Sorption equilibrium of methanol on new composite sorbents "CaCl$_2$/silica gel"

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Abstract This paper presents experimental data on methanol sorption on new composite sorbents which consist of mesoporous silica gels and calcium chloride confined to their pores. Sorption isobars and XRD analysis showed the formation of a solid crystalline solvate CaCl$_2$·2MeOH at low methanol uptake, while at higher uptake the formation of the CaCl$_2$–methanol solution occurred. The solution confined to the silica pores showed the sorption properties similar to those of the CaCl$_2$–methanol bulk solution. Calorimetric and isosteric analyses showed that the heat of methanol sorption depends on the methanol uptake, ranging from 38 ± 2 kJ/mol for the solution to 81 ± 4 kJ/mol for the solid crystalline phase CaCl$_2$·2MeOH. The above mentioned characterizations allowed the evaluation of the methanol sorption and the energy storage capacities, clearly showing that the optimal applications of these new composite sorbents are the methanol removal from gaseous mixtures, heat storage and sorption cooling driven by low temperature heat.

Keywords Sorption · Methanol · Silica gel · Confined calcium chloride · Heat storage

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1 Introduction

A new family of composites for sorption of water vapor based on a chemical active salt confined to pores of a host matrix has recently been presented (Aristov et al. 1996a, 1996b, 1997; Gordeeva et al. 2002). The initial idea was to modify the conventional adsorbents, like silica, alumina, etc., by hygroscopic salts in order to increase their ability to adsorb water. In fact, the composites "salt inside porous matrix" (so called, Selective Water Sorbents, SWSs) appeared to possess advanced sorption properties, low regeneration temperature and thus are promising for various applications such as the drying of air and other gases, low temperature heat storage, adsorption heat pumps, etc. (Aristov et al. 1999, 2000; Tokarev et al. 2001).

It is known that the properties of a composite material can differ from individual properties of the components (Nedeljkovic 2000; Simonova and Aristov 2005). Actually, the confinement of inorganic salts to mesopores of various matrices appeared to affect essentially the physico-chemical properties of these salts, namely, the melting point of the salt crystalline hydrates (Aristov et al. 1997), the sorption equilibrium with water vapor (Aristov et al. 1996a, 1996b; Gordeeva et al. 2002), the phase composition of the salt (Gordeeva et al. 1997), etc. It can occur due to either the dispersion of the confined salt to nano-sized particles, which have increased surface energy respect to the bulk salt, or due to the interaction between the salt and the matrix surface. Since the salt properties change, the properties of the composite material can not be considered as a linear superposition of the individual properties of the components (Simonova and Aristov 2005).

Based on the same concept, we present here new sorbents of methanol (MeOH), which consist of calcium chloride impregnated inside pores of two types of mesoporous silica gel,

Table 1 Properties of the host matrices and synthesized sorbents (the BET specific surface area S_{sp}, the pore volume V_{pore}, the average pore diameter d_{av} of the matrices, and the salt content C_{CaCl_2} in the sorbent)

No.	Composition	C_{CaCl_2}, g/g	S_{sp}, m^2/g	V_{pore}, cm^3/g	d_{av}, nm
S6	$CaCl_2/SiO_2$(SP18-8749.01)	0.23	580	0.85	6
S15	$CaCl_2/SiO_2$(KSK)	0.25	350	1.0	15

namely, a KSK type (average pore diameter $d_{av} = 15$ nm), S15, and a SP18-8749.01 type ($d_{av} = 6$ nm), S6. Methanol is considered as a promising working fluid for low temperature heat storage and adsorptive cooling due to its relatively high vapor pressure and low freezing point (Lourdudoss and Stymne 1987; Meunier 1999; Offenhartz 1980). The silica gels used are conventional adsorbents with a well-defined porous structure. The calcium chloride was chosen because of its good ability to absorb methanol vapor forming crystalline solvates (methanolates) $CaCl_2 \cdot N$MeOH, $N = 1, 2, 3, 4$ and 6 (Offenhartz et al. 1980; Pietsch 1957; Bixon et al. 1979). The properties of the bulk crystalline methanolates and the $CaCl_2$–MeOH solution are well studied, allowing the comparison between the bulk and confined systems.

