



CaCl₂-containing composites as thermochemical heat storage materials



Amira Jabbari-Hichri^a, Simona Bennici^{b,*}, Aline Auroux^a

^a Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de Recherches sur la Catalyse et L'Environnement de Lyon, 2 avenue Albert Einstein, F-69626 Villeurbanne, France

^b Institut de Science des Matériaux de Mulhouse, UMR CNRS 7361, 15 rue Jean Starcky, 68057 Mulhouse, France

ARTICLE INFO

Keywords:

Thermochemical heat storage
Mesoporous materials
Calcium chloride
Water sorption
Calorimetry

ABSTRACT

The purpose of this paper is to enhance the heat storage and mass transfer performances of mesoporous materials by adding a hygroscopic salt. Silica-gel, alumina, and bentonite were chosen as supports of 15 wt% of calcium chloride. Comparison between the three series of composites was done by analyzing the impact of the salt addition on the physico-chemical and sorption properties of the three host matrixes. Moreover, the water sorption/desorption kinetics on the different composites under operating conditions, close to those of heat pump application, has been studied. The thermal behavior of the composite materials was examined by TG/DSC analysis.

The addition of calcium chloride increased the quantity of sorbed water and released heat. The composite silica gel/CaCl₂ showed the highest sorption capacity (0.27 g_{H₂O} g_{sample}⁻¹) accompanied with the highest heat storage (746 J g_{sample}⁻¹). The activation energy determined for the desorption process was following the silica-gel/CaCl₂ < bentonite/CaCl₂ < alumina/CaCl₂ order, opposite to the pore size of the various composites, that was the larger for silica-gel based materials. Finally, the experimental results of rehydration were fitted with kinetics model in order to describe the kinetics of water vapor adsorption of the three mesoporous composites. Moreover, using the experimental data of rehydration a kinetic model was applied to describe water vapor diffusion in the three mesoporous composites.

1. Introduction

Thanks to their physicochemical properties, porous materials, especially mesoporous materials, have received significant attention for their use in various applications [1,2], as membranes, chemical sensors and materials for thermochemical storage (TCS). In particular, the applications in gas drying, air conditioning, and seasonal heat storage systems are widely described [3]. Energy storage is one of the most critical problems to use solar energy as a source of energy for buildings [4]. The main advantage of using this storage system is to bridge the gap between the maximum availability of solar radiation in summer (dehydration step) and the energy demand for heating houses in winter (hydration step) [5]. For better energy efficiency, the improvement of the adsorption properties of materials for TCS plays an important role. Traditionally, the materials used as water vapor adsorbents are activated carbons, carbon molecular sieves, silica gels, activated aluminas, zeolites, clay minerals, and metal-organic microporous and mesoporous materials [6]. Recently, composite materials have been used as

adsorbents for thermochemical heat storage applications [7]. In order to reach good performances, the adsorbents should be adapted to the specific use conditions. Stach et al. [8] showed that the most important properties for adsorption system are the maximum working temperature and the energy storage density. Moreover, composites must adsorb water in a short time, thus improving the kinetics of water vapor sorption remains a key issue for applying hydrophilic porous materials in thermochemical heat storage systems. Composite materials [9–11] are usually prepared by combining porous host materials and hygroscopic salt hydrates; improved properties as high specific surface area, defined degree of hydrophilicity, accessibility of the pore network, thermal and hydrothermal stability are required to improve the heat storage capacities [11].

Increasing attention has been given to mesoporous materials used as supports [12]. The combination of mesoporous host matrixes and salts (such as CaCl₂, LiNO₃) changes the water sorption mechanism, improving the storage capacity and enlarging the working temperature range of the resulting composites, which render them suitable to a

Abbreviations: TCS, ThermoChemical Storage; S, Silica gel; A, Alumina; B, Bentonite; SCa₁₅, CaCl₂ deposited on silica gel; BCa₁₅, CaCl₂ deposited on bentonite; AlCa₁₅, CaCl₂ deposited on Alumina; BET, Brunauer, Emmett et Teller; BJH, Barret Joyner and Halenda; ICP, Inductively Coupled Plasma; OES, Optical Emission Spectroscopy; TG, ThermoGravimetry; DSC, Differential Scanning Calorimetry; RH, Relative Humidity; IUPAC, International Union of Pure and Applied Chemistry; DTG, Derivative of thermogravimetric curves

* Corresponding author.

E-mail address: simona.bennici@uha.fr (S. Bennici).

<http://dx.doi.org/10.1016/j.solmat.2017.07.037>

Received 21 December 2016; Received in revised form 17 July 2017; Accepted 26 July 2017

Available online 29 July 2017

0927-0248/ © 2017 Elsevier B.V. All rights reserved.

Nomenclature

S_{BET}	Surface Area
V_p	Pore Volume
\emptyset	Average pore diameter
W	Water sorption capacity
m_h	Mass of hydrated sample
m_d	Mass of dried sample
M	Molar weight
N_A	Avogadro number
T_p	Peak temperature
β	Heating rate

R	Perfect gas constant
E_d^{app}	Apparent activation energy
q	Adsorbed phase concentration
D	Effective diffusivity
t	Time
A	External surface area
V	Particle volume
m_t	Average water uptake for $t > 0$
m_∞	Average water uptake for $t = K$
R_p	Particle radius
K	Rate constant
τ	Characteristics time of the adsorption process

wider range of applications (heat pumps and refrigerators). The physico-chemical properties of the support, the chemical nature and amount of deposited salt, and the preparation conditions affect the sorption properties of the composite [13]. It has been shown that the water sorption capacity is higher in the case of composites than for pure salts or mesoporous host materials used separately [13,14]. Many of these materials exhibit high surface areas and pore volumes leading to interesting uptakes of water vapor. Pires et al. [15] claimed that the hydrophobic/hydrophilic behavior (that is connected to the surface sites nature) is a fundamental property to explain the extent of water vapor sorption capacity. Cases et al. [16] indicate that the magnitude of the heat of adsorption depends on the choice of efficient water adsorbents, and that the amount of water adsorbed on the surface of different clays is governed by the size and the charge of the saturating cation.

