

Sustainable thermochemical energy storage through eco-friendly zeolites - A characterization study

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Abstract:

Judicious utilization of natural resources always helps protect the environment from several ill-effects. This paper was aimed at exploring the merits of natural and environment friendly zeolites towards sustainable thermochemical energy storage. Sorption behaviour of selected zeolites were investigated using a differential thermogravimetric analyser. The desorption kinetics was studied by heating the materials from room temperature to 600 °C. The materials lose their water molecules on heating and become anhydrous mostly around 300 °C. The desorption enthalpies due to heating were noted to decrease with increase of heating rate, and found low for Zeolite-Mordenite (334.5 Jg^{-1}) and high for Molecular Sieves-4A (1060 Jg^{-1}). Materials' adsorption enthalpies were determined by subjecting them to single cycle tests comprising of heating, cooling and hydration processes in sequence. The desorption and adsorption enthalpies of a single cycle were found to vary with the material and temperature program used. To understand the desorption and adsorption kinetics better, the materials were also tested on X-ray photoelectron spectroscopy, Brunauer–Emmet–Teller, and thermal constants analysers respectively for their elemental composition, structural properties, and thermal conductivity. This paper concludes that many of the naturally available zeolites stand as potential candidates for a sustainable thermochemical energy storage and recovery.

Keywords:

Environment; zeolites; sorption; thermochemical energy storage; thermal conductivity; differential thermogravimetric

Abbreviations:

| | |
|-------|---|
| BET | Brunauer–Emmet–Teller |
| BJH | Barrett-Joyner-Halenda |
| DTA | Differential Thermal Analysis |
| DTG | Differential Thermogravimetric |
| IUPAC | International Union of Pure and Applied Chemistry |
| LHS | Latent Heat Storage |
| MS | Molecular Sieves |
| SHS | Sensible Heat Storage |
| TCES | Thermochemical Energy Storage |
| TCM | Thermochemical Material |
| TES | Thermal Energy Storage |
| XPS | X-ray Photoelectron Spectroscopy |
| Z | Zeolite |

1. Introduction: Demand for energy is ever increasing across the globe due to the rapid growth in human population and their lifestyle, industrialization etc. Energy is being used in manufacturing industry, transportation sector, residential and commercial buildings, power or electricity generation etc. Buildings' energy consumption was noted to be one-third of the total energy produced and anticipated to increase by 50% by the year 2050 [1]. Nearly 60 to 70% of this energy alone is used for heating and cooling applications. These energy needs are traditionally supported by the non-renewable sources, mostly the fossil fuels. Despite being a prime energy-supplier, their increasing cost and decreasing availability have forced the researchers to consider new and alternate sources of energy for sustainable growth.

Of the several renewable energies (e.g. solar, wind, biomass, geothermal), solar energy is considered as a promising resource due to its abundant availability across the globe. However, the uniform availability of solar energy across the day and seasons stands as a major challenge in its successful utilization. This limitation can be addressed by devising suitable thermal energy storage (TES) systems for the short-term and long-term energy needs like cooling and heating applications. On the basis of energy storage principle, TES methods are broadly classified into sensible heat storage (SHS), latent heat storage (LHS) and thermochemical energy storage (TCES). Both the SHS and LHS methods are well-researched and matured techniques, hence being used for commercial systems. In contrast, the TCES method is an emerging technique and not yet established.

Good energy storage characteristics, zero heat losses, long-term storage capability, and long-distance transport possibilities are a few attractive features of the TCES method against the traditional SHS and LHS methods [2]. The TCES method permits to store and retrieve large quantities of heat through reversible chemical reactions consisting of charging (i.e. endothermic reaction) and discharging (i.e. exothermic reaction) processes. These reversible reactions can be any of the following combinations: dehydration-hydration, desorption-adsorption, decarbonation-carbonation, reduction-oxidation etc., all subject to the kind of material in consideration. The material here deals both the thermal and chemical forms of energy; hence referred to as thermochemical material (TCM). On heating i.e. charging, a sorption based TCM stores energy in the sorbent in chemical form while dissociating the sorbate. Such stored energy shall be released when the sorbate reacts back with the sorbent.

Sorption materials are categorized on the basis of pore diameter, as microporous (less than 2 nm), mesoporous (range from 2 to 50 nm) and macroporous (greater than 50 nm) materials. Micro and mesoporous materials such as zeolites, silica-alumina phosphates, metal organic frameworks, activated carbons, and silica gels were used for energy storage and refrigeration applications. A TCM should be non-corrosive, non-toxic, stable under rapid reaction kinetics, and possess high energy storage density [3]. Interestingly, zeolites fulfil most of these requirements. Charging temperatures were relatively high ($> 200 - 300\text{ }^{\circ}\text{C}$) [4], yet they exhibited good desorption tendency at lower temperatures, as good as 80% by $150\text{ }^{\circ}\text{C}$ temperature [5].

Porous materials were reviewed for low temperature heat storage, adsorptive pumping [6] and chillers applications [7]. These reviews highlighted the need for systematic testing, development of new porous materials, and suggested further studies to examine their long-term durability. Calorimetric investigations were performed on zeolites (LiNaX, AlPO_4 , and SAPO-34), and $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ impregnated with attapulgite for thermochemical energy storage [8]. The experiments showed that the attapulgite based composite offered high energy storage density (1500 kJ kg^{-1}) and attributed this to the larger uptake of water. Similar kind of investigations were also performed on Zeolite 5A and $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ for TCES applications, and found relatively higher energy storage density for the latter [9]. Thermal stability of zeolites was investigated by subjecting them for a limited number of cycles [10]. The tested zeolites experienced a notable mass gain during the cooling period of each cycle, hence suffered from poor hydration capacity. Zeolite NaY and Zeolite HY were noted to display good cyclability and yield satisfactory sorption enthalpies. Recently thermal properties of several zeolites were investigated to develop a low cost salt loaded composite material for thermochemical energy storage applications and found that the two high purity crystal zeolites yielded higher water uptake [11].

Zeolites were also tested on open type TCES prototypes for applications like water and space heating, adsorption heat pump and chiller, and refrigeration applications. An open TCES system was experimentally investigated with novel composite material (porous concrete- CaCl_2) along with the proven materials (Vermiculite- CaCl_2 and zeolite-13X) for heat storage applications [12]. For the studied operating conditions, the porous concrete- CaCl_2 exhibited better energy storage density. Considering the zeolites as TCMs, an open sorption TCES system was built and studied experimentally for low-temperature heat storage applications [13]. Among the tested samples, the zeolite-13X exhibited higher heat storage density during the desorption and adsorption processes.

Poor heat and mass transfer rates, high investment cost, complexity in designing closed systems are a few challenges of this technique for large scale applications. Composites were prepared using zeolites to address the agglomeration [14] and low hydration rate [15] problems exhibited by the pure or authentic materials like salt hydrates and hydroxides. Further, most of the zeolites exhibited very poor thermal conductivity. The zeolite-NaX (packed powder form) was investigated at room conditions and obtained thermal conductivity as $0.08 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.16 \text{ W m}^{-1} \text{ K}^{-1}$ respectively for 800 nm and 2 μm size particles [16]. Zeolite-NaY was tested at 20 °C and 1 atm and yielded thermal conductivity as $0.1 \text{ W m}^{-1} \text{ K}^{-1}$ [17]. Apart from the experimental studies, silica zeolite was investigated using non equilibrium molecular dynamics simulations and found the thermal conductivity in the range from 0.6 to 4 $\text{W m}^{-1} \text{ K}^{-1}$ at different crystallographic directions. Metals [18] and additives or binders [19] were used to alter the zeolites' desorption temperature and thermal conductivity respectively. Thermal conductivity of a porous material, and zeolite in particular, depends on several factors including its pore size and distribution, framework density [20] and crystal structure [21]. Addition of metal (copper/ nickel) foams helped to increase the thermal conductivity of Zeolite NaX [22]. This composite was expected to scale down the adsorber size at least by 5 to 10 times.

