The Performance of Small-Pore Microporous Aluminophosphates in Low-Temperature Solar Energy Storage: The Structure–Property Relationship

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The utilization of the reversible chemical and physical sorption of water on solids provides a new thermal energy storage concept with a great potential for lossless long-term storage. The performance of microporous aluminophosphates in heat storage applications is highlighted by a comparative thermogravimetric and calorimetric study of three known materials (SAPO-34, $AlPO_4$-18, APO-Tric) and is correlated with their structural features. The maximum water sorption capacity is similar for all three samples and results in a stored energy density of 240 kWh m^{-3} in the 40–140 °C range. The elemental composition influences the gradual (silicoaluminophosphate SAPO-34) or sudden (aluminophosphates $AlPO_4$-18, APO-Tric) water uptake, with the latter being favourable in storage systems. The driving force for the determined sorption process is the formation of highly ordered water clusters in the pores, which is enabled by rapid and reversible changes in the Al coordination and optimal pore diameters. The ease with which changes in the Al coordination can occur in APO-Tric is related to the use of the fluoride route in the synthesis. The understanding of these fundamental structure/sorption relationships forms an excellent basis for predicting the storage potential of numerous known or new microporous aluminophosphates and other porous materials from their crystal structures.

1. Introduction

Large-scale utilization of solar energy for heating and cooling applications, which represent almost half of the final energy demand in developed countries, depends on effective thermal energy storage systems that reduce the time or the rate mismatch between energy supply and energy demand. Most of the current technologies store thermal energy as sensible heat; the temperature of sensible heat storage materials (SHS), such as water, rises when they absorb heat, and vice versa. The disadvantages of SHS are a low energy density (energy stored per unit volume) of approximately 53 kWh m^{-3} and high thermal losses over long periods of time. An alternative to sensible heat storage is latent heat storage (LHS), which uses the heat of liquefaction of phase-change materials (PCM) for storage. However, for long-term thermal storage, PCM systems are not considered to be superior to hot water tanks, even with twice the energy density, because of accelerated degradation (segregation of material in the system upon melting, supercooling, corrosion, etc.), considerable heat-loss over time, and higher costs.[1]

A new and very promising concept of heat storage consists of systems that utilize reversible physicochemical sorption phenomena (mostly water adsorption on solid sorbents) to store energy. Under the influence of a heat supply, water is desorbed from the material and is then stored separately (an endothermic phenomenon referred to as the charging or activation of material). When water and sorbent are put into contact, there is a heat release (an exothermic phenomenon referred to as a material's discharge or deactivation; **Figure 1**). Energy can therefore be stored with negligible thermal loss because heat is not kept in either sensible or latent form, but as a chemical potential. The quick and fully reversible hydration processes are superior to those in crystallohydrates, which are also attractive thermochemical storage materials that offer high energy storage density at a relatively low cost but suffer from very slow sorption kinetics and materials degradation.[2]

In sorption storage systems, low-cost crystalline or amorphous silica-based porous materials and their composites with hygroscopic inorganic salt hydrates (e.g., $CaCl_2$) have been considered as the most promising adsorbents.[3–6] Despite many scientific efforts, none of these materials currently meet the requirements for large-scale applications: a charging temperature below 140 °C, energy density (energy stored per unit volume) above 250 kWh m^{-3}, and resistance to material degradation.[1] Zeolites A, X, and Y have high charging temperatures (>170 °C), and amorphous silica gels provide only low material energy densities (a maximum of 135 kWh m^{-3}). Additionally, the total storage density, which includes all of the components (in particular tanks and heat-exchangers), is sometimes barely

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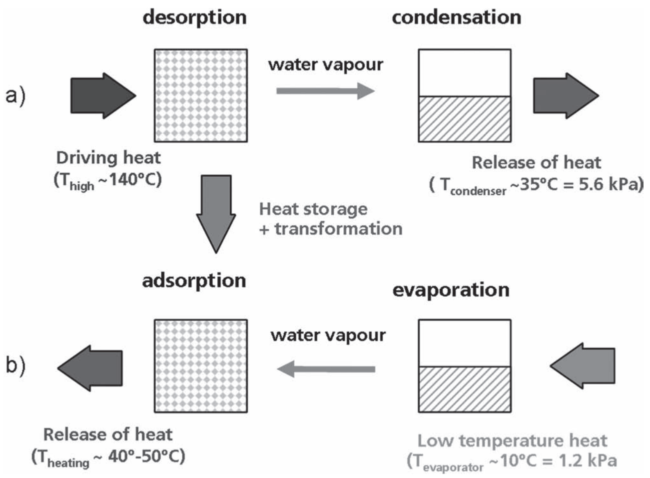

