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Material Selection for Adsorption Heat Storage Systems

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Abstract: Several materials were tested for their suitability as an adsorption heat storage medium. The main objective of the research was to test their adsorption properties in combination with water. The main observed properties were adsorption uptake, relative pressure of the adsorption and adsorption energy. The examined materials were selected from the groups of mesoporous silica nanoparticles (MSNs) and zeolites. From the observed materials the MSNs materials are showing the highest adsorption uptake up to 0.8 g/g of water which is due to their higher pore volume. However, most of the adsorption is occurring through the capillary condensation and the adsorption energy is then roughly equal to the water latent condensation energy which is about 41 kJ/mol. The zeolites are showing much higher adsorption energies but are greatly limited by the adsorbed amounts.

Keywords: Zeolite; Mesoporous Silica Nanoparticles; Adsorption; Water; Heat Storage

1. INTRODUCTION

The continuing research effort on the nanostructured materials led to several discoveries in the field of artificial highly organized materials such as zeolites, mesoporous silica nanoparticles (MSNs), metal-organic frameworks (MOFs) and some other materials with high surface area such as silica gel and activated carbon. Among these materials the MSNs are particularly intriguing thanks to their variability and high thermal and hydrothermal stability[1]. The MSNs can be tailored to have any size of pores, though the most typical are sizes around 2-20 nm[2]. The most basic manufacturing process of the MSNs is built on liquid-crystal topology of surfactants with self-assembly and self-organization as shown in Fig. 1. This process has been described and modified by many authors and can provide us with great variability in the form of pore size, shape and particle morphology[3].

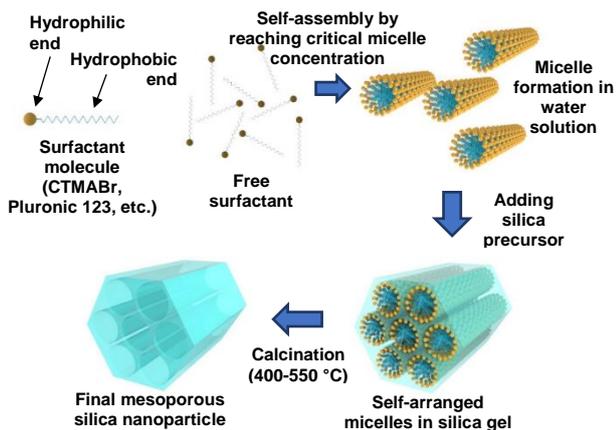


Fig. 1. Preparation of mesoporous silica nanoparticles

To store the energy in porous materials an adsorption process is utilized. Depending on the material, we can talk about two processes: physisorption and chemisorption. The energy storing in clean porous materials is governed by the process of physisorption, where the adsorbate (in our case water vapor) is adsorbed

on the surface of the material which is accompanied by energy release.

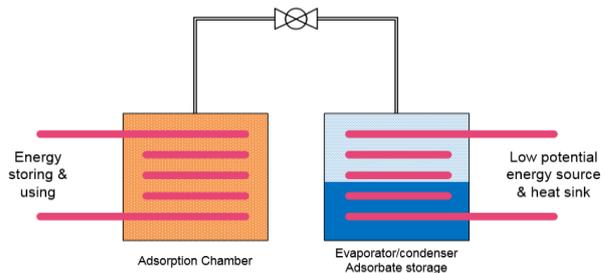


Fig. 2. Simplified schema of adsorption heat storage

The amount of released energy is generally decided by the interaction forces between the adsorbent and adsorbate (storage medium and water vapor) and partially by pore size. Therefore, materials with higher affinity towards water (hydrophilic) will yield more energy. The adsorption heat storage system works in two regimes governed by respective physical processes. In the first one, governed by adsorption, the energy is released and in the second one the energy is stored in form of surface-deficiency potential by desorption of the adsorbate from it. Simplified schema of such energy storing device is shown in Fig. 2.

At the present the main research activities are focused on study of new materials and development of a storage medium[4]. In this work are analyzed materials from the group of mesoporous silica nanoparticles and aluminophosphate zeolites.

2. EXPERIMENTAL

2.1 Materials

The basic characteristics of the observed materials are summarized in Table 1. The first apparent difference between the selected groups is the pore size. While the MSN-x (x = numerical designation of the sample) materials with their pore size belong to the group of mesoporous materials the zeolite with their set crystalline structure and much smaller pore size are typical microporous materials' representatives. The difference is

also visible in the case of particle size as shown in Fig. 3.