The reported investigations primarily focused on determining the materials' properties (e.g. desorption temperature, energy storage density, water adsorption capacity) and their suitability for intended applications. Notably no comprehensive results are available on dehydration, hydration and thermal conductivity for the well-known zeolites. This paper was aimed at exploring the merits of many of the commonly used zeolites and addressing the aforementioned aspects. Therefore, a select few zeolites were examined for their suitability in using the low temperature (150 ~ 200 °C) industrial waste heat. Towards this, the samples were tested on a DTG analyzer to assess their mass changes and the associated enthalpies due to desorption and adsorption. Further, these zeolites were characterized for their elemental composition, structural properties, thermal conductivity using respectively the XPS spectroscopy, BET, and thermal constants analyzers. This paper presents the zeolites' desorption characteristics at different heating rates and the enthalpies due to sorption processes. The mass variation due to heating is illustrated for Zeolite NaY, and depicted its anhydrous condition.

2. Experiments:

2.1 Materials: Zeolites are microporous, aluminosilicate based minerals and used commonly as adsorbents for catalysis processes and gas separations [23]. Considering these materials as potential TCMs, a select few, listed in the Table 1, were examined to establish their properties and sorption kinetics. The generic chemical formula of these materials is $M_xD_y[Al_x + 2ySi_n - (x + 2y)O_{2n}].mH_2O$, where M and D represents respectively mono-valent cations (e.g. Li, Na, K), and di-valent cations (e.g. Mg, Ca, Sr, Ba) and m indicates the number of water molecules [24]. The materials' (listed in the Table 1) exact elemental composition was not available from the manufacturers, and the chemical formulae stated therein correspond to the references cited. The zeolites employed in the present study were obtained in the powder form from Alfa Aesar, and used them without further purification.

2.2 Methodology: In the present study, chemical composition of the selected materials was analyzed using X-ray photoelectron spectroscopy (XPS) with monochromatic Al K α X-rays. This instrument helps scanning all the chemical elements present, except the hydrogen (H) and helium (He). The materials' spectrum was charge corrected by the carbon element (C_{1s}) at the binding energy of 284.8 eV. Structural properties were measured by the Brunauer–Emmet–Teller (BET) analyzer. Here, the sample was initially degassed at 250 °C temperature for two hours duration under vacuum conditions before measuring the nitrogen (N₂) adsorption at 77 K. The BET N₂ adsorption method was used to measure the total specific surface area, total pore volume and mean pore diameter of selected materials. Similarly, t-plot and Barrett-Joyner-Halenda (BJH) methods were employed to determine respectively the micro- and meso-pore distribution. Thermal conductivity was evaluated at room temperature using the TPS 500S, a Hot Disk's transient plane source based thermal constants analyzer.

Materials' desorption and adsorption kinetics were evaluated using the DTG-60H, a Shimadzu's differential thermogravimetric analyzer. Towards this, the DTG-60H was configured as shown in Fig.1 and the materials were subjected to heating and single cycle test runs as illustrated in Fig.2. For each test run, approximately 10 mg of sample was loaded to evaluate the material's desorption and adsorption kinetics. During the heating or desorption process, nitrogen gas with a flow rate of 50 ml min⁻¹ was supplied as a purge gas to the sample chamber. The purge gas was also helpful in driving out residual water molecules present, if any. During the adsorption process, water vapor generated in a thermal bath at 30 °C was supplied along with the nitrogen gas to the sample chamber. The relative humidity of this gas (nitrogen + water vapor) was measured with a humidity

sensor having $\pm 1\%$ accuracy, and noted it to be 76%. Glass wool was used to prevent entry of moisture, if any, to the sample chamber. The instruments' specifications are furnished in Table 2.

To understand the desorption kinetics of a material, its sample was heated up to 600 °C at different heating rates (5, 10 and 20 °C min⁻¹), as shown in Fig.2(a). Different heating rates were considered here to predict the materials' thermal behavior when subjected to TCES systems or prototypes. These test runs help determining the materials' desorption temperature and the associated enthalpy. To determine the adsorption enthalpy, the sample was subjected to sequential heating (or desorption), cooling and hydration (or adsorption) processes, henceforth referred to as single cycle, as shown in Fig.2(b). Keeping the temperature program constant for hydration, different single cycles were performed by varying the temperatures of heating (150 °C, 200 °C, and 250 °C).

3. Results and discussion:

3.1. Elemental composition: To interpret the desorption and adsorption kinetics and the associated enthalpies of a material, a thorough understanding of its elemental composition is helpful; as the adsorption and desorption tendencies are predominantly influenced by the ionic forces due to the cations present and Si/Al ratio. The survey scan spectrums of various zeolites derived from the XPS analysis are presented in Fig.3. Apparently, basic photoelectron elements such as Al_{2p}, Si_{2p}, Na_{1s}, and O_{1s} occur at almost similar binding energies for the tested zeolites. Noticeably, each zeolite has adventitiously presented C_{1s}, a carbon element, at the binding energy of 284.8 eV [28]. Further, these spectrums show Auger electron peaks (NaKLL and OKLL) due to the de-excitation of the photoion through Auger transformation [29].

Table 3 presents the atomic weight based elemental composition of the selected materials derived from the XPS. These results confirm the presence of mono-valent and di-valent cations, though not shown them explicitly in the chemical formulae cited in the Table 1. The quantity of aluminosilicate, an identifier for zeolites, derived in terms of Si/Al ratio, almost matches with that of equivalent estimated from the respective chemical formula. The minor deviations in the elemental composition of a material against the cited chemical formulae can be attributed to the synthesis procedure followed and the purity of raw materials used.

3.2. Structural properties: Materials with high surface area and pore volume exhibit tendency for water adsorption during the hydration period, and may also favor impregnation with another material of interest. Fig.4 shows the BET analyzer based N_2 isotherms for adsorption and desorption processes. The adsorption and desorption curves for Z-NaX, Z-NaY, Z-HY and Z-MORD, shown in Fig.4, are almost similar to that of type I isotherms suggested by the International Union of Pure and Applied Chemistry (IUPAC) standards [30]. Whereas the MS-3A and MS-4A, in the present study, did not exhibit such isotherms, as their smaller cavities could not adsorb the relatively larger N_2 molecules. The structural properties are derived from these N_2 adsorption and desorption isotherms and furnished in Table 4. These properties are found to vary in proportion to the N_2 adsorbed.

3.3. Thermal conductivity: Since a TCES system deals with heat energy during the charging and discharging periods, its performance is invariably dependent on in-situ heat transfer rates. Among the several influencing parameters, thermal conductivity of working medium/ material plays an important role on the heat transfer rates. Hence, an assessment of material's thermal conductivity becomes vital. As described earlier, the selected materials were tested on the TPS-500S for thermal conductivity and the same are shown in Fig.5. For each material, at least six readings were taken to estimate the uncertainty in measurement. The mean thermal conductivity of these materials ranges from $0.065 \text{ W m}^{-1} \text{ K}^{-1}$ to $0.096 \text{ W m}^{-1} \text{ K}^{-1}$. For Z-NaX, it is $0.091 \text{ W m}^{-1} \text{ K}^{-1}$ and matches with the reported literature [22]. Table 5 presents the thermal conductivity values of the zeolites reported in the literature. Majority of the tested materials exhibit very low thermal conductivity, and the deviations among them can be attributed to various factors including the crystal structure and pore characteristics. Owing to their poor thermal conductivity, the tested materials are suggested for impregnation with suitable and good heat conducting media, before considering them for a TCES application.

