

WATER SORPTION OF COMPOSITE CaCl₂-FEKIL2 FOR SOLAR THERMAL ENERGY STORAGE

Alenka Ristić¹, Stefan K. Henninger² and Venčeslav Kaučič¹

¹National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia

²Fraunhofer Institute for Solar Energy Systems, Heidenhofstr. 2, 79110 Freiburg, Germany
e-mail: alenka.ristic@ki.si

ABSTRACT

Composite water sorbent CaCl₂-FeKIL2, containing a disordered mesoporous iron silicate as a matrix and CaCl₂ as a hygroscopic salt, has been developed for sorption-based solar thermal energy storage. The maximum water sorption capacity of FeKIL2 is 0.21 g/g, while the composite possesses 3 times higher maximum water sorption capacity due to the presence of the salt in the matrix. Heat of adsorption of the composite is 50.4 kJ/mol. A short-term cycling test between temperatures of 150 °C and 40 °C at a water vapour pressure of 5.6 kPa confirms a comparatively good hydrothermal stability of the composite.

Keywords: CaCl₂-FeKIL2, FeKIL2, water sorption, solar thermal energy storage

INTRODUCTION

Thermal energy storage is an important technology for renewable energy systems and energy efficiency. The effectiveness of all renewable energy technologies that supply heat can be improved by improving the effectiveness of thermal storage. Thermal energy storage is essential particularly for solar thermal systems. To reach high solar fractions, it is necessary to store heat efficiently for longer periods of time. Until now, no cost-effective compact storage technologies are available to do this. For high solar fraction systems, hot water stores are expensive and require very large volumes of space. Alternative storage technologies, such as phase change materials (PCMs) and thermochemical materials (TCMs) are available on a laboratory scale. It is well known that materials are the main bottleneck for finding effective solutions for compact thermal energy storage, and that there is a need for new storage materials with a higher specific energy storage density and lower material cost.

Thermally stable mesoporous adsorbents can be used as storage materials mostly in combination with water as working fluid for application in adsorption heat pumps and thermo-chemical heat storage.¹ Mesoporous disordered silicas (silica gels) are widely studied as hydrophilic compounds due to the high affinity to water vapour, large water sorption capacity at low humidity and moderate temperatures for solar thermal energy exploitation regeneration (~ 150°C).² The advantage of mesoporous silica gels is their low charging temperature. Thus, these materials can be used for storage of low temperature heat (e.g. solar energy) and industrial waste heat.¹

The preparation of the composite (two-component) materials by combining the advantages of hygroscopic salts (halides, sulphates and nitrates of alkali and alkali-earth metals) with those of the pure porous materials (matrix) is another strategy to improve sorption capacity. Different matrices are used, mostly disordered porous silicas, ordered mesoporous silica, alumina and natural clays. The matrix absorbs water and serves as a dispersion medium, which forms a required salt particle size and high salt surface area. In addition this affects the state and properties of the salt, and conducts heat through the solid. Usually the porous matrix has lower water sorption capacity than the hygroscopic salts, which have an active role and interact with water to increase the sorption capacity.³

A study of water sorption properties of the composites revealed that the formation of salt hydrates in the dispersed state happened at a lower relative pressure of water vapour with respect to the bulk state. This makes the salts dispersed within mesoporous matrix much more efficient than a common bulk salt. The main disadvantage of the composite sorbents is the corrosion and leakage of the hygroscopic salt from the mesopores, resulting in a degradation of the adsorption properties.⁴

In this work, we present the study of the sorption properties of new water composite sorbent, consisting of iron silicate with disordered mesopores as the matrix and CaCl_2 as salt hydrate for low-temperature heat storage application.

EXPERIMENTAL

FeKIL2 with a molar ratio of Si/Fe 80 has been prepared by the modified two-step synthesis.⁵ The composite was prepared by wet impregnation of the initial FeKIL2 with 2.1 M aqueous solution of calcium chloride.⁶

Thermogravimetric investigation was performed with a SDT 2960 Thermal Analyzer. Prior to the TG measurement, samples were stored in a desiccator over saturated ammonium chloride solution for 7 days.