Figure 1. Water adsorption is an exothermal process that provides the heat released or discharged from the storage. The charging of a material is performed with the reverse endothermic process of desorption using, for example, solar energy. The desorption temperature of 140 °C coincides with the current maximum temperature reached by solar thermal collectors (e.g., evacuated tube collectors), and the temperature of 95 °C can readily be achieved by flat-plate solar collectors.

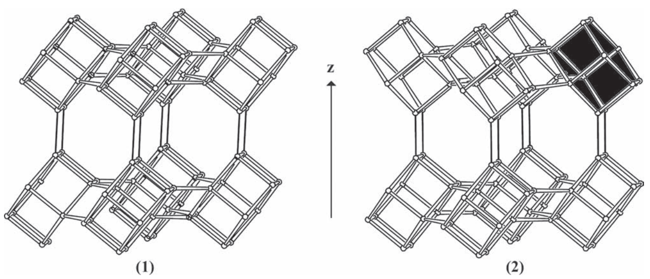

Figure 2. Connection mode in **CHA (1)** and **AEI (2)** structure topologies viewed along the *x*-axis.[14] The lines connect the centers of AlO_4 and PO_4 tetrahedra, which are schematically presented as small white circles in the picture. The double-six-ring building units (marked black in the figure) are forming the same type of layers in both structures. The difference in layer-to-layer deposition in the two structures (only by transition in **CHA** and rotation by 180° in **AEI**) leads to different sizes and shapes of the pores and cavities.

above that of water because of the space required by the setting up of these components. Major disadvantages of composite materials, where mesoporous silicates with pore openings of up to 50 nm are impregnated with hygroscopic salts, are the corrosion and leakage of salt species from the mesopores.[7]

Recent investigations of microporous aluminophosphates (APO-n or AlPO-n; n = structure type) and their modified analogues (SAPO-n and MeAPO-n; S = Si, Me = transition metal) have revealed their advantages over silicates concerning charging temperature and storage density.[2,8,9] To date, the emphasis in heat storage research has been on aluminophosphates with incorporated silicon or metal cations, where the presence of dopants enhances the water sorption capacity because structural defects enable better interactions of polar water molecules with the surface.[10,11] However, dislodgement of silicon or metal cations from the framework sites and framework structure degradation, which is quite common after a few water desorption/sorption cycles, lowers the performance of these aluminophosphate materials.[10–13]

Despite the great importance of heat storage in enabling a high percentage of renewable energy in the fuel mix, there have been no systematic studies of the possible mechanisms for heat storage enhancement concerning materials optimisation. The crucial questions that remains to be answered are whether and how we can further increase the materials storage performance by controlling their structural features to a higher degree.

In this paper, we report a study of the structure/sorption-behavior relationship of three aluminophosphates with interconnected small pores with the aim of improving the design of storage materials. We show, for the first time, the crucial correlation between both the crystal structure and materials synthesis procedure and heat storage performance. For the study, we selected silicoaluminophosphate SAPO-34 with chabazite topology (CHA) (5 µm crystal size), aluminophosphate $AlPO_4$-18 (AEI topology) (3 µm crystal size), and aluminophosphate APO-Tric with triclinically distorted chabazite topology (10 µm crystal size) (**Figure 2**).[14] This is the first test of APO-Tric for sorption applications, whereas SAPO-34 and $AlPO_4$-18 water sorption studies have already been performed.[12,13]

2. Results and Discussion

2.1. Water Sorption Capacity

With regard to the applications in the focus of this work, we have chosen two parameters to estimate the sorption-based storage performance of each material: the maximum water vapor uptake at optimal sorption temperatures and the heat of adsorption. The sorption isotherms for all three samples are shown in **Figure 3**. As can be seen, the APO-Tric sample displays a water loading uptake of 318 g kg^{-1} within a narrow