2 Experimental

Commercial silica gels KSK (Reakhim, Russia) and SP18-8749.01 (Grace Davison, Germany) with different pore diameter (Table 1) were used as host matrices. The silica gel was dried at 200 °C for 2 hours and then cooled to ambient temperature. Afterwards, it was impregnated with 25 wt.% $CaCl_2$ aqueous solution and dried at 150 °C until the sample weight became constant. The properties of the samples prepared are presented in Table 1.

Sorption equilibrium between methanol vapor and the composites was studied in the temperature range $T = 20$–160 °C and at partial methanol pressure $P_{MeOH} = 21$–300 mbar using a CAHN C2000 thermal balance. Before measurements the sample of 15–30 mg mass was heated at 160 °C under continuous evacuation (residual pressure ≈ 0.01 mbar) until reaching the dry weight m_0. Then, the measuring cell of the balance was connected with an evaporator to maintain fixed pressure of methanol vapor over the sample and the sorption process started. The evaporator temperature was set by a thermostat with the accuracy of ± 0.1 °C. The amount of methanol $m(P_{MeOH}, T)$ sorbed at equilibrium was measured as the final increase of the sample weight at fixed T and P_{MeOH}. Typical time of the equilibrium reaching was 0.5–2 hours, depending on the measuring conditions. The methanol sorption was characterized either by the methanol content $w = m(P_{MeOH}, T)/m_0$, or by the equilibrium number of sorbed

molecules of methanol related to one molecule of calcium chloride $N(P_{MeOH}, T) = [(m(P_{MeOH}, T)/\mu_{MeOH})]/(m_0 * C_{CaCl_2}/\mu_{CaCl_2})$, where μ_{MeOH} and μ_{CaCl_2} are the molecular weights of methanol and $CaCl_2$, respectively, $m(P_{MeOH}, T)$ is the equilibrium amount of methanol sorbed at fixed P_{MeOH} and T, and C_{CaCl_2} is the salt content in the sorbent.

Calorimetric data were obtained with a Setaram Tian-Calve calorimeter. The sample was placed into a measuring ampule on a layer of quarts glass grains of 0.25–0.4 mm size, preliminary washed with nitric acid and distilled water and then dried at 450 °C. The ampule was connected with the pump through a valve and a trap filled with a liquid nitrogen and pumped. Then, methanol portions of 1–100 μl were injected into the ampule with a micro-syringe. The accuracy of the calorimetric measurements was 3–4%.

The formation of the phase of crystalline methanolates during MeOH sorption was studied *in situ* by an X-ray diffraction (XRD) using a Siemens D-500 diffractometer and Cu K_α radiation (Krieger et al. 2000). The sample was placed in a camera-reactor fixed at the diffractometer and heated at $T = 200$ °C and the diffraction pattern of the dry sample was measured. Then the flux of He with MeOH vapor was passed through the camera-reactor and the diffraction pattern was recorded at $T = 30, 60, 80$ and 100 °C.

3 Results and discussion

3.1 Sorption properties

Isobars of methanol desorption on the S15 composite are shown in Fig. 1. All isobars appear to be similar in shape but demonstrate a shift toward higher temperature with the increase in the vapor pressure. Each curve has a plateau corresponding to $N \approx 2$. The plateau indicates the formation of a solid crystalline solvate (methanolate) $CaCl_2 \cdot 2$MeOH (Offenhartz 1980; Offenhartz et al. 1980) due to reaction

