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New materials for adsorption heat transformation and storage

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ABSTRACT

Great current progress in the materials science offers an enormous choice of novel adsorbents which may be promising for transformation and storage of low temperature heat, e.g. from renewable heat sources. This paper gives an overview of recent trends and achievements in this field. We consider possible optimization of zeolites by dealumination, further development on aluminophosphates, composites "salt in porous host matrice" and metal-organic frameworks which are currently receiving the largest share of scientific attention. The particular attention is focused on the chemical nano-tailoring and tunable adsorption behavior of these materials to satisfy the demands of appropriate heat transformation cycles. We hope that this review will give new impact on target-oriented research on the novel adsorbents for heat transformation and storage.

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1. Introduction

Resource and energy security are issues to be solved in near future. As a response to this challenge, severe efforts are being undertaken towards both renewable and unconventional energy and resource exploration. In this scope, heat transformation such as thermally driven chillers or heat pumps as well as heat storage based on adsorption processes in highly porous materials can play a key role to enhance energy efficiency in the heating and cooling sector [1].

The main principle of the adsorption heat transformation (AHT) is based on the consecutive adsorption and desorption processes [2]. At the adsorption phase the working fluid (usually water, methanol) is evaporated at lowest temperature using up the evaporation heat Q_{ev}, and then the vapor is adsorbed by dry adsorbent releasing the heat Q_{ads} at medium temperature. During the regeneration stage the vapor is desorbed by applying the regeneration heat Q_{reg} from the external heat source (the driving heat). The working fluid is then condensed from the gas phase releasing the heat Q_{con}. The AHT units can work in cooling, heat pumping and heat storage mode. In the cooling mode, the useful effect is produced in the evaporator by taking Q_{ev} from the user device, while Q_{con} and Q_{ads} are dissipated to the environment. In the heating mode the heats Q_{con} and Q_{ads} are useful and Q_{ev} is taken from the environment. In the heat storage mode during the endothermal desorption the heat is stored and during the exothermal adsorption the heat is released.

The efficiency and cost-effectiveness of such processes are critically governed by the performance of the applied adsorbents [3,4]. Furthermore, the operating conditions of these adsorption heat transformation applications differ in a wide range. Consequently, depending on the application, the desirable temperature of the useful heat and the temperature level of the available heat

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source, different specifically optimized materials have to be utilized [5]. Recently, it has been shown that the adsorbents which adsorption equilibrium with working fluid is characterized by s-shaped adsorption isotherms are advantageous for the adsorption heat transformation [5]. For most applications the steep increase in the adsorption should take place in a relative pressure range of 0.05–0.3. In this vein, the possibility to intently modify the properties of applied adsorbent can essentially help in harmonizing the adsorbent and the cycle. Nowadays, activated carbons, silica gels, silica-aluminophosphates and zeolites are employed, and it is generally agreed that new achievements in the field of micro- and meso-porous adsorbents will open new market opportunities.

Recent advances in materials sciences have substantially promoted the development of micro- and mesoporous adsorbents, and a wide range of related materials is available for the use in adsorption heat pumps. As their adsorption characteristics vary in a wide range, a comparatively large area of applications can already be realized.

Therefore various adsorption-driven heat pumps have been marketed lately by e.g. Invensor, Sortech [6], Vaillant [7], Viessmann [7] and Mitsubishi Plastics [8].

Within this article recent developments on optimization of zeolites by dealumination, further developments on SAPOs, composites based on the salts and porous matrices and especially metal-organic frameworks (MOFs), as certainly the material class that is currently receiving the largest share of scientific attention, will be covered. The particular attention is focused on the chemical tailorability and tunable adsorption behavior of these materials.

2. Tailoring adsorbents

2.1. Optimization of zeolites by dealumination

The large group of crystalline (alumino-)silicates comprises a considerable number of members with pore sizes and pore volumes large enough to be considered for heat transformation applications, e.g. Zeolite A or the faujasites Zeolite X and Y. Zeolites are composed of vertex-sharing $[SiO_4]$ and $[AlO_4]^-$ tetrahedrons connected in such a way that a crystalline structure, which forms channels and cavities with diameters of 0.3–1.5 nm, is obtained [9].

Forty-eight different zeolites have been found to occur naturally, but when high purities and porosities are desired, synthetic zeolites are preferred – also because another 150 structures that are not found naturally can be obtained synthetically [10]. Unfortunately, zeolites A, X and Y are typically too hydrophilic to be used in adsorption chillers or heat pumps with regeneration temperatures of up to 120 °C.

