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Influence of Characteristics of Methanol Sorbents "Salts in Mesoporous Silica" on the Performance of Adsorptive Air Conditioning Cycle

Larisa G. Gordeeva,*,† Angelo Freni,‡ Giovanni Restuccia,‡ and Yuri I. Aristov†

Boreskov Institute of Catalysis, Novosibirsk, Russia, and Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", S. Lucia sopra Contesse, Messina, Italy

In this paper a new family of methanol sorbents "salts in mesoporous silica" is proposed for utilization in an adsorptive air conditioner driven by a low-temperature heat ($T = 338−373$ K). The methanol sorption capacity of composites, under typical cooling cycle conditions, was measured by an express method based on the Polanyi principle of temperature invariance. An estimation of the cooling coefficient of performance (COP) was carried out in order to compare the performance of such sorbents with other methanol and water sorbents. Results obtained showed that most of the synthesized composites present methanol sorption ability higher than that of common methanol sorbents (e.g., active carbons). The composite LiCl (30.6 wt %)/SiO$_2$ shows the highest sorption capacity, $w_{ads} = 0.8$ g/g, and uptake variation per cycle, $\Delta w = 0.71$ g/g. The corresponding cooling COP is 0.74 (maximum $T_{des} = 363$ K, single-bed cycle), which is comparable to typical COP values for the best water sorbents.

1. Introduction

Adsorptive cycles based on methanol as a working medium are considered promising for air conditioning (AC) driven by low-temperature heat: solar energy, automotive waste heat, etc.[1−3] Unlike water vapor, methanol presents a lower freezing temperature ($T = 175$ K) and a higher operating pressure ($P = 0.06−0.35$ bar). The main drawback of using methanol as a refrigerant in comparison to water is the lower latent heat of evaporation, which limits the cooling efficiency of an air conditioner. To compensate for this, adsorbent materials with improved sorption properties adapted for demands of particular cycle are required.[4,5]

Typical materials used for methanol adsorption are activated carbons and hydrophobic zeolites.[6−10] However, the net desorption per cycle under typical AC conditions does not usually exceed 0.14−0.18 and 0.15−0.25 kg/kg for zeolites and activated carbons, respectively.

It is well-known that inorganic salts MeA as well as "methanol−salt" solutions can absorb methanol vapor by forming crystalline solvates or lower salt concentration solutions:

$$MeA + nCH_3OH = MeA \cdot nCH_3OH$$

$$\text{solution 1} (C_1) + CH_3OH = \text{solution 2} (C_2)$$
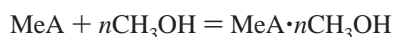
where the salt concentration C_2 is lower than C_1.[2,11−13] The number of methanol molecules n can reach 3−6 for different salts,[2,11,12] resulting in a large amount of methanol absorbed. For example, the reaction LiCl + 3CH$_3$OH = LiCl·3CH$_3$OH presents a sorption ability of 2.25 kg of CH$_3$OH per 1 kg of LiCl, which far exceeds the typical value of methanol adsorption by zeolites and activated carbons. Consequently, the formation of methanol solvates is very attractive for sorption cooling/heating.[2] Specifically, the formation of calcium chloride methanol solvate due to the reaction CaCl$_2$ + 2CH$_3$OH = CaCl$_2$·2CH$_3$-OH was proposed for solar heating, cooling, and energy

storage.[2,3,14] CH$_3$OH/LiBr−CH$_3$OH solution is considered as a working pair for the storing and pumping of heat.[15,16] However, the use of bulk salt in a sorption system is limited by the following factors:

(1) The formation of crystalline solvates from salt is accompanied by the intense reorganization of the crystalline structure and proceeds with a certain inertia, especially in a low-temperature range. The presence of inhibitions, i.e., a pronounced pressure−temperature region around equilibrium where the reaction is inhibited, is typical for such a reaction. Only outside this region does the reaction proceed at a measurable rate.[17] This inhibition region reflects that the formation (adsorption) and decomposition (desorption) branches do not coincide on the sorption isobars, so a sorption/desorption hysteresis occurs.

(2) Reaction between the salt crystallites and the methanol vapor results in the formation of a crystalline solvate phase on the surface of the salt. Further reaction requires the diffusion of methanol vapor through the layer of the solvate,[17] which could be a very slow process.

(3) Swelling of the salt during the formation of solvate leads to its mechanical destruction and dust formation.

These three factors can strongly restrict the application of bulk salts for adsorption cooling/heating; for this reason, in this paper a new family of sorbents, specifically designed for methanol sorption, is presented. This new class of sorbents is directly derived by the well-known selective water sorbents "inorganic salts confined in porous matrixes" that have already been proposed for water vapor sorption.[18−20] The selective water sorbents (SWSs) combine the advantages of porous adsorbents and solid absorbents. Due to the volume sorption of vapor by salt nanoparticles inside pores, they possess a large water sorption capacity (up to 0.6−0.8 g/g). The diffusion restrictions and adsorption/desorption hysteresis typical of the reactions with bulk salts appeared to become negligible due to the dispersion of the salt to nanosize.[21−23] Furthermore, the possibility to vary the chemical nature of the salt and the matrix as well as the porous structure of the matrix allows a wide-range modification of composite sorption properties to meet the demands of particular applications.

