DESIGN OF WATER SORBENTS FOR ENERGY STORAGE AND TRANSFORMATION

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ABSTRACT

Great current progress in the material science offers novel sorbents which may be promising for storage and transformation of low temperature heat. This paper gives an overview of recent achievements in these fields at National Institute of Chemistry Slovenia. Design of efficient storage sorption materials with advanced properties is motivated by two driving forces: to increase of the water sorption capacity and to regenerate the sorbent at low temperature (up to 150^{o}C). Developments on two-component silica-based materials and aluminophosphates will be highlighted.

Keywords: inorganic sorbents, water sorption capacity, heat transformation, heat storage

INTRODUCTION

Thermal energy storage (TES) is becoming a crucial technology in enabling more efficient use of renewable energy and contributing to the reduction of our dependency on fossil fuels. Recent research activities are focused on the development of new generation for heat storage systems that would enable efficient utilization of low-temperature solar energy or waste heat for heating and cooling applications. Sensible heat storage (water tanks) which is currently available suffers from severe heat losses and low energy storage density. Another two new storage concepts appeared; latent heat storage (LHS), which uses the phase change enthalpy of phase-change materials (PCM) for storage, and thermochemical heat storage (TCS), which utilise the reversible chemical and physical sorption of gases, mostly water vapor, in solids. This technology has the potential to store ten times more heat energy per mass or volume than LHS technologies.

Thermally stable porous adsorbents can be used as storage materials for application in thermo-chemical heat storage and heat transformation such as heat pumps or thermally driven adsorption chillers, where the main principle is based on the consecutive adsorption and desorption processes. During the last decade a lot of attention has been devoted to the synthesis of inorganic porous water sorbents due to the needs of materials with high sorption capacity and low charging temperature.

A large number of sorbents are currently considered for sorption thermal energy storage, traditional such as silica gels and zeolites, and innovative like aluminophosphates, MOFs and composites. The most versatile class of sorbents for thermal energy storage are two-components or composites, which have been prepared for the enhancement of thermo-physical properties of sorption materials, like 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). These sorbents have the advantage to tailor sorption capacity by varying content of salt and porous structure. Further advantages are a low desorption temperature, a low price and a simple production method. Highly hydrophilic zeolites with water vapour systems have been one of the most studied and tested adsorbent/adsorbate pairs. The main shortcoming of zeolites is their high charging temperature (up to 250°C). Several attempts to adapt adsorption performance of zeolites to the characteristics of adsorption chillers and heat pumps have been done. Modification of zeolites by ion exchange (with magnesium cations) increase water sorption capacity, while steaming[1] treatments reduce it. Manufacturing of granulated binder-free zeolites (A, X and Y) have been enabled increasing the water sorption capacity of these materials, for example 14% for zeolite A[1] and 16% for zeolite X[1], but charging temperature has still remained high. Recently new opportunity such as the functionalization of zeolites with organosilanes resulted in the increase of hydrophobicity and preservation of maximum water capacity.[2] In the last decade, new adsorption materials have been succesfully proposed, namely microporous aluminophosphates[3,4] have revealed their advantages over zeolites concerning low charging temperature due to low hydrophilic character, high water capacity and high adsorption/desorption enthalpy. Recently, it has been shown that the adsorbents which adsorption equilibrium with working fluid is characterized by s-shaped adsorption isotherms are advantageous for the heat pumps and chillers. For most applications the steep increase in the adsorption should take place in a relative pressure range of 0.05–0.3.[2] MOFs - another material class possesses very large water sorption capacity and heat storage capacity, s-shaped adsorption isotherms and require low charching temperature. Their key drawback is too low temperature lift.

This paper addresses the overview of the design of efficient water sorption materials, which properties match well the working conditions of heat storage and transformation applications, in the last few years.

