

Effective Inorganic Hybrid Adsorbents of Water Vapor by the Sol–Gel Method

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The SiO₂/CaCl₂ hybrid porous materials were obtained by the two-step hydrolysis and condensation of tetraethoxysilane with (a) replacement of ethanol from alcogel by supercritical CO₂ to obtain aerogel morphology and (b) drying alcogel at ambient to obtain xerogel structures. Aerogels and xerogels containing ~17 and ~30 wt % of CaCl₂ (dry matter) were prepared and investigated for adsorptivity of water vapor to obtain sorption capacities in excess of 1 kg of water/kg of adsorbate. The adsorbates obtained can be dried and reused. No notable loss in adsorption capacity was observed during 50 cycles.

Introduction

The need to improve effectiveness of heat transformation and storage devices promotes investigations of the pertinent adsorbent–adsorbate systems and drives the search for new adsorbents suitable for this purpose. Adsorption energy recovery systems which utilize water as a working fluid are particularly attractive, not only owing to their environmental acceptance but also due to the promising technical/thermodynamic characteristics. Zeolites (both synthetic and natural) and silica gels exhibit remarkable water sorption capacities and hence are most widely applied in such systems.^{1–4} Water sorption capacity of zeolites can be as high as 0.3 kg of H₂O/kg of adsorbent, and for silica gels even over 0.4 kg/kg.⁵ Upgrading of silica gels by incorporating inorganic hygroscopic compounds (e.g., CaCl₂, LiBr), investigated most recently,^{6,7} results in materials with sorption capacities reaching 70–75% w/w. These materials are virtually two-phase solids consisting of a porous host matrix (silica gel, ~70 wt %) and a hygroscopic substance (HS, ~30 wt %) introduced into the pore space by the conventional impregnation with aqueous solution.⁶ Apparently, such an approach is

convenient but too simple to ensure the desired end content of the HS and its uniform distribution within the sample. Sol–gel science offers an alternative, equally simple, yet potentially far more effective approach, viz., a straightforward entrapment of the target compound within the sol–gel matrix, which hopefully should result in its atomic dispersion across the sample. Such a method has already proved effective to give highly active catalysts and biocatalysts,^{8–10} and excellent accounts of this and other more advanced concepts are available.^{11,12} In the present paper we report on the preparation of inorganic hybrid adsorbents (IHA) of water vapor by the sol–gel route and on adsorption and structural properties of the materials obtained.

Experimental Section

Materials. Four different samples of IHA (labeled 1–4) were prepared by the sol–gel route described in detail in Figure 1, and one (5), for comparison, by impregnating 2–5 mm pieces of silica aerogel with 14 wt % aqueous solution of CaCl₂. Samples 1 and 3 were prepared to achieve a target CaCl₂ content of 17 wt % (dry matter), while samples 2 and 4 to achieve a 30 wt % content, respectively. The alcogel samples were synthesized from tetraethoxysilane (TEOS), ethanol, H₂O, HCl, NH₄OH, and CaCl₂ following the two-step preparation procedure described by Brinker et al.¹³ The total molar ratio of the compounds was 1:9:4:8 × 10⁻⁴:8 × 10⁻³. In the first stage TEOS was hydrolyzed under reflux for 1 h at 50 °C in a solution with molar ratio TEOS/EtOH/H₂O/HCl equal to 1:4.5:y:8 × 10⁻⁴, where y was determined to meet the total H₂O/TEOS molar ratio *r* = 4 accounting for water introduced into the system in the second stage with the solution of calcium