The same concept as SWSs, that is, the confinement of the active salt into pores of the host matrix, was applied to develop

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* To whom correspondence should be addressed. Tel./Fax:+7 383 330 95 73. E-mail: gordeeva@catalysis.ru.
† Boreskov Institute of Catalysis.
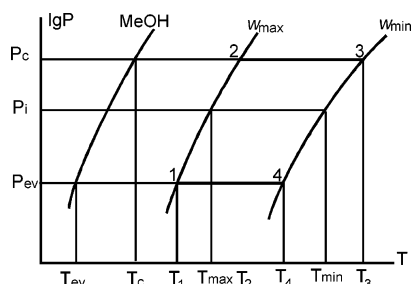‡ Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano".

Figure 1. Thermodynamic cycle of adsorptive cooling.

new materials for methanol sorption. The results of the experimental study for a number of composites "salts inside porous matrixes" in methanol sorption are presented. In particular, the methanol sorption ability of the synthesized samples was measured under typical conditions of a basic cooling cycle. Finally, estimation of the cooling coefficient of performance (COP) was carried out in order to identify the most promising composites for application in an adsorptive air conditioner.

2. Theoretical Basis

A single-bed adsorptive AC unit consists of an adsorber filled with adsorbent, an evaporator, and a condenser. The working cycle, which consists of four stages, is presented in Figure 1 in a pressure−temperature diagram. During the first stage (1−2 in Figure 1) the adsorber, isolated from the evaporator and condenser, is isosterically heated from temperature T_1 to T_2. When the pressure of the adsorber reaches P_c, it is connected to the condenser and continues to be heated to T_3 (stage 2−3). During this isobaric desorption stage, methanol is desorbed from the adsorbent and condenses in the condenser. Then, the adsorber is isolated and isosterically cooled (stage 3−4) to T_4. When the methanol pressure reaches P_{ev}, the adsorber is connected to the evaporator and isobarically cooled to T_1 (stage 4−1). During this stage, the adsorbent adsorbs methanol vapor from the evaporator and the useful effect is produced.

The operating conditions of the cycle are determined by four temperatures, namely, the temperatures of condensation T_c, evaporation T_{ev}, the maximum temperature of desorption T_3, and the minimum temperature of adsorption T_1. T_1 and T_c depend on the temperature of the environment where the heat is dissipated, and are in the temperature range from 298 to 318 K. T_{ev}, which is determined by the desirable temperature of the cold produced, is between 278 and 288 K. Finally, T_3 depends on an external heat source available for adsorbent heating. For low-temperature heat sources, such as solar energy and waste heat, this temperature range is 338−373 K.

The coefficient of performance of a single-bed cooling cycle (COP) is the ratio of the evaporation heat Q_{ev} to the heat supplied to the adsorbent during the isosteric heating 1−2 (Q_{ish}) and desorption 2−3 (Q_{des}). The contribution of sensible heat of the liquid methanol flowing from the condenser to the evaporator is neglected.

$$COP = \frac{Q_{ev}}{Q_{ish} + Q_{des}} \quad (1)$$

Taking into account that

$$Q_{ev} = \Delta L \Delta w; \quad Q_{ish} = C_p(w_{max})(T_2 - T_1);$$
$$Q_{des} = \Delta H \Delta w + C_p(w)(T_3 - T_2) \quad (2)$$

the COP of the cycle can be written as

$$COP = \frac{\Delta L \Delta w}{\Delta H \Delta w + C_p(w_{max})(T_2 - T_1) + C_p(w)(T_3 - T_2)} =$$
$$\frac{\Delta L \Delta w}{\Delta H \Delta w + \Theta} = \frac{\Delta w}{A \Delta w + B} \quad (3)$$

where the following coefficients were introduced:

$$A = \frac{\Delta H}{\Delta L}; \quad B = \frac{\Theta}{\Delta L};$$
$$\Theta = C_p(w_{max})(T_2 - T_1) + C_p(w)(T_3 - T_2) \quad (4)$$

Thus, the COP increases with the rise in the net desorption per cycle Δw, asymptotically approaching $\Delta L / \Delta H$. Consequently, to increase the COP, the optimal adsorbent should exchange a large amount of methanol between the rich and weak isosters of the cycle (1−2 and 3−4, Figure 1).

The amount of methanol adsorbed/desorbed by the composite under typical cooling cycle conditions is determined from the isosteric chart. The measurement of a full set of sorption isosters is a very time-consuming procedure, which cannot be used for fast screening of a large number of sorbents. Consequently, an express method was developed for scanning methanol sorption under typical cooling cycle conditions. The theoretical basis of the express method is the Polanyi principle of temperature invariance.[24] According to this principle, at different temperatures T_a and T_b, an equal volume of adsorbed phase v can be achieved at the vapor pressures T_a and T_b, linked in the formula

$$T_a \ln\left(\frac{P}{P_s}\right)_a = T_b \ln\left(\frac{P}{P_s}\right)_b \quad (5)$$

where P/P_s is the relative pressure of adsorbate. This approach allowed Dubinin and Astakhov to introduce free sorption energy:

$$\Delta F = -RT \ln \frac{P}{P_s} \quad (6)$$

This shows a one-to-one correspondence between the adsorbed volume and ΔF for many microporous materials.[25−27] Let us consider that the density of methanol adsorbed ρ is equal to the density of the bulk methanol.[25] The difference in the methanol density at 40 and 90 °C does not exceed 0.049 g/cm³, that is, only 6%.[28] Therefore, for simplification purposes, the density ρ of the adsorbed phase is assumed constant in the temperature range of the cycle described. Subsequently, using the Polanyi approach for the amount of methanol adsorbed $w = V\rho$, the equilibrium methanol content can be uniquely determined by the product $T \ln(P/P_s)$.[29] For the rich isoster of the cycle (stage 1−2 in Figure 1), corresponding to $w = w_{max}$, the following equation is true:

$$\Delta F(w_{max}) = -RT_1 \ln \frac{P_{ev}}{P_s(T_1)} = -RT_2 \ln \frac{P_{con}}{P_s(T_2)} \quad (7)$$

whereas for the weak isoster (stage 3−4) ($w = w_{min}$), the equilibrium can be written as

$$\Delta F(w_{min}) = -RT_3 \ln \frac{P_{con}}{P_s(T_3)} = -RT_4 \ln \frac{P_{ev}}{P_s(T_4)} \quad (8)$$

Thus, to estimate the sorption ability of different adsorbents under the cycle conditions, it is sufficient to compare the methanol adsorption normalized to the weight of dry adsorbent
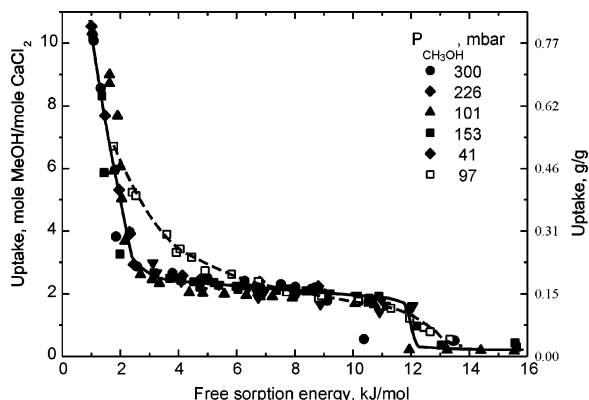
Figure 2. Methanol uptake on CaCl$_2$/SiO$_2$ d_{av} = 15 nm (filled symbols) and CaCl$_2$/SiO$_2$ d_{av} = 6 nm (open symbols) composite vs free sorption energy ΔF.

at one methanol pressure P_i and two temperatures T_{min} and T_{max} (Figure 1), which satisfy the expressions

$$\Delta F(w_{max}) = -RT_{max} \ln \frac{P_i}{P_s(T_{max})};$$

$$\Delta F(w_{min}) = -RT_{min} \ln \frac{P_i}{P_s(T_{min})} \quad (9)$$

The most promising materials for the adsorptive cooling are those that have a maximum difference in methanol sorption $\Delta w = w_{max} - w_{min}$ between the temperatures T_{min} and T_{max} based on the thermodynamic considerations discussed above. For such an estimation, it is sufficient to measure just two methanol uptakes which correspond to the rich and weak isosters, instead of the common measuring of a full set of isobars or isotherms.

In general, the limits of a basic cycle for adsorptive machines (see points 1 and 3 of Figure 1) depend on the temperature level of the external heat source and sink. In the case of an adsorptive air conditioner driven by low-temperature heat, typical pressures and temperatures for methanol adsorbate are the following: $P_1 = P_{ev} = 61$ mbar; $T_1 = 303$ K; $P_3 = P_{con} = 274$ mbar; $T_3 = 358-363$ K. The corresponding values of free sorption energy, calculated by eq 6, are the following: $\Delta F(w_{max}) = 3158$ J/mol and $\Delta F(w_{min}) = 6216-6922$ J/mol.

The temperature T_4 of the basic cycle is unknown, but it can be estimated considering that $P_4 = P_1 = 61$ mbar, and that during the isosteric cooling 3−4 the uptake remains constant. In the examined case, if we assume $T_4 = 328$ K, then $\Delta F = 6565$ J/mol, which is close to the estimated value of $\Delta F(w_{min})$.

Thus, the comparison of different sorbents was performed by the measurement of the methanol uptake at $P = 61$ mbar, $T_{max} = 303$, and $T_{min} = 328$ K. This made it possible the estimation of the difference in methanol uptake on the sorbents over the cycle. This two-point method can be recommended for sorbents that obey the Polanyi principle.

Many comprehensive water sorption studies on composites based on several inorganic salts (halides, sulfates, nitrates of alkali and alkaline-earth metals, etc.) confined into pores of various matrixes (silica gel, alumina, porous carbons, etc.)[21,30−32] demonstrated that these composites follow the Polanyi principle.[33] Unfortunately, methanol sorption on such composites has not been thoroughly investigated yet.

