Novel Materials for Adsorptive Heat Pumping and Storage: Screening and Nanotailoring of Sorption Properties

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The brief review of innovative materials for adsorptive pumping and storage of low temperature heat as well as current trends in this field showed their great potential. To implement it in the near future it is reasonable to follow two complementary lines: (a) systematic testing for this application novel adsorbents initially developed for other targets (gas drying, separation, etc.), and (b) tailoring of new specific porous materials adapted just to variety of adsorptive cooling, heating and storage cycles under different climatic and boundary conditions. The main idea of the latter approach is that for each particular adsorptive cycle there is an optimal adsorbent, the thermodynamic characteristics of which could allow perfect performance of this cycle. The first step of the analysis is the formulation of requirements to this desirable (ideal) adsorbent. Then, the final step is to design and synthesize a new adsorbent with sorption properties close or even equal to those determined before as perfectly fitting the cycle. Particular examples of nanotailoring of adsorption properties are given for two phase materials, composites “a salt in a porous host matrix”, which can be used as efficient adsorbents of water, methanol and ammonia.

Introduction

Fulfillment of the Kyoto protocol requires the replacement of fossil fuels with renewable energy sources and rational use of heat in industry, transport and dwellings (re-use of exhaust heat, energy storage, etc.). These new heat sources have lower temperature potential that opens a niche for applying adsorption technologies for energy transformation and storage. Therefore current progress in this field is essentially related to the development of innovative materials which are properly adapted to the new targets. In particular, novel nanoporous materials are required for adsorptive heat pumps (AHP) and adsorptive heat storage (AHS).

Porous structures are divided into microporous (pore diameters less than 2 nm), mesoporous (pores of 2 to 50 nm) and macroporous (more than 50 nm) in the IUPAC classification. The designation as “nano” is a fashionable prefix recently introduced and frequently used at present to highlight materials and phenomena with typical spatial scale 1–100 nm (Klabunde, 2001). Many nanoporous materials such as common zeolites, silicas, clays, carbaceous molecular sieves, etc. are known for many decades and widely used for industrial catalysis. Last decades many efforts were devoted

to synthesize new nanoporous materials with advanced structural and adsorption properties. Here we give a brief review of “old” and “new” nanomaterials and discuss current trends in their application for AHP and AHS.

1. The State-of-the-Art and Current Trends

1.1 “Old” and “new” adsorbents

Classification into “old” and “new” is very relative as within a short period of time many new families of porous materials progressed from the initial idea to complete development, hence, passed the way from “new” to “old” status. For instance, the development of crystalline porous phosphates was started in 1982 with the synthesis of adsorbents with aluminophosphate composition (Wilson *et al.*, 1982). Due to incorporation of different transition metals next to phosphorus and aluminum, by 1994 the variety of phosphate based porous materials—metalloalumino-phosphates had become comparable with that of the common silicate based (“old”) zeolites (Martens and Jacobs, 1994). Both structure and adsorption properties of these “new” materials depend on the type and amount of incorporated metal.

Extremely fast progress was made with mesoporous materials (MCM, SBA, FSM, etc.) (Beck *et al.*, 1992; Inagaki *et al.*, 1993), carbon nanotubes (Iijima, 1991), nanohorns (Harris *et al.*, 1994), aerogels (Pekala *et al.*, 1992), activated carbon fibers (ACF) (Kaneko and Ishii, 1992) and many others.

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Fig. 1 MCM-41 material with mono-sized pores used for SWS synthesis (Tokarev *et al.*, 2002)

Fig. 2 Water adsorption isotherms: 1, SWS-1L; 2, FAM-Z02; 3, SWS-5L; 4, zeolite 13X; 5, FAM-Z01; 6, silica Fuji Silys RD; 7, carbon aerogel a-CA-54 (Hanzawa and Kaneko, 1997); 8, pitch-based ACF P5 (Miyawaki *et al.*, 2001)

Now similar progress is being made with new family of supramolecular materials (so called, metal organic frameworks, MOF, or porous coordination polymers, PCP) (Yaghi *et al.*, 2003; Janiak, 2003; Kitagawa *et al.*, 2004; Kitagawa and Uemiy, 2005). Numerous techniques for synthesis of versatile structures from molecular building blocks have been developed so far. “In a surprisingly short time, the structural chemistry has attained a very mature level. Coordination polymers have now taken an important position in the porous-materials area” (Kitagawa *et al.*, 2004).