3.4. Heating: In the present study, heating tests were performed at different heating rates as illustrated in the Fig.2(a), to determine the desorption temperature and the associated enthalpy. Differential thermogravimetric-differential thermal analysis (DTG-DTA) curves for Z-NaY due to heating up to 600°C at a heating rate of 5°C min^{-1} are shown in Fig.6. On heating to an elevated temperature, a sorption material begins to release water molecules sequentially before it becomes anhydrous. Such anhydrous material may begin to decompose, if heated further. Since the material loses water molecules by virtue of heating, the process is also referred to as desorption. In the process of desorption, a fraction of supplied heat energy is stored in the base material in

chemical form. The temperature at which the material becomes anhydrous, for brevity, is taken as desorption temperature.

Since a desorption process deals with removal of water molecules, its interpretation becomes easy if the material's structural information (including the total number of H₂O molecules present and their position) is known a priori. The mass curve shown in Fig.6 is almost similar to the trend reported by Whiting et al. [5]. By relating the instant mass against the initial mass of the sample, in terms of material's molecular weight, the number of water molecules present at such temperature was determined. Fig.6 depicts the sequential loss of H₂O molecules due to the heating, till the material (Z-NaY) becomes anhydrous at 281.3 °C. The desorption enthalpy was estimated on the basis of simultaneously derived DTA curve, and found to be 977.5 kJ kg⁻¹.

Fig.7 shows the mass variation of all selected materials due to heating up to 600 °C at a heating rate of 5 °C min⁻¹. Each of these curves follow almost similar trend, suggesting that the materials exhibit tendency to desorb the water molecules on heating. As a curve gradually turns into flat, the opportunity for further drop in the mass ceases, and thus material becomes anhydrous. Mass drop of each material is understood to be affected by the (i) elemental composition and the relative mass contribution of the water molecules, (ii) structural framework, and (iii) heating rate. The mass curves shown in Fig.7 suggest that the selected materials lose most of their water molecules by around 150 °C, and turn into flat at around 300 °C. These temperature limits (150 ~ 300 °C), interestingly align with variety of heat sources including the industrial waste heat and solar energy, hence the selected materials stand as potential candidates for the TCES applications. The mass drop is found to be the lowest for Z-MORD and highest for Z-NaY, when heated only to 150 °C. Most of the materials exhibit thermal stability without a major decomposition for heating up to 600 °C.

Desorption temperature of a material can be determined by identifying the anhydrous mass condition on its mass curve due to heating, as illustrated in the Fig.6. Towards this, an exact and complete chemical formula is crucial. Assuming that the chemical formulae furnished in the Table 1 approximate the materials under present study, the anhydrous mass percentage was calculated in terms of their respective molecular weights and the same is provided in Table 6. Desorption temperatures are not determined for Z-HY and MS-3A due to the lack of reliable and complete chemical formulae. Based on the available limited data, the desorption temperatures are

found to be high for materials with relatively larger weightage of total cations. Accordingly, they are low for Z-MORD and moderately high for MS-4A.

Desorption enthalpy of a material indicates its maximum possible energy storage capacity, thus decides its suitability for a TCES application. Table 6 presents the desorption enthalpies of selected materials at different heating rates. These enthalpies mostly decline as heating rate increases. Further, the desorption enthalpies are low for Z-MORD and high for MS-4A.

A material with lower desorption temperature yet having higher desorption enthalpy is preferred over the others as it allows to use low temperature energy sources like industrial waste heat, solar energy etc. Its suitability for a specified temperature of heat source can be decided in terms of the extent of desorption, i.e. the ratio of actual amount of desorption to the maximum possible amount of desorption when the material becomes anhydrous. Table 6 also provides the extent of materials' desorption at 150 °C, a temperature that matches with the aforementioned sources of heat. As heating rate increases, the extent of material's desorption is observed to decline. Hence the desorption enthalpies due to heating shall be better at lower heating rates. These heating studies are thus helpful in identifying the right material for a given heat source.

3.5 Single cycle: The energy stored in a material through desorption process can be retrieved either partially or fully through the reverse process, i.e. adsorption. To determine the adsorption enthalpy, the material in consideration was subjected to single cycle as illustrated in Fig.2(b). Energy retrieval therefore depends mainly on the temperature program considered for the cyclic processes. As described in section 2, single cycle tests were performed by varying the temperature of heating (150 °C, 200 °C, and 250 °C), while keeping the temperature program constant for hydration.

Among the materials tested, the Z-NaY exhibits a greater extent of desorption when heated to 150 °C (refer Table 6), hence envisioned good desorption and adsorption enthalpies from it. Fig.8 shows the DTG and DTA curves of Z-NaY for a single cycle with isothermal heating at 150 °C. Prior to begin the heating from room temperature, the sample was exposed to nitrogen gas for 30 min, purely to drive away the physisorbed water content present, if any. The sample was then heated at 5 °C min⁻¹ heating rate to 150 °C and maintained at this temperature for 30 min to drive away the chemisorbed water molecules. Due to this heating, the sample

experiences a drop in mass as reflected on the mass curve. The simultaneously derived DTA curve shows peaks corresponding to this period of mass change, hence yields an adsorption enthalpy. Since the sample was not heated to its desorption temperature, the mass drop due to loss of water molecules is partial. This partial desorption yielded lower desorption enthalpy (577.6 J g^{-1}) as against the desorption enthalpy due to complete desorption (977.5 J g^{-1}), furnished in the Table 6.

On completion of the heating, the sample was cooled in the presence of nitrogen gas at $5 \text{ }^{\circ}\text{C min}^{-1}$ cooling rate, so as to facilitate it for hydration process at room temperature. Since that the sample chamber could not attain room temperature due to non-linear cooling at lower temperatures, an isothermal cooling was employed for 30 min duration. During this period of cooling, the sample experienced a noticeable mass gain while no moisture or water molecules was present in the sample chamber. A similar observation was reported by Fraenkel et al. [35] when a zeolite sample was subjected to cyclic heating and cooling processes. Mass gain during the cooling period was attributed to the adsorption of permanent gases (e.g. nitrogen), which in turn said to be affected by the sample's surface area and aluminum content. Soon after the cooling program completed, water vapor generated from the thermal bath at $30 \text{ }^{\circ}\text{C}$ was supplied along with nitrogen gas to the sample chamber for 60 min duration. Correspondingly, the sample began to adsorb the supplied water vapor marking a gain in its mass. This was reflected on the simultaneously derived DTA curve with a marked peak. This cyclic processes resulted to 418.9 J g^{-1} as adsorption enthalpy, a value smaller than its counterpart due to desorption (577.6 J g^{-1}), and well below the enthalpy due to complete desorption (977.5 J g^{-1}).

The above results suggest that the adsorption enthalpy can be improved if its counterpart due to partial desorption was increased. This is possible if the temperature of heating was increased to say $200 \text{ }^{\circ}\text{C}$ or $250 \text{ }^{\circ}\text{C}$. The single cycle tests for Z-NaY were performed for these two temperatures while keeping the remaining temperature program unchanged. Fig.9(a) shows the changes in mass of the sample during various stages of a single cycle (viz. heating, cooling and hydration) when it was performed for different temperatures of heating ($150 \text{ }^{\circ}\text{C}$, $200 \text{ }^{\circ}\text{C}$, and $250 \text{ }^{\circ}\text{C}$). The changes in mass shown in the bar chart were evaluated against the sample's mass at the start of heating, and marked with either negative or positive sign to indicate the respective loss or gain. The extent of material's desorption, shown in negative figures, is found to increase with the temperature of heating. Mass gain during the cooling period tends to decrease with the increase in temperature of heating. The increased extent of desorption helps improving the desorption enthalpy, if not proportionately, as shown in

Fig.9(b). The cumulative benefit due to the (i) increase in the extent of material's desorption, and (ii) drop in the mass gain during the cooling period, has not shown an equivalent improvement in the sample's mass gain during the hydration. Due to this, no benefit is realized in the adsorption enthalpy as the temperature of heating increases.

