DESIGN OF TWO-COMPONENT SORBENTS FOR SORPTION HEAT STORAGE

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ABSTRACT

A design of composites with PHTS matrix (plugged hexagonal templated silicate) with average pore size of 5.7 nm and different amounts of calcium chloride (4, 10, 20 wt %) for solar thermal energy storage is presented. The novel composites have been developed by incipient wetness impregnation. Preparation procedure of the matrix increased its hydrophilic properties, showing its active role in water sorption. Calcium chloride is shown to be located in the pores of the matrix. The presence of $CaCl_2$ in PHTS leads to a partial deformation of ordered pore structure ($10\text{-}CaCl_2$) or a collapse of the ordered pore arrangement ($20\text{-}CaCl_2$) into the disordered mesostructure. The increased salt content in the composites impacted the sorption performance of these composites, e.g. higher content of the salt higher energy storage capacity.

Keywords: composites, $CaCl_2$, active matrix, water sorption, sorption capacity, heat storage.

INTRODUCTION

The efficiency of sorption heat storage technology is governed by the performance of the applied sorbents. Thus, sorbents with high water sorption capacity and regeneration temperature from 80 to 150 °C are required. Hydrothermally stable porous adsorbents can be used as storage materials for application in sorption heat storage. The main principle is based on the consecutive adsorption and desorption processes. A large number of sorbents are currently considered for sorption thermal energy storage (TES). The most versatile class of sorbents are two-components or composites, which have been prepared for the enhancement of water sorption capacity, heat and mass transfer on one side, and on the other hand to avoid or diminish the deliquescence, swelling and agglomeration of salt hydrates during sorption/desorption cycles, thus combining the advantages of the pure porous material which act as a matrix and hygroscopic salt hydrates (mainly chlorides and sulphates of alkali and alkali-earth metals) [1]. These sorbents have the advantage to tailor sorption capacity by varying content of salt and porous structure of the matrix.

Here wepresent the design and structural properties of efficient water sorption composites, for low temperature sorption heat storage.

EXPERIMENTAL

The composite was prepared by incipient wetness impregnation of the PHTS with different concentrations (4 wt%, 10 wt%, and 20 wt%) of calcium chloride solution [2]. The X-ray powder diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO high-resolution diffractometer with Alpha1 configuration. Nitrogen physisorption measurements were performed at -196 °C on a Tristar volumetric adsorption analyzer (Micromeritics). Prior to the evaluation of textural properties of the composites the amount of the nonporous salt was taking into account which does not contribute to nitrogen adsorption to a large extent. Thus nitrogen isotherms and all specific values (surface area, pore volume) were corrected. The BET specific surface area, S_{BET}, was calculated using the adsorption branch in the relative pressure range between 0.05 and 0.16 [3]. The total pore volumen, Vt, was estimated from the

amount adsorbed at a relative pressure of 0.96. The pore size distributions (PSDs) were calculated from nitrogen adsorption data using an BJH algorithm [4]. The maxima on the PSD are considered as the primary mesopore diameters for given samples. Water sorption measurements were performed at 40 ^{o}C on IGA-100 gravimetric analyzer (Hiden Isochema Ltd.). The hydrothermal stability of the materials were evaluated with 20-cycles measurements at 56 mbar in a helium gas flow (10 mL/min) with 75 % relative humidity by varying the temperature between 40 and 140 °C. The water loading capacity of materials were measured at the beginning, and after 20 cycles.

RESULTS AND DISCUSSION

The PHTS matrix pattern indicated three diffraction peaks corresponding to the reflections typical for two-dimensional hexagonal pore arrangement. It can be seen that after loading of 4 wt. % of calcium chloride, the channels with good order were preserved during the preparation procedure of the composite. The impregnation of larger amounts of calcium chloride leads to the change of the diffraction patterns; only one less intensive diffraction peak was observed for the composite with 10 wt.% of the salt, while a broad diffraction peak was determined for the composite with 20 wt.% of the salt. These results indicate the collapse of ordered arrangement of mesopores of these composites into disordered mesopore arrangement. XRD pattern in the wide-angle range (not shown) of the composite with 4 wt. % and 10 wt. % of calcium chloride did not show any reflections of calcium chloride, which could be explained with the presence of highly dispersed calcium chloride with nanosized dimensions that are located on the surface and within the pores. Only one broad peak was observed in the range ($15°< 2\theta< 30°$) corresponding to glass-like amorphous silicate particles. While the XRD pattern of the composite with 20 wt.% of calcium chloride showed diffraction peaks of the salt. Porous structure of the PHTS matrix and all composites were examined by nitrogen sorption isotherms. Structural parameters determined on the basis of these isotherms are listed in Table 1. Due to the synthesis procedure PHTS sample exhibits sorption isotherm typical for PHTS-like material [5]. Plugged hexagonal templated silica has the same 2D hexagonal symmetry as SBA-15 with some of its cylindrical mesopores have internal plugs, while others are open as inferred from gas adsorption-desorption data. N_2-sorption isotherms of PHTS are of type IV according to the IUPAC classification with H5 hysteresis loop [6], showing a one-step capillary condensation, two-step desorption, and an appreciable widening of hysteresis loops. The first step is similar to desorption in pure SBA-15 and is assigned to the desorption of N_2 from the open pores; the second desorption step can be attributed to the nanoparticles (plugs) within the mesopores (the narrowed mesopores). The second step on the desorption branch indicates the existence of plugged mesopores. The presence of $CaCl_2$ in PHTS leads to a marked change in the shape of the hysteresis loops, showing on partial deformation of ordered pore structure ($10-CaCl_2$) into a collapse of the ordered pore arrangement ($20-CaCl_2$), which finds some evidence in XRD analyses.