To date only the methanol sorption equilibrium on composite CaCl$_2$ confined to pores of silica gel with pores of diameter d_{av} = 15 nm has been studied in detail over the methanol pressure range of 40−300 mbar in the temperature range 298−423 K.[34,35]

Table 1. Main Characteristics of the Silica Gels Used

silica gel	V_p, cm^3/g	S_{sp}, m^2/g	d_{av}, nm
Davisil Grade 646	1.15	300	15
Grace GmbH SP2-8926.02	1.5	326	15
Grace GmbH I 254	0.9	500	6

Table 2. Methanol Solvates of Various Salts

salt	no. of methanol molecules in solvates
LiCl	1, 3
LiBr	1, 3
CaCl$_2$	1, 2, 3, 4, 6
CaBr$_2$	1, 2, 3, 4, 6
CuCl$_2$	1, 2, 3, 4, 5
CuBr$_2$	2, 4
MgCl$_2$	4, 6
MgBr$_2$	6
NiCl$_2$	1, 2, 4, 6
NiBr$_2$	6
Ca(NO$_3$)$_2$	1.8 (2)
MnCl$_2$	1.91 (2)
MnBr$_2$	1.87 (2)

The relevance of the Polanyi principle for describing the methanol sorption equilibrium was verified for this composite. All the sorption isobars follow the same curve when presented as methanol uptake N vs free sorption energy ΔF (Figure 2). This means that methanol sorption on this composite is a function of only the parameter ΔF and follows the Polanyi principle.

Generally, sorption of both water and methanol vapor by bulk salts results in the formation of crystalline solvates (hydrates or methanolates, respectively) and solutions of salt in water or methanol.[11,12] The main regularities of sorption equilibrium of the composites with methanol and water vapor are revealed to be similar.[18,30,34] Consequently, it can be assumed that methanol sorption on such composites obeys the Polanyi principle of temperature invariance. Hence, the developed express method can be applied for scanning various salts that could be of interest for methanol sorption over a typical cooling cycle.

3. Experimental Section

3.1. Synthesis of Composites. Silica gels Davisil Grade 646, Grace SP2-8926.02, and Grace I 254 were used as host matrixes (Table 1). Different inorganic salts which react with methanol to form solvates were used as active substances (Table 2).[11−16]

The composites were synthesized by impregnation of the silica gel with an aqueous solution of the salts followed by thermal drying at 473 K.[18] The salt content in the composites was determined by weighing dry samples before and after impregnation. The composites prepared and their basic properties are displayed in Table 3.

3.2. Sorption Measurements. Sorption measurements were carried out according to the following procedure. The air flow saturated with methanol vapor up to the methanol partial pressure $P_{ev} = 61$ mbar was passed through the adsorber filled with dry composite at temperature $T_{max} = 303$ K until the weight became constant. Then the temperature of the adsorber was increased up to $T_{min} = 328$ K and the desorption stage was carried out. Methanol uptake after adsorption and desorption stages was measured as

$$w\left(\frac{g_{MeOH}}{g_{sorbent}}\right) = \frac{m}{m_0}$$

Table 3. Chemical Composition of the Composite Sorbents Synthesized

no.	composition	silica gel	C, wt %	V_p, cm³/g
1	LiCl/SiO₂(b)	Grace SP2-8926.02	30.6	1.05
2	LiBr/SiO₂(b)	Grace SP2-8926.02	29.2	1.05
3	MgCl₂/SiO₂(a)	Davisil Grade 646	25.4	0.85
4	Ca(NO₃)₂/SiO₂(a)		28.4	0.82
5	NiBr₂/SiO₂(a)		28.2	0.82
6	MnCl₂/SiO₂(a)		28.2	0.82
7	CuCl₂/SiO₂(a)		28.0	0. 83
8	CoCl₂/SiO₂(a)		27.0	0.84
9	MgBr₂/SiO₂(a)		20.8	0.91
10	BaCl₂/SiO₂(a)		26.4	0.85
11	CaBr₂/SiO₂(a)		25.5	0.86
12	LiCl/SiO₂(c)	Grace I 254	24.6	0.68
13	NiBr₂/SiO₂(b)	Grace SP2-8926.02	44.6	0.83
14	CaBr₂/SiO₂(b)		45.9	0.84
15	CaCl₂/SiO₂(a)	Davisil Grade 646	25.0	0.85
16	CaCl₂/SiO₂(c)	Grace I 254	23.0	0.69

Table 4. Sorption Properties of Composite Sorbents: Methanol Uptake after Adsorption and Desorption Stages and Amount of Methanol Exchanged under Conditions of the Cycle Related to Weight and Volume of the Sample

no.	sorbent	w_{ad}, g/g	w_{des}, g/g	Δw, g/g	Δw_v, g/cm³
1	LiCl/SiO₂(b)	0.81	0.09	0.71	0.47
2	LiBr/SiO₂(b)	0.73	0.33	0.40	0.26
3	MgCl₂/SiO₂(a)	0.29	0.14	0.15	0.08
4	Ca(NO₃)₂/SiO₂(a)	0.20	0.03	0.17	0.09
5	NiBr₂/SiO₂(a)	0.28	0.02	0.26	0.14
6	MnCl₂/SiO₂(a)	0.15	0.09	0.05	0.03
7	CuCl₂/SiO₂(a)	0.09		<0.09	<0.05
8	CoCl₂/SiO₂(a)	0.20	0.03	0.17	0.09
9	MgBr₂/SiO₂(a)	0.14	0.05	0.09	0.04
10	BaCl₂/SiO₂(a)	0.08		<0.08	<0.04
11	CaBr₂/SiO₂(a)	0.24	0.06	0.17	0.09
12	LiCl/SiO₂()	0.64	0.10	0.49	0.24
13	NiBr₂/SiO₂(b)	0.48	0.06	0.42	0.27
14	CaBr₂/SiO₂(b)	0.47	0.23	0.24	0.16
15	CaCl₂/SiO₂(a)	0.17	0.15	0.02	0.02
16	CaCl₂/SiO₂(c)	0.29	0.12	0.17	0.09