$$CaCl_2 + 2MeOH \Leftrightarrow CaCl_2 \cdot 2MeOH \qquad (1)$$
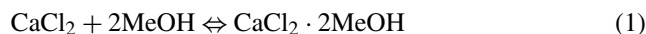
This methanolate is stable over the temperature range of 20–35 °C. At temperature higher than the right boundary of the plateau the solvate undergoes the decomposition towards the dry salt. The solid system MeOH–$CaCl_2$ consists of two components and three phases, so according to
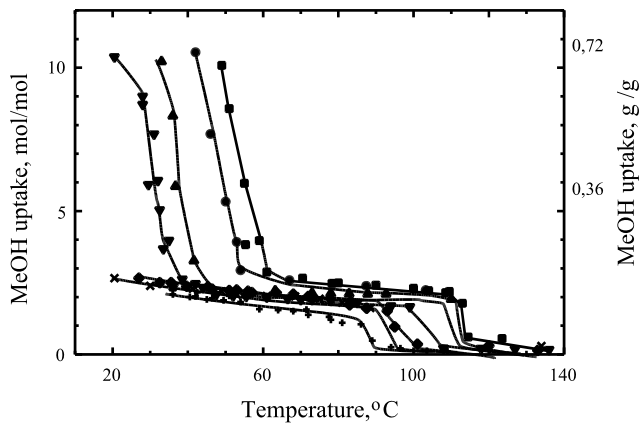
Fig. 1 Isobars of methanol desorption for S15 composite at $P(MeOH)$ = 21 (✗), 41 (✚), 53 (◆), 101 (▼), 153 (▲), 226 (●) and 300 (■) mbar
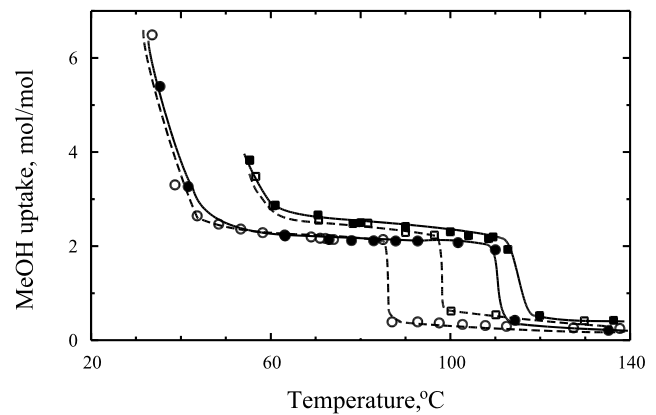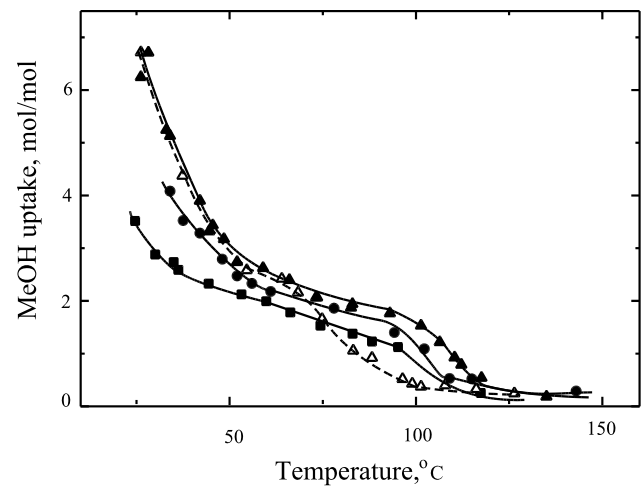

Fig. 2 Isobars of methanol sorption (□, ○) and desorption (■, ●) for S15 sorbent at $P(MeOH) = 153$ (○, ●) and 300 (□, ■) mbar

Fig. 3 The isobars of methanol adsorption (▲) and desorption (△) for S6 composite $P(MeOH) = 95$ (▲, △), 71 (●) and 40 (■) mbar

the Gibb's phase rule, the number of freedom of the system equals 1. For this reason the temperature of $CaCl_2 \cdot 2MeOH$ decomposition is completely independent on the extent of reaction and depends only on the methanol pressure. As the temperature becomes lower than that of the left boundary of the plateau, the system exhibits a sharp increase of methanol uptake to $N \approx 7$–9. No plateau corresponding to formation of other crystalline methanolates $CaCl_2 \cdot NMeOH$ ($N = 1, 3, 4, 6$), which are stable in the bulk system (Pietsch 1957), was detected.