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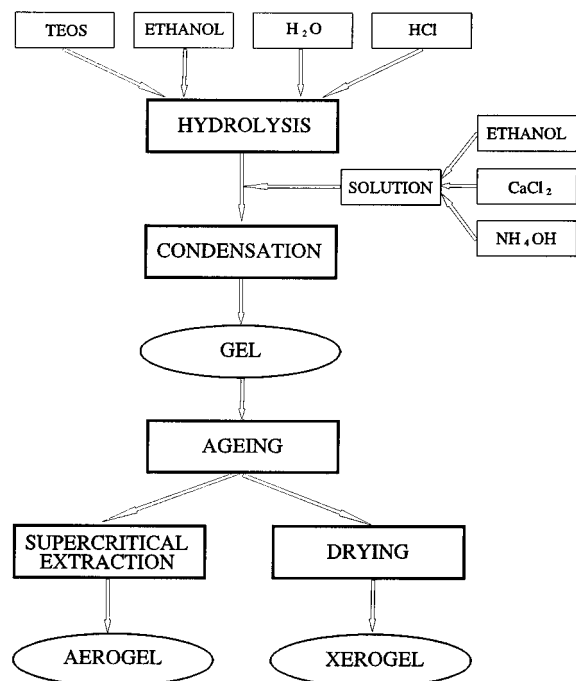


Figure 1. Schematic representation of the preparation procedures.

chloride. Then the solution was mixed with the remaining ethanol, NH_4OH and 35 wt % aqueous solution of CaCl_2 to obtain 40 mL samples which were kept at 25 °C. Gelation took place within 1.5–2.5 h. Alcolgel samples were aged for 6 days at room temperature, and then they were dried either in supercritical carbon dioxide at 45 °C and 15 MPa, to obtain the hybrid $\text{SiO}_2/\text{CaCl}_2$ aerogels (sample 1 and 2), or at ambient, for some 30 days, to get the hybrid xerogel materials (sample 3 and 4). To remove residual water and ethanol, the samples thus obtained were dried for 2 h at 200 °C. The earlier DTG investigations showed that these conditions were sufficient to obtain dry materials. Then the samples were weighed, to determine the actual content of calcium chloride, and stored in a desiccator. The similar drying procedure preceded every structural and adsorption examination of the samples. Sample 5 was obtained as follows: first the silica aerogel monolith¹⁴ (mesopore volume $V_{p(\text{N}_2)} = 2.8 \text{ cm}^3/\text{g}$, mean pore diameter = 32 nm, apparent density $\rho_a = 0.11 \text{ g/cm}^3$, dried at 290 °C and 20 MPa) was crushed and 2–5 mm pieces were selected, dried for 1 h at 200 °C and weighed. Then they were impregnated for a week at 20 °C by immersing in a 14 wt % aqueous solution of calcium chloride. After separating from the solution and rinsing quickly with water two times the material was dried for 2 h at 200 °C and weighed to determine the content of calcium chloride.

Methods. Sorption Experiments. Nitrogen isotherms were measured by a Micromeritics ASAP 2000 instrument at 77 K. Water vapor adsorption isotherms were measured volumetrically using a standard device.⁴ A nanometric pressure stabilizer of the manostat type guaranteed that measurements were isobaric, and a system of thermostats ensured that the process was isothermal. The measurements were carried out within the temperature range 25–150 °C.

Apparent Density. The apparent density ρ_a was determined by mercury porosimetry using Micromeritics Auto Pore II 9220.

Transmission Electron Microscopy. Transmission electron micrographs were obtained on a JEOL 2000SX instrument operating at 160 kV. The IHA samples were dried for 2 h at 200 °C and subsequently ground to a size of about 60–100 mesh, and the particles were suspended in dry cyclohexane and sonicated for 1–2 min. The solution was allowed to settle 5 min and a droplet of the resulting supernatant was placed on a holey carbon film and dried.