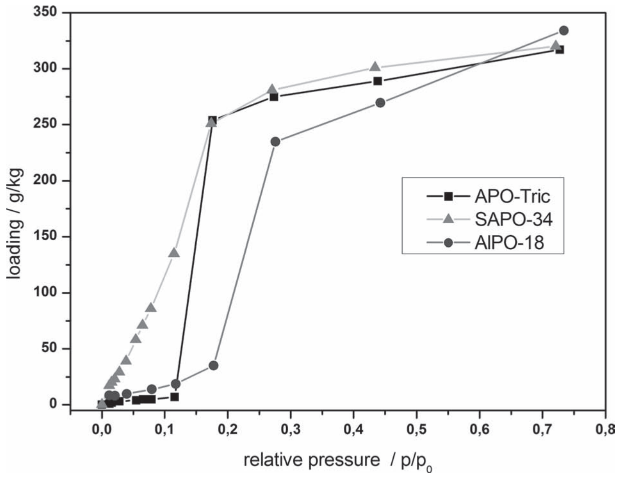

Figure 3. Water adsorption isotherms of SAPO-34 (isotherm Type I), $AlPO_4$-18 (isotherm Type V) and APO-Tric (isotherm Type V) obtained at 40 °C. The suitable relative pressure range for water uptake in storage systems is from 0.1 to 0.5.

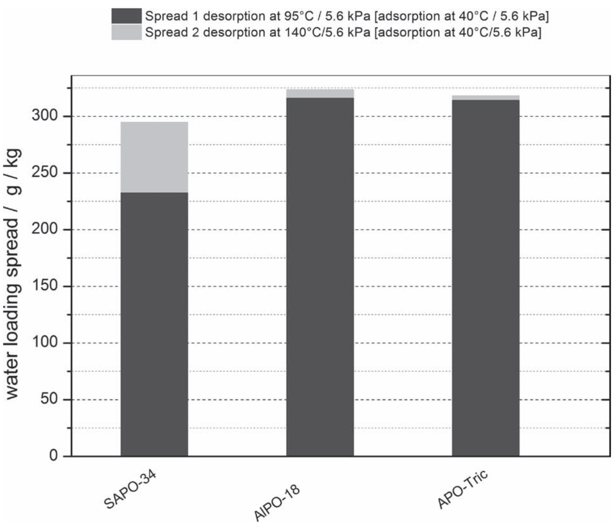

Figure 4. Water loading spread at two different desorption temperatures for SAPO-34, AlPO$_4$- 18, and APO-Tric. The dark grey parts of the bars show the water loading spread at the lower desorption temperature (95 °C), and the whole bar indicates the water loading spread at the higher temperature (140 °C).

relative pressure range. In particular, the shape with a steep isotherm is advantageous for low-desorption-temperature applications. The water isotherm for AlPO$_4$-18 material has a similar shape but is shifted to higher relative pressures. The adsorption isotherm of SAPO-34 reveals water uptake at lower relative pressures due to the presence of Si in the framework (strong hydrophilic sites). This type of water sorption reduces the useable water loading spread within the cycle because the relative operating pressures (p/p_0) usually exceed 0.1.

The additional advantage of the two pure aluminophosphate structures (AlPO$_4$-18 and APO-Tric) over SAPO-34 (silicoaluminophosphate) for low-temperature applications is demonstrated in **Figure 4**. Desorption temperatures of 140 and 95 °C and a minimum adsorption temperature of 40 °C at a water vapor pressure of 5.6 kPa were used in our study, according to a principle process in a storage system. The three materials show similar water loading at a desorption temperature of 140 °C. However, the AlPO$_4$-18 and APO-Tric materials exhibit considerably higher loading spreads than SAPO-34 at a lower desorption temperature of 95 °C. This is an important issue for the implementation of storage in heating systems because solar heat collectors can easily reach 95 °C.