The rate of the $CaCl_2 \cdot 2MeOH$ decomposition is low at $T < 90\,°C$ due to the fact that solid-gas reactions involving a first order phase transformation proceed with certain inertia, especially at a low temperature range. The presence of pressure-temperature region around equilibrium where the reaction is essentially inhibited resulted from an extensive reorganization of crystalline structure. Another consequence of such reorganization necessary for the $CaCl_2 \cdot 2MeOH$ decomposition is that the sorption-desorption isobars are essentially irreversible at low methanol uptakes ($0 \leq N \leq 2$) (Fig. 2). As the MeOH vapor pressure rises, the temperature of $CaCl_2 \cdot 2MeOH$ decomposition increases (Fig. 1) and the rate of $CaCl_2 \cdot 2MeOH$ decomposition is likely to rise. Consequently, the area of hysteresis loop decreases (Fig. 2).

Isobars of methanol sorption on composite S6 are presented in Fig. 3. The uptake monotonically increases with the decrease in temperature, so that, no plateau at $N = 2$ was found. The inflection is likely to be caused by the fact that the crystalline methanolate $CaCl_2 \cdot 2MeOH$ coexists with solution or solid phase $CaCl_2$–MeOH of variable composition. The hysteresis loop of adsorption/desorption isobars (Fig. 3) is another indirect indication of the formation of crystalline methanolate $CaCl_2 \cdot 2MeOH$. Indeed, the hysteresis might be caused by the reorganization of crystalline structure of $CaCl_2$ and $CaCl_2 \cdot 2MeOH$ during methanol sorption/desorption. When the temperature decreases lower the inflection, the isobars become smooth curves and the

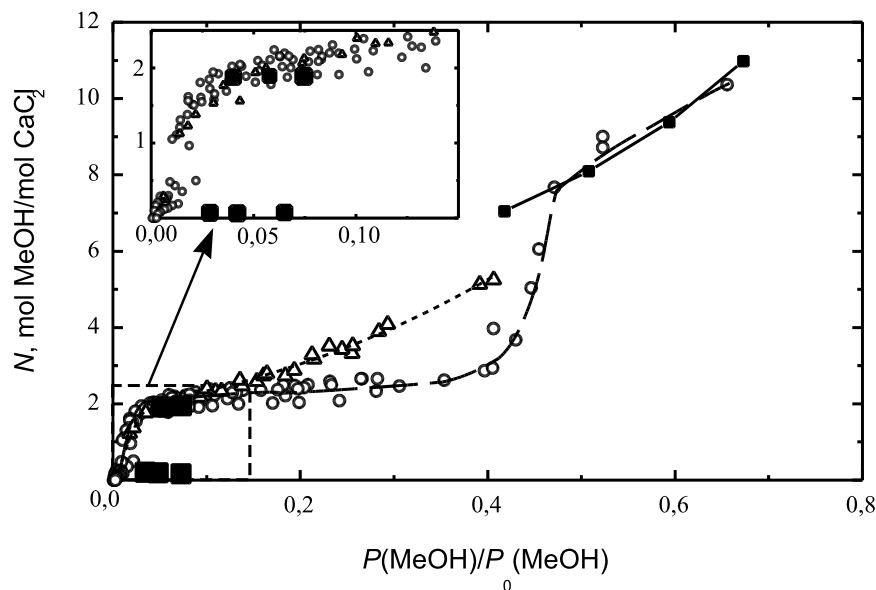methanol uptake growths gradually. This indicates the formation of a $CaCl_2$–methanol solution inside the pores.

If we present the sorption data as a function of the methanol relative pressure $\phi = P_{MeOH}/P_0$, where P_0 is the pressure of saturated methanol vapor at fixed temperature T, the temperature invariant curves of methanol sorption on S6 and S15 composite can be obtained (Fig. 4). The shape of the curves confirms the main features of the sorption isobars. The temperature invariant curve for the S15 composite exhibits the plateau at $0.02 \leq \phi \leq 0.4$, which is attributed to the existence of stable crystalline methanolate $CaCl_2 \cdot 2MeOH$. The plateau is followed by a sharp increase of the sorption at $0.4 \leq \phi \leq 0.5$ and a moderate growth at $\phi > 0.5$. Gradual growth of uptake at $\phi > 0.5$ indicates clearly the formation of $CaCl_2$–MeOH solution inside the silica pores (Pietsch 1957; Bixon et al. 1979; Chou and Tanioka 1997). According to the Gibb's phase rule the confined system $CaCl_2$–MeOH, which consists of two phases (liquid and gaseous), becomes divariant one.