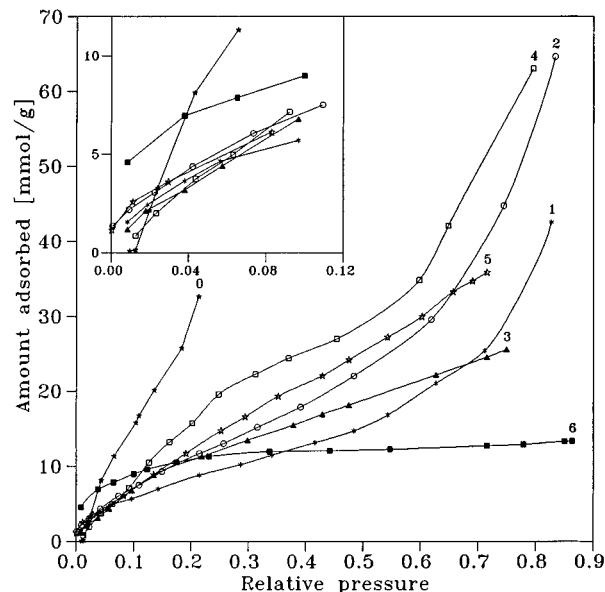


Figure 2. Water vapor adsorption isotherms at 298 °C. 100% CaCl_2 (sample 0), aerogel 17 wt % of CaCl_2 (1), aerogel 29% (2), xerogel 17% (3), xerogel 29% (4), impregnated silica aerogel 32% (5), 4.0 Å molecular sieve (6).

Table 1. Characteristic Parameters of the Texture of IHA Samples

| sample | type ^a | CaCl_2 (wt %) | $V_{p(\text{N}_2)}$ (cm^3/g) | S_{BET} (m^2/g) | ρ_a (g/cm^3) |
|--------|-------------------|------------------------|--|--|------------------------------|
| 1 | a | 16.7 | 3.9 | 886 | 0.21 |
| 2 | a | 28.9 | 1.9 | 640 | 0.25 |
| 3 | x | 16.6 | 0.45 | 276 | 1.07 |
| 4 | x | 28.9 | 0.54 | 200 | 1.06 |
| 5 | i | 31.6 | 0.54 | 152 | 1.08 |

^a a, aerogel, x, xerogel, i, impregnated silica aerogel.

Results and Discussion

As can be seen from Figure 2, all the materials obtained demonstrate a strong affinity for water. The adsorption isotherms from all IHAs are generally of the IUPAC type II, thus similar to those depicting water adsorption on silica gels and other mineral substances. However, the adsorptivities given in Figure 2 are markedly higher than ever reported before for silica-based materials, and sorption capacities exceeding 1 kg of $\text{H}_2\text{O}/\text{kg}$ of adsorbent exhibited by samples 2 and 4 in the higher relative pressure region are at least 2- or 3-fold larger than observed in zeolites. Surprisingly enough, more detailed examination of Figure 2 reveals that adsorptivity of water vapor on sample 5 (impregnated silica aerogel) in the low and intermediate relative pressure region may be even higher than of the hybrid sol-gel samples. However, in the higher relative pressure range the small water droplets were observed on the surface of sample 5, most probably indicating the separation of CaCl_2 (dissolving out) from the host structure. This rendered immaterial further investigations of adsorptivity of sample 5. Such water droplets were never observed on samples 1–4, even after prolonged saturation with water vapor. Thus, on the whole the adsorbents afforded by the sol-gel route, regardless of the mode of drying, appear to be superior to those with the similar content of calcium chloride, and similar $\text{CaCl}_2/\text{SiO}_2$ composition, yet prepared by impregnation of silicagels⁶ or aerogels. This corroborates earlier expectations regarding a strong positive effect of the

