

NEW COMPOSITE SORBENT "CaCl₂ in MESOPORES of MCM-41" FOR SORPTION COOLING/HEATING

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Abstract

New working material "CaCl₂ confined to mesoporous host matrix MCM-41" is synthesised and studied keeping in mind its application for sorption cooling/ heating. For this *mesoporous* system water sorption isobars, isosters and isotherms are obtained at temperature 20-150 °C and vapour partial pressure 8.7 – 50.3 mbar. The calorimetric heat of vapour sorption is measured at water uptakes $w = 0 - 48.2$ wt.%. The water sorption is found to be a combination of liquid absorption and heterogeneous adsorption. The results obtained evidence considerable change of the salt properties due to its confinement to the MCM-41 nanopores. Brief comparison of this sorbent with a pure silica gel for cooling/heating application is done.

KEYWORDS

calcium chloride, water sorption, MCM-41, heat of sorption

INTRODUCTION

Development of sorption cooling/heating systems which are driven by low temperature heat is attracting increasing interest as they allow utilisation of the huge amount of industrial waste heat and low grade solar energy and fit the requirements of zero Ozone Depletion and Global Warming Potentials. The large scale dissemination of the sorption systems requires searching new advanced working pairs.

We have recently presented a new family of composite working materials called as selective water sorbents (SWSs) that were invented, developed and studied at the Boreskov Institute of Catalysis (Novosibirsk) [1-7]. An SWS material is a two-phase system which consists of a porous host matrix and a hygroscopic substance (commonly an inorganic salt) impregnated into its pores. Due to their physical structure the materials take an intermediate position between solid adsorbents and pure hygroscopic salts and can be organised in a way to demonstrate the best features of the both systems. In this communication we describe a new SWS material, namely, calcium chloride in MCM-41 matrix, and present its physico-chemical properties: "water vapour - SWS" equilibrium, specific water sorption capacity, heat of water sorption and specific energy storage capacity. The MCM-41 matrix has unique properties as it consists of monosized cylindrical mesopores with good gas transport properties (for more details see [8]). Improved mass transfer is considered to be necessary for efficient application of the sorbent in modern cooling/heating systems.

EXPERIMENTAL

Sample preparation

Previously dried at 150 °C granules of MCM-41 [8] (specific surface area $S_{\text{BET}} = 1050$ m²/g, pore volume $V_{\text{por}} = 1.1$ cm³/g, pore diameter $D_{\text{por}} = 3.8$ nm) were impregnated at 20 °C with saturated calcium chloride aqueous solution up to complete pores filling and then dried at 150 °C until the sample weight remains constant. The salt content in the sample synthesised turned out to be equal to $C_{\text{CaCl}_2} = 37.7$ wt.%. BET measurements have shown no MCM-41 porous structure collapse due to salt impregnation while its specific surface area reduces down to 325 m²/g that indicates a partial blockage by the confined salt of the access to internal volume of pores.

Measurements of sorption equilibrium curves

Sorption equilibrium in "water vapour - CaCl₂ - MCM-41" system was investigated by a TG method over 20-150 °C temperature range at water vapour partial pressures P_{H₂O} of 8.7 to 50.3 mbar using a Rigaku Termoflex thermobalance. Dry sample of 20 mg weight (m_{dry}) was placed in a standard Al crucible and the dependence of the sorbed water uptake m_{H₂O} on T at fixed P_{H₂O} was registered both at adsorption and desorption modes which gives us a sorption isobar. The water uptake is presented here as a number N of sorbed water molecules related to one molecule of the confined salt:

$$N = (m_{H_2O} \cdot 111) / (m_{CaCl_2} \cdot 18), \quad (1)$$

where 111 and 18 are molecular weights of calcium chloride and water respectively and m_{CaCl₂} is a salt weight in the sample equal to m_{CaCl₂} = 0.377 m_{dry}.

Calorimetric measurements

For direct measurements of calorimetric heat ΔH_{cal} of water sorption at 40 °C a Setaram Tian-Calve HT calorimeter was used. A sample of 300 mg dry weight was placed in a glass ampoule connected to a vapour injector and vacuum system. Before measurements the sample was heated up to 150 °C under evacuation at 10⁻³ Pa for 2 hours. During the experiments small amount of water vapour (10⁻⁴ - 10⁻³ moles) was injected inside the ampoule and the heat released due to water sorption by the sample was measured by the calorimeter. Average error of sorption heat measurements was not higher than 4%.

