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Further improvement of the synthesis of silica gel and $CaCl_2$ composites: Enhancement of energy storage density and stability over cycles for solar heat storage coupled with space heating applications[☆]

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ABSTRACT

Composite materials based on a silica gel loaded with $CaCl_2$ are of great interest for seasonal thermochemical heat storage. In order to improve the performance of these materials for this application, and to evaluate their multi-cycle stability, a new synthesis protocol is proposed, based on successive impregnation/drying steps by using a matrix with a broad pore size distribution. Through this method, a $CaCl_2$ content of 43 wt%, a high cycle loading lift of 0.40 g/g and an unprecedented energy storage density for this type of material of 211 kW h/m^3 of packed bed composite, in conditions of a solar heat storage system (adsorption at 30 °C, desorption at 80 °C, and water vapor pressure of 12.5 mbar) can be reached. Moreover, the distribution of the salt inside the pores and the absence of any salt crust outside the matrix prevent salt leakage, leading to an outstanding preservation of the cycle loading lift after 10 cycles. Based on Polanyi theory, it can be assumed that the energy storage density can exceed 350 kW h/m^3 for water sorption at 20 °C, desorption at 80 °C, with both steps at a water vapor pressure of 12.5 mbar.

1. Introduction

Promoting the use of renewable energy sources is one of today's main challenges. Solar energy is one of the most promising options thanks to its high availability and low cost. To solve the problem of the discrepancy between the availability of solar heat and space heating needs, long-term storage systems have to be developed. Long-term heat storage systems need some specific requirements. For example, the storage material will be submitted to one charging phase and one discharging phase per year. As the system should be used for at least 20 or 25 years, the storage material should keep the same performance over at least 20–25 cycles. The long-term heat storage should be able to produce enough energy (e.g. 3000 kW h/year for a single-family house in Belgium) to cover the heat demand of a building, and so the material's energy storage density should be as high as possible to reduce the volume of storage needed to cover the heat demand of the building. Thermochemical heat storage, using a reversible sorption/desorption reaction, is the most promising solution due to the high energy storage density of thermochemical storage materials (up to 780 kW h/m^3) (Aydin et al., 2015; N'Tsoukpoe et al., 2014, 2009). Water has often been chosen as a sorbate due to its nontoxicity and low cost; that is why, in this paper, this is the only sorbate considered. A wide range of thermochemical storage materials have been discussed including salt hydrates ($MgSO_4$ (Ferchaud et al., 2014, 2013, 2012; van Essen et al., 2009b), $CaCl_2$ (Mugnier and Goetz, 2001; van Essen et al., 2009a), Li_2SO_4 (Ferchaud et al., 2013, 2012), $CuSO_4$ (Ferchaud et al., 2012; van Essen et al., 2009a), $MgCl_2$ (Ferchaud et al., 2013; Mugnier and Goetz, 2001; van Essen et al., 2009a; Zondag et al., 2013), Na_2S (Mugnier and Goetz, 2001), LiCl (Mugnier and Goetz, 2001) and $SrBr_2$ (Fopah Lele et al., 2015; Hennaut et al., 2014; Lahmidi et al., 2006; Michel et al., 2014, 2012)), physical adsorbents (such as activated carbons, silica gels, zeolites, metal organic frameworks (Elsayed et al., 2016; Permyakova et al., 2017)) and composite materials (salt encapsulated in a porous matrix). Among these materials, salt hydrates have the highest energy storage densities (several hundreds of kW h/m^3) (Trausel et al., 2014). However, for some of these salts, their high water content in the conditions of thermal heat storage systems may cause their dissociation in solution and/or provoke morphological instability

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or aggregation of particles, which make their use in a thermochemical storage reactor difficult (Bouché et al., 2016; De Jong et al., 2014; Donkers et al., 2016; Solé et al., 2012; Whiting et al., 2014). Hence, composite materials have been developed with the aim of stabilizing the salt while keeping a high energy storage density, thereby limiting the volume of the storage system to be installed in the building architecture.

Among the salt hydrate candidates, calcium chloride is an interesting candidate for thermal heat storage thanks to its large availability, low cost and hydration rate of 5 mol of water per mole of $CaCl_2$ under thermochemical storage for space heating conditions. However, $CaCl_2{\cdot}6H_2O$ is prone to transform spontaneously into a solution, which makes the use of $CaCl_2$ as pure salt in a thermochemical reactor difficult.

To solve the problem of the instability of pure $CaCl_2$, a lot of research has been devoted to the development of efficient composites based on $CaCl_2$. The incorporation of $CaCl_2$ into the pores of silica gel using a wet impregnation protocol with a large quantity of salt solution followed by filtration and drying steps, with possibly an additional washing step, has already been described (Aristov et al., 2002, 1996b). The influence of physical-chemical parameters on the salt content and on sorption properties was studied (Aristov et al., 1997, 1996a; Gordeeva et al., 2006; Tokarev and Aristov, 1997; Wu et al., 2007; Zhu et al., 2006). It was shown that salt content is closely dependent on both the pore size of the matrix (Zheng et al., 2014) and the salt concentration during the impregnation step (Elsayed et al., 2016), while the sorption capacity of composites is strongly linked to the salt content (Gordeeva et al., 2006; Wu et al., 2007; Zhu et al., 2006).