Table 1. Basic properties of selected samples[5]

Sample	Pore size ^a (\varnothing nm)	Pore volume ^b ($\text{cm}^3 \cdot \text{g}^{-1}$)	Surface area ^c ($\text{m}^2 \cdot \text{g}^{-1}$)	Bulk density ^d ($\text{g} \cdot \text{cm}^{-3}$)
MSN-1	1.7	0.357	833.2	0.274
MSN-2	2.3	0.465	722.5	0.169
MSN-3	2.7	0.651	825.1	0.200
MSN-4	3.6	0.807	809.6	0.175
Z01	0.73	0.085	191.3	0.512
Z02	0.38	0.279	695.4	0.675
Z05	0.73	0.101	244.5	0.690

^aDFT model – according to pore vol. distribution, ^bNitrogen absolute adsorbed volume, ^cBET multipoint model, ^dConsolidation force of $\sim 523 \text{ N} \cdot \text{m}^{-2}$

The particle cells of the MSN-x materials have typically around 200 nm in diameter and have spherical shape. These cells also have the tendency to aggregate into bigger clusters. The crystals of the Z0x aluminophosphate zeolites have much wider variety of sizes with a typical size in the lower units of micrometers (1-5 μm).

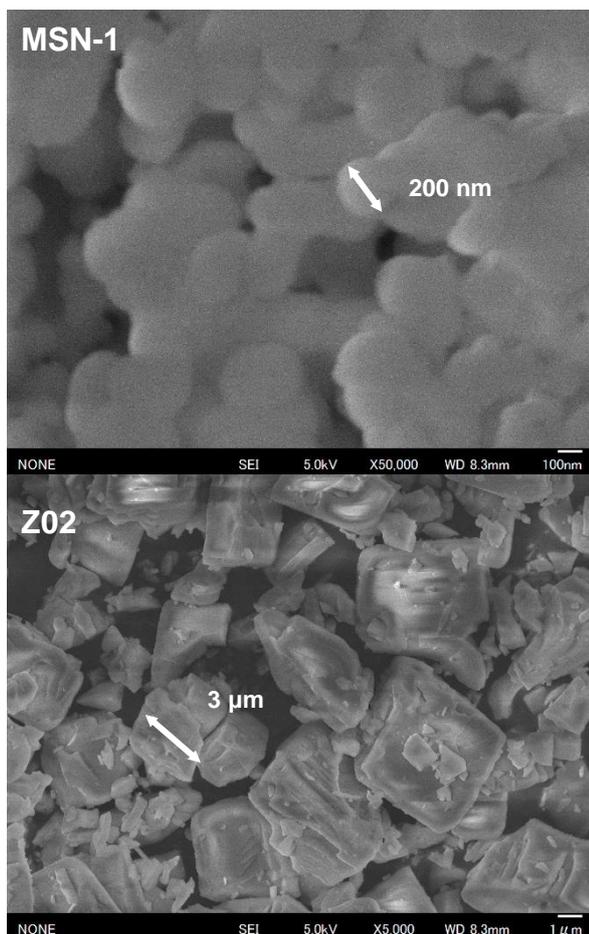


Fig. 3. SEM images of the MSN-1 mesoporous silica nanoparticles and the Z02 zeolite crystals

2.2 Methods and equipment

The adsorption isotherms were measured on the 3Flex instrument from Micromeritics. Prior to the measurement the samples were degassed at 200 °C in vacuum for 5 hours to measure the weight of the dry samples and after the weighting for another 5 hours at 200 °C to eliminate any residues adsorbed during the weighting. The

preparation of samples was conducted in the same manner for all of the material species.

The SEM images were acquired by JOEL JSM-6700F field emission scanning electron microscope.

3. RESULTS AND DISCUSSION

The materials in this work were originally selected on the prospect of combination with water as an adsorbate and therefore their good affinity towards it. The high adsorption uptakes show that the basic prerequisite has been met and all the selected materials are readily adsorptive for water. The collections of water adsorption isotherms are shown in Fig. 4 for the MSN-x and Z0x material series respectively.

The results on adsorption prove that the materials are highly water adsorptive and can adsorb a significant amount of it. The aluminophosphates generally adsorb less water compared to mesoporous materials due to their microporous inner structure. The bulk density shows much higher density of zeolites despite the similar absolute density of silica and aluminophosphate ($\rho_{\text{silica}} = 2.65 \text{ g/cm}^3$, $\rho_{\text{zeolite}} = 2.566 \text{ g/cm}^3$) which demonstrated the higher content of the material but less free space for the adsorption sites.

However, the adsorption amount is only a part of the evaluation of a successful thermal storage medium. Another important factor is the heat of adsorption and temperature gain expressed as relative pressure of adsorption.

