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A hygrothermal modelling approach to water vapour sorption isotherm design for mesoporous humidity buffers

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ABSTRACT

This paper describes the development of a design technique using hygrothermal numerical modelling for top-down predictive design and optimisation of water vapour sorption isotherms to match any humidity buffering application. This was used to inform the design and synthesis of two new mesoporous silica (MS) materials suitable for specific applications. To validate the technique, the new materials were experimentally assessed using gravimetric dynamic vapour sorption (DVS). The experimental isotherms closely matched the optimised isotherm predictions from the design stage, and a positive correlation was observed between the rate of change in adsorbed water content, Δw and the time taken to exceed the permissible upper limit of humidity, $\varphi_{i,U}$ in a closed environment. A positive non-linear correlation was determined between the interior volumetric moisture load, ω_{ml} and the mass of adsorbent required to fully achieve humidity buffering between specified lower/upper limits ($\varphi_{i,L}$ and $\varphi_{i,U}$). The kinetics of water vapour sorption/desorption were found to have general agreement when using the current hygrothermal numerical model. Current hygrothermal models appear to significantly underestimate the rate of adsorption/desorption in rapid-response mesoporous silica type materials. This is perhaps largely due to the current lack of consideration for scanning curve prediction within hysteresis loops and so is a priority for future research.

1. Introduction

Regulation of the psychrometric variables within pre-defined upper/lower limits, to match the requirements of ‘closed environments’ (*e.g.* cars, aircraft, buildings, incubators, laboratories, archives, *etc.*) accounts for the vast majority of global energy consumption and all associated emissions [1–3]. The study of hygrothermics considers an enclosed volume of air in which the psychrometric conditions are isolated from the exterior environment by limiting the exchange of heat, air, and moisture. In relative humidity (RH) buffering applications desirable hygrothermal behaviour is a material's capacity for simultaneous buffering of fluctuations in energy (air enthalpy) and mass (water vapour) concentration with respect to equilibrium moisture content [4,5]. Some examples of moisture buffering applications in closed environments are preventing mould formation [6–9], building fabric damage [10–12], regulating thermal comfort for human activities [13–17], and energy efficient retrofit of existing/older buildings [18–20]. On the other hand, disregarding RH buffering from hygrothermal materials lead to energy and cost penalties. These are caused by relying on continuous use of air conditioning (normally oversized) regardless of occupation, reducing the efficiency of the systems and increasing the energy consumption [21–23]. Advanced mesoporous materials could be then used to fully buffer fluctuations in psychrometric variables by designing them to have hygrothermal properties compatible with the pre-defined upper/lower limits of any closed environment.

Hygrothermics studies the coupled phenomena in porous solids that occur as a result of adsorption, diffusion, and desorption of heat and moisture (liquid and vapour phases). The moisture storage function is one of several hygrothermal functional properties, where $w = f(\varphi)$ defines the non-linear relationship between the mass of adsorbed water and the ratio of vapour pressure to saturation vapour pressure; known as a sorption isotherm when at constant temperature. The maximum value for w depends on n, corresponding to total pore volume, whilst $\lambda(w)$ describes the positive dependency of thermal conductivity on w. The summation of c_p for the adsorbent and adsorbate describe stored energy, whilst

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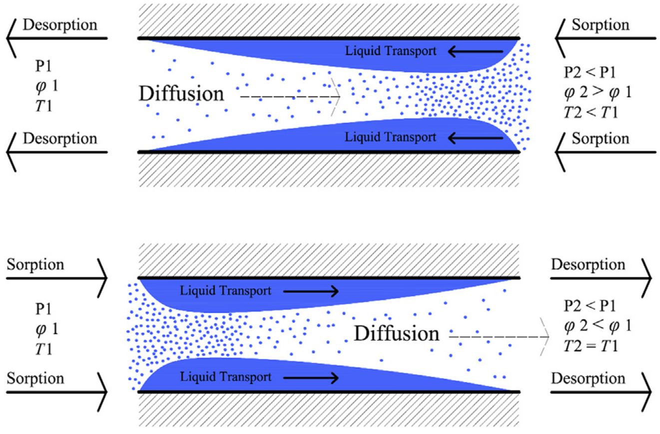
Nomenclature