RESULTS AND DISCUSSION

Sorption equilibrium in "water - calcium chloride - MCM-41" system

A set of sorption isobars is presented on Fig. 1 as a dependence of water uptake on temperature at various partial vapour pressures. These curves demonstrate a divariant type of sorption equilibrium over the whole range of water sorption that is typical for sorption equilibrium of vapour with salt solutions. No solid crystalline hydrates formation is observed. This is in line with our previous results on "salt-water" sorption equilibrium inside small pores [2].

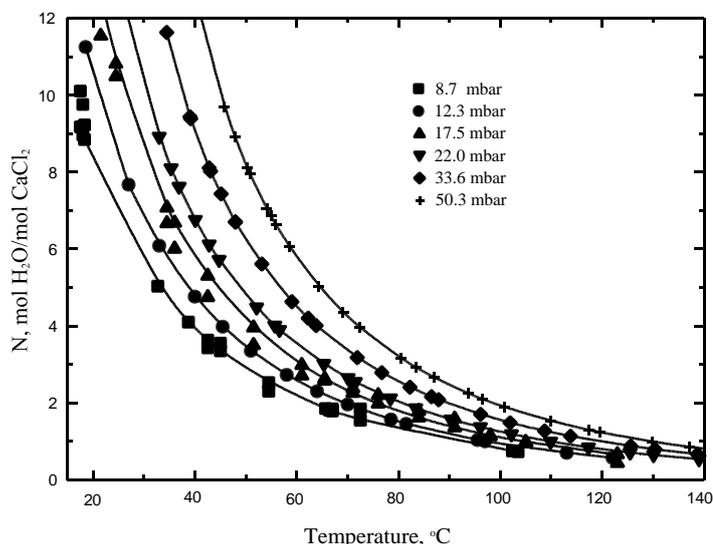


Fig. 1 Isobars of water sorption on " calcium chloride - MCM-41" composite.

Based on experimentally measured isobars a family of sorption isosters is calculated and displayed as straight lines in a ln(P_{H₂O}) vs 1/T presentation (Fig.2):

$$\ln(P_{H_2O}) = A(N) + B(N)/T, \quad (2)$$

where A(N) and B(N) are coefficients. The slope of these lines allows to obtain the isosteric heat of water sorption ΔH_{is}(N) = B(N)·R, where R is an universal gas constant. Values of ΔH_{is}(N) are presented in Table 1 for N = 1 – 7.

The ΔH_{is} -value tends to slightly decrease with the water content increase and at $N = 7$ it approaches the evaporation heat of a bulk CaCl_2 aqueous solution.

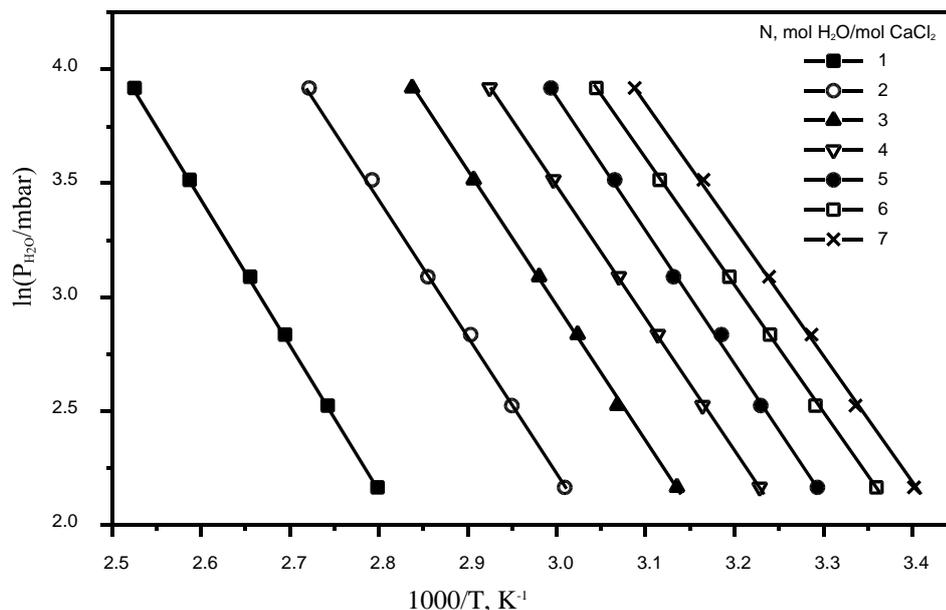


Fig. 2. Water sorption isosters for " calcium chloride - MCM-41" sorbent.