Fig.10(a) shows the mass changes of all the selected materials during a single cycle with 150 °C as the temperature of heating. Based on this data, a few observations can be discerned. More or less, each of the tested zeolites experiences mass gain during the cooling period, which reduced the possible adsorption opportunity. Notably, these mass gains are relatively less, thanks to the additional isothermal cooling employed in the current study, against the previous work of this research group [10]. Some of the materials (viz. Z-NaX, Z-HY and MS-4A) experienced greater mass gain (the cumulative effect of cooling and hydration) than their respective absolute mass drop (due to the heating). This hydrophilic nature can be attributed to several influencing parameters including the strong electrostatic interaction, structural properties and their framework, materials' chemical composition and the Si/Al ratio [18,36]. The desorption and adsorption enthalpies shown in Fig.10(b) almost match to the orders of mass changes shown in Fig.10(a). For the present temperature program, Z-MORD yielded lesser desorption and adsorption enthalpies, while the rest exhibit moderate to good performance. Based on the present study, the desorption and adsorption enthalpies during a single cycle are found to vary with temperature program and the material. For better results, therefore, an appropriate temperature program need to be identified for each material independently. This finding also justifies as why the adsorption enthalpies for Z-NaX, Z-NaY, Z-HY and Z-MORD of the present study differ from the reported results in the literature [5].

4. Conclusions:

Selected zeolites were tested for their sorption kinetics in terms of desorption temperatures, extent of material's desorption for a given temperature of heating, and enthalpies due to desorption and adsorption. Towards this, the samples were subjected to different temperature programs namely, heating and single cycles. The elemental composition, structural properties and thermal conductivity of these materials are also presented. Based on the current study, the following conclusions are drawn.

- XPS results confirm the presence of mono-valent and di-valent cations. The Si/Al ratio is an identifier for zeolites and almost matches with that of equivalent estimated from the respective chemical formula. Lower the value of Si/Al ratio, better the water vapour adsorption capacity.

- Most of the tested materials exhibit measurable pore volume (0.1688 to $0.3354 \text{ cm}^3 \text{ g}^{-1}$) and surface area (460 - $900 \text{ m}^2 \text{ g}^{-1}$) that supports the sorption reactions.
- Thermal conductivity of these materials is very poor ($\sim 0.1 \text{ W m}^{-1} \text{ K}^{-1}$), and matches with that of commonly used thermal insulators. This challenge can be overcome by impregnating them with suitable heat conducting media, thanks to their favorable porous structure.
- These materials exhibit tendency to desorb water molecules on heating, thus leading to simultaneous drop in their mass. The amount of mass drop is affected by the (i) elemental composition including the water molecules, (ii) structural framework, and (iii) heating rate.
- The number of water molecules present at any temperature was determined by relating the instant mass of the sample against its initial mass. The desorption temperature of a material is therefore influenced by the material's structural framework and elemental composition. Majority of the materials lose their water molecules mostly by heating to $150 \text{ }^\circ\text{C}$ and become anhydrous at around $300 \text{ }^\circ\text{C}$, a range that permits to use commonly available heat sources for TCES.
- Desorption enthalpy of a material indicates its maximum possible energy storage capacity, thus decides its suitability for a TCES application. The desorption enthalpies are observed to decline as heating rate increases. Further, they are low for Z-MORD (334.5 J g^{-1}) and high for MS-4A (1060 J g^{-1}).
- Zeolites experience a noticeable mass gain during the cooling period that follows a heating process. This was attributed to the adsorption of permanent gases.
- The desorption and adsorption enthalpies during a single cycle are found to vary with temperature program and the material. In the present study, Z-MORD yields lesser desorption and adsorption enthalpies, while the rest exhibit moderate to good performance. Better results can be realized by fine-tuning the temperature program for each material independently.
- Therefore, the authors opine that the selected materials stand as potential candidates for sustainable storage and recovery of thermochemical energy towards space, water and process heating applications.
- Further, these zeolites can be tested on a lab scale experimental prototype for sufficient number of cycles to determine their suitability for the TCES applications.
- The zeolites may also act as a matrix or base material for inorganic salt hydrates that suffer from agglomeration, gel-like formation, etc. in making suitable composite materials.

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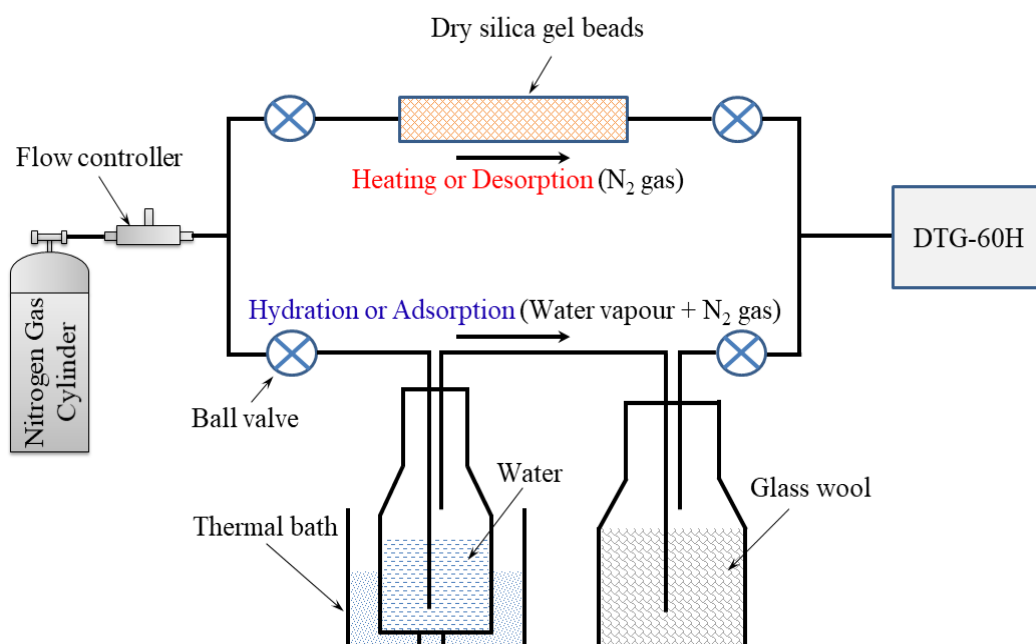