The chemical composition and pore structure of host porous materials strongly affect the water sorption capacities of the final composites [17]. Another factor influencing the sorption properties is the surface interaction between the matrix and the hydrate salt [18]. In a recent work our group focused on the enhanced performances of silica-alumina based composite materials obtained by dispersing different types of hydrate salts on the support surface [19]. The composites containing calcium chloride presented the highest water sorption and heat storage capacities. Jia et al., 2006 [20] developed a new composite by depositing LiCl into the pores of a silica gel, proving that, at high relative humidity, the adsorption capacity of the composite was 2–3 times higher than that of the pure host matrix. Simonova et al. [21] studied the enhancement of water uptake (up to 0.2–0.3 g_{H2O} g_{sample}⁻¹) of a silica gel after deposition of Ca(NO₃)₂. Recently, Posern et al. [22] reported that by varying the amount of deposited salt and tuning the pore size of the host matrices, the water sorption capacity of the composite can be improved. It is worth to notice that the most suitable composites for TCS applications mentioned by various scientific researchers are those presenting calcium chloride as active phase [19,23,26,27].

Calcium chloride is a hygroscopic salt that is able to absorb water molecules even at room temperature and to release them when heated, providing high energy values [23,24]. N'Tsoukpoe et al. [25] reviewed the recent studies on thermal energy storage systems using calcium chloride based composites. Some disadvantages, as swelling and agglomeration phenomena, can be overcome by depositing calcium chloride on a support. It is then important to select a porous matrix that offers a larger surface and internal pore volume, in order to enhance the interaction between the salt and the water vapor. Besides, once dispersed into the matrix pores the properties of the salt can vary. Aristov et al. [9] showed that the sorption behavior of CaCl₂ hydrates radically changes due to deposition into mesoporous silica gel. The same research group [10] studied the water sorption process on expanded vermiculite/ calcium chloride composites. The authors claimed that the confinement of CaCl₂ into vermiculite pores can strongly influence the hydration process that can already take part at low water vapor pressure. At higher water uptakes, a CaCl₂ aqueous solution is formed inside

the pores and the isosteric sorption heat has been shown to depend only on the amount of water adsorbed (the isosteric heat changing from 76.3 kJ mol⁻¹ for solid hydrates to 39.1–46.6 kJ mol⁻¹ range value, close to the value of water condensation enthalpy). Dawoud et al. [28] investigated the kinetics of water vapor sorption on two composite materials containing 34 and 28 wt% of calcium chloride deposited respectively on silica gel and alumina. Due to the increased diffusion resistance to water, resulting from the salt impregnation, the authors showed that the kinetics of water sorption into the two different composites was lower than into the two host matrixes. Kerskes et al. [29] measured the water uptake and the released heat for a composite obtained by depositing 40 wt% of CaCl₂ on bentonite (heat storage capacity of 700 J g_{sample}⁻¹), while Zhu et al. [30] claim an energy storage capacity of 950 J g_{sample}⁻¹ for a composite formed by 40 wt% CaCl₂ deposited on silica gel.

The objective of this paper is to highlight the impact of the physico-chemical properties of different mesoporous supports on the final performance of CaCl₂-containing composites. The amount of heat stored and released is here directly measured during two successive cycles of hydration/dehydration. Moreover, kinetic models have been applied to the experimental rehydration data in order to better understand the link between physicochemical properties and heat storage performances of the studied composites.

2. Experimental

2.1. Composite materials preparation

The mesoporous materials used in this study as supports (silica gel (S), alumina (Al), and bentonite (B)) have been respectively purchased from Grace Divison, Rhône-Poulenc and Süd-Chemie. Composites were prepared by incipient wetness impregnation, and 15 wt% of calcium chloride ($\geq 99.0\%$, Sigma-Aldrich) was deposited on the three different host matrices. Prior to deposition, the mesoporous host matrixes were dried at 110 °C, then CaCl₂ (dissolved in the required volume of water to completely wet the support) intimately mixed with the support powders. The obtained samples were dried in static air at 110 °C overnight, and successively dehydrated in air flow for 8 h at 260 °C before use. The composite materials were labelled as follows: SCA₁₅, BCa₁₅, and AlCa₁₅. The amount of 15 wt% of calcium chloride was chosen as the maximum amount to avoid the problem of crust formation on the surface of porous host materials, which can block the diffusion of H₂O molecules through the pores of the support [23]. Besides, samples containing higher quantities of calcium chloride show lower heat conductivity than samples with smaller salt loadings [31]. The heat transfer performance is indeed a very important property of thermochemical heat storage systems and it is controlled by the thermal conductivity of the solid storage material.

The minimum temperature required for the sample activation was determined by thermogravimetry performed from 25 to 500 °C with a heating rate of 5 °C min⁻¹ in air flow on a Labsys-TG instrument from

Download English Version:

<https://daneshyari.com/en/article/6456913>

Download Persian Version:

<https://daneshyari.com/article/6456913>

[Daneshyari.com](https://daneshyari.com)