Since other well-known zeolites as for instance ZSM-5 or zeolite beta are too hydrophobic to be applied in thermally-driven heat transformation dealumination of the hydrophilic faujasite-type zeolites X and Y was suggested. Many dealumination techniques have been reported in literature [11]. The grade of dealumination has to be controlled carefully due to the loss of the crystalline structure under harsh conditions on one hand and the rising hydrophobicity on the other hand. Herzog et al. investigated the application of steaming and the degree of dealumination of zeolite Y with respect to water adsorption properties [12]. They started with a commercially available NaY with a Si/Al-ratio of 2.7 and a water adsorption capacity of about 0.28 g/g. The capacity was found constant for Si/Al-ratios up to 3.2 and decreasing for rising Si-/Al-ratios. Water adsorption isotherm for the best performing dealuminated material showed a s-shape with a rise in water uptake of approx. 0.2 g/g between the relative pressures 0.01 and 0.3 compared to the uptake of 0.1 g/g for the unmodified NaY in the same range. This shows the opportunities coming with dealumination of zeolites but also the demand for a sensitive and good controllable process.

2.2. Further strategies for use of classical zeolites

The possible use of alumino-silica zeolites in adsorption applications needs the substantial modification of their high hydrophilic character by reducing the strong electrostatic interaction with water molecules. The reason for the elevated water affinity of zeolites, indeed, is related to the electrostatic charge of the zeolitic framework that promotes the adsorption of polar molecules. Differently from modifications of the zeolites structure by cations exchange or variation of the Al/Si ratio by dealumination, an alternative way is the functionalization of zeolites by chemisorption of organosilanes. Silanes are a family of organic-inorganic compounds where the silicon atom is bonded to some hydrolysable groups and an organic radical group. The hydrolysable part of the silane molecule allows the chemical bonding with hydroxyl groups on the zeolite surface particles forming stable Si–O bonds. The silanes chemisorption plays a dual effect: partially compensating the structure charge influencing the zeolite electrostatic potential and partially interacting with the zeolite pores during the water molecules adsorption. Interesting results have been obtained by mixing zeolites with bifunctional and trifunctional silanes to form zeolite hybrid coatings for adsorption heat exchangers [13]. However, reacting zeolite 4A, X and Y with dimethoxydimethyl and propyltrimethoxy silanes in diluted concentrations and proper conditions has conducted to an effective functionalization of the original structures [14]. The functionalized zeolites did not show modification of the original framework when characterized by X-ray diffractometry or the variation of the Al/Si ratio. The reaction conditions, indeed, induce a chemical bond between the silane molecules and the superficial silanol groups that are always present on the zeolite surface, according to following the mechanism:

$$3[4A, X] - OH + Si(OCH_3)_3 - R \rightarrow [4A, X] - O)_3 - Si - R + 3\ CH_3OH$$

In Fig. 1 the isotherm curves (T = 298 °C) of a zeolite A treated with dimethoxydimethyl silane and a zeolite X treated with propyltrimethoxy silane are shown compared to the isotherms of the pristine zeolites. From the comparison, it is evident how the silane chemisorption caused a shift in the low P/P0 range of the water uptake curves of the original zeolites. The consequence was, as shown in Fig. 1, an increased hydrophobicity of the functionalized zeolites, which caused the traditional Type I isotherm to transform in a Type V-similar isotherm, typically observed in AlPOs and SAPOs materials. The silanes bonding, however, due to the low concentration of hydroxyl group on the zeolite crystals surface, did not cause a decrease of the maximum water capacity of the original zeolites, being effective only at low vapor pressure (Fig. 1).

The desired, expected, consequence of the functionalization is the evidence of an increased hydrophobicity that correspond to a shift from the typical Type I isotherm of microporous hydrophilic materials toward the characteristic Type V isotherm of SAPOs and AlPOs zeotypes, where water adsorption begins at certain level of vapor partial pressure. All possible functionalization, however, to be applicable have to comply with some minimum requirements: a final high structural stability, low cost of raw materials and a simple preparative.

2.3. Aluminophosphates and silico-aluminophosphates (AlPOs and SAPOs)

Synthetic aluminophosphates (AlPOs) with the empirical formula $AlPO_4$ can be compared to neutral, pure-silica zeolites. An

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