The isosteric heat of adsorption ΔH°_{ad} describes the energy release during the adsorption process and in this work was calculated according to the following equation:

$$\Delta H^{\circ}_{ad} = R \left\{ \frac{[\partial \ln p]}{[\partial \frac{1}{T}]} \right\}_{\theta} \quad (1)$$

where R is the gas constant and $[\partial \ln p]/[\partial \frac{1}{T}]$ are the individual isosteric plots calculated for respective relative pressure and absolute temperature. Because the adsorption is an exothermic process the equation has natural negative results due to the grow of the pressure with the temperature increase, here expressed as an inverse value. The full data on the isosteric heat are presented in the Fig. 6. It is apparent that the energy yields during the adsorption are mostly constant with very little aberrations. That signifies constant adsorption rates and steady conditions.

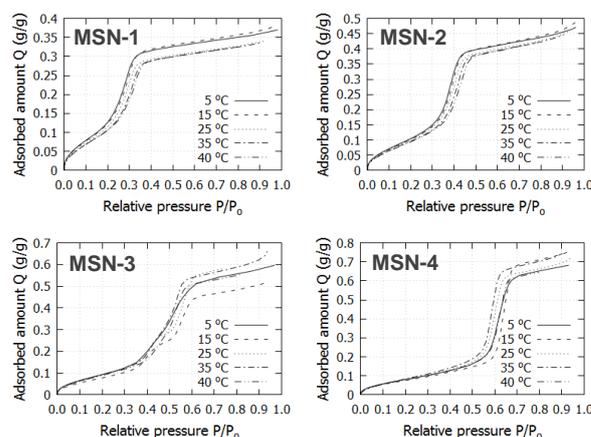


Fig. 4. Water adsorption isotherms on the MSN-x and Z0x materials

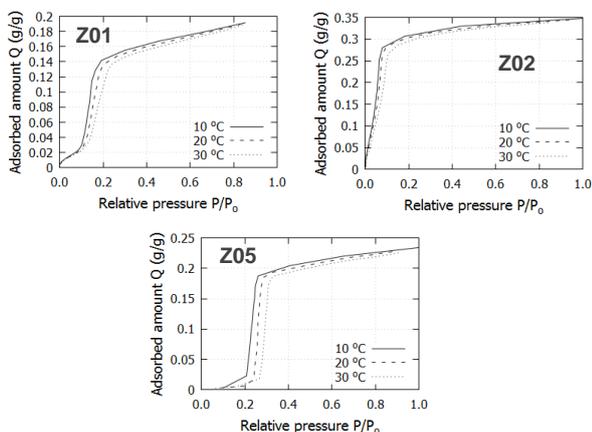


Fig. 4. Water adsorption isotherms on the MSN-x and Z0x materials (continuing)

The disparity between the energy of adsorption and density is clearly visible in Fig. 5. Due to the lower density the adsorption amount and the pore volume is significantly bigger in case of the MSN-x which leads to higher uptake rates for the MSN-x materials. Consequently, that means higher adsorption energy per unit of the storage material. However, if we compare the acquired data further we see that the situation is different if we plot the values by the unit of the source water vapor. In that case the zeolites show higher affinity towards water and higher energy yields. That is also supported by the lower source temperatures which in case of Z02 drops down to 6.4 °C. This temperature is necessary to load 80 % of the full capacity of the material at the target temperature of 40 °C.

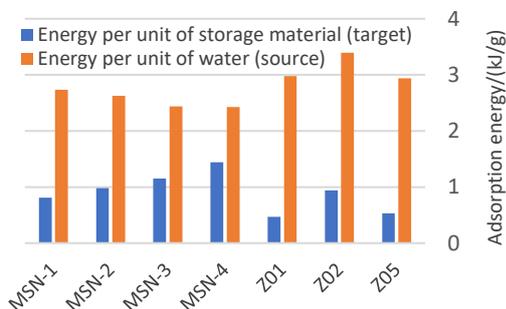


Fig. 5. Adsorption energy of the MSN and Z0 materials in relation to the material and source

The source temperatures are evidently better (lower) in case of aluminophosphates. That means that for using the discharging a source with lower temperature is sufficient. However, the situation for the Z02 is more complicated during the charging process. Because the adsorption occurs at very low relative pressure the desorption (charging) requires even lower pressure or charging higher temperature. That is also another issue with zeolite adsorbents, which require higher desorption temperature typically higher than 150 °C[6]. Compare to that, MSN materials can be charged with temperature as low as 80 °C. However, the setback of the MSN materials for the use as a thermal storage material of small temperature gain remains.