Fig.1 Schematic layout for material's characterization on DTG-60H

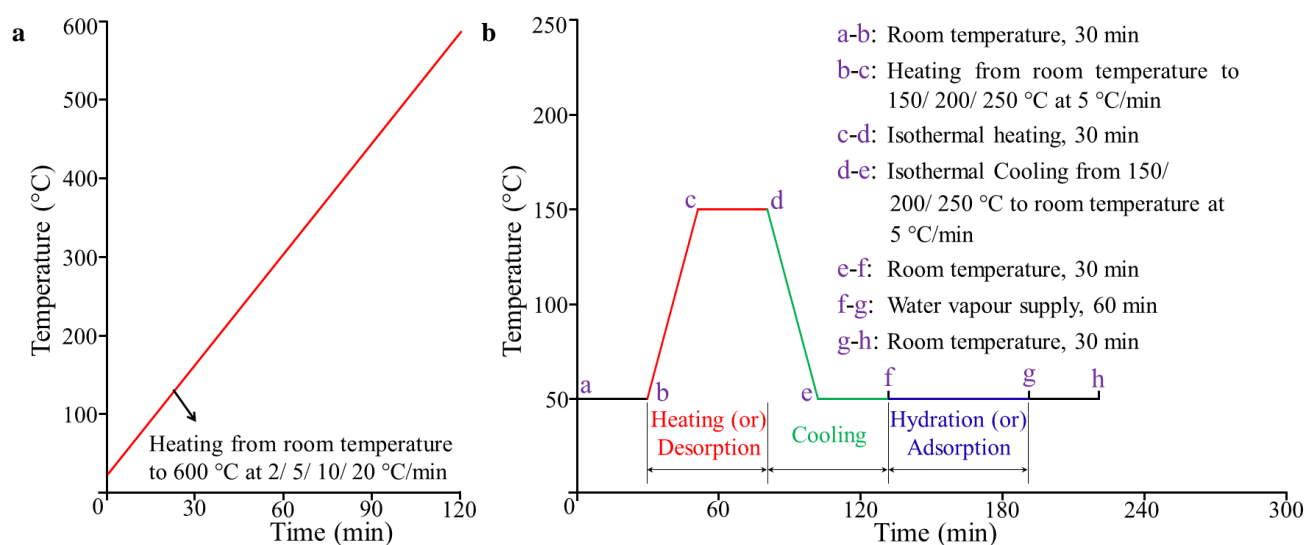


Fig.2 Temperature programs for heating (a), and single cycle (b)

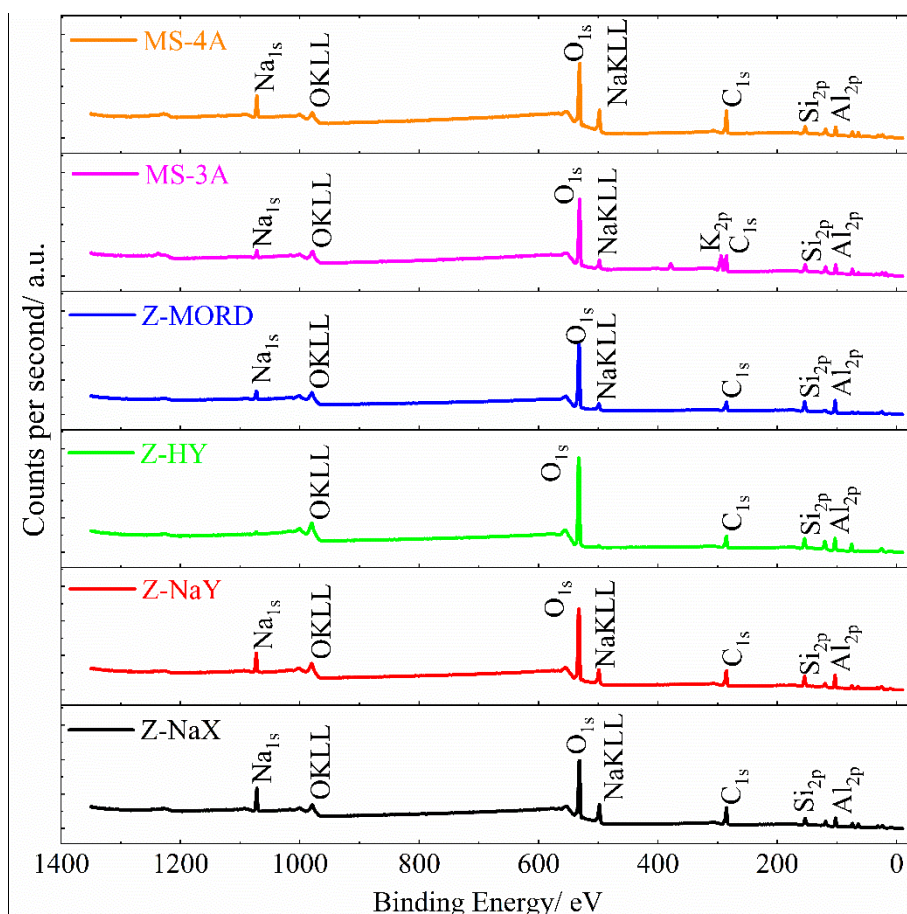


Fig.3 XPS survey scan spectrum of the selected materials

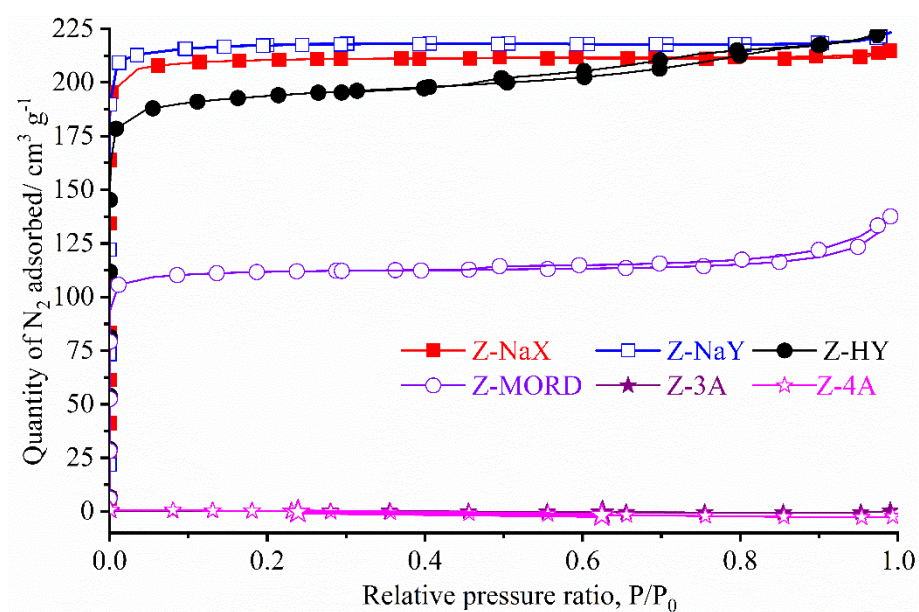


Fig.4 BET analyzer based N₂ adsorption and desorption isotherms of the selected materials

