

MICROPOROUS ADSORBENTS FOR HEAT AND HYDROGEN STORAGE APPLICATIONS

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ABSTRACT

The commitment of EU states to achieving 20% share of renewable energies in Europe's final energy consumption by 2020 has maximized research activities in solar energy utilization in Europe and world-wide. At the same time, hydrogen is a proposed system for delivering energy in the future. However, the storage of solar heat and hydrogen is still a technological challenge that hinders their large-scale utilization. Microporous adsorbents are currently the most promising candidates for storage applications, mainly because of the possibility for a precise tuning of their atomic structure. This paper focuses on the latest approaches in synthesis and structure characterization of microporous aluminophosphates and metal-organic framework structures for sorption-based storage applications.

Keywords: microporous materials; adsorbents; gas storage; hydrogen storage; heat storage

INTRODUCTION

Heating and cooling account for almost half of the European final energy demand in industry and households. Large-scale utilization of solar thermal energy in buildings for heating and cooling applications would have a huge impact on the world energy supply, but the development of full potential of these applications is not possible without effective thermal energy storage systems that would provide an optimum tuning between energy delivery and request. In the last few years, utilization of the reversible chemical and physical sorption of water on solids has become a subject of great interest, since it provided a new storage concept with a potential for loss-free long-term (seasonal) storage of high power density, which would be much more effective than conventional condensing boiler heating systems. However, up to now there is no mature long term sorption heat storage system yet, because no storage material that would ensure high enough energy densities (energy stored per unit volume) at water desorption temperatures below 140 °C (that would coincide with a reasonable temperature reached by solar thermal collectors, e.g. evacuated tube collectors) as been proposed so far [1-2].

Hydrogen technologies are facing similar problems. Hydrogen has very low density at normal conditions and its storage requires too large and too heavy containers. Compressed hydrogen at pressures up to 800 bar represents a safety risk and requires tough and non-permeable materials. Liquefaction of hydrogen at cryogenic temperatures (-253°C) is technologically very demanding and very expensive. Hydrogen storage in solid materials based on adsorption of molecular hydrogen on high-surface-area porous materials or chemical bonding of atomic hydrogen in covalent and ionic compounds. For economically acceptable hydrogen storage, material should sorbs minimum 9 wt. % or 81 kg/m³ of hydrogen in a few minutes at moderate temperatures and pressures. However, there are no materials available at the moment that could fulfill all the requisite goals [3-5].

Recent sorption studies of some known and new microporous materials, which has traditionally been used in gas drying and purification, revealed their great and so far unexploited potential also in storage applications [6-8]. The microporous aluminophosphates

(APO) with incorporated silicon (SAPO) at framework sites (e.g. SAPO-34) and mesoporous silicates impregnated with hygroscopic inorganic salts (e.g. $\text{CaCl}_2/\text{SBA-15}$) showed high energy densities up to 150 kWh/m^3 at temperatures around 100°C , which is close to the required values for heat storage applications. However, dislodgement of silicon from the framework sites, structure degradation (quite common after a few water desorption/sorption cycles), corrosion and leakage of salt solution from mesopores of silicates decrease their storage potential. For hydrogen storage, porous metal-organic framework materials (MOF) are the most promising materials. So far, up to 10 wt. % or 53 kg/m^3 of hydrogen can be stored in MOF, which is related to their large surface areas up to $6000 \text{ m}^2/\text{g}$ and low densities $< 1 \text{ g/cm}^3$ [9]. The sorption process is quick and reversible, which is crucial for on-board (transport) applications. The main disadvantage is that the process requires unfavorable p, T conditions (low temperature and pressure), which are caused by weak van der Waals interactions among hydrogen molecule and solid surface.

In the present paper we report on the strategies that have been applied recently to enhance the storage capacities of microporous materials for heat storage and hydrogen storage applications.

MICROPOROUS ADSORBENTS FOR HEAT STORAGE

The adsorption of water vapor on the surface of a solid adsorbent like microporous zeolite or aluminophosphate is an exothermal process that provides the heat released or “discharged” from the storage (Figure 1). Preventing the discharge simply requires to keep the dry solid adsorbent and the adsorbing fluid, called adsorptive, in separate closed vessels. Charging of material is performed with a reverse endothermic process of desorption using, for example, solar or waste heat.