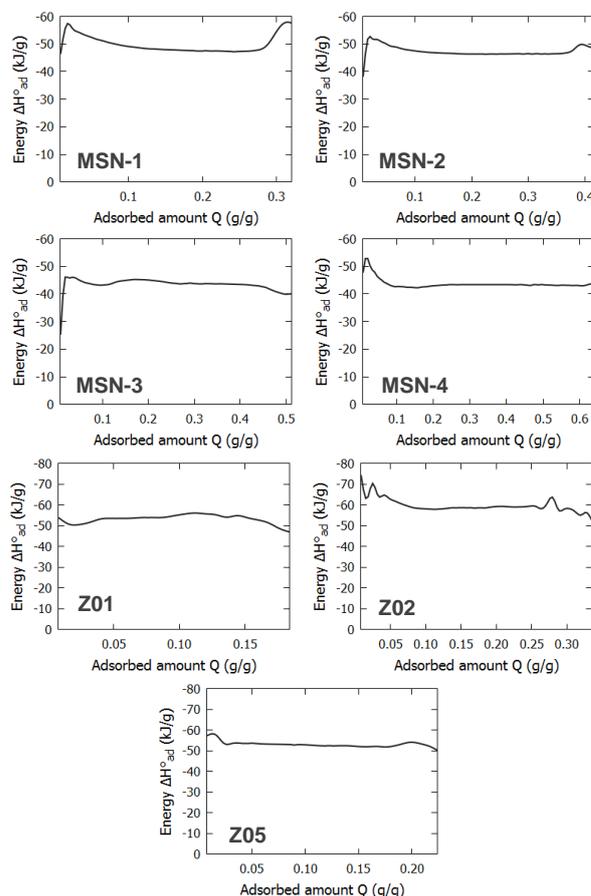


Fig. 6. Change of free energy of adsorption of the zeolite and MSN materials – isosteric heat of adsorption

The data shown in the Table 2 are collection of the main characteristics of the selected materials for the use a thermal energy storage. For practical applications the storage energy density is calculated per kilogram of the storage material only. The actual value per kilogram of the system is directly dependent on the setting of individual system and for obvious reasons it cannot be listed without a full description of such system.

Table 2. Characteristic capabilities of the selected materials as an adsorption thermal storage medium

Sample	Water adsorption capacity ^a (g·g ⁻¹)	Temperature of the vapor source ^b (°C)	Isosteric adsorption energy ^c (kJ·g ⁻¹)	Storage energy density ^d (Wh·kg ⁻¹)
MSN-1	0.36	22.5	0.81	225.0
MSN-2	0.44	26.9	0.98	272.5
MSN-3	0.58	29.5	1.15	320.0
MSN-4	0.85	32.1	1.44	398.6
Z01	0.20	23.8	0.47	130.5
Z02	0.34	6.4	0.94	260.1
Z05	0.23	21.6	0.53	147.2

^aAt 0.95 P/P₀, ^bFor the considered output at 40 °C and 80 % of the capacity, ^cPer weight of the storage material, ^dStorage material only (at 80 % of the capacity)

If we further compare the values of the storage energy density with other materials such as Silica gel[7] or Zeolite 13X[7,8] as shown in Fig. 7 we can see that all the materials signify distinctive improvement in the storage energy densities. The distinguishable rising trend in the MSN-x series is given by the increase in the pore volume. However, the highest amount of MSN-4 does

not necessarily mean the highest suitability as the source temperature is too high for practical operation conditions.

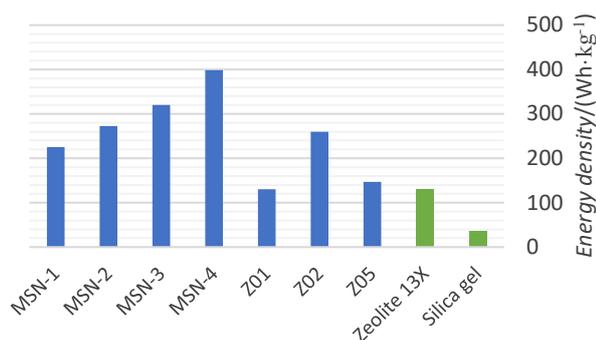


Fig. 7. Storage energy density per material with comparison to zeolite 13X and silica gel

4. CONCLUSION

- Several material samples from the group of mesoporous silica and aluminophosphate zeolites have been tested on adsorption capabilities of water.
- All of the MSN materials exhibit higher adsorption uptakes of water per unit of the material compares to the zeolites
- The MSN materials show higher storage energy densities per unit of the storage material, however, lower adsorption energies per unit of the source adsorbate (water)
- The investigated materials from this work show high potential in the application as the thermal energy storage media.

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