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). The experimental setup and the corresponding error analysis are described in detail elsewhere⁷. The chosen operating conditions were the following: a maximal desorption temperature of 150 °C and a minimal adsorption temperature of 40 °C or 20 °C for water vapour pressures of 5.6 kPa and 1.2 kPa, respectively. To evaluate the hydrothermal stability of the materials, the samples have been exposed to a short-cycle hydrothermal treatment consisting of 20 cycles between temperatures of 150 °C and 40 °C at a water vapour pressure of 5.6 kPa. The water uptake for each cycle between 150 °C and 40 °C has been determined as a first benchmark.

RESULTS AND DISCUSSION

For a first estimation of the water capacity⁸ for the mesoporous FeKIL2 and the composite, the samples were stored in high humidity atmosphere (75% at 25 °C) and subsequently subjected to TG analysis (not shown). Water is desorbed up to 120°C due to physically bonded water molecules in the mesostructure. DTG curves evidence one adsorption site for water molecules for both samples, probably in the mesopores. The water loss up to 150°C for FeKIL2 is 18.8%, while the composite shows a loss of 42.2%. The water capacity, determined by dividing the weight loss due to water desorption with the weight of the sorbent⁸ at 150°C as the reference mass, is 0.23 g/g for the matrix and 0.73 g/g for the composite. Out of these non-equilibrium measurements it can be concluded that the presence of CaCl_2 in the composite increase the amount of water in the sorbent.

As the above mentioned measurements only give a first estimation on the possible water capacity, detailed equilibrium measurements under defined humidity conditions were performed. The water sorption uptake curves of the FeKIL2 matrix and the composite in Figure 1 show typical characteristics of the mesoporous hydrophilic adsorbents. The adsorption isobars at 1.2 and 5.6 kPa, respectively, show a nearly linear uptake up to a relative pressure of 0.5, with an increase at higher relative pressure. The water sorption capacity of the composite is improved due to the presence of CaCl_2 , which interacts with water³. The composite shows a maximum water uptake of 0.58 g/g under the given conditions. The difference to the above given maximum uptake is probably due to slow adsorption dynamics

and therefore non-equilibrium, although isothermal hold time for the last adsorption point was more than 10 h in the TG-DSC measurement. The matrix shows an uptake of 0.21 g/g, which is in good agreement to the results of TG measurements.

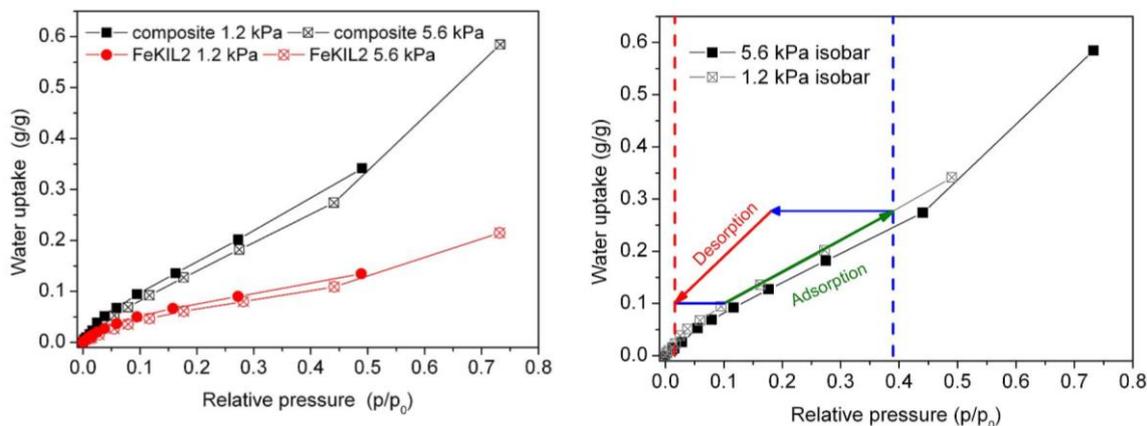


Figure 1: (left): Water sorption isobars at 1.2 and 5.6 kPa, displayed versus the relative pressure thus giving an isothermal representation of mesoporous FeKIL2 and the composite CaCl₂-FeKIL2 and (right): Thermodynamic cycle of the composite CaCl₂-FeKIL2. The maximum working range of a typical sorption heat storage cycle is indicated by perpendicular lines.