The heat of adsorption, H_{ads}, for APO-Tric was determined to be 2978 J g^{-1} or 53.6 kJ mol^{-1}. The integral heat, including the heat capacity of the material and the adsorbed water, Q_{int}, was determined to be 3367 J g^{-1} (60.6 kJ mol^{-1}) for the desorption step and 3414 J g^{-1} (61.5 kJ mol^{-1}) for the adsorption step. Similar values were obtained for SAPO-34 and AlPO$_4$-18 (**Table 1**).[2,12] The calculated energy density for APO-Tric based on the packed bed density is 240 kWh m^{-3} and is comparable to the values for the other two studied materials.

To evaluate the hydrothermal stability of the material, the APO-Tric sample was exposed to a short-cycle hydrothermal treatment consisting of 50 cycles between temperatures of 140 and 40 °C at a water vapor pressure of 5.6 kPa. In the following step, the water uptake for each cycle between 140 and 40 °C was determined as a first benchmark. As can be seen in **Figure 5**, there is only a small loss of water uptake capacity in APO-Tric, which confirms the stability of the structure under the operating conditions. Furthermore, the crystallinity of the APO-Tric material remains unchanged after the cycling test, as determined by X-ray powder diffraction (XRPD) (**Figure 6**). This is an additional advantage over the SAPO-34 material, which becomes amorphous after 50 cycles of hydrothermal treatment.[13]

Table 1. Maximum loading spread, heat of adsorption, and range of the maximum loading spread found in the literature[12] for simultaneous TG/DSC measurements for SAPO-34, AlPO$_4$-18, and APO-Tric.

Sample	Average maximum spread [g kg^{-1}]	H_{ads} [kJ mol^{-1}]	Range of maximum spread [g kg^{-1}]
AlPO$_4$-18	323	55.1	284–381
SAPO-34	295	55.5	267–312
APO-Tric	318	53.6	318

2.2. Structure–Property Relationship

The obtained results revealed similar water sorption capacities for all three selected materials with slightly different sorption mechanisms. We concluded that APO-Tric has a high and sudden water uptake because of the exothermic formation of ordered hydrogen-bonded water clusters at comparatively low relative pressure p/p_0 (step of the isotherm). The ordered water distribution in the pores, which was observed by an XRPD study of hydrated APO-Tric and confirmed by ab initio density functional theory (DFT) calculations of water confinement in a similar material, is initiated by the covalent bonding of water molecules to specific Al sites in the aluminophosphate structure (first water layer) (**Figure 7**).[15,16] The rest of the water stabilises in the pores by the formation of strong H-bonds with

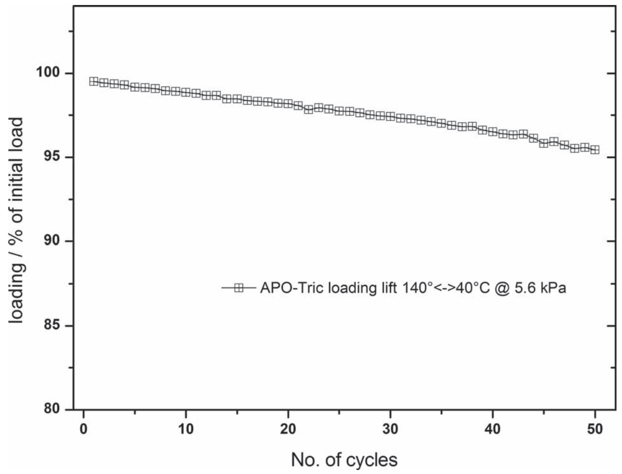

Figure 5. Water loading lift compared to initial loading (100%) for 50 cycles between 140 and 40 °C at a water vapor pressure of 5.6 kPa for APO-Tric.

