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Int. J. Therm. Sci. 41 (2002) 470–474

International Journal of Thermal Sciences

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New composite sorbent $CaCl_2$ in mesopores for sorption cooling/heating

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Received 24 January 2001; accepted 2 August 2001

Abstract

New working material "$CaCl_2$ confined to mesoporous host matrix MCM-41" is synthesised and studied keeping in mind its application for the sorption cooling/heating. For this *mesoporous* system the isobars, isosters and isotherms of the water sorption are obtained at the temperatures 293–423 K and the vapour partial pressures 8.7–50.3 mbar. The water sorption is found to be a combination of a liquid absorption and a heterogeneous adsorption. The obtained results evidence the considerable change of the salt properties due to its confinement to the MCM-41 nanopores. A brief comparison of this sorbent with a pure silica gel for the cooling/heating application is made. © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Keywords: Calcium chloride; Water sorption; MCM-41; Heat of sorption

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1. Introduction

Development of the sorption cooling/heating systems, which are driven by the low-temperature heat, attracts the increasing interest. These systems allow utilisation of the huge amount of industrial waste heat as well as the low-grade solar energy and fit the requirements of the Zero Ozone Depletion and the Global Warming Potentials. The large-scale dissemination of the sorption systems stimulates the search of the advanced working pairs.

We have recently presented a new family of the 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) confined into the matrix pores. Due to their physical structure, the materials take an intermediate position between the solid adsorbents and the 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 the MCM-41 matrix, and present its physicochemical properties: the equilibrium "water vapour–SWS", the specific capacity for the water sorption, the heat of the water sorption and the specific capacity for the energy storage. The MCM-41 consists of the monosized cylindrical mesopores (Fig. 1). The good gas-transport properties of this structure explain the use of the MCM-41 as a host matrix (for more details see [8]). The improved mass transfer is considered to be necessary for the efficient application of the sorbent in the modern cooling/heating systems.

2. Experimental

2.1. Sample preparation

Granules of MCM-41 [8] (the specific surface area $S_{BET} = 1050\ m^2 \cdot g^{-1}$, the pore volume $V_{por} = 1.1\ cm^3 \cdot g^{-1}$, the pore diameter $D_{por} = 3.8$ nm) were preliminary dried at 423 K. Then they were impregnated at 293 K with a saturated aqueous solution of calcium chloride until the complete pore filling and then dried again at 423 K until the sample weight remained constant. The salt content in the sample synthesised was equal to $C_{CaCl_2} = 37.7$ wt.%.

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PII: S1290-0729(02)01339-X

Nomenclature

T_{ads}	adsorption temperature	K
S_{BET}	BET surface area	$m^2 \cdot g^{-1}$
C_{CaCl_2}	calcium chloride content	wt.%
m_{CaCl_2}	calcium chloride weight	g
COP	coefficient of performance	
T_{cond}	condenser temperature	K
m_{dry}	dry sample weight	g
T_{ev}	evaporator temperature	K
T_{max}	maximal temperature of cycle	K
w_{max}	maximal water uptake	$g \cdot g^{-1}$
w_{min}	minimal water uptake	$g \cdot g^{-1}$
MCM-41	Mobil Composite Material	
D_{por}	pore diameter	nm
V_{por}	pore volume	$cm^3 \cdot g^{-1}$
P_0	saturated vapour pressure	mbar
E_{sp}	specific energy storage capacity	$J \cdot g^{-1}$
A_{sp}	specific water sorption capacity	$g \cdot g^{-1}$
T	temperature	K
R	universal gas constant $= 8.31\ J \cdot mol^{-1} \cdot K^{-1}$	
m_{H_2O}	water uptake	g
w	water uptake	$g \cdot g^{-1}$
N	water uptake	$(mol\ H_2O) \cdot (mol\ CaCl_2)^{-1}$
P_{H_2O}	water vapour partial pressure	mbar
Greek symbols		
η	relative vapour pressure	
ΔH_{cal}	calorimetric sorption heat	$kJ \cdot mol^{-1}$
ΔH_{is}	isosteric sorption heat	$kJ \cdot mol^{-1}$
Δw	water uptake difference	$g \cdot g^{-1}$

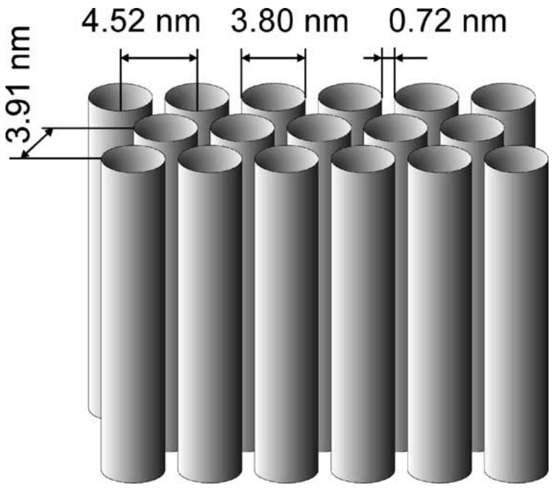

Fig. 1. Structure of the MCM-41 material.