Increasing demand for new porous adsorbents is continuously submitting from the industry side. No doubt that various zeolites are the most widely used industrial catalysts as they are very efficient for oil refining, fine organic chemistry, petrochemistry, etc. (Corma, 1997). Another huge application of new porous materials concerns adsorption technologies—gas

purification, separation, storage, etc. (Ruthven, 1984). Vast number of novel adsorbents with diverse structure and properties is synthesized every year for these aims. Even just counting and classification of these materials present difficulties. That is why we will give here just a very brief review of “old” and “new” nanomaterials and refer to special literature.

Common zeolites and silicas, clays (pillar-layered silicates, vermiculite, bentonite, etc.), carbonaceous molecular sieves and activated carbons present the “old” adsorbents. Innovative nanoporous materials, like large-pore zeolites (AIPO, SAPO, MAIPO, etc.), mesostructured silicates (MCM (**Figure 1**), SBA, FSM, etc. (Corma, 1997)), MOF, composites “salt in nanoporous matrix” (SWS) (Aristov *et al.*, 1996, 2002), new carbonaceous materials (ACF, carbon aerogels, mesocarbon microbeads (Kaneko *et al.*, 1998), super-high-surface-area carbons (Otowa *et al.*, 1993)) can be conventionally ascribed to the “new” adsorbents the list of which can be continued.

1.2 Known adsorbents for AHP and AHS

However, only a few “old” and “new” adsorbents have already been tested for AHP (AHS). The AHP working pairs “zeolite (3A, 4A or 13X)–water”, “silica gel (types 3A and RD Fuji Silysia Chemical Ltd.)–water”, “carbon (AC35, TA90)–methanol”, “carbon (PX21)–ammonia” and several others were invented for the past few decades and still used in the majority of AHP units. For water as a working fluid, common aluminosilicate-based zeolites exchange large amount of water (0.2–0.3 g/g) in narrow temperature and humidity range which is shifted to high T and low P/P_0 (**Figure 2**). This allows a large temperature lift, however, needs a high temperature for regeneration ($T_{\text{des}} > 150\text{--}200^\circ\text{C}$). Silica gels, quite the contrary, exchange water over wide temperature range, have a low temperature lift, but can be easily charged ($T_{\text{des}} > 60\text{--}100^\circ\text{C}$). Other oxide-based single component adsorbents take an intermediate position.

Thus, it is reasonable to expect that just a screening of already known nanoporous materials to assess their feasibility for AHP systems can result in new efficient working pairs. We consider as example the aluminophosphate nanostructures (AIPO) already mentioned above. Application of aluminophosphates (AIPO-5, AIPO-17 and AIPO-18) for low grade heat utilization was first analyzed in (Jaenchen *et al.*, 2002). The authors concluded that these materials “loose the adsorbed water or methanol at $T < 400\text{ K}$ that makes the microporous aluminophosphates suitable for utilization of low temperature heat”. Indeed, recently two AIPO-type adsorbents have been proposed for desiccant and AHP systems (Kakiuchi *et al.*, 2004). FAM-Z01 has an AFI type two-dimensional structure with 0.73 nm windows, and its framework consists of AlO_4 , PO_4 and FeO_4 tetrahedrons. It is suggested for adsorptive cooling driven by 60°C heat, for instance,

from fuel cell, solar energy, etc. FAM-ZO2 is a CHA-type silicoaluminophosphate with a 3D-structure (SAPO-34). The framework consists of AlO_4 , PO_4 and SiO_4 tetrahedrons and 0.38 nm windows. It is suggested for adsorptive cooling driven by 90°C heat, for instance, from car engines. Both the materials during water adsorption undergo the transition between hydrophobic and hydrophilic structures which causes exchange of large amount of water within narrow temperature and humidity ranges (Figure 2, curves 2 and 5). For AHP cycle with $T_e = 10^\circ\text{C}$, $T_c = 40^\circ\text{C}$ and $T_{\text{des}} = 90^\circ\text{C}$ the amount of water exchanged by FAM-ZO2 is 0.17–0.19 g/g that is 4.8 and 3.8 times those of Y zeolite and silica gel (Kakiuchi *et al.*, 2005). High heat of water adsorption (58 kJ/mol) of these FAMs restricts the limiting cooling COP of a basic cycle (without regeneration of heat) to 0.70, however, is favorable for AHS. Further testing of these materials under real conditions of AHP should find out the dynamic and cycling behavior of FAMs (Dawoud, 2007; Sapienza *et al.*, 2007).