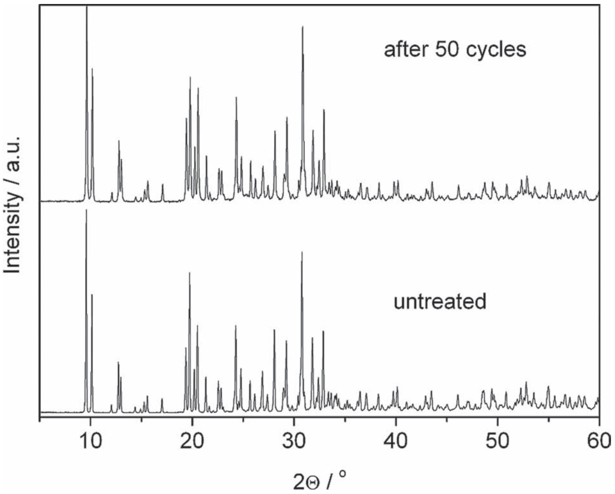

Figure 6. X-ray diffractograms of the APO-Tric material before and after 50 cycles of hydrothermal treatment.

the framework water molecules (second water layer). This type of arrangement leads to a highly ordered water cluster. The confined space in the pores (cavities) in APO-Tric does not allow additional (loosely bound) water layers in the pores.

The ordered covalent bonding of water molecules to Al framework sites in APO-Tric is related to the preparation of the material.[15] APO-Tric can only be prepared in a fluoride medium, and, in the as-synthesised form, one third of Al sites are coordinated to two fluorine and four oxygen atoms in ordered AlO_4F_2 octahedra. The crystalline product exhibits triclinic deformation of the rhombohedral chabazite structure. During calcination, which is performed to obtain pores free of extra-framework molecules, fluorine atoms are removed from the structure and all Al atoms become tetrahedrally coordinated with slightly disordered tetrahedral bond lengths and angles. The structural symmetry changes to rhombohedral. However, when this structure is exposed to humidity, the framework readily bonds one or two water molecules to the previously octahedrally coordinated Al sites. This type of Al octahedral distortion tendency, i.e., a memory-effect, is a driving force for water sorption in the APO-Tric structure and also determines the perfect ordering of the second layer of water molecules. The examination of oxygen-oxygen contacts reveals strong interactions between water molecules in the first and second water layers (O···O distances from 2.623(3) and 2.680(4) Å, respectively).

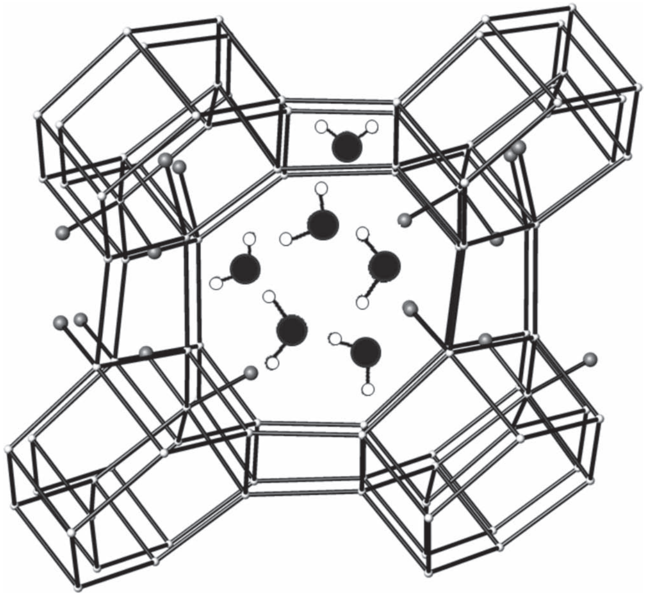

Figure 7. Schematic presentations of the position of extra-framework water molecules (dark grey clouds) in relation to the covalently bonded framework H_2O (light grey clouds) molecules, which leads to the formation of ordered water clusters associated with an additional heat release.

Water ordering consequently contributes to the heat of adsorption, which is important for storage applications. Additionally, the size of the water cluster perfectly matches the size of the cage in the structure. It is known from the literature that the heat of adsorption of molecules in microporous materials can be substantially enhanced when they are adsorbed in micropores whose dimensions closely match the size and shape of the molecules, i.e., the so-called contact surface is large.[17,18] The hydrothermal stability of the material is in accordance with the reversible hydration/dehydration process in the structure, despite constant Al–O bond cleavage and formation.

A similar mechanism of water uptake was found in $AlPO_4$-18, where a portion of the Al also changes its coordination during the adsorption and desorption processes. The $AlPO_4$-18 has an elliptical, pear-shaped cage with a small pocket, while the APO-Tric sample possesses regular elliptical cages of 0.67 nm × 1.0 nm.[14] This leads to different water loading and ordering in the structure and also causes the difference between the relative pressures at which the water adsorption occurs in $AlPO_4$-18 and APO-Tric.