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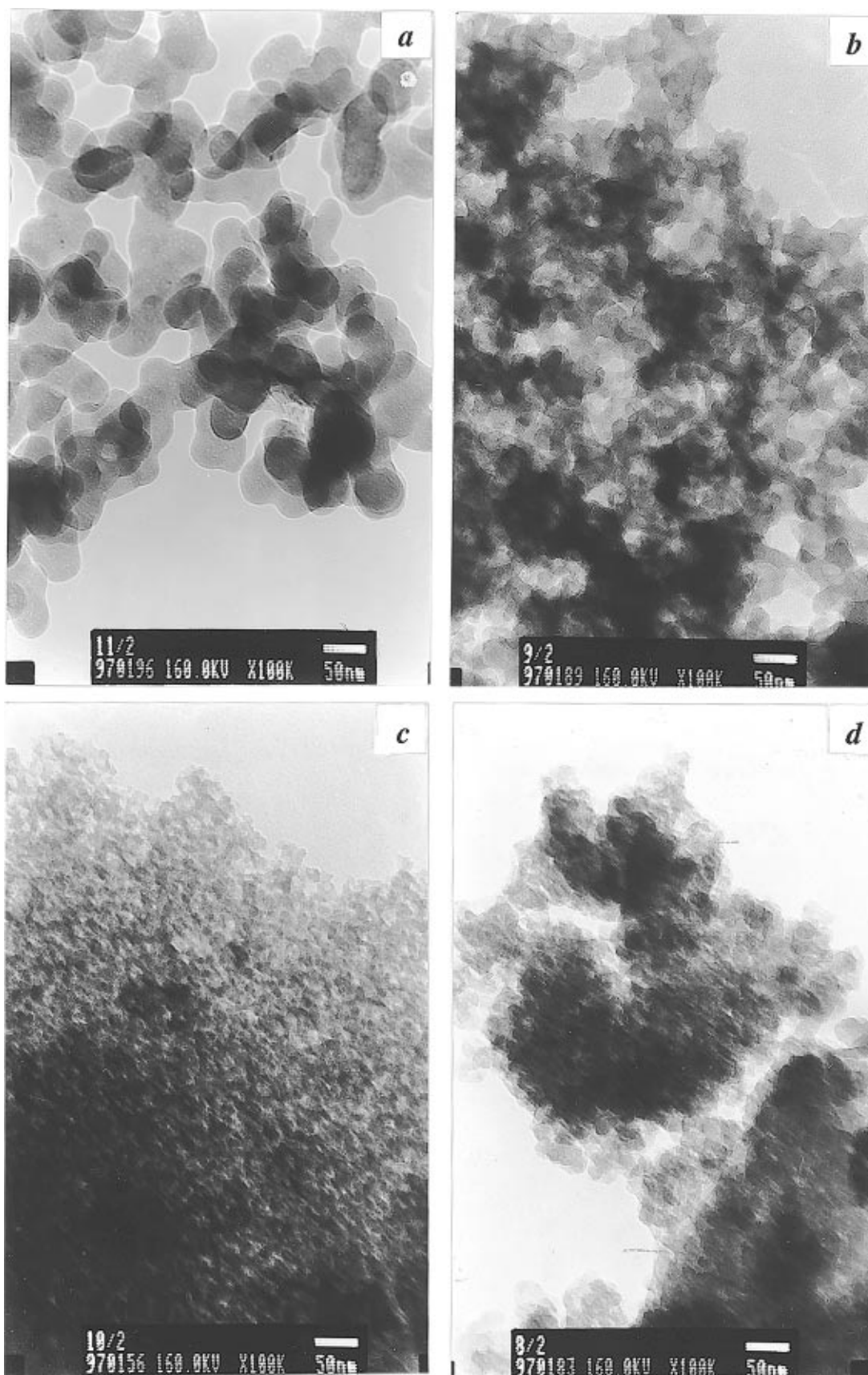


Figure 3. TEM images of IHA samples. Aerogel 29 wt % of CaCl_2 (a), aerogel 17% (b), xerogel 29% (c), impregnated silica aerogel 32% (d).

uniform distribution of calcium chloride on adsorption properties of the materials. Apparently the amount of calcium chloride embedded in silica matrix is also of prime importance. This is clearly demonstrated by markedly lower adsorptivities of water vapor shown by

samples 1 and 3 (with some 17 wt % of CaCl_2) in comparison with those of 2 and 4, which contained about 30% of calcium chloride (Figure 2). The 4.0 Å molecular sieve (Union Carbide/Fluka) adsorbs more water vapor than any of the IHA samples in the low relative pressure