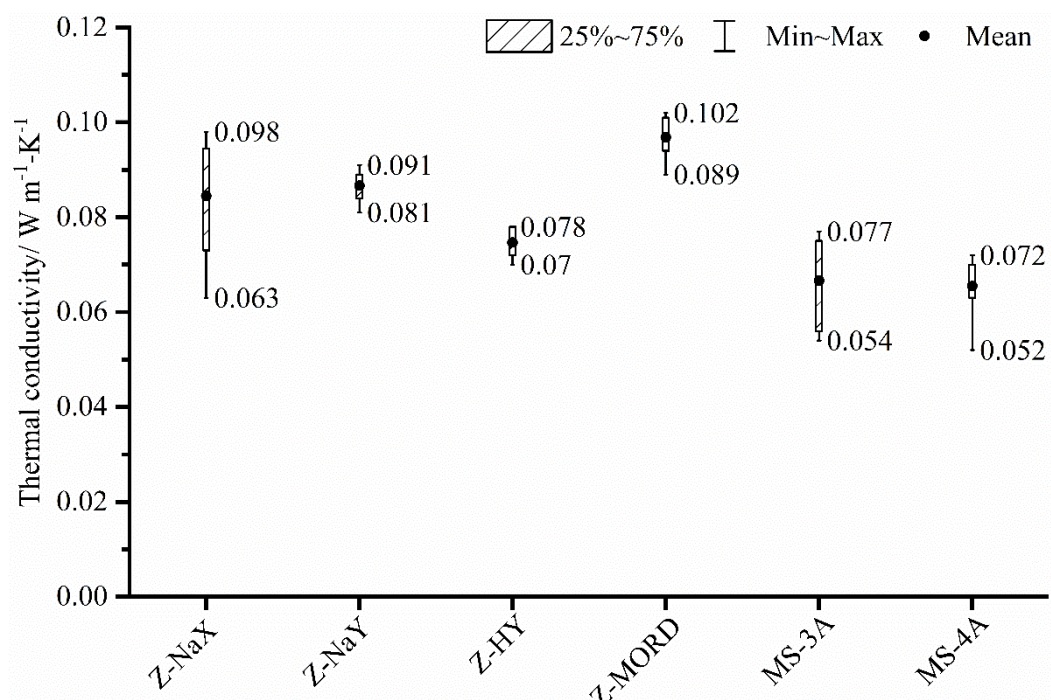


Fig.5 Thermal conductivity of the selected materials

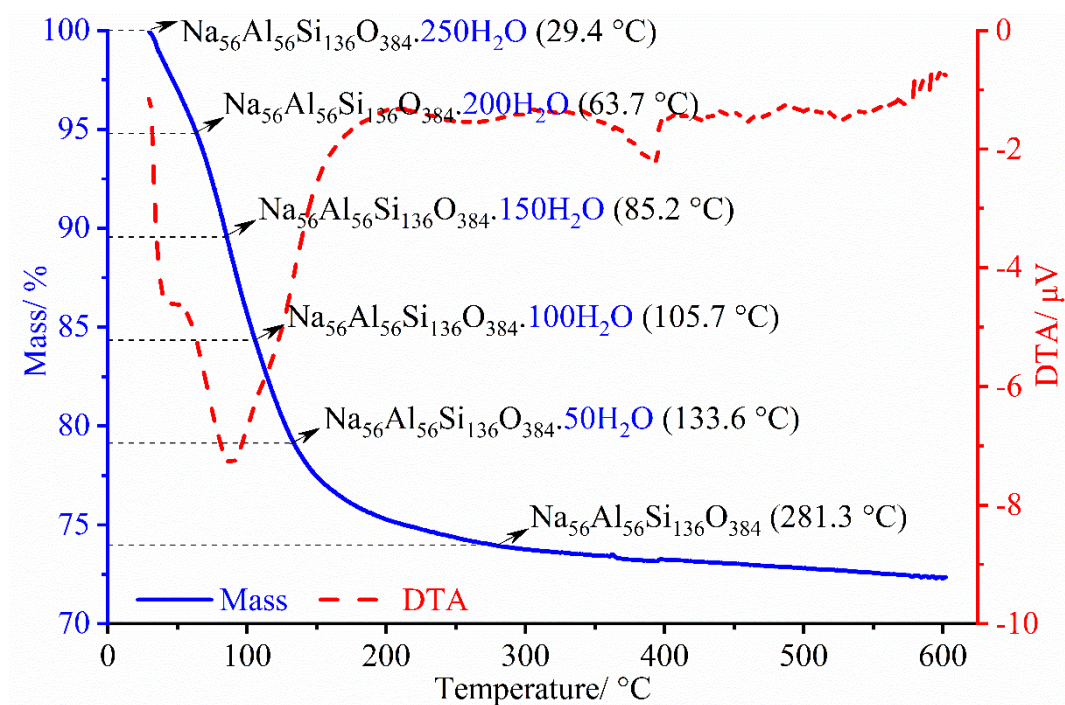


Fig.6 DTG-DTA curves of Z-NaY due to heating at 5 °C/min heating rate

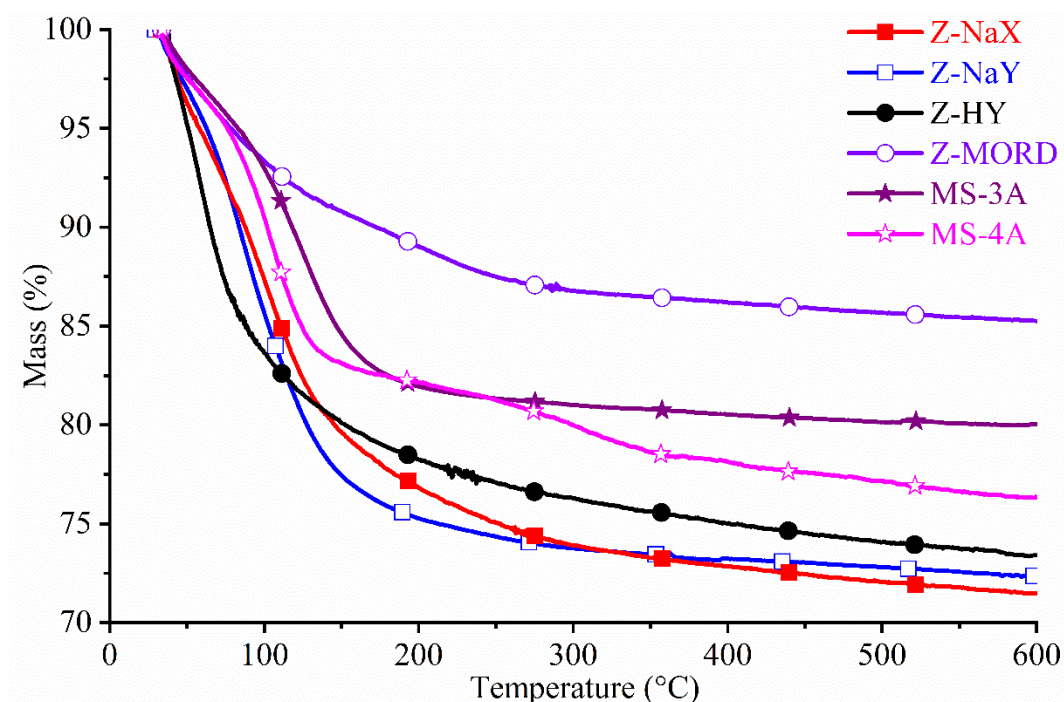


Fig.7 Mass curves of the selected materials due to heating at 5 °C/min heating rate

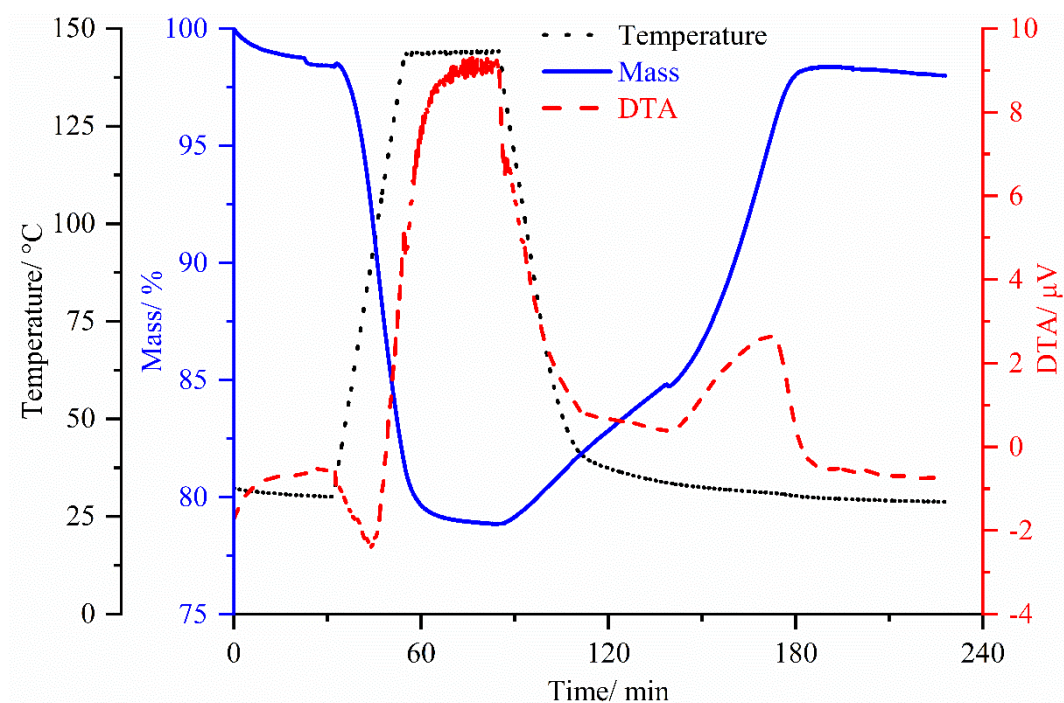


Fig.8 DTG-DTA curves of Z-NaY for a single cycle with isothermal heating at 150 °C

