

Conference Proceedings

1st International Conference on Applied Mineralogy & Advanced Materials - AMAM2015

Water vapor adsorption on porous materials for solar cooling applications

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Abstract

Water adsorption capacity of representative and innovative hydrophilic micro-, meso- and macroporous materials was examined as a function of relative humidity. Most of the studied materials showed high rates of water adsorption and the mesoporous were characterized as the more suitable for surface cooling applications

Keywords: Porous materials, Water vapor adsorption, Solar cooling.

1. Introduction

Among the most important challenge nowadays is sustaining and improving urban environmental quality and mitigating major energy and environmental problems of big cities such as microclimate changes with increased temperatures especially during the summer time. Urban areas of more than 5 °C warmer than their surrounding rural areas have been observed in Agrinio, like an “island” of heat surrounded by cooler rural areas (UHI) (Vardoulakis et al., 2013).

The last years, because of the severe consequences of the UHI effect (increase of the electricity generation due to the demand for cooling energy; deterioration of the living environment due to higher pollutants emission; increase of the chemical weathering of building materials; and increase the discomfort and even the mortality rates), there has been an impetus in research aiming in understanding its origin and developing the appropriate

mitigation measures. Roof temperatures of up to 70 °C due to solar radiation during the summer time are a major heat source for the formation of the UHI effect or the urban microclimate change. In order to alleviate the UHI adverse effects, several mitigation measures have been proposed like the reduction of the thermal and pollutants emissions of human origin, the increase of the green spaces in the urban environment, the use of cool materials as construction and roof materials and more specialized designs like those associated with humidification and albedo increase, photovoltaic canopies, super-hydrophilic photocatalyst-coated building surfaces with water film.

Evaporative cooling is among the older technique of cooling and several methods are being studied for direct or indirect evaporative cooling systems. In the last few years, the use of porous materials for the evaporative cooling of building has been started to be studied as an alternative and sustainable way to cool the roof surface of a building or the pavement of outdoor spaces by taking advantage of the properties of porous materials (Karamanis & Vardoulakis, 2012). The principle of evaporation cooling of buildings (either as a stand-alone roof material or as an additive in green roofs or roofs covered by gravel stones) is the same as in the solar heat energy storage; the night or the rainy days are the period of cold and the day of sun irradiation is the period of hot. Stored water or night sorbed moisture are evaporated during the hot day and the porous surface temperature is reduced due to the release of the latent heat. Lower surface temperatures contribute to the reduction of air temperature since the intensity of heat transfer through the cold surface is lower while the heat flow inside the building is reduced. In countries with very hot summers like the Mediterranean countries, reduced surface temperatures lead to the reduction of the cooling load. Complementary, in cases of dry summers with reduced water sources where the use of hydroelectric energy is forbidden, the reduced demand leads to reduced imports and the subsequent associated reduced costs.

The hydrophilicity, rate and capacity of the water vapor adsorption are the primary factors to consider in the selection of the porous materials. A large number of microporous (<2 nm), mesoporous (2-50 nm) and macroporous materials are currently under investigation as water vapor sorbents. Additionally, these materials have attracted much attention for solar cooling applications either passive or adsorption heat pumps and chillers. In passive designs, we have recently shown that porous materials have the ability to adsorb water and thus, they interact with solar irradiation and heat in order to cool the inner space of buildings through the water vapor adsorption-desorption cycle. The purpose of this work is to investigate in detail how pore' size affects the water adsorption capacity and the thermal properties of the materials at the three pores' size range micro (<2 nm), meso (2-50 nm) and macro (>50 nm).

2. Materials & methods

Representative and innovative hydrophilic micro-, meso- and macroporous materials have been purchased or prepared, characterized by several techniques and tested. The materials' characteristics are shown in Table 1. Pore volume was provided by the manufacturer or measured by nitrogen adsorption-desorption isotherms. Water adsorption capacity of the produced materials was examined as a function of relative humidity. Samples were placed in a humidity chamber at predefined relative humidity in the range 10- 93 % and 25 °C. Prior to measurements, samples were dried to constant mass in an air-circulated oven at 150 °C. Then, they were periodically weighed while the moisture content was calculated as the difference of mass measurements in different time periods and the initial dry state.

Table 1. Characteristics of the studied materials.

Material	Type	Pore size (nm)	Pore Volume (cm ³ /g)
4A	Zeolite	4	
13X	Zeolite	13	
Sepiolite	Clay	2 and 25	0.82
Silica gel	Silica	0.3-6	0.40
MESO	MCM-41	6	0.60
Basolite	MOF	2.2	0.35

3. Results & discussion

XRD spectra of the studied porous materials are shown in Fig. 1 where the characteristic peaks of each material are observed.

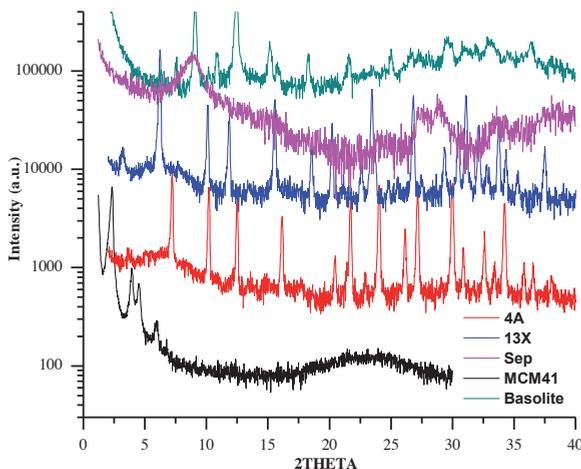


Fig. 1. XRD spectra of the studied materials.