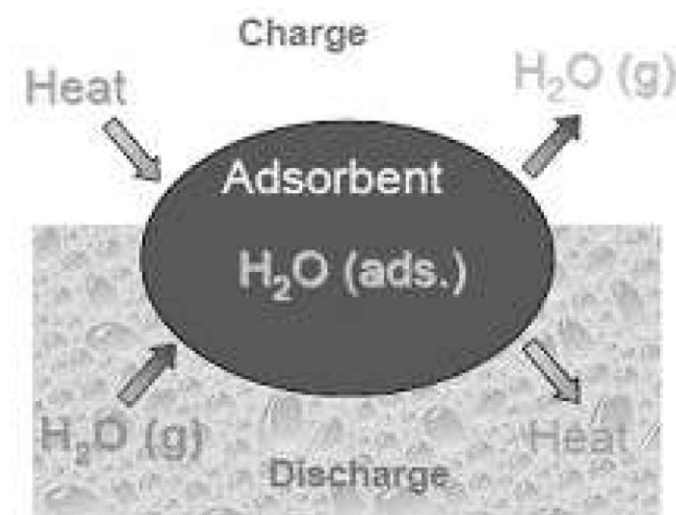


Figure 1: Adsorption process of water vapor on solid accompanied with the heat release/consumption.

Most technical adsorbents available today have been optimized for applications very different from heat transformation, primarily for gas separation and catalytic processes in the chemical industry and therefore the energy densities realized in the demonstration units were lower than expected. The materials have to be optimized for the long-term heat storage system following the criteria below:

- High storage density ($>250 \text{ kWh/m}^3$) defined by heats of adsorption; the long term aim is to arrive at thermal storage systems that are 8 times more compact than a thermal storage system using hot water (with storage density of 53 kWh/m^3);
- Regeneration (charging) temperature as low as possible (desorption of water below 140°C) to follow the solar collector operating temperatures;
- Good thermal and chemical stability under operating conditions (T, p) for many cycles of adsorption/desorption;
- Moderate operating pressure range ($\sim 5.6 \text{ kPa}$), i.e. no excessive pressure conditions and no high vacuum;
- Adequate kinetics of the absorption-desorption stages in order to match the heat supply-demand (operating conditions);
- Environmental safety, non-toxicity, low global warming potential, non-corrosiveness of materials;
- Low- to moderate-cost of materials production.

Our investigations of suitable storage materials with the above properties were directed to known and novel aluminophosphates (APO) and porous metal-carboxylates (Figure 2). The research has focused on materials with high water sorption capacity at relative pressures between 0.1 and 0.5 and with suitable sorption enthalpy. According to the literature data [10] and our recent results we concluded that proper approach could be preparation of slightly hydrophobic structures with large surface areas and small to medium sized pores (up to 0.7 nm) (e.g. Figure 2, left) or with large but properly shaped pores that would allow an appropriate arrangement of water molecules (Figure 2, right).

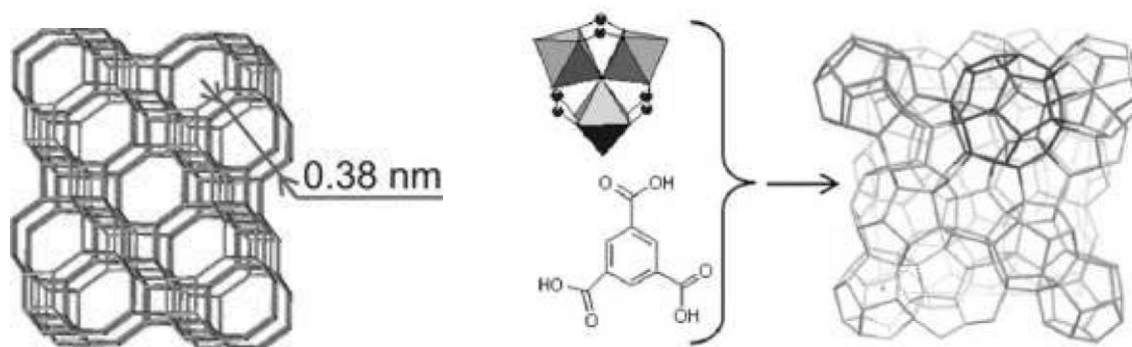


Figure 2: Structure of small pore APO (left) and metal-carboxylate with large pores from 1 to 2 nm (right).