$\boldsymbol{\rho}$	bulk density, kg/m^3
$\boldsymbol{c_p}$	specific heat capacity, J/(kg K)
$\boldsymbol{\lambda(w)}$	moisture-dependent thermal conductivity, W/(m K)
$\boldsymbol{\varphi}$	relative vapour pressure (p_v/p_{sat}), –
$\boldsymbol{n}$	bulk porosity, m^3/m^3
$\boldsymbol{w = f(\varphi)}$	water vapour sorption isotherm, kg/m^3
$\boldsymbol{\mu(\varphi)}$	water vapour diffusion factor, –
$\boldsymbol{D_w(w)}$	liquid water diffusivity, m^2/s
RH	relative humidity; where $\varphi \cdot 100$, %
$\boldsymbol{\omega_{ml}}$	volumetric moisture load, g/h/m^3
H	total enthalpy, J/m^3
h_v	latent heat of phase change, J/kg
t	time, s
T	temperature, K
δ_p	vapour permeability, kg/(m s Pa)
Suffixes	
i	interior
e	exterior
L	lower limit
U	upper limit

substantial heat transfer can occur due to both heat of adsorption and evaporation/condensation of the adsorbate during transport. In the hygroscopic domain, the (Fickian) diffusion coefficient is a function of relative vapour pressure, $\mu(\varphi)$ as a result of pore network constriction by condensation filling. In the capillary domain, the water diffusion coefficient is a function of water content, $D_w(w)$ [24,25]. This leads to the well-known contra- and counter flow mass transport scenarios in hygrothermics (see Fig. 1) [26,27].

The morphology and volume of the pore network in mesoporous silicas can be easily modulated through the synthesis process (using surfactants as a template for polycondensation of silica species) by controlling the temperature [28,29] and reaction time [30,31]. This makes them an ideal template material from which to control and synthesise hygrothermal functional properties with respect to RH buffering. Significant interest in these materials has previously focussed on catalysis [32–34], separation [35–37], gas adsorption [38–40], and drug delivery [41,42]. However, hygrothermics not only has to consider isothermal physisorption but also the temperature-dependency of heat & moisture diffusion and storage, as well as the moisture-dependency of thermal conductivity and heat storage. Hygrothermal models are constitutive and so require bulk-scale functional properties as inputs to represent mesoporous solids. The bulk-scale properties are therefore statistically-averaged representations of the mesopore-scale behaviour. In recent work, two important principles were established for the hygrothermal behaviour of mesoporous solids: (i) an empirical correlation between mesopore diameter and the kinetics of RH buffering [43], and (ii) prediction of the required adjustment to the hygrothermal functional properties of one mesoporous solid in order to duplicate the behaviour of another [20]. However, the relationships between structure (mesopore geometry, physisorption and hysteresis) and properties (hygrothermal functions) are still neither quantified nor fundamentally understood.



P = Water vapour partial pressure, φ = Relative humidity and T = Dry bulb air temperature

Fig. 1. Contra- and counter flow of mass transport. Adapted from Ref. [27].

The aim of this study was to develop a hygrothermal numerical modelling technique that enables top-down predictive design of the ideal water vapour sorption isotherm for any RH buffering application. The parameters for design would be a closed environment of volume, V in which the upper and lower limits for psychrometric variables ($T_{\max}$, $T_{\min}$, $\varphi_{\max}$, $\varphi_{\min}$) were specified. This technique was developed using three pre-existing materials from a previous study, and then used to inform the synthesis of two new MS; both having hygrothermal properties optimised to suit two different closed environment scenarios. The water vapour sorption isotherms and RH buffering behaviour of these two materials were then assessed experimentally.

2. Experimental

2.1. Synthesis and characterization

The two new pure silica MCM-41 samples were synthesized from fumed silica as silica source, cetyltrimethylammonium bromide (CTAB) as structure directing agent or template, tetramethylammonium hydroxide (TMAOH) and water. In a typical synthesis, 1.9 g TMAOH and 4.6 g CTAB were dissolved in 34.1 g of distilled water under stirring at 35 °C, following which 3.0 g fumed silica was added to the solution under stirring for 1 h to obtain a homogeneous gel of molar composition SiO_2:0.25CTAB:0.2TMAOH:40H_2O, which was left to age for 20 h at room temperature. The aged gel mixtures were then transferred into a Teflon-lined autoclave and heated, under static conditions, at 150 or 180 °C, for 48 h. The solid product was then filtered off, washed with water and dried in air at room temperature to yield the as-synthesized sample. The surfactant templates within the as-synthesised sample were removed by calcination (heating ramp rate of 5 °C/min) at 550 °C for 6 h. The final calcined silica samples were designated as MCM-41-x where x is the synthesis (crystallisation) temperature, *i.e.*, 150 or 180 °C.

2.2. Material characterisation

Powder X-ray diffraction (XRD) analysis was performed using a PANalytical X'Pert PRO diffractometer with Cu-Kα radiation (40 kV, 40 mA), 0.02 step size and 50 s step time. Nitrogen sorption isotherms and textural properties were determined at −196 °C using a conventional volumetric technique by a Micrometrics ASAP 2020 sorptometer. Before analysis, the samples were first dried at 130 °C and then outgassed under vacuum at 200 °C for 12 h. The surface area of the materials was determined using the standard Brunauer–Emmett–Teller (BET) method based on adsorption data in the relative pressure (P/P_o) range of 0.05–0.2, and pore volume was calculated from the amount of nitrogen adsorbed at P/P_o of ca. 0.99.