Results of direct calorimetric measurement of water sorption heat ΔH_{cal} are displayed on Fig.3 and presented in Table 1. The ΔH_{cal} -dependence on water uptake is in a good agreement with the isosteric data at $N > 1$, although the calorimetric heat of water sorption is higher than the isosteric heat obtained by treatment of vapour sorption data.

The direct calorimetric data also show that first portions of water (at $N < 0.05$) are sorbed with the high heat of about 90 kJ/mol that is very close to the heat of water sorption on the pure host matrix of MCM-41.

Thus, the water sorption on the composite involved can be considered as a combination of heterogeneous adsorption on surface sites of MCM matrix and liquid absorption with formation of calcium chloride aqueous solution inside MCM pores.

Table 1. Isosteric ΔH_{is} and calorimetric ΔH_{cal} heats of water sorption on "calcium chloride - MCM-41" composite as a function of water content N .

N , mol H_2O /mol CaCl_2	0.05	1	2	3	4	5	6	7	8
ΔH_{is} , kJ/mol	-	53.2	51.0	49.3	48.2	48.8	46.4	46.7	-
ΔH_{cal} , kJ/mol	89.5	61.6	65.3	64.6	62.2	56.2	55.1	54.3	53.8

The dependence of water sorption on the relative vapour pressure $\eta = P_{\text{H}_2\text{O}}/P_0$ (Fig.4) allows to compare the properties of CaCl_2 solution confined to mesoporous matrix with those for bulk salt [9]. This isotherm does not coincide with the isotherm for the bulk system neither at low nor at high η values. At low η the disperse system absorbs water much better than the bulk one, while at $\eta > 0.2$ the "isotherm" lies below the proper curve for the bulk CaCl_2 solutions [9].

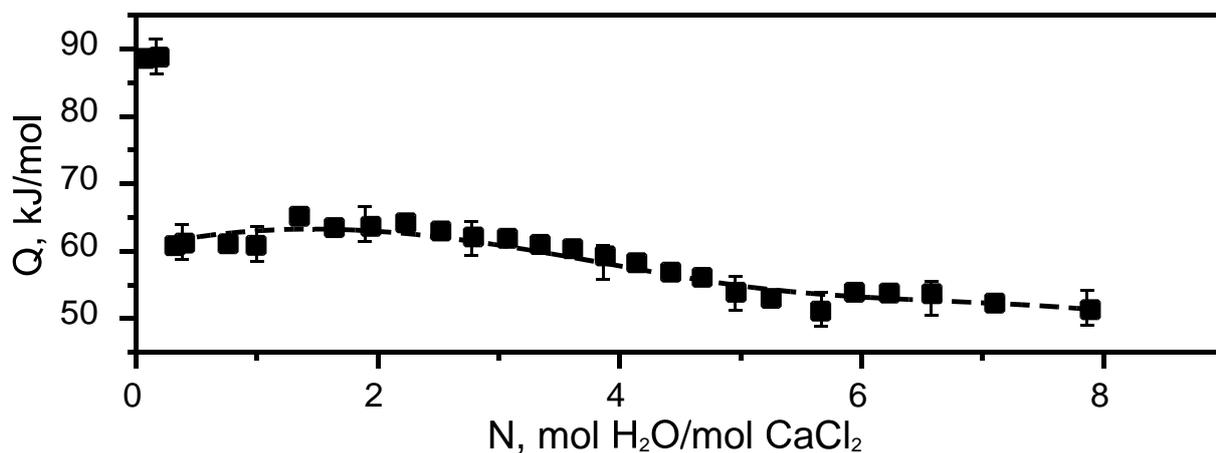


Fig. 3. Calorimetric heat of water sorption on composite studied as a function of water uptake.

Thus, the salt confinement inside nanopores of MCM-41 strongly influences calcium chloride properties, so that this opens possibility to manage water sorption properties of the composite “salt-MCM” to fit demands of particular sorbent application.

