



On the use of metal cation-exchanged zeolites in sorption thermochemical storage: Some practical aspects in reference to the mechanism of water vapor adsorption

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ABSTRACT

The sodium form of industrial X-zeolite (13X) was compared with two other samples obtained by a partial (about 70%) cation exchange with Mg^{2+} (Mg-X) or a complete exchange with Ca^{2+} (Ca-X) in view of their use as adsorbents for water vapor in energy storage systems by sorption. Various sorption methods based on the specific interactions between two probing molecules (N_2 and NH_3) and specific surface sites were employed to monitor the hydration state of the zeolite surface as a function of the temperature of sample drying performed under vacuum degassing or gas-flow conditions. X-ray diffraction, volumetric sorption technique, temperature-programmed desorption, and gas flow calorimetry were combined with Monte Carlo simulations of the mechanism of water vapor adsorption on model zeolites to demonstrate that the general tendency to operate under mild drying conditions would always result in a state of partial hydration of the zeolite surface. To increase the amount of heat released upon subsequent adsorption from a flow of helium at a relative pressure of water vapor of about 0.03, the use of Mg-X sample was demonstrated the best alternative if the activation procedure was to be performed at 200 °C. Here, the heat effect was 4–5 times greater than that measured in the case of 13X. This result is of high importance for the industrial-scale implementation of the energy storage by sorption.

1. Introduction

Converting sunlight into heat and electricity remains certainly one of the most efficient solutions to reduce greenhouse gas emissions to safer levels [1,2]. Nevertheless, numerous countries around the world may suffer from larger supply fluctuations due to the intermittent nature of such a renewable energy source, especially in the context of a progressing decentralization of energy production. Therefore, adequate energy storage systems have a key role to reduce the time and rate mismatch between energy supply and energy demand. Even though latent heat storage devices, making use of phase change materials, provide an advanced and environmentally friendly technology for storing thermal energy [3,4], reversible sorption phenomena at the solid-gas interface offer real promise in the control of seasonal solar energy storage [2,5–8].

By far the most commonly studied environmentally-friendly technology for long-term solar energy storage by sorption refers to the use of a “green” and cheap adsorbate like water vapor in open storage systems [6,7]. The sorption phenomena are carried out making use of porous solids in order to increase the adsorbate uptake and intensify the

heat exchange during each charge-discharge cycle [8–21]. Besides high specific surface areas, the target materials should be also characterized by appropriate hydrophilic character of their surface, as well as sufficient hydrothermal stability and resistance to repeated hydrothermal stress [7,8,20,22]. Fast sorption kinetics resulting in a high thermal power output is also considered as having a benefic effect on the performance of the storage system [20]. Anyhow, the choice of appropriate adsorbent for long-term solar energy storage by sorption is substantially influenced by the operating mode in which a given storage unit is working [5,7,8,23]. The “moist-air flow” mode during the discharging phase (i.e., adsorption of water vapor from outdoor air brought inside) offers the advantage of operating under atmospheric pressure and ambient temperature, with no need for a specific insulation of the reactor. Nevertheless, one more aspect deserves a great attention in fundamental studies on materials for storage applications. *From a technological point of view, perfect control of drying and storage conditions is an impossible objective.* During the charging step, the adsorbent is rather sheltered from direct sun exposure and heat required for drying will be delivered in pre-heated air that has a low relative humidity. Afterwards, the dried adsorbent will be stored at ambient temperature

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from summer to winter time under air containing, at least, a trace of water vapor. Given the diversity of the above-discussed criteria, it is not surprising that new or modified adsorbents are still reported in the literature.

Within the category of natural inorganic materials, the energy released upon water adsorption onto zeolites and swelling clays was demonstrated to reach even about 90 kJ mol^{-1} for low water contents [21,24–27]. Nevertheless, insufficient thermal and hydrothermal stability of clay minerals was considered as an important obstacle to their successful implementation. Very intensive studies undertaken on water adsorption by a variety of zeolite structures under different experimental conditions have evidenced their usefulness as potential adsorbents in the context of long-term solar energy storage by sorption [8,12,13,20–22,25,26,28–30]. A typical illustration has been provided by Cindrella and Dyer who compared the storage performances of three types of zeolites containing various compensating cations. [31] This has certainly motivated the first practical use of zeolite 13X in sorption energy storage on district heating net in Munich to store about 1300 kWh during off-peak hours for the subsequent heating of a school building [6,23]. The easiness with which the adsorptive properties of zeolites may be tuned through varying crystal structures, Si:Al ratios, or compensating extra-framework cations is certainly a great advantage [12,13,21,26,32–34]. Their main drawback is their great sensitivity to deactivation by insufficient regeneration, which may compromise the reversibility of the charge-discharge cycle upon energy storage. Harsh desorption conditions are necessary upon drying to restore the maximum energy during the discharging step [8,15,25,35]. It should be also remembered that the hydration and dehydration of zeolites is paralleled by the migration of extra-framework cations among various crystallographic sites [21,26,28,30,32,35–38], thereby modifying their accessibility or even blocking the entrance of some pores. Moreover, some evolution of the pore structure of a pre-shaped sample of Na^+ saturated 13X zeolite subject to a great number of repeated charge-discharge cycles under hydrothermal conditions was evidenced by Storch et al. [22].