Table 1. Structural properties of the matrix and the prepared composites.

Sample	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{mi} (cm^3/g)	Average Pore Size (nm)
PHTS	810	0.705	0.122	5.7
4-CaCl$_2$-PHTS	461	0.492	0.037	5.6
10-CaCl$_2$-PHTS	322	0.377	0.022	5.8
20-CaCl$_2$-PHTS	163	0.189	0.016	6.2

Abbreviations: S_{BET}, the BET surface area; V_{tot}, total pore volume evaluated from adsorption isotherm at the relative pressure 0.96

The maximum of PSD for 4-CaCl$_2$-PHTS due to CaCl$_2$ nanoparticles shifted to a lower pore size value (5.6 nm), while in 10-CaCl$_2$ and 20-CaCl$_2$ composites they shift to 5.8 nm and 6.2 nm, respectively. The reason could be the partial destruction of mesoporous structure caused by the corrosive action of calcium chloride solution [7]. Maxima are less intensive with higher amounts of CaCl$_2$. The ordered mesoporous matrix and the composites exhibit water sorption isotherms Type V. The water uptake curve of the matrix showed typical characteristics of weak hydrophilic or hydrophobic mesoporous materials with low sorption at low relative pressure and moderate sorption at the middle relative pressure, and sudden high water sorption at higher relative pressure [8]. The maximal water upload of the matrix was 0.65 g/g, showing the active role of the matrix. Maximal water sorption capacities of the composites increased to 0.78 g/g (4-CaCl$_2$), 1.20 g/g (10-CaCl$_2$), and 2.24 g/g (20-CaCl$_2$). The shape of the uptake curves was evidently changed. For a relative pressure of 0.4, the composite containing 10 wt.% CaCl$_2$, showed double water sorption capacity (0.16 g/g vs. 0.38 g/g), while the composite with 20 wt.% of the salt revealed three times larger water sorption capacity than the matrix (0.16 g/g vs. 0.58 g/g). It can be concluded that the presence of calcium chloride in the matrix increased the water sorption capacity of the composites; thus, the salt content impacted the sorption performance of these composites. The most relevant parameter for evaluating the effectiveness of sorbent for TES is the integral heat of adsorption. It is well known that the adsorbents with low water uptake after desorption and high water uptake after adsorption, resulting in high water loading lift to reach high storage densities, are needed for sorption heat storage. The integral heat of adsorption was calculated for the given boundary conditions for space heating: adsorption temperature at 40 °C, desorption temperature at 120 °C, and a dew point temperature was set at 10 °C. The integral heat of adsorption Q$_{ads}$ of all composites is listed in Table 2.

Table 2.Water loading lift and the integral heat of adsorption for the composites.

Sample	Δw (kg/kg)	Q$_{ads}$ (Wh/kg)	Q$_{ads}$ (kJ/kg)
PHTS	0.073	71	256
4-CaCl$_2$-PHTS	0.100	81	292
10-CaCl$_2$-PHTS	0.142	119	428
20-CaCl$_2$-PHTS	0.239	193	694

The increased amount of the salt in the composites increased the calculated water loading lifts, and consequently, the energy storage capacity. Cycling stability of these composites during 20 cycles of sorption and desorption between 40 and 140 °C at 56 mbar was tested, showing a small reduction of water uptake (2–6 %) after the last cycle for each composite.

CONCLUSION

Novel composites composed of PHTS (plugged hexagonal templated silicate) with hexagonal pore arrangement as the matrix and 4 wt.%, 10wt.%, and 20 wt.% of calcium chloride have been developed by incipient wetness impregnation. The preparation procedure of the matrix increased its hydrophilic properties, showing its active role for water sorption. Calcium chloride is shown to be located in the pores of the matrix. The presence of CaCl$_2$ in PHTS leads to a partial deformation of ordered pore structure (10-CaCl$_2$) or a collapse of the ordered pore arrangement (20-CaCl$_2$) into the disordered mesostructure.The water sorption capacities of composite sorbents were improved by the preparation of the matrix with smaller average pores (5.7 nm), adding highe ramount of calcium chloride (from 4 wt% to 20 wt% of the salt) and by changing the preparation method of the composites (incipient wetness impregnation). The comparatively good initial stability of these composites under the

operating conditions was determined without any salt leaching. These composites are promising candidates for low-temperature termal energy storage.

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