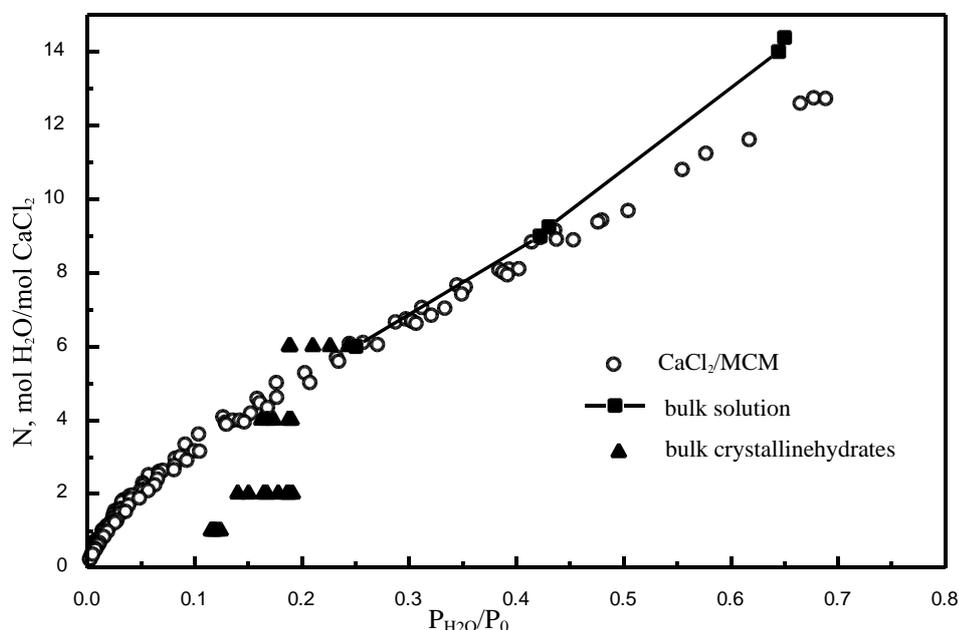


Fig. 4. “Universal isotherm” of water sorption on composite studied and literature data on water sorption by bulk crystalline hydrates and aqueous solution of CaCl_2 .

The study of the sorption equilibrium allows an estimation of the specific water sorption capacity A_{sp} and specific energy storage capacity E_{sp} of composite involved. The former value strongly depends on the relative pressure (see Fig.4), and reaches $A_{sp}=0.7\div 0.75$ g of water sorbed by 1 g of the dry sorbent at $P/P_0 \approx 0.7$. Evidently, this value is far beyond that of common adsorbents such as silica gels, alumina, zeolites, *etc.* So, the large A_{sp} value causes an extremely encouraging specific energy storage capacity E_{sp} of this sorbent, that is defined as the maximum energy stored during complete water desorption calculated per 1 g of a dry SWS material. Taking into account the isosteric sorption heat ΔH_{is} and sorption capacity A_{sp} , E_{sp} can be estimated as 2.0-2.1 kJ/g.

Thus, the composite “calcium chloride inside MCM-41 matrix” is an artificial sorbent intermediate between solid adsorbents and liquid absorbents. Its water sorption properties are defined by the porous structure of the host matrix (MCM-41), chemical nature and amount of the impregnated salt (CaCl_2). To analyse a thermodynamic cycle of sorption cooling/heating units utilising this sorbent one should base on isosteric chart of this sorbent. This is exemplified by Fig. 5 where a basic cycle of solid sorption system is

briefly outlined in a (LnP, T) presentation with operating parameters common for cooling machine driven by low grade heat ($T_{ev} = 5^{\circ}\text{C}$, $T_{cond} = T_{ads} = 40^{\circ}\text{C}$, $T_{max} = 130^{\circ}\text{C}$).

Fig. 5 shows that for “CaCl₂-MCM” composite the water desorption begins at 76°C (initial water uptake $w_{max} = 22$ wt.%) and at highest cycle temperature of 130°C the rest of water is $w_{min} = 5$ wt.%, so that $\Delta w = w_{max} - w_{min} = 17$ wt.% of water is involve in the cycle. For KSK silica this value is much lower ($\Delta w = 5$ wt.%) (Fig. 5). This results from the experimental fact that for the composite sorbent isosteric lines are more closely spaced than for the pure silica. A direct consequence is the large increase in the specific cooling energy that is proportional to the mass of cycled working liquid.