Additional point to consider was chemical composition of the material. In aluminophosphates (APO) the number of defect sites (Al-OH, P-OH) on the framework and the reversible changes in Al structure during water sorption (4- to 5- and 6-coordinated Al) control the adsorption mechanism. APOs show water loading uptakes up to 381 g/kg within a narrow relative pressure range (Figure 3, left). In silicoaluminophosphates (SAPO) the presence of Si at the framework sites increase hydrophilicity of the material, which results in a gradual water uptake starting already at very low relative pressures [6, 10]. The broad relative pressure range of the water uptake in SAPOs is a significant drawback of the material in storage

applications, because the system needs to respond quickly to the temperature and pressure changes during sorption/desorption. We concluded that aluminophosphates (APO) with Al that can change coordination during hydration/dehydration and sorb in a narrow relative pressure range with a steep isotherm (Type V) are very perspective inorganic materials for heat storage. Our investigations of MOFs for heat storage applications were focused on the structures that poses properly distributed and accessible metal sites in the framework or outside the framework. The water uptake measurement for porous iron-carboxylate (Figure 3, right) revealed excellent water loading capacity, but within a broad p/p_0 range. The present hysteresis loop is also unfavorable for the application. However, the overall performance for water uptake between p/p_0 of 0.1 and 0.5 is approximately 0.37 g/g, which is still a great result. The study of reversible water sorption revealed hydrothermal stability of APO material an operating temperatures and operating pressures for more than 50 cycles and for at least 10 cycles for MOF material.

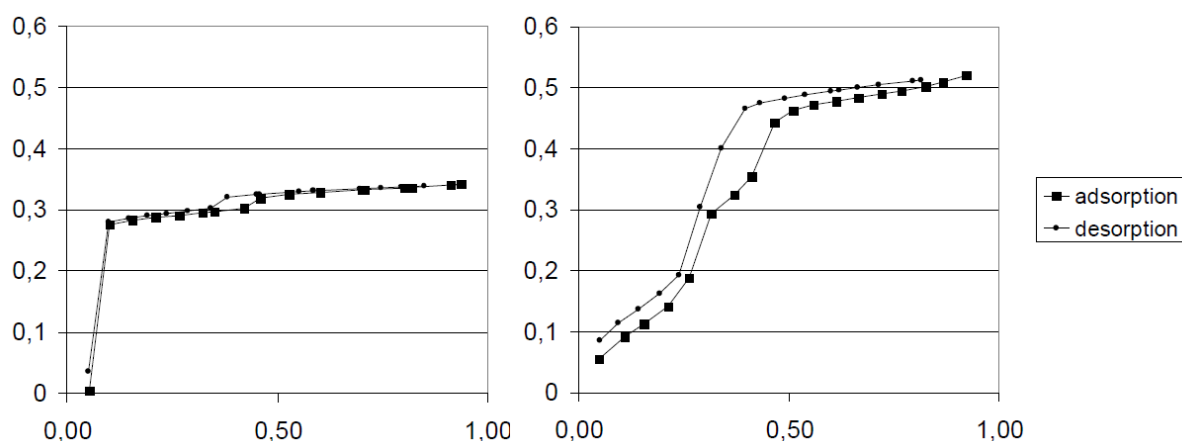


Figure 3: Water adsorption isotherm obtained by the volumetric method (Autosorb Station 1, 293 K) for medium-sized aluminophosphate (left) and iron-carboxylate (right) showing dependence of water loading (g of water/g of material) of relative pressure change (p/p_0) measured.

MICROPOROUS ADSORBENTS FOR HYDROGEN STORAGE

According to DOE ((Department Of Energy) 2015 targets [5], materials for on-board hydrogen storage applications should meet the following criteria:

- Minimum 9 wt. % and 81 kg/m³ of stored hydrogen;
- Store 5 kg of hydrogen in maximum 2.5 minutes for transport applications;
- At temperatures from -40 to 85°C;
- At pressures from 3 to 100 bar;
- Structural and mechanical stability must not change during at least 1500 cycles of sorption/desorption;
- Environmental safety, non-toxicity, low global warming potential, non-corrosiveness of materials;
- Low- to moderate-cost of materials production.

Figure 4 shows the potential of different solid materials that have been intensively studied in the recent years for hydrogen storage applications. The drawbacks of metal and covalent hydrides, which covalently bond hydrogen atom, are low structure stability in cycling processes, extremely slow sorption/desorption of hydrogen and high desorption temperature. The storage of hydrogen in porous solids is based on weak van der Waals interactions of hydrogen molecules with the surface of the materials. Majority of known porous materials, including zeolites and carbon sorbents, have very low storage capacity. At the moment MOFs seem to be the best candidates to meet the required criteria.