Although the specific surface area of the MCM-41 reduces to 325 $m^2 \cdot g^{-1}$ during the salt impregnation, the BET measurements showed no collapse of the MCM-41 porous structure. This reduction indicates that the confined salt partially blocks the access to the internal volume of the matrix pores.

2.2. Measurements of sorption equilibrium curves

The sorption equilibrium in the system "water vapour–$CaCl_2$–MCM-41" was investigated in the temperature range 293–423 K and at the partial pressures P_{H_2O} of the water vapour from 8.7 to 50.3 mbar by a TG method with the use of a Rigaku Termoflex thermobalance. Before the measurements of a sorption isobar, a dry sample of 20 mg (m_{dry}) was placed in a standard Al crucible and slowly heated to 150 °C until reaching a constant weight. Then the internal balance volume was connected with an evaporator in order to maintain fixed water vapor pressure over the sample, and the sorption process started. The evaporator temperature was set by a thermostat with an accuracy of $\pm 0.1\,^\circ C$. The accuracy of the sample temperature regulation was about $\pm 0.4\,^\circ C$. The equilibrium amount of sorbed water m_{H_2O} was measured directly as a final increase in the sample weight at fixed T and P_{H_2O}. It usually took 0.5–2 hr to reach the equilibrium. The sorption isobars were recorded as a dependence of the sorbed water uptake m_{H_2O} on temperature T at the fixed P_{H_2O} both at the adsorption and desorption modes with the accuracy ± 0.1 mg. The water uptake is presented here as a number N of the sorbed water molecules related to one molecule of the confined salt:

$$N = \frac{m_{H_2O}/M_{H_2O}}{m_{CaCl_2}/M_{CaCl_2}} \tag{1}$$

where $M_{CaCl_2} = 111\ g \cdot mol^{-1}$ and $M_{H_2O} = 18\ g \cdot mol^{-1}$ are molecular weights of calcium chloride and water, respectively, and m_{CaCl_2} is the weight of the salt in the sample equal to $m_{CaCl_2} = 0.377 \cdot m_{dry}$.

3. Results and discussion

3.1. Sorption equilibrium in the system "water–calcium chloride–MCM-41"

A set of the sorption isobars measured at the various partial pressures of the vapour is presented in Fig. 2. These curves demonstrate a bivariant type of the sorption equilibrium over the whole range of water sorption N that is typical for the sorption of vapour by the salt solutions. No formation of the solid crystalline hydrates can be observed. This is in line with our previous results on the sorption equilibrium in the system "salt–water" inside the small pores [2].

Based on the experimentally measured isobars, a family of the sorption isosters is calculated and displayed as the straight lines in a $\ln(P_{H_2O})$ vs. $1/T$ presentation (Fig. 3):

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

where $A(N)$ and $B(N)$ are coefficients. The slope of these lines allows us to obtain the isosteric heat of the water sorption $\Delta H_{is}(N) = B(N) \cdot R$, where R is the universal gas constant. The values of $\Delta H_{is}(N)$ are presented in Table 1 for $N = 1$–7.

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

The dependence of ΔH_{is} on the water uptake is in a good agreement with the results of the direct calorimetric measurement of the water sorption heat ΔH_{cal} [9], also presented in Table 1.

The dependence of the water sorption on the relative vapour pressure $\eta = P_{H_2O}/P_0$ (Fig. 4) allows us to compare the properties of the $CaCl_2$ solution confined to mesoporous matrix with those for the bulk salt [10]. This isotherm does not coincide with the isotherm for the bulk system both at low and at high η values. At the low partial pressure η, the disperse system absorbs water much better than the bulk one, whereas at $\eta > 0.2$, the "isotherm" lies below the corresponding curve for the bulk $CaCl_2$ solutions [10].

Thus, the salt confinement inside the nanopores of the MCM-41 strongly influences the calcium chloride properties. Such an influence opens the possibility to manage the properties of the composite "salt–MCM" in respect with the water sorption to fit the demands of a particular sorbent application.