With regard to a sorption heat storage application the important property is the possible loading lift within the thermodynamic cycle. Depending on the boundary conditions, a possible loading lift for the composite is approximately 0.20 g/g as illustrated in Figure 1. Here, the working conditions are a maximum desorption temperature of 150 °C at 5.6 kPa condenser pressures and a very low minimum adsorption temperature of 25 °C at 1.2 kPa evaporator pressures. These are typical temperatures for heat transformation application, as e.g. 5.6 kPa condenser pressures corresponds to a condensing temperature of 35 °C. This temperature can either be reached for heat rejection devices in summer or for direct heating in winter. The evaporator pressure of 1.2 kPa corresponds to an evaporation temperature of 10 °C, which is either a good value for low temperature heat source in winter or a good value for a cooling application in summer. It has to be mentioned, that the minimum adsorption temperature of 25 °C is slightly too low for direct heating purposes, however, this marks a maximum working windows. The heat of adsorption for the high energy sites has been determined to be 55.2 kJ/mol, whereas the major part of the adsorption takes place with a heat of adsorption of 50.4 kJ/mol, which is approx. 8% higher than the evaporation enthalpy of water and 10% higher than the heat of adsorption of silica gel-CaCl₂ composite, containing 40% of the salt.⁹ Therefore, the heat storage capacity under the above given conditions can roughly be estimated to 560 kJ/kg for the composite material.

Beside the loading lift within the cycle and the possible heat of adsorption, the repeated hydrothermal stability is the third important value with regard to a cyclic adsorption process for heat storage applications.¹⁰ Although the leakage of the salt is mentioned as a possible problem⁴, the repeated hydrothermal treatment was, to the best of our knowledge, not performed so far on comparable composites.

To evaluate the hydrothermal stability of the composite, the sample has been exposed to a short-cycle hydrothermal treatment consisting of 20 cycles between temperatures of 150 °C and 40 °C at a water vapour pressure of 5.6 kPa. In the following step, the water uptake for each cycle between 150 °C and 40 °C has been determined as a first benchmark. Only a small loss of water uptake capacity in FeKIL2 (0.6%) and in the composite (3.6%) is observed, which confirms the comparatively good initial hydrothermal stability of FeKIL2 and the composite under the operating conditions. However, the composite shows a continuous,

nearly linear degradation, which may result in a significant decrease of the capacity after hundreds of cycles.

No leaching of CaCl₂ was directly observed after the cycling test, as it is usually observed for these materials⁴. It can be concluded that the FeKIL2 matrix can prevent the first stage CaCl₂ leaching from the mesopores of the matrix. The composite CaCl₂-FeKIL2 shows a promising hydrothermal stability for the first 20 cycles between temperatures of 150 °C and 40 °C at water vapour pressure of 5.6 kPa.

CONCLUSION

New composite CaCl₂-FeKIL2 is the material with potential applications as water sorbent for thermo-chemical heat storage. The introduction of CaCl₂ in the FeKIL2 matrix improves the maximal water sorption capacity for approximately 3 times, which makes the composite a potential water sorbent material for low temperature heat storage. Desorption of water from the composite can be achieved at 120 °C. The repeated hydrothermal stability of CaCl₂-FeKIL2 is evaluated for the first time showing that this two-component sorbent is comparatively good hydrothermally stable after 20 cycles between temperatures of 150°C and 40°C at water vapour pressure of 5.6 kPa.

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