The shape of the temperature invariant curve of S6 composite is essentially different. A step-wise increase of sorption at $0.01 \leq \phi \leq 0.02$ is followed by the smooth growth of sorption at $\phi > 0.03$. This indicates the formation of CaCl$_2 \cdot$2MeOH, which is likely to coexist with a CaCl$_2$–MeOH solution or the solid phase, the composition of which changes continuously.

For comparative purposes the data on sorption equilibrium for the bulk CaCl$_2$–MeOH system are also shown in Fig. 4 (Offenhartz et al. 1980; Bixon et al. 1979; Chou and Tanioka 1997). It can be seen that at $\phi \geq 0.5$ a CaCl$_2$–methanol solution is inside pores and the confined CaCl$_2$–MeOH system exhibits the sorption properties similar to the bulk system. Thus, the confinement of CaCl$_2$–MeOH solution to the KSK pores (S15 composite) does not affect its sorption equilibrium with methanol vapor. On the contrary, the sorption equilibrium of the confined and the bulk systems does not coincide at low relative pressure of methanol. The decomposition of CaCl$_2 \cdot$ 2MeOH towards CaCl$_2$ in the pores of the both silica gels occurs at relative pressure ϕ equal to 0.01–0.02, while in the bulk state it occurs at $0.025 < \phi < 0.075$. The dispersion of CaCl$_2 \cdot$ 2MeOH inside silica pores results in the decrease of the relative pressure of its decomposition. This conforms to the data on water sorption on CaCl$_2$ confined to silica gel pores (Aristov et al. 1996a, 1996b).

The isosters of methanol sorption on S15 composite plotted from the isobaric data are shown in Fig. 5 for $N = 0$–8 as $\ln(P_{MeOH})$ vs $1/T$ presentation. They are straight lines with the slope sharply dependent on the methanol uptake. The isosteric heat of methanol sorption ΔH_{is} was calculated from the slope to be 38 ± 2 kJ/mol at $N > 2$, that is close to the heat of methanol evaporation $\Delta H_{ev} = 35.4$ kJ/mol. As the methanol uptake decreases down to
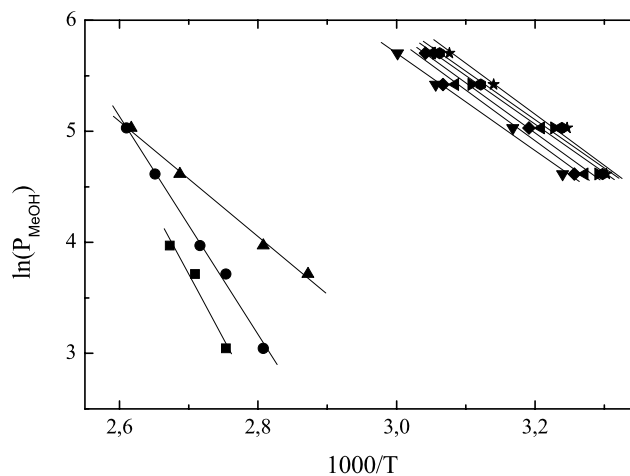

Fig. 5 The isosters of methanol desorption from S15 at $N = 0$ (■), 1 (●), 2 (▲), 3 (▼), 4 (◆), 5 (◄), 6 (►), 7 (⬟) and 8 (★)

$N < 2$ (point of the right boundary of the plateau at $N = 2$) ΔH_{is} rises up to 81 ± 4 kJ/mol. The increase of the isosteric heat can be attributed to the formation of crystalline solvate CaCl$_2 \cdot$2MeOH with strong chemical bonds between CaCl$_2$ and methanol molecules. The sorption isosters of S6 composite follow the same trend. The value of ΔH_{is} increases from 35 to 89 kJ/mol, when N decreases from 4 to 1 mol/mol.