The encouraging example of FAMs showed that adsorbent screening can reveal which already known materials can be efficiently used in AHP and AHS sector. On the other hand, the comprehensive study of sorption properties of a huge number of available adsorbents is extremely time-consuming as it requires careful measuring a set of sorption isobars (isosters, isotherms) in a wide range of temperature and pressure. To hasten the screening a fast but quite accurate experimental method based on the Polanyi potential theory was suggested (Chalaev and Aristov, 2006; Gordeeva *et al.*, 2007a).

1.3 Pre-screening of known adsorbents

This principle declares that, at different temperatures T_a and T_b , equal uptake can be achieved at the vapor pressures P_a and P_b which are linked through the formula (Polanyi, 1932)

$$T_a \ln h_a = T_b \ln h_b \quad (1)$$

where $h = P/P_s$ is a relative pressure of adsorbate. It postulates a one-to-one correspondence between the adsorption uptake and the product $T \ln h$. Dubinin introduced the similar value $\Delta F = -RT \ln h$, the so called free energy of adsorption or the adsorption potential. He showed that for variety of microporous solids the specific adsorption volume V (normalized to the weight of the dry adsorbent, cm^3/g) can be expressed in general form as a unique function of ΔF (Dubinin, 1975)

$$V = f(\Delta F)$$

If the adsorbate density does not depend on temperature similar relation is valid for the specific uptake (g/g)

$$w = f(\Delta F) \quad (2)$$

Since the Polanyi invariance principle is rather universal, the application area of this relation turned out to be wider, and it can be generalized for non-microporous adsorbents as well (Jaroniec, 1997). In the latter case a polynomial expression

$$w = a + b\Delta F + c\Delta F^2 + d\Delta F^3 \dots \quad (3)$$

can be used for describing the equilibrium uptake (Nunez *et al.*, 1999; Prokopiev *et al.*, 2000). Thus, Eqs. (2) and (3) give a one-to-one correspondence between the equilibrium uptake and a single parameter $\Delta F = -RT \ln h$, instead of usual two (P , T).

According to this unique correspondence the rich isoster of the cycle related to $w = w_{\text{max}}$ can be unambiguously characterized by the potential

$$\Delta F(w_{\text{max}}) = -RT_1 \ln[P_1/P_s(T_1)] = -RT_2 \ln[P_2/P_s(T_2)] = K_1$$

K_1 is determined only by T_e and T_c , and does not depend on T_d . For the weak isoster with $w = w_{\text{min}}$ this parameter can be written as

$$\Delta F(w_{\text{min}}) = -RT_3 \ln[P_2/P_s(T_3)] = -RT_4 \ln[P_1/P_s(T_4)] = K_2$$

K_2 is uniquely determined by T_c and T_d , but not by T_e .

Thus, to compare different adsorbents, it is sufficient to present the specific water adsorption in the form of temperature-invariant curve of sorption $w(\Delta F)$. Those materials, for which the difference in sorption Δw at $\Delta F_1 = K_1$ and $\Delta F_2 = K_2$ is maximal, can be considered from the thermodynamic point of view as the most promising for the adsorptive cooling.

The advantages of the suggested approach are:

- Already published data on sorption properties of materials can be used for the analysis, including those that have been obtained at temperatures and pressures different from those realized in the real cycle;
- Analysis can be based on a single isotherm or isobar of sorption.

What only matter is that relation (1) should be valid and experimental data be obtained in the proper range of adsorption potential $K_1 \leq \Delta F \leq K_2$. Example of such fast screening of new and known adsorbents to be applied for air conditioning (AC) driven by low temperature heat (e.g., in vehicles) can be found in (Gordeeva *et al.*, 2007a, 2007b).