or as a number of methanol molecules adsorbed by one salt molecule:

$$N\left(\frac{\text{mole}_{MeOH}}{\text{mole}_{sorbent}}\right) = \frac{m/M_{MeOH}}{m_o C/M_{salt}}$$

The sorption per cycle Δw was calculated as the difference in the methanol uptakes at $T_{max} = 303$ K and $T_{min} = 328$ K.

4. Results and Discussion

4.1. Sorption Properties. The influence of the chemical nature of confined salt on the sorption ability of composites is presented in Table 4 and Figure 3. The composites based on LiCl and LiBr appear to demonstrate the highest net methanol sorptions under the cycle conditions described above. The net sorptions of composites containing MgCl₂, NiBr₂, and CaBr₂ are lower, but they can be also of interest.

The composite no. 1 LiCl (30.6%)/SiO₂(b) appears to show a very high sorption capacity $w_{ads} = 0.8$ g/g. The methanol uptake after the desorption stage decreases to $w_{des} = 0.09$ g/g, giving the variation of uptake per cycle $\Delta w = 0.71$ g/g, which is much larger than that for conventional adsorbents, such as porous carbons and zeolites (Figure 3).[6-10]

The composite no. 2 LiBr (29.2 wt %)/SiO₂(b) possesses a high ability to sorb methanol, $w_{ads} = 0.73$ g/g. However, the temperature of desorption fixed at the cycle is not likely to be high enough to desorb the methanol adsorbed. The uptake after the desorption stage remains rather high, $w_{des} = 0.33$ g/g, giving the variation of uptake per cycle $\Delta w = 0.4$ g/g. It is 2 times lower than that of LiCl-based composites, but nevertheless far

exceeds the sorption per cycle for conventional adsorbents. The increase in the desorption temperature T_{min} will result in a rise of the sorption difference in a cycle. Thus, the LiBr-based composite could be of interest when the heat source with a higher temperature T_3 is available for regeneration of a sorbent.

The composite no. 3 MgCl₂ (25.4 wt %)/SiO₂(a) possesses quite good sorption ability ($w_{ads} = 0.29$ g/g), but the methanol adsorbed cannot be desorbed under the cooling cycle conditions described above ($w_{des} = 0.14$ g/g).

The methanol sorption ability of composite no. 5 NiBr₂ (28.2 wt %)/SiO₂(a) is quite high ($w_{ads} = 0.28$ g/g), and the majority of the methanol adsorbed can be desorbed under the chosen cycle conditions ($w_{des} = 0.02$ g/g), giving the sorption per cycle $\Delta w = 0.26$ g/g. The composite no. 14 with a larger NiBr₂ content of 44.6 wt % possesses a higher sorption ability $w_{ads} = 0.47$ g/g and sorption per cycle $\Delta w = 0.42$ g/g. The composites nos. 4, 6, 7, 8, 9, 10, and 11 based on the salts Ca(NO₃)₂, MnCl₂, CuCl₂, CoCl₂, MgBr₂ BaCl₂, and CaBr₂ appear to be of no interest because of their low sorption ability ($w_{ads} \leq 0.2$ g/g) or small sorption difference during the cycle ($\Delta w \leq 0.17$ g/g).