Diffraction and NMR studies, and theoretical calculations showed that, in the as-synthesised form of $AlPO_4$-18, which was prepared in a fluoride-free medium, tetrahedral and 5-coordinated Al are present, the latter due to the bonding of OH groups to Al.[19,20] In the presence of water, the calcined structure with all tetrahedral Al transforms to a rehydrated one, where one third of Al holds the octahedral coordination. Interestingly, the octahedral Al is not the same as the 5-coordinated Al in the as-synthesised form, so no memory effect, which was recognised as the driving force for water sorption in APO-Tric, is present here.

In SAPO-34 (4.5 wt% of Si in our sample), the gradual water uptake is governed by the presence of randomly distributed Si in the framework. Si^{4+} atoms usually replace P^{5+} in the aluminophosphate structure, leading to the formation of highly acidic bridging OH groups (Si–OH–Al), which are supposed to be the primary sites for water bonding and are associated with very rapid sorption and high heat of adsorption. This causes water to sorb at too low relative pressures (Figure 3) and higher desorption temperatures (Figure 4), which is unfavourable in solar heat storage systems. Higher amounts of Si in the SAPO-34 material shift the water uptake to even lower relative pressure values.[12,21] Strong interactions between water and the framework in SAPOs was demonstrated, for example, by an in situ NMR study of hydrated SAPO-34, which revealed that the hydration of acidic bridging OH groups (Brønsted acid sites) was followed by the coordination of water to aluminium atoms.[22] It was also shown that a significant hydrolisis of SAPO-34 in water, along with the formation of an amorphous silica phase, occurred after six months. A similar study of the effect of high coverages of water on the aluminosilicate zeolite surface revealed that it even caused proton transfer from the framework acidic OH group to water and the formation of H_3O^+ ions.[23] In contrast, the disordered distribution of Si sites results in disordered water arrangement in the pores that mimic the bulk fluid phase and in a smaller heat release as compared to water cluster formation in APO-Tric.

Comparison of our results with water sorption measurements of medium- or large-pore microporous aluminophosphates (pore diameter approximately from 0.55 to 0.75 nm) revealed that larger pores do not enable better water sorption performance.[8,24] This is mainly due to the weaker water–framework interactions that result from the inadequate/larger Al–O–P angles (lower ability to confine water) and the weaker interaction between the water molecules that are not close to the surface. DFT calculations for water sorption in $AlPO_4$-5 and $AlPO_4$-11 revealed that the initial loading of water in the large cavity was associated with the mild acidity of the framework (i.e., framework structural defects might enhance the hydrophilicity in aluminophosphates). The subsequent isobaric increase in loading was attributed to the H-bonding between adsorbed water molecules at higher water loading; the water molecules are arranged in the middle of the pores in the liquid-like form with no or very weak interactions with the framework.[25]

3. Conclusions

To gain a higher fraction of (solar) thermal energy and to increase the efficiency of a number of existing heating/cooling technologies in buildings and industries, which all contribute to a decrease in fossil fuel consumption, improvements in heat storage systems are required. This field of research has been neglected for a long time due to great interest in photovoltaic systems. However, the advantage of direct heat production without any energy-conversion losses should be a great stimulus for further investigation on this subject, with an obvious emphasis on materials research.

In our study, we have shown that the small, microporous aluminophosphates, which can i) change the framework Al coordination, ii) allow the formation of ordered water clusters, and, consequently, iii) allow sudden water uptake in a narrow pressure range, are among the most suitable materials for low-temperature (solar) heat storage. The so-called memory effect, where Al, previously coordinated to up to two F^- ligands and four framework oxygen atoms, instantly coordinates to water, is another important issue that was noted in this study.