1.4 Screening and IUPAC classification

Basing on this approach, let us make brief general discussion on applicability of known types of the adsorbents in AHP systems. It is well known that most isotherms of adsorption can be ascribed to one of five types, from I to V, according to classification first suggested in Brunauer *et al.* (1940). Besides, we will

Fig. 3 Typical adsorption isotherms (Greg and Sing, 1967) and their derivatives

consider the relatively rare step-like isotherms of adsorption, which were ascribed in Greg and Sing (1967) to type VI.

As mentioned above, those materials will be promising for the use in AHP that can reversibly adsorb/desorb a large amount of water in a relatively narrow range of the adsorption potential ΔF (or of relative vapor pressure h), means those with the large derivative $dw/d(\Delta F)$ or dw/dh . A sight on the typical isotherms and their derivatives shows that this criterion can be apparently fulfilled for the adsorbents with the isotherms of type I, IV, V or VI (**Figure 3**).

The isotherms of type I are typical of solids with micropores, for example, zeolites. Commonly, the jump of uptake is observed at rather low $h \approx 0.01$ – 0.02 (or $\Delta F > 15$ – 20 kJ/mol) that leads to the desorption temperature $T_{\text{des}} > 200^\circ\text{C}$, that is quite far from the conditions considered in this paper.

The isotherms of type IV are common for adsorption on mesoporous solids, e.g., inorganic oxides, like silica, alumina, etc. (Greg and Sing, 1967). Characteristic feature of these materials is a hysteresis caused by a capillary condensation of adsorbate. The hysteresis makes the AHP and especially AHS operation worse because desorption occurs at higher temperature than the adsorption. For water the condensation is typically observed at the relative pressures $h > 0.5$ – 0.7 that is too large to be used for AHP (acceptable is h

of about 0.3 and lower).

The isotherms of type V are typical for weak sorbent-sorbate interaction (Greg and Sing, 1967), for example, in the system “water–porous carbon”. Even for microporous carbons, sharp increase in the uptake is observed when the relative pressure h becomes high enough and ranging between 0.35–0.45 and 0.6–0.7 (Figure 2, curves 7 and 8). Easy desorption at $h > 0.35$ could be of interest only for adsorptive AC systems driven by low temperature heat, e.g., working at $T_c = 10^\circ\text{C}$ and $T_c \leq 27^\circ\text{C}$ that is not interesting for practice. Thus, hydrophobic adsorbents based on various activated carbons can be done more attractive for adsorptive AC, if manage to shift the adsorption/desorption transition to $h = 0.2$ – 0.3 . Another crucial point of these water adsorbents is a strong adsorption/desorption hysteresis (Miyawaki *et al.*, 2001) which, however, can be nearly neglected for carbon based aerogels (Hanzawa and Kaneko, 1997). Contrarily, activated carbons, both standard (AC35, TA90, RX11) and innovative (ACF A-20), are widely used for adsorption of alcohols (methanol, ethanol) (Douss and Meunier, 1988; Saha *et al.*, 2007) and ammonia (Critoph and Zhong, 2005).

The most promising are step-like isotherms of type VI, which first were observed for adsorption of inert gases on non-porous adsorbents (Greg and Sing, 1967). Each step was found to correspond to the formation of successive monolayers on the surface that leads to a sharp but small change in the uptake. Figure 2 shows that similar isotherms have been recorded for adsorption of water on new adsorbents of FAM and SWS type. In this case the uptake change is larger and reaches 0.15–0.20 g/g. For FAMs it is due to the structural transition from hydrophobic to hydrophilic state. For SWSs each step is caused by a chemical reaction between water vapor and salt S (or its hydrate) (Aristov *et al.*, 1996)

Thus, the screening procedure is expected to be successful, first of all, for those adsorbents which have step-wise adsorption equilibrium curves.