3.2. *Application in sorption heat pumps*

The study of the sorption equilibrium allows an estimation of the specific capacity A_{sp} for the water sorption and the specific capacity E_{sp} for the energy storage of the composite involved. The former value strongly depends on the relative pressure (see Fig. 4), and reaches $a_{sp} = 0.7$–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 the 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 the complete water desorption calculated per 1 g of a dry SWS material. Taking into

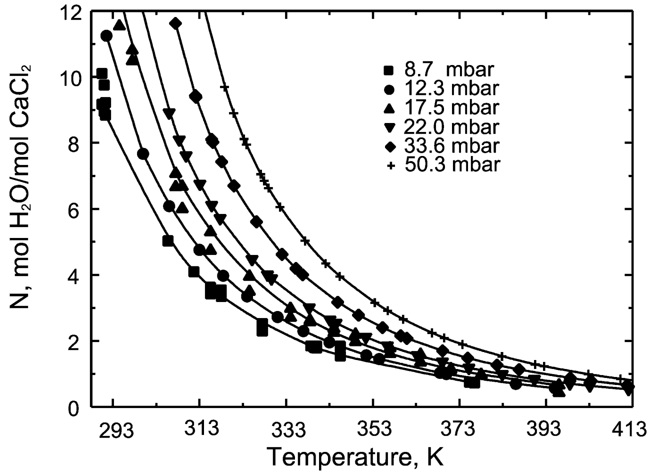

Fig. 2. Isobars of water sorption on the composite "calcium chloride–MCM-41".

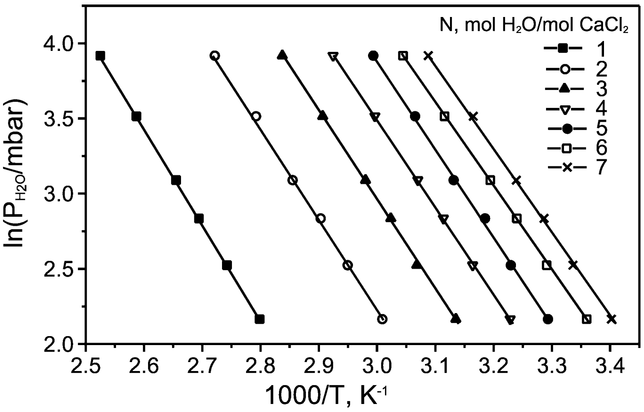

Fig. 3. Water sorption isosters for the sorbent "calcium chloride–MCM-41".

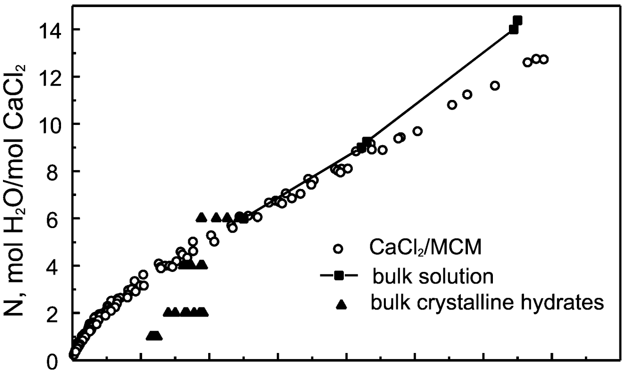

Fig. 4. "Universal isotherm" of water sorption on the composite studied and literature data on the water sorption by bulk crystalline hydrates and by the aqueous solution of $CaCl_2$.

Table 1
Isosteric ΔH_{is} and calorimetric [9] ΔH_{cal} heats of water sorption on the composite "calcium chloride–MCM-41" as a function of the water content N

N, $(\text{mol } H_2O)\cdot(\text{mol } CaCl_2)^{-1}$	0.05	1	2	3	4	5	6	7	8
ΔH_{is}, kJ·mol^{-1}	–	53.2	51.0	49.3	48.2	48.8	46.4	46.7	–
ΔH_{cal}, kJ·mol^{-1}	89.5	61.6	65.3	64.6	62.2	56.2	55.1	54.3	53.8

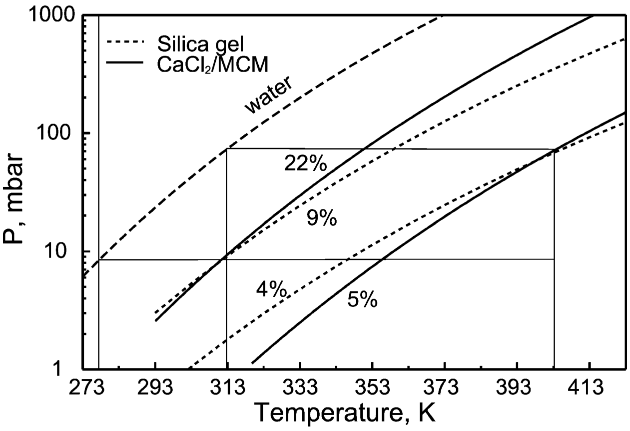

Fig. 5. Comparison of operating cycles for the composite “$CaCl_2$–MCM” (solid lines) and the pure commercial silica gel of the KSK type (dashed lines), plotted from the experimental data on the water sorption.