The composite no. 15 CaCl₂ (25.0 wt %)/SiO₂(a) demonstrates negligible sorption per cycle $\Delta w = 0.02$ g/g due to the presence of a plateau in the range F of the cycle described. This plateau is caused by the formation of stable crystalline solvate CaCl₂·2CH₃OH in pores of silica gel (Figure 2).[34] A decrease in the pore size of the silica gel d_{av} from 15 to 6 nm results in the disappearance of the plateau. The composite no. 16 CaCl₂ (25.0 wt %)/SiO₂(c) demonstrates a methanol sorption ability $w_{ads} = 0.29$ g/g and a sorption per cycle $\Delta w = 0.14$ g/g. Therefore, the matrix's pore size allows the sorption properties of the composites to vary.
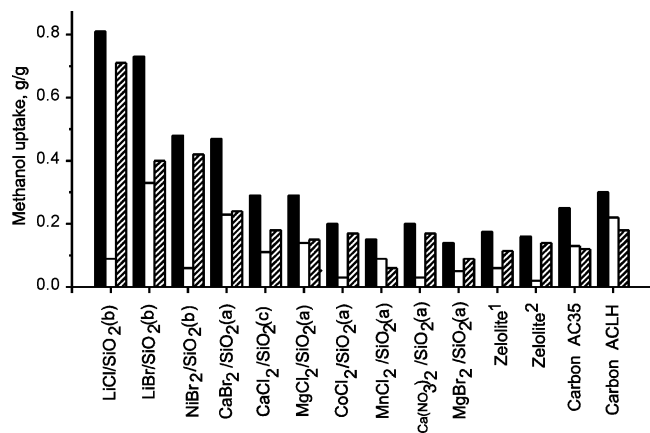
Figure 3. Methanol uptake by composite sorbents and conventional adsorbents: zeolites and activated carbons after adsorption (shaded bars), desorption (white bars) stages, and variation of uptake per cycle (black bars).
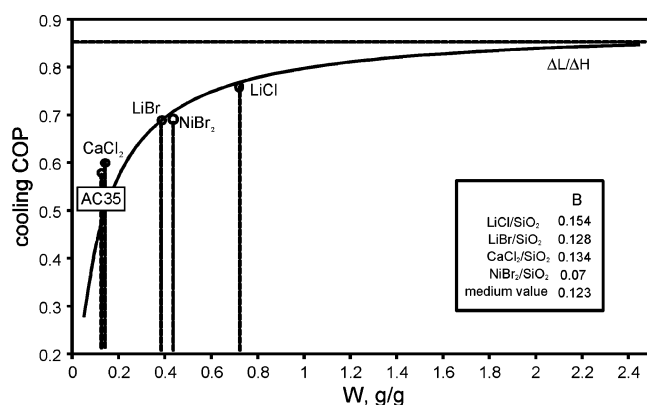
Figure 4. Thermodynamic cooling COP calculated for the most promising composites (T_3 = 363 K).

Thus, most of the composites "salt inside pores of silica gel" appear to demonstrate high values of net methanol sorption under cooling cycle conditions within the range 0.3−0.8 g/g.

4.2. COP Evaluation. For accurate calculation of the thermodynamic COP by eq 1, specific measurements of the sorption properties and of the equivalent specific heat of each composite are required. However, a reasonable estimation of these values can be done considering the following approximations:

(1) The equivalent specific heat of each composite is calculated as a sum of the specific heat of the host matrix, of the salt, and of the methanol adsorbed:[36]

$$C_{p,eq}(w) = C_{p,salt}C_{salt} + C_{p,SiO_2}(1 - C_{salt}) + wC_{p,MeOH}$$
(10)

The specific heat of the composites at stage 2−3 in the cycle (Figure 1) was calculated for medium methanol uptake w_{med} = $(w_{min} + w_{max})/2$.

(2) The latent heat of methanol is calculated considering the medium temperature of the working cycle.

(3) The desorption enthalpy is calculated as a sum of the latent heat of methanol and the free sorption energy ΔF, for a medium value of methanol adsorbed w_{med}:

$$\Delta H = \Delta L + \Delta F(w)$$
(11)

which is derived from the fundamental expression between the desorption enthalpy and the free sorption energy under the assumption that the density of the methanol adsorbed is constant.[25,29,37]

The above-described approximation made it possible to calculate the coefficients A, B, and Θ in eq 4 and, thus, the cooling COP for the most promising composites. Considering $\Delta F(w) = [\Delta F(w_{min}) + \Delta F(w_{max})]/2 \approx 4830$ J/mol = 150 J/g and ΔL = 1140 J/g, $A = \Delta H/\Delta L$ = 1.13.

Figure 4 shows the cooling COP as calculated for the composites based on LiCl, NiBr$_2$, and LiBr in silica gel pores d_{av} = 15 nm and CaCl$_2$ in pores d_{av} = 6 nm[34] (maximum temperature of desorption T_3 = 363 K). In the same figure, the B coefficients estimated for the four composites are reported. The curve plotted in the same figure was calculated considering the value of A = 1.13 and the medium value of B = 0.123. We can assume that all the composites present COP values that are in proximity on this general curve, which tends to 1/A for infinite values of uptake variation.

It is evident that the composite LiCl/SiO$_2$ allows a thermodynamic COP of 0.74, which is close to the maximum theoretical value COP$_{max}$ = 1/A = 0.88. The other composites considered present performances similar to the thermodynamic COP values for the best water sorbents.[38] Such good performances are due to a very high methanol sorption ability which overcomes the intrinsic problem of low latent heat of methanol.

5. Conclusions

A new family of methanol sorbents "salts in mesoporous silica" was presented. The measurement of methanol sorption capacities of composites, under typical AC cycle conditions, showed that most of the composites synthesized present a net methanol sorption ability Δw = 0.3−0.8 g/g, which is higher than that of common methanol sorbents. The LiCl-based composite is likely to be the most promising due to the maximum value of methanol absorbed w_{ads} = 0.8 g/g, which can be removed by heating by some 25 °C. Thus, the net sorption per cycle reaches Δw = 0.7 g/g, which makes the composite very attractive for adsorption air conditioning driven by low-grade heat. The LiBr-based composite possesses high methanol sorption w_{ads} = 0.73 g/g, but for removing methanol sorbed a higher desorption temperature is required. It could be a good candidate for sorption cooling/heating driven by an energy source with a temperature T_3 higher than 363 K. The estimated COP values range between 0.6 and 0.74, which are comparable with the COP values for the best water adsorbents. The promising results obtained encourage us to continue our research, focusing on the full measurement of the sorption properties for the LiCl/SiO$_2$ composite.