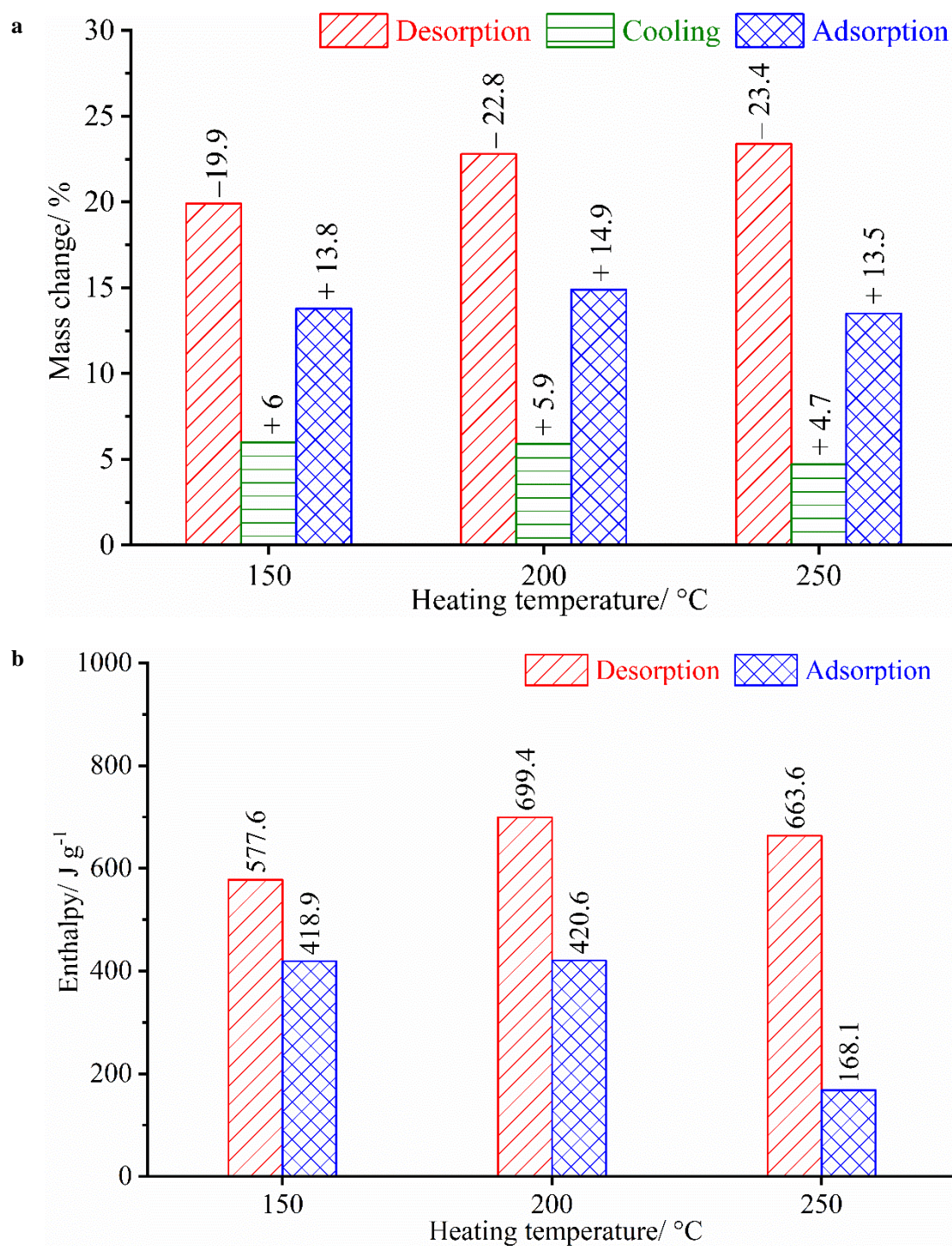


Fig.9 Mass changes (a), and desorption and adsorption enthalpies (b) of Z-NaY during a single cycle with different temperatures of heating

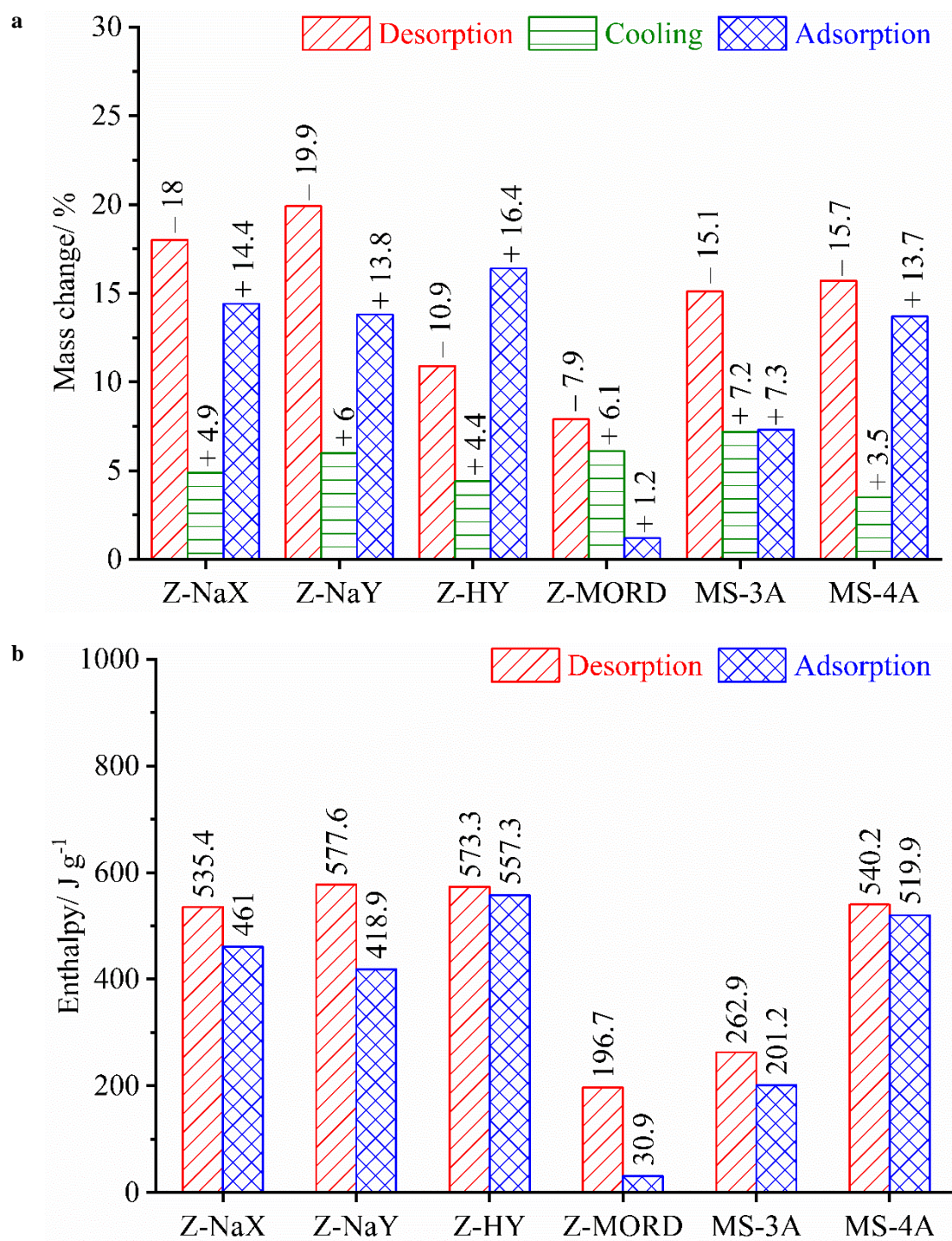


Fig.10 Mass changes (a), and desorption and adsorption enthalpies (b) of the selected materials during a single cycle with 150 °C as the temperature of heating