Different kinds of amorphous silicas and aluminosilicates have been also proposed in the scientific and technical literature related to the subject [6,9–11]. In particular, the deposition of a thin layer of a hygroscopic salt on the surface of an ordered mesoporous material was demonstrated to increase the molar heat effect of water vapor adsorption [10,11]. Nevertheless, some difficulties in preventing blockage of the pore space in such composites were evoked, thereby leading to a decrease in the amount adsorbed. Hybrid organic-inorganic solids or Metal Organic Frameworks (e.g., MIL-101) represent a second class of model porous materials recently tested for the present application [14–19], owing to the presence of unsaturated metal centers in the structure which can yield strong interactions with water molecules [39]. Appropriate functionalization of the organic moieties undertaken to improve the hydrothermal stability of the MOF structure did not result in a drastic decrease in material performance since still relatively high values of adsorption enthalpy of the order of 50 kJ mol^{-1} were observed for a water uptake close to 0.14 g g^{-1} in the presence of hydrophilic ligands [40].

It is useful to underline that the fruitful use of zeolite 13X as a water vapor adsorbent in short-term energy storage was the main motivation for the present study. The principal goal with respect to seasonal thermal energy storage was to avoid potentially detrimental conditions of high water vapor partial pressure in combination with elevated temperatures. The design of adequate adsorbents was inspired from high enthalpy of hydration for multivalent cations compared to that of Na^+ [41]. Several metal cation-exchanged zeolites of the X type containing divalent extra-framework cations were prepared. The possibly mild conditions of their drying were determined, while ensuring sufficiently high energy values released during the discharging phase in comparison with the pristine 13X sample. The incomplete dehydration of the zeolite surface as a function of the drying conditions applied was

demonstrated by combining various experimental techniques including N_2 gas adsorption at -196°C , two-cycle adsorption of gaseous NH_3 at 80°C , temperature-programmed desorption of NH_3 , or gas flow microcalorimetry operating in the pulse mode. Despite this imperfection of the energy charging stage, gas flow microcalorimetry experiments carried out under dynamic conditions of water adsorption, at a low relative pressure of water vapor of about 0.03 from a flow of helium as carrier gas at room temperature, provided evidence for the improved storage performance of the Ca- and Mg-exchanged samples. Taking into account the difficulty in controlling the surface state of the zeolite samples and thus in determining the absolute adsorption isotherms, Monte Carlo simulations were utilized within this study to supplement the interpretation of the experimental results in reference to the mechanism of water vapor adsorption.

2. Experimental

2.1. Materials

The 13X zeolite powder sample used in the present study was a kind gift from the Mediterranean Company of Zeolites (SOMEZ, France). The sample was repeatedly washed with deionized water. The cation-exchanged samples were obtained by making use of aqueous solutions of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. In a typical ion-exchange procedure, 30 mL of 1 mol L^{-1} nitrate solution were added to about 0.5 g of zeolite 13X and the suspension was stirred for 2 h. Then the mixture was centrifuged for 10 min at 3000 rpm at room temperature to separate the supernatant from the solid. The whole exchange procedure was repeated afterwards. A third centrifugation was performed over a period of 14 h. The resulting solid powder was washed with 30 mL of deionized water by stirring for 2 h. The two-phase mixture was subsequently centrifuged 5 times, with the last centrifugation run lasting again 14 h. The solid sample was finally dehydrated by freeze-drying under vacuum in a Cryonext freeze-drier and stored in unsealed vials.

2.2. Materials characterization methods

X-ray diffraction (XRD) measurements were performed to check the stability of zeolite structures by using a PANalytical X'Pert MPD (Philips 1710) diffractometer controlled by a computer. The XRD patterns were collected using a $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405980 \text{ \AA}$), the 2θ diffraction angles being recorded at a scan rate of 0.039° and a time step of 415 s in the 2θ range from 5° to 70° . The samples were analyzed at room temperature without any preliminary thermal treatment. Additional XRD patterns were collected following the same procedure at different temperatures in order to verify the thermal stability of the crystalline structure. A Wavelength Dispersive X-Ray Fluorescence (WDXRF) spectrometer (Axios Max, PANalytical, Netherlands) was used to analyze the materials composition. The Rh-anode X-ray tube was operated at a maximum power of 4 kW with a maximum voltage of 60 kV or maximum current of 160 mA. To obtain high resolution spectra, eight dispersive $\text{LiF}200$, $\text{LiF}220$, $\text{PE}002$, $\text{Ge}111$, $\text{PX}1$, $\text{PX}4a$, $\text{PX}5$, and $\text{PX}7$ crystals were employed. 14 scans were collected under vacuum, each scan covering a range of the expected elements, and the peak areas of the characteristic radiations were assessed. Gas scintillation proportional counters and gas flux detector were used to record the intensity of the characteristic radiations. The quantitative analysis was based on the use of PANalytical's proven SuperQ software. Using both calibration curves to estimate the proportion of the different elements and the crystallographic structure (in which Al and Si elements have to be distributed inside the 192 sites), it was therefore possible to calculate the various chemical formula for each sample.

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