3.2 Phase composition

The formation of crystalline phase CaCl$_2 \cdot$2MeOH due to the methanol sorption on the S15 composite is clearly confirmed by XRD *in situ* measurements (Fig. 6). At high temperature ($T \geq 80$°C at $P_{MeOH} = 21$ mbar and $T \geq 110$°C at $P_{MeOH} = 101$ mbar) the sample comprises the

dry $CaCl_2$. As the temperature decreases, the intensity of reflexes attributed to $CaCl_2$ diminishes and the reflexes of $CaCl_2 \cdot 2MeOH$ appear (Gillier-Pandraud and Philoche-Levisalles 1979). Dry $CaCl_2$ undergoes to dimethanolate $CaCl_2 \cdot 2MeOH$ omitting the monomethanolate formation $CaCl_2 \cdot MeOH$ that agrees with the results reported in Offenhartz et al. (1980). The parameters of the crystalline structure of $CaCl_2 \cdot 2MeOH$ appear to change slightly due to the confinement inside the silica pores, namely, the interlayer distance (100) decreases from 19.90 to 19.06 Å. At temperature lower than the left boundary of the plateau ($T = 30\,°C$ at $P_{MeOH} = 101$ mbar, Fig. 6a) the intensity of reflexes of $CaCl_2 \cdot 2MeOH$ decreases but no other reflexes appear, that indicates the formation of $CaCl_2$–MeOH solution due to the dissolution of $CaCl_2 \cdot 2MeOH$. The temperatures of the
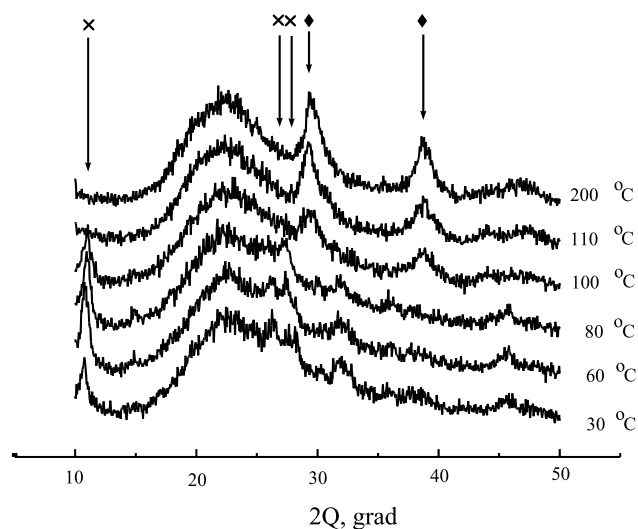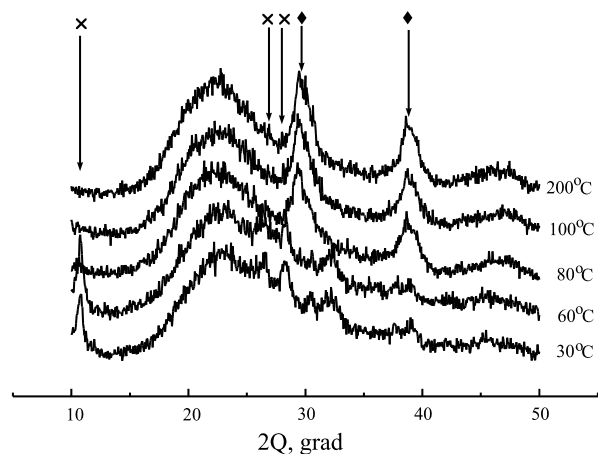
$CaCl_2 \cdot 2MeOH$ transitions towards the dry salt and $CaCl_2$–MeOH solution correlate well with those evaluated from the sorption measurements (Fig. 1). Thus, no formation of other crystalline solvates $CaCl_2 \cdot NMeOH$ with $N = 1, 3, 4, 6$ typical for the bulk system has been detected by the XRD analysis of S15 composite.