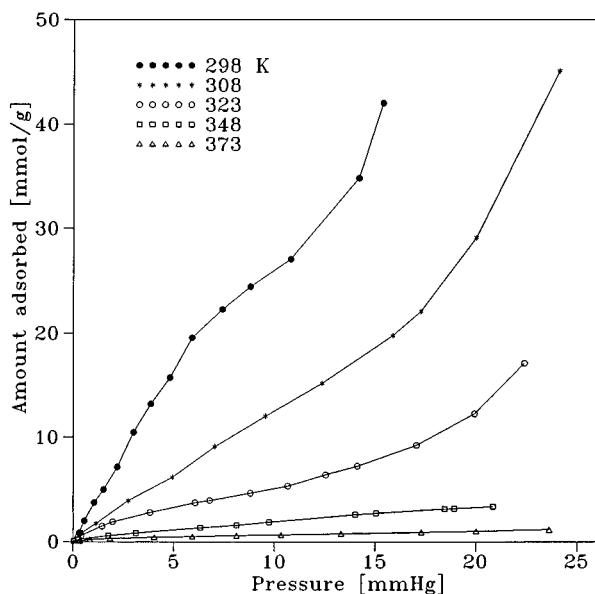


Figure 4. Water vapor adsorption on xerogel 29% at different temperatures.

Table 2. Isosteric Heats of Water Vapor Adsorption on Sample 4 at Different Adsorptivities

| | | | | | | | |
|--------------|-------|------|-------|------|------|------|------|
| w (kg/kg) | 0.006 | 0.01 | 0.025 | 0.05 | 0.1 | 0.2 | 0.3 |
| Q (kJ/mol) | 57.2 | 55.7 | 53.8 | 51.3 | 48.2 | 49.6 | 46.6 |

region $P/P_0 < 0.15$ shown in detail in the inset. This is associated with the lack of micropores and a marginal mesopore volume in the pore size range of 2–5 nm determined in all IHA samples by the nitrogen adsorption method (data not shown here). More surprising, perhaps is the very low amount of water vapor adsorbed by pure calcium chloride in the relative pressures less than 0.01 (cf. inset in Figure 2).

The characteristic parameters of IHA porous texture determined by the nitrogen adsorption method and mercury porosimetry are given in Table 1. As was expected, the evacuation of ethanol from hybrid alcogels by supercritical carbon dioxide afforded aerogel materials characterized by an open porous structure in the meso- and macropore size range. In contrast, the conventionally dried xerogel structures have a majority of pores in the size range of 5–12 nm. This can be also inferred from the TEM images given in Figure 3. The micrographs clearly show an open polymeric structure of hybrid aerogels (Figure 3a,b) and a uniform xerogel-type morphology of sample 4 (Figure 3c). The morphology of sample 5 (Figure 3d) is somewhat obscured and can hardly be categorized; most likely the calcium chloride effectively masked the bulk of its details during the process of impregnation. The type of morphology shown in micrographs 3a and 3b perfectly conforms with that of aerogels. It is, however, totally different from the very tenuous branched polymeric structures usually observed in silica aerogels afforded by the two-step acid–base procedure.¹⁵ The uniform secondary particles of diameters in the range 30–40 nm seen in sample 2 (Figure 3a) are quite large, in fact even larger than observed in typical colloidal silica aerogels. However, the branched polymeric structure displayed in micrograph 3a, despite its rather massive outlook, seems very