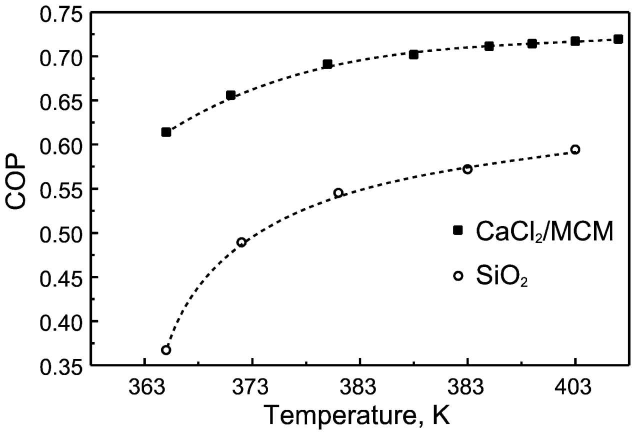

Fig. 6. Dependence of COP on maximum desorption temperature for the adsorption cooling device utilising the composite “$CaCl_2$–MCM” and the pure commercial silica gel of the KSK type.

account the isosteric sorption heat ΔH_{is} and the sorption capacity A_{sp}, E_{sp} can be estimated as 2.0–2.1 $\mathrm{kJ{\cdot}g^{-1}}$.

Thus, the composite “calcium chloride inside MCM-41 matrix” is an artificial sorbent intermediate between the solid and liquid absorbents. Its water sorption properties are defined by the porous structure of the host matrix (MCM-41), the chemical nature and the amount of the impregnated salt ($CaCl_2$). To analyse a thermodynamic cycle of the sorption cooling/heating units based on this sorbent, one should use the isosteric chart of this sorbent. This is exemplified by Fig. 5 where a basic cycle of the solid sorption system is given in a $(\mathrm{Ln}\,P, T)$ presentation with the operating parameters common for the cooling sorption unit driven by the low-grade heat ($T_{\mathrm{ev}} = 278$ K, $T_{\mathrm{cond}} = T_{\mathrm{ads}} = 313$ K, $T_{\max} = 403$ K).

Fig. 5 shows that for the composite “$CaCl_2$–MCM”, the water desorption begins at 349 K (initial water uptake $w_{\max} = 22$ wt.%). At the highest cycle temperature of 403 K, the water residual is $w_{\min} = 5$ wt.%. So, $\Delta w = w_{\max} - w_{\min} = 17$ wt.% of water is involve in the cycle. For KSK silica this value is much lower ($\Delta w = 5$ wt.%) (Fig. 5). Such a high value of Δw for the composite sorbent results from the experimental fact that for this material, the isosteric lines are closer spaced than those for the pure silica. A direct consequence is the large increase in the specific cooling energy that is proportional to the mass of the cycled working liquid.

Our calculations of the thermal performance of the adsorption refrigeration unit based on the composite “$CaCl_2$–MCM” at the operating conditions mentioned above demonstrate that the COP value reaches 0.71 (Fig. 6), whereas in case of pure silica this value does not exceed 0.6.

The data on the water sorption equilibrium presented above allow us to analyse only thermodynamic behaviour of the adsorption refrigeration unit, while the dynamics of water sorption and the heat transfer in the sorbent layer can be of high importance for decreasing the cycle time and creating powerful and compact refrigeration units. To perform this analysis we are going to follow the procedures previously developed for studying heat and mass transfer in the SWS materials [4,11–13].

4. Conclusions

The study has shown that the composite material based on $CaCl_2$ as an impregnated salt and MCM-41 as a host matrix is able to absorb up to 0.75 g of H_2O per gram of the dry sorbent. That high absorptivity can ensure the high values of the energy storage capacity (2.1 $\mathrm{kJ{\cdot}g^{-1}}$). Moreover, most of water sorbed can be removed at the relatively low temperature between 343 and 393 K that facilitates drastically the usage of heat sources with the low temperature level, like industrial heat wastes, geothermal or 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 the solid MCM matrix is likely to allow overcoming the crystallisation and corrosion problems that are crucial for liquid absorption units.

Thus, the results of this study demonstrate that the new SWS material “$CaCl_2$ inside MCM pores” can be competitive with the common working materials, like zeolites, silica gels, etc. and should be considered as a good candidate for the thermal applications driven by the low-temperature heat sources.

Acknowledgements

Authors thank the Russian Foundation for Basic Researches (Grant 99-03-32312), Cooperation Program between the Russian Academy of Sciences and CNR (Italy) and the Program “Russian Universities” (Grant N-901065) for partial financial support of the research activity.

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