For instance, step-wise isotherm was reported for methanol adsorption on porous coordination polymer $\{[\text{Cu}_2(\text{pzdc})_2(\text{dpyg})] \cdot 8\text{H}_2\text{O}\}_n$ (**Figure 4**) (Kitaura *et al.*, 2002). Adsorption takes place at $P/P_0 = 0.22$ – 0.36 while desorption occurs at $P/P_0 = 0.09$ – 0.11 . This hysteresis is accompanied by reversible crystal-to-crystal transformation induced by adsorption and desorption of MeOH molecules which resembles the FAM transformation. A precise structural study reveals that contraction and re-expansion of the channels with the layer-layer separation varying between 9.6 and 13.2 Å is observed for the process of desorption/adsorption of methanol molecules. The amount of methanol exchanged

Fig. 4 Adsorption (A)/desorption (D) isotherms of MeOH on $[\text{Cu}_2(\text{pzdc})_2(\text{dpyg})]_n$ at 298 K (Kitauro *et al.*, 2002). Tentative cooling cycle is shown by arrows

during this transformation reaches 0.16–0.19 g/g that could be of practical interest. Therefore, this PCP can be suggested for further testing in adsorption AC units.

In principle, a huge amount of PCPs have already been synthesized, but only for a few of them the adsorption of various gases has been studied (mostly of O_2 , N_2 , CO_2 , CH_4 for gas separation and storage). We believe that future screening of PCPs for AHP (AHS) application will reveal novel and highly efficient working pairs.

Although we presented here several tricks which can prompt rational way of screening, this approach, in general, is a palliative one as it gives an intermediate solution rather than an ultimate one. Indeed, the selected adsorbent, being the best among the tested materials, may quite differ from an adsorbent optimal for a particular cycle.

In any case it is reasonable to perform such a screening in tight cooperation between material scientists and thermal engineers, because 1) many new materials are not commercially available yet and can be obtained only from the laboratories where they have been developed, 2) the preliminary knowledge of material's basic properties and restrictions is important for its proper testing, and 3) joint analysis of what kind of adsorbent is needed for particular cycle could make the screening more focused and less time-consuming. Therefore, it would be very helpful to develop simple requirements to an optimal adsorbent and use them as a lodestar. There important issues will be discussed further on.

2. Nanotailoring Approach

The second approach described below requires even more intimate and coordinated actions of these two scientific communities. The main idea of this approach is that for each adsorptive cycle (heating, cooling, storage, etc.) there is an optimal adsorbent, the

thermodynamic characteristics of which could allow perfect performance of this cycle (Aristov, 2005). Hence, after the parameters of the particular cycle have been determined, the next step is the **formulation** of the requirements to this desirable (ideal) adsorbent. Then, the final step is to **design and synthesize** a new adsorbent with sorption properties close or even equal to those determined before as perfectly fitting the cycle. This approach, in general, can give an ultimate solution instead of a palliative one most probably resulting from the first methodology. It seems reasonable if the formulation of the requirements will come from the thermal engineering side where a deep knowledge of the various adsorptive cycles has been accumulated. Here we consider first attempts to realize this approach, which concern a non-regenerative cooling cycle.

2.1 Requirements to an optimal adsorbent

For this cycle mentioned demands can be formulated using a universal relation between the three temperatures of the basic cycle: the evaporator temperature T_e , the condenser temperature T_c and the temperature of the external heat source T_g . The minimal desorption temperature T_2 is obtained as an intersection of the line $\ln P = \ln P_0(T_c) = \text{const}$ with the rich isoster. If the rich and weak isosters and the equilibrium line $\ln P(1/T)$ for the pure adsorbate intersect at T approaching infinity (the so called Trouton's rule (Alefeld and Radermacher, 1994)), the following simple relation can be obtained (Critoph, 1988; Aristov, 2005; Saha *et al.*, 2006)

$$T_c^2 = T_2 T_e \quad (5)$$

Hence, the minimal temperature of an external heat source that is necessary to drive the cycle with fixed T_c and T_e can be calculated without detailed knowing of the isosteric sorption chart of a particular pair adsorbate–adsorbent (**Figure 5**). The validity of Eq. (5) was justified for working pairs which are commonly used for adsorption units: water–silica gel, water–zeolite 13X, water–SWSs, methanol–carbon (AC-35, TA90), methanol–zeolite CBV 901 Y and ammonia–carbon PX31 (Aristov *et al.*, 2007). **Table 1** demonstrates that for the working pair “water–silica Fuji Silysia Ltd. RD” the difference ΔT between the minimal desorption temperature directly obtained from experimental isosters ($T_{2\text{ex}}$) and calculated from Eq. (5) at fixed T_c and T_e ($T_{2\text{cal}}$) is surprisingly low and does not exceed $\pm 1.0^\circ\text{C}$.