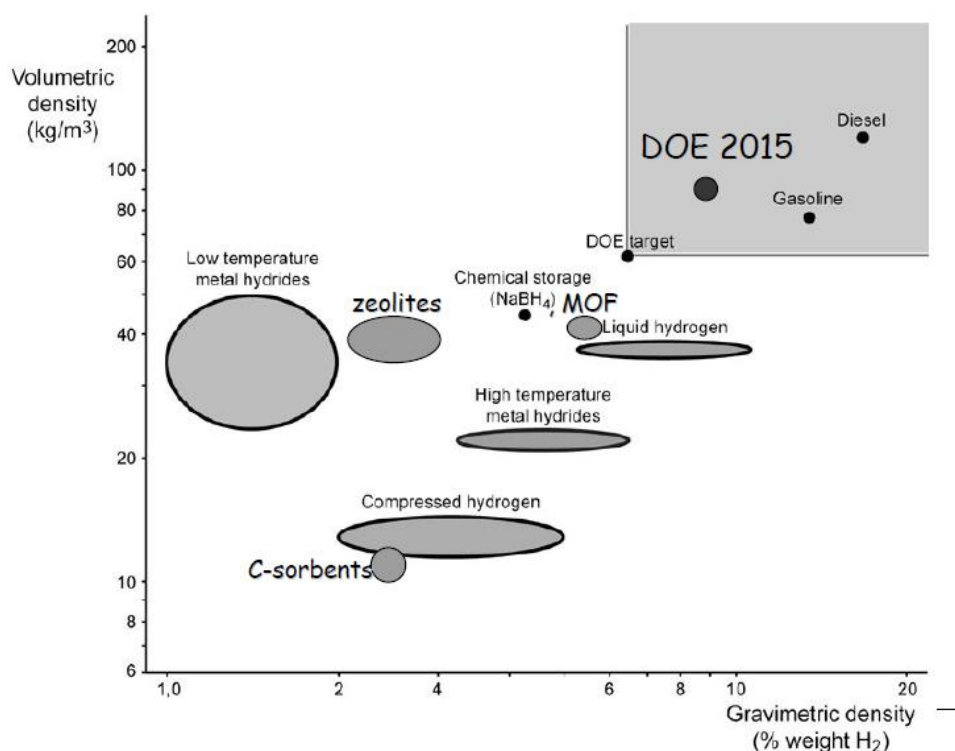


Figure 4: The potential of different solid-state systems for hydrogen storage. The MOFs and liquid hydrogen storage performances are the closest to DOE 2015 targets in terms of storage capacity. Taking into account also the kinetics, thermodynamics, safety and other issues, MOFs are materials of choice.

The strategies for the synthesis of new MOFs with desired properties are concentrated on achieving high sorption capacity with significantly improved H₂-MOF surface interactions to enable effective storage also at moderate temperatures. The procedures are [13-15]:

- Optimized chemical composition and suitable pore size for better interactions with hydrogen (up to 15 kJ/mol), which concentrates on the control of the type, number, distribution and accessibility of metal sites in the frameworks, since coordinatively unsaturated metal sites in MOF frameworks represent primary sites for hydrogen loading (Figure 5). Suitable (and cheap) reactants are functionalized aromatic di- and tri-carboxylates and inorganic salts of Mg, Ca, Fe and Ti;
- Structures with high surface area for high storage capacity;
- Stable crystalline structure that would assure materials homogeneity;

- Post-synthetic modification of prepared structures with metals (Ni, Mg) to ensure additional metal sites for hydrogen bonding.

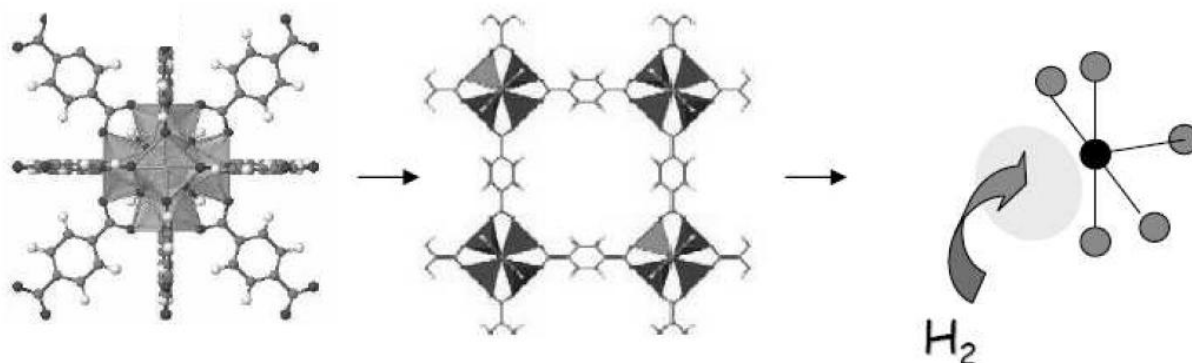


Figure 5. The finely distributed and coordinatively unsaturated metal sites are suitable sites for hydrogen uptake since they provide the strongest hydrogen-framework interactions.

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