Table 1 Selected materials and their details

| Materials | CAS No | Cat. No | Label/ Code being used | Chemical formula |
|---------------------|-------------|---------|------------------------|--|
| Zeolite NaX | 63231-69-6 | A10378 | Z-NaX | $\text{NaAlSi}_{1.23}\text{O}_{4.46} \cdot 3.07\text{H}_2\text{O}$ [25] |
| Zeolite NaY | 1318-02-1 | 045862 | Z-NaY | $\text{Na}_{56}\text{Al}_{56}\text{Si}_{136}\text{O}_{384} \cdot 250\text{H}_2\text{O}$ [26] |
| Zeolite HY | 1318-02-1 | 045866 | Z-HY | - |
| Zeolite Mordenite | 1318-02-1 | 045876 | Z-MORD | $\text{Na}_8\text{Al}_8\text{Si}_{40}\text{O}_{96} \cdot 24\text{H}_2\text{O}$ [25] |
| Molecular Sieves 3A | 308080-99-1 | B21165 | MS-3A | - |
| Molecular Sieves 4A | 70955-01-0 | A11535 | MS-4A | $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$ [25,27] |

Table 2 Instruments' specifications

| Instrument | Make and model | Specifications |
|----------------------------|---|---|
| XPS | Thermo Fisher Scientific & K-Alpha | Kinetic energy: 5-1500 eV Low power charge compensation: 72W max Duel beam source Aluminum K-Alpha micro-focused monochromator Low energy co-axial electron |
| BET | MicrotracBEL & BELSORP-mini II | Resolution: $0.01 \text{ m}^2 \text{ g}^{-1}$ Pore size: 0.35 to 200 nm Gas flow: N_2 , CO_2 , H_2 & Ar Accuracy: $\pm 0.25\%$ |
| Thermal constants analyzer | TPS 500S, a Hot Disk's transient plane source | Thermal conductivity: $0.03\text{-}200 \text{ W m}^{-1} \text{ K}^{-1}$ Accuracy: $\pm 2\%$ |
| DTG | SHIMADZU | Temperature range: Ambient to 1500°C Heating/ cooling rate range: 0.1 to $99.9^\circ\text{C min}^{-1}$ Accuracy: $\pm 2\%$ |

Table 3 Elemental composition of the selected materials

| TCM | Elemental composition (wt.%) | | | | | | | | | | |
|--------|------------------------------|------|------|-----------|------|-------|-------|-------|-------|-------|-------|
| | Cations | | | | | | O | C | Al | Si | Si/Al |
| | Mono-valent | | | Di-valent | | Total | | | | | |
| | Li | Na | K | Mg | Sr | | | | | | |
| Z-NaX | - | 6.02 | - | - | 0.04 | 6.06 | 42.52 | 31.33 | 8.06 | 12.02 | 1.49 |
| Z-NaY | 0.63 | 5.23 | - | 0.06 | - | 5.92 | 46.28 | 25.88 | 5.59 | 16.33 | 2.92 |
| Z-HY | - | 0.85 | - | 0.08 | - | 0.93 | 51.56 | 19.45 | 12.89 | 15.17 | 1.18 |
| Z-MORD | 1.53 | 3.21 | - | - | - | 4.74 | 50.03 | 20.08 | 3.56 | 21.59 | 6.06 |
| MS-3A | 0.5 | 2.27 | 6.05 | 0.16 | - | 8.98 | 41.5 | 26.36 | 10.56 | 12.54 | 1.19 |

| | | | | | | | | | | | |
|-------|---|------|---|------|---|------|-------|-------|------|-------|------|
| MS-4A | - | 6.03 | - | 0.12 | - | 6.15 | 39.27 | 34.03 | 8.96 | 11.60 | 1.29 |
|-------|---|------|---|------|---|------|-------|-------|------|-------|------|

Table 4 Structural properties of the selected materials

| Material | Total surface area (m ² g ⁻¹) ^a | Total pore volume (cm ³ g ⁻¹) ^a | Mean pore diameter (nm) ^a | Micro-pore area (m ² g ⁻¹) ^b | Micro-pore volume (cm ³ g ⁻¹) ^b | Meso-pore area (m ² g ⁻¹) ^c | Meso-pore volume (cm ³ g ⁻¹) ^c |
|----------|---|---|--------------------------------------|--|---|---|--|
| Z-NaX | 824.4 | 0.3323 | 1.61 | 781.1 | 0.3131 | 7.0 | 0.0099 |
| Z-NaY | 900.1 | 0.3453 | 1.53 | 869.6 | 0.3354 | 7.5 | 0.0127 |
| Z-HY | 795.2 | 0.3484 | 1.75 | 692.0 | 0.2780 | 46.5 | 0.0698 |
| Z-MORD | 460.3 | 0.2125 | 1.84 | 418.6 | 0.1688 | 11.3 | 0.0450 |

^a BET method; ^b t-plot method; ^c BJH method

Table 5 Thermal conductivity of the zeolites reported in the literature

| Material | Thermal conductivity (W m ⁻¹ K ⁻¹) |
|---------------------|---|
| Z-NaX [22] | 0.09 |
| Z-NaX [16] | 0.08-0.16 |
| Z-NaX [31] | 0.082 |
| Z-NaY [17] | 0.1 |
| Z-NaY [32] | 0.0065-0.25 |
| Silica zeolite [33] | 0.6-4 |
| MS-4A [34] | 0.65 |

Table 6 Desorption results for the selected materials

| Material | Anhydrous mass (%) | Desorption temperature (°C) | | | Desorption enthalpy (J g ⁻¹) | | | Extent of material's desorption at 150 °C (%) | | |
|----------|--------------------|--------------------------------------|-------|-------|--|-------|-------|---|------|------|
| | | Heating rate (°C min ⁻¹) | | | | | | | | |
| | | 5 | 10 | 20 | 5 | 10 | 20 | 5 | 10 | 20 |
| Z-NaX | 73.8 | 305.6 | 276.9 | 254.2 | 820.6 | 742.4 | 843.7 | 77.8 | 69.8 | 65.6 |
| Z-NaY | 73.9 | 281.3 | 276.8 | 295.8 | 977.5 | 745.3 | 728.2 | 86.5 | 79.1 | 78.4 |
| Z-HY | - | - | - | - | 775.7 | 545.6 | 609.1 | - | - | - |
| Z-MORD | 87.6 | 244.6 | 231.1 | 265.2 | 334.5 | 314.5 | 283.3 | 74.2 | 74.7 | 68.9 |
| MS-3A | - | - | - | - | 893.2 | 851.5 | 833.0 | - | - | - |
| MS-4A | 77.8 | 419.8 | 333.4 | 368.9 | 1060.0 | 833.9 | 592.1 | 76 | 76.2 | 71.6 |

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