Nomenclature

A = coefficient of eq 2
B = coefficient of eq 2
C = salt concentration, wt %
COP = coefficient of performance
C_p = heat capacity, J/K
ΔF = Dubinin−Polanyi potential, J/mol
ΔH = enthalpy of methanol desorption, J/g
ΔL = heat of methanol condensation, J/g
M = molar mass, g/mol
m = mass of methanol adsorbed, g

m_o = mass of dry sorbent, g
N = methanol uptake, mol/mol
P = pressure, bar
P_s = saturation pressure, bar
Q = heat, J/kg
R = gas universal constant, J/(mol K)
T = temperature, K
V = volume of adsorbed phase, cm^3/g
w = methanol uptake, g/g
Δw = variation of uptake per cycle, g/g

Greek Symbols

ρ = density of methanol adsorbed, g/cm^3
Θ = coefficient of eq 2

Subscripts

ads = adsorption
con = condensation
des = desorption
ev = evaporation
ish = isosteric heating

Literature Cited

(1) Meunier, F. Adsorption heat pump technology: possibilities and limits. *Proceedings of the International Sorption Heat Pump Conference*, March 24−26, 1999, Munich, Germany; Lang Offsetdruck GmbH: Unterschlibheim, Germany, 1999; p 25.

(2) Offenhartz, P. O'D.; Brown, F. C.; Mar, R.; Carling R. W. A heat pump and thermal storage system for solar heating and cooling based on the reaction of calcium chloride and methanol vapor. *J. Sol. Energy Eng.— Trans. ASME* **1980**, *102*, 59.

(3) Lai, H.; Li, C. Application of periodic reversal flow reactors to chemical heat pump systems based on solid/vapor non-catalytic reaction. *Chem. Eng. Sci.* **1996**, *51*, 2951.

(4) Follin, S.; Goetz, V.; Guillot, A. Influence of microporous characteristics of activated carbons on the performance of an adsorption cycle for refrigeration. *Ind. Eng. Chem. Res.* **1996**, *35*, 2632.

(5) Schmidt, F. P.; Luther, J.; Glandt, E. D. Influence of adsorbent characteristics on the performance of an adsorption heat storage cycle. *Ind. Eng. Chem. Res.* **2003**, *42*, 4910.

(6) Leite, A. P. F.; Daguenet, M. Performance of a new solid adsorption ice maker with solar energy regenereation. *Energy Convers. Manage.* **2000**, *41*, 1625.

(7) Douss, N.; Meunier, F. Effect of operating temperatures on the coefficient of performance of active carbon-methanol system. *Heat Recovery Syst. CHP* **1988**, *8*, 383.

(8) Chernev, D. Waste heat driven automotive air conditioning system. *Proceedings of the International Sorption Heat Pump Conference*, March 24−26, 1999, Munich, Germany; Lang Offsetdruck GmbH: Unterschlibheim, Germany, 1999; p 65.

(9) Gordeeva, L.; Aristov, Yu.; Freni, A.; Restuccia, G. Preparation of zeolite layers with enhanced mass transfer properties for adsorption air conditioner. *Proceedings of the International Sorption Heat Pump Conference*, Sept 24−27, 2002, Shanghai, China; Science Press: Beijing, China and Science Press New York Ltd.: New York, 2002; p 625.

(10) Restuccia, G.; Freni, A.; Russo, F.; Vasta, S. Experimental investigation of a solid adsorption chiller based on a heat exchanger coated with hydrophobic zeolite. *Appl. Therm. Eng.* **2005**, *25*, 1419.

(11) *Gmelins Handbuch der Anorganischen Chemie, Calcium Eraganzungs band.* Pietsch, E. H. E., Ed.; Verlag Chemie: Weinheim, Germany, 1957; Sn. 28, Tl. B, Rf. 2, p 523.

(12) *Gmelin Data: 2000−2005 Gesellschaft Deutscher Chemiker*; licensed to MDL Information Systems GmbH; 1988−1999: Gmelin Institut fuer Anorganische Chemie und Grenzgebiete der Wissenschaften.

(13) Bixon, E.; Guerry, R.; Tassions, D. Salt effect on vapor pressure of pure solvents: methanol with seven salts at 24.9 °C. *J. Chem. Eng. Data* **1979**, *24*, 9.

(14) Riffat, S. B. A combined chemical storage and vapour-compresion heat pump using CH$_3$OH/CaCl$_2$ and R12 refrigerant. *J. Inst. Energy* **1991**, *64*, 77.

(15) Lourdudoss, S.; Stymne, H. An energy storing absorption heat pump process. *Energy Res.* **1987**, *11*, 263.

(16) Ruiter, J. P. Simplified thermodynamic description of mixtures and solutions. *Int. J. Refrig.* **1990**, *13*, 223.

(17) Andersson, J. Y. *Kinetic and mechanistic studies of reactions between water vapour and some solid sorbents*. Department of Physical Chemistry, The Royal Institute of Technology, S-100 44, Stockholm, Sweden, 1986; pp 27−44.

(18) Aristov, Yu. I.; Resticcia, G.; Cacciola, G.; Parmon, V. N. A family of new working materials for solid sorption air conditioning systems. *Appl. Therm. Eng.* **2002**, *22*, 191.

