_{\text{ads}}}^{T_{\text{reg}}} \left[c_{p,s} + c_{\text{ads}} \left\{ c_{p,l} + Q_{\text{st}} \left(\frac{1}{T} - \frac{1}{v_g} \frac{dv_g}{dT} \right) \right\} \right] dT$$

$$+ \int_{c_{\text{des}}}^{c_{\text{ads}}} \{ h_a(P, T, c) - h_g(T) \} dc$$

$$+ \int_{P_{\text{evap}}}^{P_{\text{cond}}} Q_{\text{st}} \left. \frac{\partial c}{\partial P} \right|_T dP + \int_{T_{\text{reg}}}^{T_{\text{des}}} \left[c_{p,s} + c_{\text{ads}} \left\{ c_{p,l} + Q_{\text{st}} \left(\frac{1}{T} - \frac{1}{v_g} \frac{dv_g}{dT} \right) \right\} + Q_{\text{st}} \left. \frac{\partial c}{\partial T} \right|_P \right] dT,$$

where c_p is the specific heat and h is the enthalpy. T_{reg} is the regeneration temperature. The subscripts “a,” “s,” “g,” and “l” indicate adsorbate, solid, gaseous, and liquid phases. The subscripts “ads” shows adsorption, “des” indicates desorption, “cond” defines condensation, and “evap” is the evaporation. The cooling capacity is calculated as

$$Q_{\text{evap}} = \int_{c_{\text{des}}}^{c_{\text{ads}}} h_{fg}(T_{\text{evap}}) dc - \int_{c_{\text{des}}}^{c_{\text{ads}}} \int_{T_{\text{evap}}}^{T_{\text{cond}}} (c_{p,l} dT) dc$$

$$- \int_{c_{\text{des}}}^{c_{\text{ads}}} \{ h_g(P, T) - h_g(T) \} dc.$$

The performance (η) of the adsorption cooler can be evaluated by $Q_{\text{evap}}/Q_{\text{des}}$.

We calculate and plot E and Q_{st}^* as a function of silica gel pore widths for the adsorption of water vapor, and these are shown in Fig. 2. It is observed that a rapid change in E and Q_{st}^* occurs for pore sizes smaller than 3 Å, where there is no cooling capacity. For larger pores, there is a rapid decrease in Q_{st}^* and E . The relationship between E and pore size was correlated on the basis of experimental data resulting from x-ray scattering in micropores of carbonaceous materials.²³ These results showed that the E in the micropore decreases when the pore width increases, which indicates the validity of the proposed formulation [Eq. (1)]. In the present analysis, the DFT method is used to calculate the PSD of silica gel pores. The plots of incremental pore volume against pore width for three types of silica gels namely type “A,” type “RD” and CaCl_2 -in-silica gel are shown in Fig. 3. Both “RD” and “A” types silica gels have similar PSD curves and their local maxima are observed at 12.2 Å and 12.7 Å, respectively. The local maximum of CaCl_2 -in-silica gel²⁹ is found at 15 nm. The system performances (η) at

different pore widths and volumes of silica gels are shown in Fig. 4. η is an increasing function of pore width up to 8 Å and remains slightly lower at higher pore width. η also increases at higher pore volume due to an increase in the mass of refrigerant exchanged during the adsorption phase. For normal silica gel such as type A, type RD, type 3A, n is found 1.3. However, n is found to be 1.5 for CaCl_2 -in-silica gel due to the change in surface-structural heterogeneity of normal silica gel by calcium chloride.

From the present analysis, it is observed that there is no cooling performance for pore widths varying from 0 to 0.3 nm. The best performance of silica gel-water based ADC is obtained at pore width of 0.8 nm with higher pore volume. The characteristics energy (E) is found to be higher in micropore ranges. This indicates that the adsorption and desorption rates are higher in micropores. The adsorbent materials like silica gel should be designed with micropores ranging from 0.8 to 1 nm and higher micropore volume for adsorption cooling applications. Employing the proposed formulations, it is possible to estimate the performances of ADC for any type of adsorbent-adsorbate pair.

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