Interesting sorption properties were obtained for composites based on MCM-41 and $CaCl_2$ at 37.7 wt%, with a water sorption capacity and energy storage capacity at $p/p_s = 0.7$ of 0.7 g/g and 580 W h/kg respectively (Tokarev et al., 2002), and also for a silica gel/$CaCl_2$ composite with a salt content of 30 wt% with a sorption capacity and energy storage capacity at 25 °C and 80% RH of 1.2 g/g and 940 W h/kg respectively (Gordeeva et al., 1999; Tohidi et al., 2009). A composite SBA-15/$CaCl_2$ with a salt content of 43 wt% adsorbed 0.47 g/g at 50 °C and 37 mbar (Ponomarenko et al., 2010). In those studies, the water vapor pressure chosen for the adsorption step is high compared to real working conditions. Besides, the energy storage capacity is calculated assuming the composite is completely dry after the desorption step, which is not always the case depending on the heat source temperature.

Concerning seasonal heat storage applications, some composites based on $CaCl_2$ have already been studied in lab scale prototypes. A silica gel/$CaCl_2$ composite with a salt content of 35 wt% (Zhu et al., 2006), which can adsorb 0.73 g/g at 30 °C and 80% RH, was tested in an open system. The water vapor pressure is particularly high in comparison to that used in heat storage systems (solar space heating). The performance of this composite was stable for 500 cycles, with a heat storage capacity of 264 W h/kg (no indication was given concerning the bed density to calculate the energy storage density). Ristić et al. (2012) developed a composite based on $CaCl_2$ and on sorbent FeKIL2 with a salt content of 7 wt%. The cycle loading lift, between the adsorption step at 25 °C and 12 mbar, and desorption step at 150 °C and 56 mbar, was 0.2 g/g, which corresponds to a heat storage capacity of 155 W h/kg (no indication concerning the bed density was given) with 3.6% loss of water uptake after 20 cycles between 40 °C and 150 °C at 56 mbar. The highest energy storage density was reported for a composite based on aluminosilicate and $CaCl_2$ in an open system: 180 kW h/m^3 between 20 °C and 150 °C at 7.8 mbar (Jabbari-Hichri et al., 2015). These conditions were different from the reference conditions for solar thermal energy storage and space heating applications. The desorption temperature of 150 °C is quite high for thermal solar collectors, for which temperatures lower than 100 °C are typically used. In solar heat storage applications, the main challenge is to reach high energy storage density with a low temperature heat source for desorption ($<$ 100 °C). Moreover, the adsorption temperature of 20 °C is too low for space heating applications as it corresponds to the target comfort temperature of the room.

Despite the fact that numerous studies have been focused on $CaCl_2$ based composites, it is not always possible to evaluate their potential as thermochemical storage materials for solar thermal energy storage for space heating applications. The main reason for this is the lack of information about the energy density that can be reached – high energy storage density is required to limit the volume of the system – in conditions close to the application ones. The water uptake is not always measured in an adequate range of temperature and pressure for this application. The composite packing density is rarely provided, preventing the determination of the energy storage density.

Moreover, the stability over successive cycles is still the main issue (Ji et al., 2007), as the salt becomes liquid in the pores past a certain point of high water uptake, and problems of salt solution leakage from the matrix pores were reported, leading to a loss of performance after several cycles. For a good multi-cycle stability, the salt content of the composite should be limited and not exceed around 30 wt% (Wu et al., 2007), which also limits the sorption capacity and hence the energy storage density. For space heating applications, the energy storage density should be at least 150 kW h/m^3, which represents a 20 m^3 storage to cover the needs of a passive house. With this low salt content, this value of energy storage density would not be reached. Therefore, further improvements to the synthesis protocol are required in order to increase both the salt content of the composite and the energy storage density as well as enhancing the multi-cycle stability, which is of primary importance for seasonal heat storage for space heating applications.

When composites present high salt contents (Ponomarenko et al., 2010; Tokarev et al., 2002; Tokarev and Aristov, 1997), the location of the salt (on the surface of the matrix or in the pores) and the stability of composites have not been previously investigated. Concerning the target value of the energy density, one can refer to the most promising results that have been published so far when considering other salts than $CaCl_2$, for example, zeolite 13X/$MgSO_4$ (Hongois et al., 2011), silica gel/$Ba(OH)_2$ and silica gel/$LiNO_3$ (Jabbari-Hichri et al., 2015). The best results were reported for the composite zeolite 13X/$MgSO_4$ with an energy storage density of 166 kW h/m^3 (desorption temperature of 150 °C, adsorption at 30 °C and 17–19 mbar) (Hongois et al., 2011). This composite required a high desorption temperature, which is too high for using thermal solar collectors (loss of efficiency of the collectors).

In this work, a composite based on silica gel and on $CaCl_2$, synthesized with a different protocol than those previously reported, will be presented. The objectives are to optimize the salt content of the composite, its energy storage density, and multi-cycle stability. The energy storage density of the composite will be determined in conditions of a solar heat storage system coupled with space heating. The complete structural and chemical characterization of this composite will be performed in order to understand the mechanism of sorption and evaluate its stability.

2. Materials, synthesis and characterization

2.1. Materials

The silica gel used as a porous matrix in this study is Davisil grade 62 from Grace, hereafter called SG62. This silica gel has a broad pore size distribution, mainly with mesopores. The anhydrous calcium chloride (Caso®granules) with 94% purity was provided by Solvay.

2.2. Synthesis protocol

A few grams of composite were synthesized using the following protocol: the silica gel was first dehydrated in an oven at 200 °C for 4 h until the mass remained constant. The matrix was then cooled down to

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