(19) Restuccia, G.; Freni, A.; Vasta, S.; Aristov, Yu. Selective Water Sorbents for solid sorption chiller: experimental results and modelling. *Int. J. Refrig.* **2004**, *27*, 284.

(20) Aristov, Yu. I.; Restuccia, G.; Tokarev, M. M.; Cacciola, G. Selective water sorbents for multiple applications. 10. Energy storage ability. *React. Kinet. Catal. Lett.* **2000**, *69*, 345.

(21) Tokarev, M. M.; Aristov, Yu. I. Selective water sorbents for multiple applications. 4. CaCl$_2$ confined in the silica gel pores: sorption/desorption kinetics. *React. Kinet. Catal. Lett.* **1997**, *62*, 143.

(22) Dawoud, B.; Aristov, Yu. I. Experimental study on the kinetics of water vapor sorption on selective water sorbents, silica-gels and alumina under typical operating conditions of sorption heat pumps. *Int. J. Heat Mass Transfer* **2003**, *46*, 273.

(23) Aristov, Yu. I.; Glaznev, I. S.; Freni, A.; Restuccia, G. Kinetics of Water sorption on SWS-1L (calcium chloride confined to mesoporous silica gel): influence of grain size and temperature. *Chem. Eng. Sci.* **2006**, *61*, 1453.

(24) Polanyi, M. Therories of the adsorption of gases. A general survey and some additional remarks. *Trans. Faraday Soc.* **1932**, *28*, 316.

(25) Bering, B. P.; Dubinin, M. M.; Serpinsky, V. V. Theory of volume filling for vapor adsorption. *J. Colloid Interface Sci.* **1966**, *21*, 378.

(26) Dubinin, M. M.; Stoeckli, H. F. Homogeneous and heterogeneous micropore structures in carbonaceous adsorbents. *J. Colloid Interface Sci.* **1980**, *75*, 34.

(27) Dubinin, M. M. *Progress in Surface and Membrane Science*; Academic Press: New York, 1975.

(28) *Spravochnik Khimika*; Goskhimizdat: Leningrad, 1963; Vol. 1.

(29) Andersson, J. Y.; Bjurstrom, H.; Azoulay, M.; Carlsson, B. Experimental and theoretical investigation of the kinetics of the sorption of water vapour by silica gel. *J. Chem. Soc., Faraday Trans. 1* **1985**, *11*, 2681.

(30) Gordeeva, L. G.; Restuccia, G.; Cacciola, G.; Aristov, Yu. I. Selective water sorbents for multiple applications: 5. LiBr confined in mesopores of silica gel: sorption properties. *React. Kinet. Catal. Lett.* **1998**, *63*, 81.

(31) Mrowiec-Bialon, J.; Lachocski, A. I.; Jarzebski, A. B.; Gordeeva, L. G.; Aristov, Yu. I. SiO$_2$-LiBr nanocomposite sol-gel adsorbents of water vapor: preparation and properties. *J. Colloid Interface Sci.* **1999**, *218*, 500.

(32) Gordeeva, L. G.; Freni, A.; Restuccia, G.; Aristov, Yu. I. Water sorption on "LiBr in porous carbons". *Fuel Process. Technol.* **2002**, *79*, 225.

(33) Prokop'ev, S. I.; Aristov, Yu. I. Selective water sorbents for multiple applications. 9. Temperature independent curves of sorption from theory of volume filling of micropores. *React. Kinet. Catal. Lett.* **1999**, *67*, 345.

(34) Aristov, Yu. I.; Gordeeva, L. G.; Pankratiev, Yu. D.; Plyasova, T. M.; Bikova, I. V.; Freni, A.; Restuccia, G. "Sorption Equilibrium of Methanol on New Composite Sorbents "CaCl$_2$/Silica Gel". *Adsorption*, in press.

(35) Gordeeva, L. G.; Restuccia, G.; Tokarev, M. M.; Freni, A.; Pankratiev, Yu. D.; Kraynov, A. V.; Aristov, Yu. I. Methanol sorption on "CaCl$_2$/silica gel" composite: sorption equilibrium, calorimetry. *Proceedings of the 13th International Congress of Chemical Process Engineering, CHISA*, August 27−31, 2000, Prague, Czech Republic; Process Engineering Publisher: Praha, Czech Republic, 2000; Vol. 2, p 250.

(36) Pons, M.; Poyelle, F. Adsorptive machines with advanced cycles for heat pumping or cooling applications. *Int. J. Refrig.* **1999**, *22*, 27.

(37) Tokarev, M. M.; Okunev, B. N.; Safonov, M. S.; Kheifets, L. I. Approximation Equations for Describing the Sorption Equilibrium between Water Vapor and a CaCl2-in-Silica Gel Composite Sorbent. *Russ. J. Phys. Chem.* **2005**, *79*, 1490.

(38) Pons, M.; Meunier, F.; Cacciola, G.; Critoph, R. E.;, Groll, M.; Puigjaner, L.; Spinner, B.; Ziegler, F. Thermodynamic based comparison of sorption systems for cooling and heat pumping. *Int. J. Refrig.* **1999**, *22*, 5.