Moreover, it was shown that the Trouton's rule is always valid if the sorption equilibrium obeys the Polanyi potential theory (Aristov *et al.*, 2007). We showed that Eq. (5) also allows simple and quite precise evaluation of the other two boundary temperatures of the basic cycle: the minimal temperature which can be obtained in the evaporator at fixed T_c and T_g and the

Table 1 Minimal desorption temperatures for “water–silica Fuji Silysia Ltd. RD” ($\Delta T = T_{2\text{cal}} - T_{2\text{ex}}$)

T_c [°C]	T_c [°C]	$T_{2\text{ex}}$ [°C]	$T_{2\text{cal}}$ [°C]	ΔT [°C]
5	37.1	73.8	72.8	-1.0
5	31.2	59.8	59.8	0.0
5	26.8	49.8	50.3	0.5
5	23.5	42.5	43.1	0.6
10	43.1	80.1	80.0	-0.1
10	36.8	65.8	66.2	0.4
10	32.3	55.5	56.3	0.8
10	28.7	47.9	48.7	0.8
20	54.2	92.3	92.4	0.1
20	47.8	77.5	78.3	0.8
20	38.8	58.1	58.9	0.8
20	36.0	51.8	52.8	1.0

Fig. 5 T_2 vs. T_c calculated according to Eq. (5) for various cooling applications: deep freezing ($T_e = -30^\circ\text{C}$), ice making ($T_e = -5^\circ\text{C}$) and air conditioning ($T_e = 10^\circ\text{C}$)

maximum temperature can be obtained in the condenser at fixed T_c and T_g .

Figure 5 shows that for adsorptive freezing in hot climate ($T_c = 45^\circ\text{C}$) a heat source has to have temperature level of at least 145°C and an adsorbent has to still retain the working fluid at this temperature, while for air-conditioning this threshold is at much lower temperature (85°C). It means that optimal adsorbents for these two applications at the same climatic zone are very different. Besides, quite different adsorbents are needed for the same cooling application in different climatic zones: for ice making in hot climate optimal adsorbent should retain the working fluid at least up to $T_2 = 105^\circ\text{C}$, whereas for moderate zones ($T_c = 25^\circ\text{C}$)—only up to 60°C .

If the temperature of external heat source is fixed at T_g and the optimal adsorbent is used (means that complete desorption occurs right at this temperature, $T_2 = T_g$), then the minimal temperature can be obtained in the evaporator at adsorption stage $T_e = T_c^2/T_2$ (**Figure 6**). Evidently, the highest second law efficiency

Fig. 6 Minimal evaporator temperature T_e as a function of available desorption temperature T_g at various condenser temperatures T_c

can be reached if complete desorption happens at $T_2 = T_g$ (the case of a reversible chemical heat pump) (Sharonov and Aristov, 2007). If the adsorbent is not optimal and the sorbate is desorbed at temperature $T_2 < T_g$, then (a) the evaporator temperature increases, and (b) the second law efficiency of the adsorptive chiller goes down due to the thermal entropy production caused by the external thermal coupling (Meunier, 1985).

Similar reasoning can be used to analyze various AHP cycles without heat regeneration. Requirements to an adsorbent that is optimal for regenerative cycles can be quite different from those described above, and will be a subject of future analysis.

If it has become clear which the optimal adsorbent has to be, the next step is a nanotailoring of real structure with the sorption properties as close to the predetermined ones as possible. Among the most powerful procedures to synthesize single phase nanoporous materials are:

- Template synthesis based on the use of template molecules as structure directing agents that are eliminated at the end of the synthesis (Corma, 1997);
- Supramolecular synthesis, where a nanoporous material is formed in a self-assembly process from discrete molecular building blocks (Yaghi *et al.*, 2003; Janiak, 2003; Kitagawa *et al.*, 2004, 2005).

Many developed procedures are intermediate between these two as they use both templates and self-organization phenomenon, and the self-assembly can be driven by donor/acceptor or/and covalent interactions either by hydrogen bonding between metal complexes and organic molecules. All these methods have an advantage over conventional synthesis because the final structures can be systematically modified by a rational selection of the appropriate templates or build-

ing blocks in order to get the desired architectural, chemical, and physical properties.