The adsorption of water on a porous material affects its properties and phases transitions due to the confinement that results in major differences than those in the free space. This is mainly due to the liquid-pore wall interactions upon water adsorption in the porous matrix and adhesive forces of the water molecule with polar or non-polar blocks of porous structure in addition to the liquid-liquid interactions and cohesive forces of free water. Therefore, the isothermal study of the water vapour adsorbed or desorbed on the surfaces of a porous solid as a function of the relative pressure can provide significant information on how the water's heat exchange properties are related to the geometrical constraints and the nature (hydrophilic or hydrophobic) of the porous matrix (Karamanis, 2015).

Depending on the driven forces of the water vapour adsorption process, six different isothermic curves are usually observed, categorized from type I to type VI. The type I curve is usually observed for materials with high water adsorption capacity and very fast sorption saturation at low partial pressure (P/P_0) due to steric effects, followed by consistent adsorption over a wide range of P/P_0 due to water saturation in the pores.

As a rule, the adhesive forces between water molecules and porous walls are much stronger than the water cohesive forces. These adsorbents are classified as very hydrophilic due to high affinity to water even at low P/P_0 . Such behaviour is being followed by the zeolite sample (4A and 13X) and silica gel (Fig. 2). A Langmuir function was used to describe the monolayer water vapour and the equation

$$q = \frac{ab\left(\frac{P}{P_0}\right)^{(1-c)}}{1+b\left(\frac{P}{P_0}\right)^{(1-c)}} \quad (1)$$

was fitted to the experimental data where q is the sorbed vapour at relative pressure P/P_0 . The hydrophilic type II isotherm was observed in Basolite and Sep (Fig. 2) and was normally associated with monolayer-multilayer sorption on the nonporous or macroporous surface of a powder. The S-shape is controlled by surface-water interactions and capillary effects in the porous solids for higher relative humidity and is appropriate for heat storage applications.

The water vapour adsorption isotherm was fitted by the curve following the Dubinin-Astakhov equation as

$$q = q_m e^{\left(\frac{RT \ln\left(\frac{P}{P_0}\right)}{E}\right)^n} \quad (2)$$

where q is the sorbed vapour at temperature T and relative pressure P/P_0 and q_m the saturation value while n and E are the temperature invariant parameters and $RT \ln(P/P_0)$ is the adsorption potential ΔG . In these hydrophilic materials that follow adsorption isotherms of type II, a considerably high sorption capacity of water at low P/P_0 and moderate P/P_0 was measured.

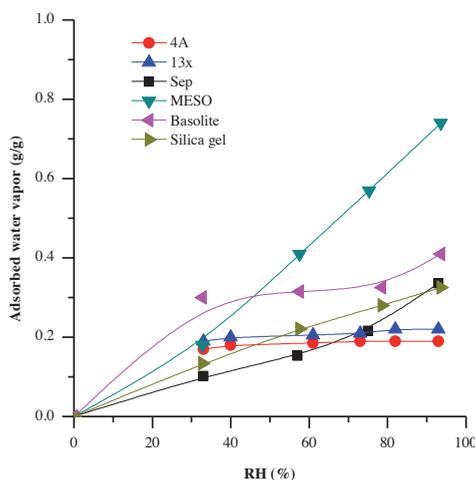


Fig. 2. Water vapour adsorption isotherms of the studied materials.

The isotherms of MESO sample showed different type behaviour. The water adsorption isotherm on the MESO sample was at the limit of type V and IV. This is indicative of a relatively low hydrophilic character in the low-pressure region of the adsorption isotherm but with a capillary condensation step 0.55-0.6 relative pressure leading to a total filling of the pore volume and thus to a type-V isotherm (with maximum uptake more than 0.7 g g⁻¹ at 93% RH). In type V adsorption which is of interest in building integrated evaporative cooling, the initial low water affinity can be considered from the point of view of nonpolar or weakly polar framework that resemble a rather hydrophobic porous solid. Due to this hydrophobicity, low thermal temperatures will be needed for water desorption. The step increase in water vapour adsorption for types IV and

V are characteristic for water vapour capillary condensation in the pores and is responsible for mesopore and macropore filling.

Therefore, the MESO materials showed high rates of water adsorption and the more suitable for surface cooling applications were determined. Additionally, phenomenological models were also applied to describe both kinetics and equilibria experimental data.

4. Conclusions

In order to evaluate the potentiality of hydrophilic materials for evaporative cooling applications, adsorbed amount of water vapour was determined by moisture sorption measurements for several adsorbents. Among the studied materials, aluminosilicates of the MCM exhibited substantial mesoporosity and appropriate properties as water vapour adsorbents for solar cooling applications.

5. Acknowledgements

This work is supported from the SOL-NANO (14-TUR) project co-financed by the European Union and the Greek State, Ministry of Education and Religious Affairs / General Secretariat for Research and Technology, O. P. Competitiveness & Entrepreneurship (EPAN II), ROP Macedonia - Thrace, ROP Crete and Aegean Islands, ROP Thessaly-Mainland Greece -Epirus, ROP Attica and Tubitak (Turkey).

References

- Vardoulakis E., Karamanis D., Fotiadi A., Mihalakakou G. (2013). The urban heat island effect in a small Mediterranean city of high summer temperatures and cooling energy demands. *Solar Energy* 94, 128-144.
- Karamanis D., Vardoulakis E. (2012). Application of zeolitic materials prepared from fly ash to water vapor adsorption for solar cooling. *Applied Energy* 97, 334-339.
- Karamanis D. (2015) Solar cooling with hydrophilic porous materials for reducing cooling needs, In: F. Pacheco-Torgal, J. Labrincha, L. Cabeza, C. G. Granqvist (Eds.), *Eco-efficient materials for mitigating building cooling needs*, Woodhead Publishing, 269-305.