The APO-Tric material's performance, combining the water uptake mechanism, heat of adsorption and hydrothermal stability, is so far the most promising among the aluminophosphates for water-sorption-based heat storage applications and for heat transformation in heat pumping systems. The strong interactions between the Si-centers and water molecules have suggested that SAPO materials should be better than APO materials for heat storage. However, the gradual water uptake and amorphisation of the crystal structure after cycling treatment are the obvious drawbacks of SAPOs. An additional advantage of pure aluminophosphates over SAPOs is that they can desorb practically all water at low temperatures (95 °C), which is crucial for their utilization.

In a broader sense, this structure-property relationship model can be used to predict the storage potential of numerous known or new microporous aluminophosphates taking into account their structural properties: the size of the pores, the chemical composition, and the preparation method (e.g., fluoride or non-fluoride routes). The higher connectivity of the pores positively contributes to the kinetic performance of materials, so structures with 3D pore systems (channels are interconnected) should be the first choice.[8] Some of the possible 3D small-pore aluminophosphate candidates for heat storage applications, besides those reported here, are structures that have so far been prepared only with the incorporation of transition metal ions or Si in the framework (RHO, PHI), but might be successfully synthesised in a fluoride medium.[14] We could further speculate that the frameworks containing double-six or double-four rings would perform better because Al in such geometries shows a tendency to quickly adopt/change its coordination.[26] The drawback of other phosphate-based materials, such as porous zinc phosphates or iron phosphates, is an increasing ionic character of the framework that usually leads to lower hydrothermal stability.

4. Experimental Section

The investigated materials were prepared hydrothermally in the presence of template molecules. The SAPO-34 (Mitsubishi) and $AlPO_4$-18[27] materials were synthesised using tetraethylammonium hydroxide as a structure-directing agent. In the synthesis of APO-Tric, HF and piperidine, a structure-directing agent, were added to the reaction mixture; the molar ratio of reactants in the gel was 2 piperidine: Al_2O_3: P_2O_5: HF: 100 H_2O. The as-synthesised sample was calcined in oxygen at 600 °C overnight. The APO-Tric material showed thermal stability up to 900 °C, while the SAPO-34 and the $AlPO_4$-18 were thermally stable up to 800 °C. The XRPD patterns were collected to check the crystallinity of the samples using a PANalytical X'Pert PRO diffractometer with CuKα radiation (1.54178 Å) at room temperature. The data were collected in the 2θ range 5° to 60° in steps of 0.017° with a total measurement time of 1 h. An EDX analysis of SAPO-34 indicated 4.5 wt% of Si in the sample.

Water adsorption characteristics were measured by simultaneous thermogravimetry and differential scanning calorimetry (TG-DSC 111 Setaram). The Setaram TG/DSC allows simultaneous measurement of the water uptake and the resulting heat flow. These measurements are performed under a humidified carrier gas (Argon 5.0, purity 99.999%). The experimental setup and the corresponding error analysis are described in detail elsewhere.[12] The chosen operating conditions were the following: a maximum desorption temperature of 140 or 95 °C and a minimum adsorption temperature of 40 °C for water vapor pressures of 5.6 kPa. The heat of adsorption was determined using the following procedure: approximately 20.2 mg of APO-Tric was dried at 150 °C for 10 h at 0% RH in a continuous argon gas flow; the relative humidity was increased to 5% RH under isotherm conditions (150 °C) for another 8 h to evaluate high energy sites within the sample; the heat of adsorption at 40 °C was evaluated in an isothermal humidity step; and, finally, the sample was isobarically heated to 150 °C and then cooled to 40 °C for a relative humidity of 76.3% RH, leading to the integral heat of adsorption,

Q_{int}, for the heat transformation cycle. The procedures for SAPO-34 and $AlPO_4$-18 were the same.[12] To evaluate the hydrothermal stability of the materials, the samples were exposed to a short-cycle hydrothermal treatment consisting of 50 cycles between temperatures of 140 and 40 °C at a water vapor pressure of 5.6 kPa. The water uptake for each cycle between 140 and 40 °C was determined as a first benchmark. Before and after the cycling an equilibrium measurement is performed, showing a decrease of water uptake of 0.172 mg or 3.8% compared to the initial loading. In addition, a slight increase of the dry mass by 0.4%, or 0.056 mg, compared to the initial uptake was observed. This may indicate an accumulation of some water molecules in the framework, which reduces the free volume.

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