2.2 Two-component (composite) adsorbents

Additional ways for nanotailoring appear for two phase structures, e.g., composites “a salt in a nanoporous matrix” (Aristov *et al.*, 1996, 2002; Aristov *et al.*, 2005; Vasiliev *et al.*, 1996, 2001; Sharonov *et al.*, 2006; Gordeeva *et al.*, 2007a; Zhong *et al.*, 2007; Wang *et al.*, 2006). If the sorbate is water, these materials are called selective water sorbents (SWS). As yet, more than fifty SWSs have been synthesised at BIC RAS (Novosibirsk, Russia) and investigated together with ITAE-CNR (Aristov, 2005). They use halides, sulphates and nitrates of various metals as active salts and silica, alumina, carbons, clays as host matrices.

The main findings of this activity can be generalized as follows:

- Three mechanisms of water sorption have been found: a) adsorption by the host matrix, b) chemical reaction between water and salt resulting in the formation of crystalline hydrates, and c) absorption by the salt aqueous solution in the pores (Pankrat'ev *et al.*, 2001);
- Sorption by composite is not a linear combination of that of the host matrix and salt (Simonova and Aristov, 2005);
- The matrix can accommodate the salt swelling due to chemical reaction between the salt and water;
- Gas–solid reaction is much faster for a confined salt than for a bulk one, so that the rate of sorption process is commonly controlled by vapour intra-particle diffusion (Aristov *et al.*, 2006);
- Inside pores, the synthesis–decomposition hysteresis can be reduced or even avoided (**Figure 7**) (Simonova and Aristov, 2005).

Moreover, a host matrix provides a network for efficient transfer of heat and reagent which greatly enhances these processes, as it was conceived and reached for composite sorbents of ammonia “salt + expanded graphite” (Mauran *et al.*, 1994; Wang *et al.*, 2006) or “salt + Busofit” (Vasiliev *et al.*, 1996).

Important advantage of SWSs is a monovariant type of equilibrium in the system “water–salt”. This allows the exchange of large amount of water in a very narrow temperature range (**Figures 2 and 8**) that is the obligatory demand to adsorbent optimal for AHP. Indeed, according to the Gibb's phase rule for the system “water–salt” described by reaction (4), the number of the degrees of freedom (variance) of the equilibrium system $\nu = k + 2 - f$. Here k is the number of components in the system ($k = 2$), f is the number of phases ($f = 3$). It means that ν is equal to unity; i.e., the system is monovariant. Hence, only one of the two external parameters T and $P(\text{H}_2\text{O})$ can be varied along the equilibrium curve. For example, when the pressure is fixed ($P = P_c$ for isobaric desorption and $P = P_c$ for isobaric adsorption) the variance of system ν becomes

Fig. 7 Isobars of water sorption/desorption for $\text{Ca}(\text{NO}_3)_2$: bulk ($\blacklozenge/\blacksquare$), confined to 12 nm pores ($\triangle/\diamond$) (Simonova and Aristov, 2005)

Fig. 8 Typical isobars (A) and isotherms (B) for mono- (a) and divariant equilibrium (b) and (c). Stepwise (monovariant) curves correspond to an optimal adsorbent.

zero. Therefore, water adds to the salt (or its hydrate) stepwise at a certain threshold temperature T_r (or certain relative pressure h). This results in sharp isobars (isotherms) of water adsorption (**Figures 2, 8 and 9**).

The transition temperature is linked with the external pressure by the Van't Hoff equation

$$\ln P = -\Delta G^\circ/RT_r \text{ or } \ln P = -\Delta H^\circ/RT_r + \Delta S^\circ/R$$

where ΔG° , ΔH° and ΔS° correspond to the variation of the standard Gibb's potential, enthalpy and entropy, respectively. As there is a large difference in values of ΔH° and ΔS° for various massive hydrates, one might expect that transition (4) can occur at quite different temperatures T_r . Thus, it gives a chance to select a hydrate which at $P = P_c$ undergoes transformation (4) at temperature T_r close to the required temperature

Fig. 9 Transition temperature for hydration reaction of $\text{Ca}(\text{NO}_3)_2$ in bulk and inside the silica pores of 6 and 12 nm in size (Simonova and Aristov, 2005)