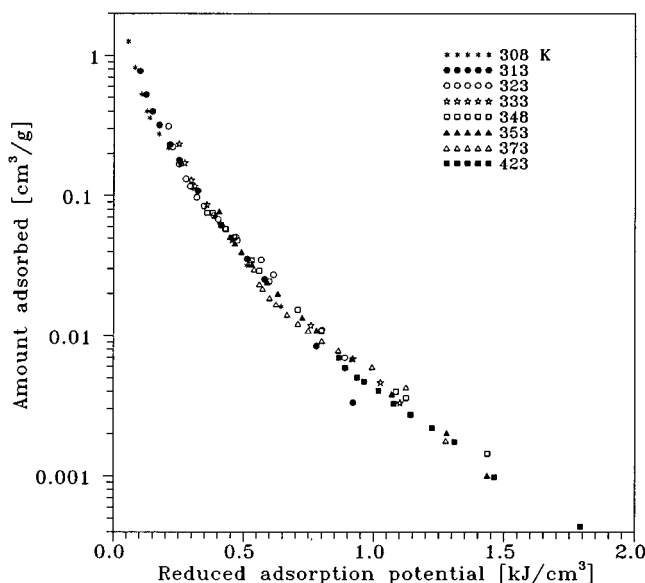


Figure 5. Volume of adsorbed water vapor on xerogel 29% against adsorption potential.

open with the bulk of voids in the macropore size range. This perfectly agrees with the projections provided by nitrogen adsorption and mercury porosimetry techniques (cf. values of apparent density and mesopore volume given in Table 1). The morphology of the sample containing only 17% of CaCl_2 shown in Figure 3b seems more compact, which may yet be misleading. Most likely this is due to the larger number of mesopores detected by nitrogen adsorption experiments (cf. Table 1) but not clearly displayed in the TEM image. The characteristic feature of the structure shown in Figure 3c is its uniformity and a remarkable presence of mesopores of size less than 20 nm. This also conforms with the pore size distribution extracted from nitrogen adsorption isotherm.

The effect of temperature on water vapor adsorption on sample 4 was investigated in the range of 25–150 °C and the isotherms obtained are presented in Figure 4. The evaluated isosteric heats of adsorption are given in Table 2. As can be seen the differential heat of adsorption falls gradually with increasing adsorption from about 57 kJ/mol H_2O at $w = 0.006$ kg $\text{H}_2\text{O}/\text{kg}$ adsorbate (0.13 mol/mol CaCl_2) to 47 kJ/mol at $w = 0.3$ w/w. Interestingly enough, similar values were found previously⁶ for the system with the same composition (34 wt % CaCl_2), yet with the CaCl_2 introduced by impregnation. In that case, however, the sharp fall was observed in the vicinity of the point where adsorption was equal to 2 mol $\text{H}_2\text{O}/\text{mol}$ CaCl_2 which clearly indicated on the chemical effect ($\text{CaCl}_2 \times 2\text{H}_2\text{O}$ formation). In the case of sample 4 this rapid decrease was not recorded, which precludes that mechanism.

We do not intend to speculate on the mechanism of water adsorption on IHA. Most likely it is a synergistic effect of silica and calcium chloride; both known for their high, yet different affinity for water. Preliminary examination performed for sample 4 indicate that the process of water adsorption tends to obey the Polanyi potential theory,¹⁶ and hence the temperature independent characteristic curve can be obtained (cf. Figure 5).

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So far only limited data have been collected on the behavior of the adsorbents (samples 2 and 4) upon repeated cycles of adsorption and drying and on their possible reuse. The results can be summarized as follows: (i) adsorbents can be effectively regenerated/dried at 200 °C; (ii) cycling repeatability (up to at least 50 cycles, – experiments still continue) has little bearing on the water vapor adsorption capacity; (iii) minor changes in the mesopore surface structure occur during initial cycles.

Conclusions

The straightforward entrapment of calcium chloride in silica matrixes using the sol–gel method results in hybrid materials with enhanced affinity for water vapor and adsorption capacities exceeding 100 wt % at higher relative pressures. These capacities are markedly

higher than those (≈ 70 wt %) exhibited by the materials similar in composition yet prepared by the impregnation of silicagels or aerogels. The hybrid materials afforded by the sol–gel route do not dissolve in water vapor, in contrast to inorganic hygroscopic materials, e.g., CaCl_2 or LiBr and to some extent also hybrid materials produced by impregnation. The adsorbents obtained can be easily regenerated/dried at 200 °C and reused. No significant loss in performance was observed during 50 cycles.

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