3.3 Calorimetric measurements

The data on isosteric heat of methanol sorption are quite consistent with the direct measurement of the heat of methanol sorption on S15 composite by a Tian-Calve calorimeter (Fig. 7). As N increases from 0 to 1 the heat of methanol sorption decreases from 97 to 60 kJ/mol. The high value of the sorption heat at $N < 0.5$ is due to the fact, that the first portions of methanol are likely to be adsorbed on active centers of the silica gel surface. Thus, the sorption heat depends on the chemical nature of these centers. At $0.5 < N < 2$ the sorption heat is essentially constant $\Delta H = 60 \pm 3$ kJ/mol. This is likely to be attributed to the formation of crystalline methanolate $CaCl_2 \cdot 2MeOH$. The value of ΔH measured is close to the formation enthalpy of the bulk methanolate $CaCl_2 \cdot 2MeOH$ $\Delta H = 51.7$ kJ/mol (Offenhartz et al. 1980). Thus, the sorption heat measured at $0.5 < N < 2$ is associated with the formation of $CaCl_2 \cdot 2MeOH$ in the silica pores. Further increase in N results in the sorption heat decreasing to $\Delta H = 38 \pm 3$ kJ/mol, which is close to the heat of methanol evaporation.

The study of the sorption equilibrium as well as the calorimetric measurements allow the estimation of the specific methanol sorption capacity A_{sp} and specific energy storage capacity E_{sp} of the composite sorbent. The former value is shown to reach $A_{sp} = 0.7$ g of MeOH per 1 g of dry sorbent at $\phi = 0.7$. It is more than three times larger than the maximum uptake for zeolites (0.2 g/g) (Tchernev
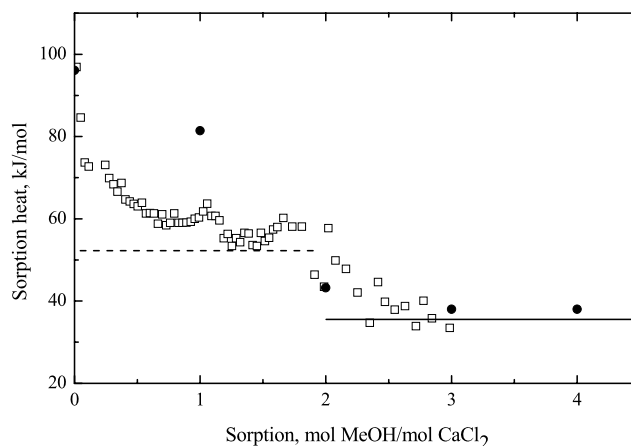

a)

b)

Fig. 6 *In situ* X-ray diffraction patterns of S15–MeOH system at the methanol partial pressure $P_{MeOH} = 101$ (**a**) and 21 (**b**) mbar at different temperature. ✕ $CaCl_2 \cdot 2MeOH$, ◆ $CaCl_2$

Fig. 7 Dependence of the calorimetric (□) and isosteric (●) heats of methanol sorption on S15. *Dashed line* represents the enthalpy of reaction (1) in bulk; *solid line* indicates the heat of the methanol evaporation in bulk