Fig. 10 Equilibrium amount of water in various hydrated salts (in bulk) vs. P/P_0 : (1) Na_2SO_4 , (2) Na_2HPO_4 , (3) $\text{Ca}(\text{NO}_3)_2$, (4) MgSO_4 , (5) CaCl_2 and (6) LiBr

determined from the analysis described above. **Figure 10** demonstrates that reaction (4) for various hydrated salts (in bulk) does occur at values of P/P_0 distributed over a wide range. Thus, first step of the salt selection should be searching salt hydrate which decomposes at transition temperature close to the desirable T_r for given cycle. Then chosen salt is to be placed inside pores of a host matrix.

For fine adjustment of the transition temperature to that required by the cycle conditions, the following parameters can be varied:

- pore size of the host matrix (Figure 9),
- amount of the salt inside the pores (Gordeeva *et al.*, 2006), and
- synthesis procedure (Aristov, 2005; Gordeeva *et al.*, 2006).

Due to the mentioned “pore size effect” interesting possibilities can be concerned with mesostructured silicates with straight monosized pores (Figure 1) (Tokarev *et al.*, 2002). In this case it becomes possible

Fig. 11 Adsorption uptake vs. relative pressure of methanol (1, LiCl/silica ; 3, LiBr/silica) (Gordeeva *et al.*, 2007a, 2007b) and NH_3 (2, $\text{CaCl}_2/\text{vermiculite}$; 4, $\text{BaCl}_2/\text{vermiculite}$) (Sharonov *et al.*, 2006). Dashed lines 1a, 2a and 4a indicate appropriate transitions in bulk

an accurate study on the effect of pore size on the transition temperature and other adsorption parameters. Thus, synthesis of a set of MCM-type adsorbents with monosize pores ranging between 5 and 20 nm is highly welcome and could give an important contribution for development of novel SWS-composites with targeted properties.

Several SWS-like materials prepared according to the discussed approach have been tested for adsorptive chilling (Restuccia *et al.*, 2004; Daou *et al.*, 2006) and energy storage (Liu *et al.*, 2004; Stach *et al.*, 2005) and demonstrated performance superior to other adsorbents.

Recently this nanotailoring approach has been extended to design novel composite adsorbents of methanol (Gordeeva *et al.*, 2007a, 2007b) and ammonia (Sharonov *et al.*, 2006; Zhong *et al.*, 2007). These materials appear to be able to exchange extra-ordinary large amount of adsorbent (up to 0.7 g/g) in very narrow temperature range (**Figure 11**). Transition temperature depends on the nature of impregnated salt and can differ from the transition in bulk (Figure 11), that allows the adjustment of the performance mentioned above.

Conclusions

The brief review of innovative materials for adsorptive pumping and storage of low temperature heat as well as current trends in this field clearly showed their great potential advantages. To implement them in the near future it is reasonable to follow the two complementary lines: a) systematic testing for this application novel adsorbents initially developed for other targets (drying, separation, etc.), and b) tailoring of new specific porous materials adapted just to vari-

ety of adsorptive cooling, heating and storage cycles under different climatic and boundary conditions. Particular examples of nanotailoring of adsorption properties are given for composites “a salt in a porous matrix” which can be used as efficient adsorbents of water, methanol and ammonia.

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Nomenclature

AHP	=	adsorption heat pumping, adsorption heat pump	
AHS	=	adsorption heat storage	
COP	=	coefficient of performance	
F	=	adsorption potential	[J/mol]
FAM	=	functional adsorbent materials	
f	=	the number of phases	
G	=	Gibb's free energy	[J/mol]
H	=	enthalpy	[J/mol]
k	=	number of components	
P	=	pressure	[bar, mbar]
PCP	=	porous coordination polymers	
S	=	entropy	[J/(mol K)]
SWS	=	selective water sorbents	
T	=	temperature	[°C]
w	=	uptake	[g/g]
Δ	=	variation	
v	=	variance	

<Subscript>

c	=	condensation
des	=	desorption
e	=	evaporation
g	=	external heat source
o	=	saturation
r	=	reaction (transition)
2	=	minimal desorption temperature

<Superscript>

o	=	standard
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