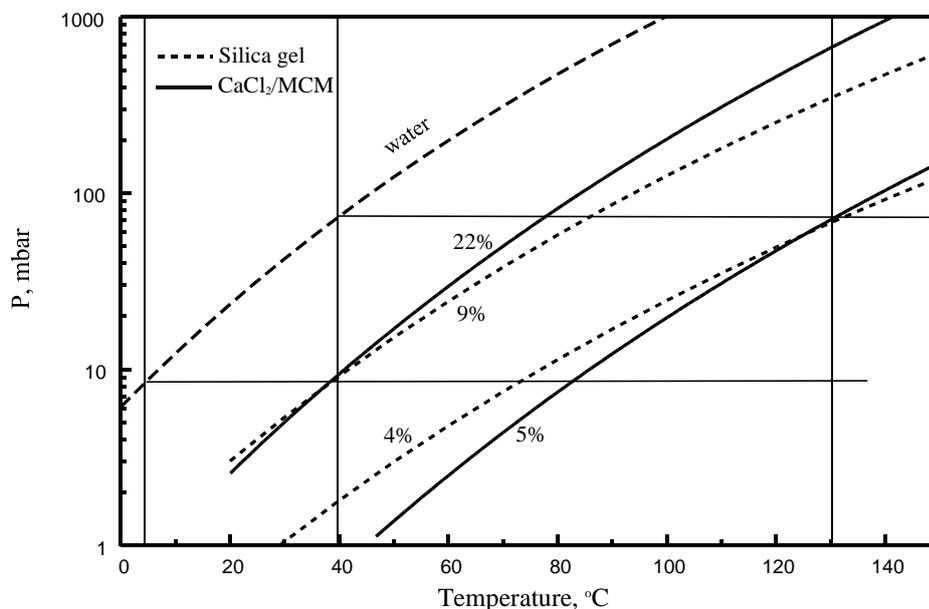


Fig. 5. Comparison of operating cycles for “CaCl₂-MCM” composite (solid lines) and pure commercial silica gel of KSK type (dashed lines), plotted from the experimental data on water sorption.

Our brief estimation has shown that the COP value for this refrigeration cycle utilising the composite “CaCl₂ – MCM” can reach 0.65-0.7.

CONCLUSIONS

The study has shown that composite material based on CaCl₂ as an impregnated salt and MCM-41 as a host matrix is able to absorb up to 0.75 g H₂O per gram of the dry sorbent, that can ensure high values of the energy storing capacity (2 kJ/g). Moreover, the most of water sorbed can be removed at relatively low temperature between 70 and 120°C that facilitates drastically using heat sources with low temperature level, like industry heat wastes, geothermal and solar energy. This material demonstrates two types of sorption behaviour (liquid absorption and solid adsorption) giving an opportunity to combine their advantages. For instance, the solution retention in solid MCM matrix is likely to allow overcoming crystallisation and corrosion problems that are crucial for liquid absorption units.

Thus, the results of this study demonstrate that the new SWS material “CaCl₂ inside MCM pores” can be competitive with the common working materials, like zeolites, silica gels, etc. and should be considered as good candidate for thermal applications driven by low temperature heat sources.

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Nomenclature

MCM-41 – Mobil Composite Material; w – water uptake, g/g; S_{BET} – BET surface area, m^2/g ; V_{por} – pore volume, cm^3/g ; D_{por} – pore diameter, nm; $P_{\text{H}_2\text{O}}$ – water vapour partial pressure, mbar; C_{CaCl_2} – calcium chloride content, wt.%; m_{dry} – dry sample weight, g; $m_{\text{H}_2\text{O}}$ – water uptake, g; T – temperature, both K and $^{\circ}\text{C}$; N – water uptake, mol $\text{H}_2\text{O}/\text{mol CaCl}_2$; m_{CaCl_2} – calcium chloride weight, g; ΔH_{cal} – calorimetric sorption heat, kJ/mol; ΔH_{is} – isosteric sorption heat, kJ/mol; R – universal gas constant, 8.31 J/molK; η – relative vapour pressure; P_0 – saturated vapour pressure, mbar; A_{sp} – specific water sorption capacity, g/g; E_{sp} – specific energy storage capacity, J/g; T_{ev} – evaporator temperature, $^{\circ}\text{C}$; T_{cond} – condenser temperature, $^{\circ}\text{C}$; T_{ads} – adsorption temperature, $^{\circ}\text{C}$; T_{max} – maximal temperature of cycle, $^{\circ}\text{C}$; w_{min} – minimal water uptake, g/g; w_{max} – maximal water uptake, g/g; Δw – water uptake difference, g/g; COP – coefficient of performance

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