Fig. 8 Cooling COP calculated for two working pairs: composite sorbent S6 CaCl$_2$/SiO$_2$–methanol, Fuji Davison Silica Gel–Water
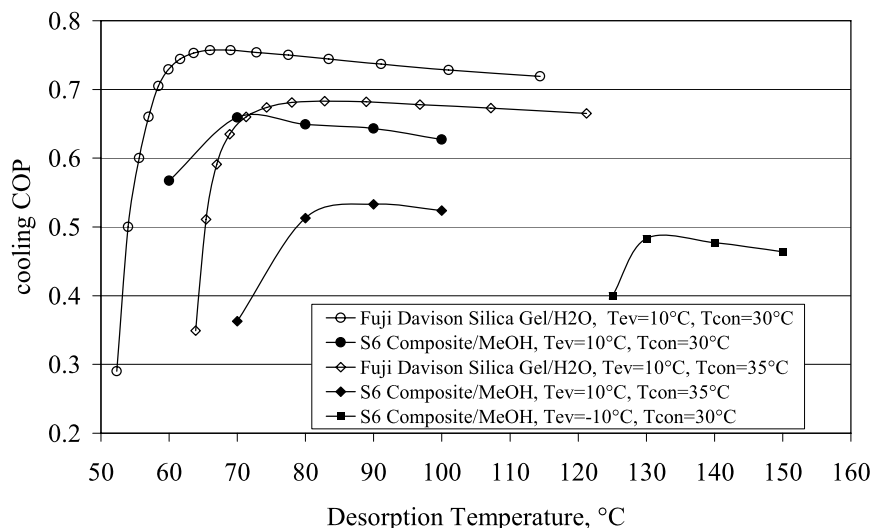
1999). It is pertinent to note that the most of methanol sorbed (75 ÷ 80%) can be desorbed by heating the sorbent by some 15 ÷ 20 °C. The remaining methanol can be removed at $T = 100 ÷ 120$ °C. The large value of A_{sp} leads to the high energy storage capacity E_{sp} of the sorbent, that is the energy needed for complete methanol desorption. The E_{sp} estimated from A_{sp} and ΔH_{is} appears to reach 0.8 kJ/g.

3.4 Performance evaluation

The high values of the methanol sorption and energy storage capacities as well as the low regeneration temperature make the composites CaCl$_2$/silica gel promising for various practical applications, like the methanol removal from gaseous mixtures, sorption cooling and low temperature heat storage. Furthermore, it was already demonstrated that the content of the confined salt, the pore size of the host matrix and synthesis conditions can be varied to adjust the properties of the sorbent composite for a specific application (Aristov 2005). Consequently, the outstanding methanol sorption capacity of the composite S15 (uptake maximum = 0.75 g/g), sounds very attractive for methanol removal and heat storage, while sorbent S6 is more suitable for sorption cooling, due to the absence of the plateau at $N = 2$ and to the relatively high sorption capacity at very low pressure. Figure 8 shows the cooling Coefficient Of Performance (COP) calculated for the composite sorbent S6 by a previously developed mathematical model (Cacciola and Restuccia 1995). The same figure reports the COP calculated for the silica gel "Fuji Davison RD"–water as working pair, which is used in commercialized adsorption chillers (Chua et al. 2002). It was found that, depending on the operating conditions, the composite sorbent S6 allows to obtain acceptable COP values that are about 15–25% lower than those calculated for the silica gel. This can be justified considering the low latent heat of methanol, which decreases the cooling effect.

However, it must be pointed out that the use of methanol is mandatory for those applications which require evaporating temperature close to or lower than 0 °C. In this case the cooling COP values calculated for a temperature of evaporation of −10 °C are close to 0.5, which is a good performance for this specific operating condition.

Furthermore, it is worthy to point out that the relatively high working pressure of methanol has positive effect on the overall dynamic performance of the machine (less pressure drops through the machine components, lower mass transfer limitation though the adsorbent bed, better sorption dynamic). In this point of view, the utilization of the methanol sorbent "CaCl$_2$/Silica Gel" S6, is particularly interesting for those applications that require high specific power and where waste heat is available, such us the automotive air conditioning.

4 Conclusions

The equilibrium of methanol sorption on the new composite sorbents based on calcium chloride confined to the silica mesopores of 6 and 15 nm diameter was studied at temperature 20–200 °C and methanol pressure 21–300 mbar. Two types of methanol sorption were found: the formation of solid crystalline solvate CaCl$_2$·2MeOH at low methanol uptake and the formation of the CaCl$_2$–methanol solution inside the pores at high uptake. The confinement of CaCl$_2$ into silica mesopores appeared to affect essentially the properties of the salt and its crystalline solvate CaCl$_2$·2MeOH. In contrast, the sorption properties of confined CaCl$_2$–MeOH solution remain the same as for the bulk solution. The methanol sorption and the energy storage capacity of the composites were found to reach 0.7 g/g and 0.8 kJ/g, respectively, that makes the composite promising for the methanol removal

from gaseous mixtures, energy storage and sorption cooling driven by low temperature heat. The calculation of the cooling COP for the composite S6, showed that this material can ensure quite good performance for different operating conditions.

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