RESULTS AND DISCUSSION

Some brief descriptions on the investigations on water sorbent composite materials for low temperature heat storage are presented. A two-component (composite) water sorbent $CaCl_2$-FeKIL2 has been developed for sorption-based solar thermal energy storage.[5] The matrix of the composite is FeKIL2 material with disordered mesopores, high surface area of 712 m2/g and mesopore dimensions between 4 and 29 nm. The mesopores of FeKIL2 matrix were formed by the aggregation of iron silicate nanoparticles, which create the network with interparticle voids. Pure silica KIL2 material showed high hydrophobic character, thus iron was introduced in the mesoporous structure during synthesis in order to create additional adsorption sites. The result of the maxilamal water uptake confirmed our prediction, namely water uptake was increase for 3 times. The composite, prepared by wet impregnation of FeKIL2 with $CaCl_2$, has lower surface area and similar mesopore dimensions as the matrix. The maximum water sorption capacity of FeKIL2 is 0.21 g/g, while the composite possesses 3 times higher maximal water sorption capacity due to the presence of the salt in the matrix, 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. Heat of adsorption of the composite is 50.4 kJ/mol, which is approx. 8% higher than the evaporation enthalpy of wáter. 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 8.5. 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. Therefore, the heat storage capacity under the above given conditions can roughly be estimated to 560 kJ/kg of the composite material. 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. Next water composite sorbents contain ordered mesoporous silica (SBA-15) matrix and different contents of $CaCl_2$ (4 wt.%, 10 wt.%, 20 wt.%). The maximal water capacities increased with higher contents of $CaCl_2$. The shifts of the water isotherms to lower relative pressure for higher amounts of $CaCl_2$ were achieved, successfully. Hydrothermal stability of the composites was tested over 20 cycles between 40°C and 140°C and a relative humidity of 76%. The lowest loss of water uptake (1.2%) after 20 cycles showed the composite containing 20 wt% of $CaCl_2$, indicating on the best heat storage performance. Temperature of regeneration of these composites was in the range from 120 to 140°C depending on the amount of the salt in the composite.

Among aluminophosphates two materials were prepared and evaluated as the most promising aluminophosphate water adsorbents for heat transformation applications regarding theirs high water uptakes, hydrothermal stabilities and energy capacities. First microporous aluminophosphate (APO-Tric)[3] shows maximal water loadings of up to 35 wt%, the energy density in the working temperature range from 40 to 140°C of 472 kWh/m^3, its hydrothermal and thermal stability (up to 900°C) and low desorption temperature at 95 °C. The main disadvantage of this material is its low thermal conductivity (~ 0.1 W/m/K). To improve it, carbon coatings on aluminophosphate were prepared.[6] The main condition for the preparation of carbon coatings on aluminophosphate is its thermal and structural stability up to 700°C, because they are usually prepared by high-temperature treatment (500-700°C). As carbon precursors, sucrose and citric acid were used. The aluminophosphate sorption material was coated with a thin layer of carbon (APO/C) by wet impregnation and dry procedure, followed by carbonization at 650°C under inert atmosphere in the furnace. The results of structure analysis showed that the preparation methods of APO/C materials had great influence on the preservation of structure and its structural properties. The amount of carbon in the composites was dependent on the type of the used carbon precursors and on method of the preparation and it was determined to be from 1.1 to 2.4%. Water sorption capacity showed that composites had similar water uptakes, while determined heats of adsorption were lower for composite materials. Thermal conductivity of the composites containing 1.1% of carbon increased for 11%. Another strategy for the improvement of thermal conductivity was the preparation of the same aluminophosphate as a coating on steinless steel plate. The thicknesses of the coatings were determined to be from 100 to 180 μm. Water sorption capacity and hydrothermal stability (cycling) was determined. The coated plate shows similar shape of the adsorption curve as the powder material, with a steep rising of the uptake between 0.1 and 0.2 relative pressures. The water uptake is lowered after 4600 cycles, due to the binder content in the coating.

Next excellent aluminophosphate water adsorbent[4] is an aluminophosphate with LTA topology (like zeolite 4A). Up to now this material shows the highest water sorption capacity (45 wt%) among aluminophosphates, low desorption temperature, s-shaped adsorption isotherm in very narrow relative pressure range, high temperature lift (30°C) and the highest energy capacity of 527 kWh/m^3. It shows also remarkable cycling stability.

CONCLUSION

New adsorbents are a prerequisite for major breakthrough in the field of adsorption heat storage and transformation. Two classes of water adsorbents such as composites and aluminophosphates prepared at National Institute of Chemistry Slovenia for low temperature heat storage and transformation applications have been presented.

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