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Influence of the aqueous medium on the energetic performances of Silicalite-1

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ABSTRACT

The energetic performance of different “Silicalite-1 – aqueous medium” systems was evaluated under high pressure. Depending on the nature of the aqueous medium, high intrusion and extrusion pressures and therefore stored and restored energies are observed. Thus, compared to the “Silicalite-1 – water” system, the stored energy is tripled in the case of “Silicalite-1 – LiCl, $3H_2O$” system.

1. Introduction

Energy production and storage are the two greatest challenges for 21st century to keep our modern life and earth sustainable. With global awareness of the crisis of conventional fossil fuels and their detrimental impact on environment, the search for clean and renewable alternative energy solutions with the possibility to store and restore the unused energy has stimulated worldwide attention [1,2]. Hydrophobic zeolites (zeosils), holds the great potential to meet our future energy storage demand. In this regard, in 2001, the intrusion–extrusion of water in strongly hydrophobic zeolites was explored by our group for applications in the field of energetic [3]. Since this pioneering work, numerous “zeosil – water” systems have been widely studied [4–9]. Recently, this process was extended to hydrophobic metal organic framework materials (MOFs) such as ZIF-8 which displays a shock absorber behavior at a quite low pressure [10].

The most studied solid was the MFI-type zeosil (Silicalite-1); a pure-silica zeolite characterized by a three-dimensional channel system with 10-membered ring (MR) openings (0.55–0.56 nm). The “Silicalite-1 – water” system acts as a molecular spring. It is able to restore 94% of the stored energy and this during several water intrusion – extrusion cycles. However, the stored energy close to $11\ J\ g^{-1}$ of zeolite is quite low [9]. In order to increase this energy, which is in first approximation related to the intruded volume and the intrusion pressure ($W=P.V$), experiments were performed to increase the pore volume by creating additional micro-, meso- and macropores using porogen (carbon black) or templating agents (surfactants), respectively [11]. However, the formation of few additional micropores led only to a slight increase of the stored energy (+20%); the presence of meso- and macropores having no real contribution. Another way to increase the stored energy can be achieved by increasing the intrusion pressure. This aim can be reached by replacing pure water with aqueous electrolyte solutions, the solid–liquid interfacial tension being usually higher compared to pure water [12]. According to the Laplace–Washburn relation, higher intrusion pressures are expected [13]. In such media, water molecules are in strong interaction with ions. Ion–dipole interactions, which depend on the size of the ion, its charge, its polarizability and the dilution of the medium, involve energies of hundreds of kJ/mol. Even if these energies are distributed over several molecules of water, generally between 4 and 6 in the first hydration layer of ions, their values for one water molecule are about 4–5 times higher than for the hydrogen bond of pure water. Consequently, in these aqueous media, the breaking of these solvation bonds needed a force and therefore an applied pressure significantly higher than for pure water. In this communication, this concept which consists in increasing the intrusion pressure is shown with different “Silicalite-1 – aqueous medium” systems. The selected media are water and highly concentrated electrolyte solutions such as LiCl, $3H_2O$, $MgCl_2$, $21H_2O$ and NaCl, $11H_2O$.

2. Experimental section

The intrusion–extrusion experiments were performed according to the procedure previously described for “zeosil – water” systems (see also supporting information) [6]. The MFI-type

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zeolite synthesis procedure and the instrumentation used in this study are also presented in the supporting information.

3. Results and discussion

For the “Silicalite-1 – LiCl, $3H_2O$” system, the pressure – volume curve, as shown in Fig. 1, exhibits one main step at around 280 MPa (P_{int}), corresponding to the intrusion of the liquid, in the pores of Silicalite-1. The intruded volume (V_{int}) is around 0.11 mL g^{-1} (Table 1), as observed for the “Silicalite-1 – water” system [9]. It is worthy to note that this volume is slightly lower than the microporous volume obtained from N_2 adsorption–desorption isotherms (*i.e.*, from 0.18 $cm^3\ g^{-1}$). A possible explanation might be similar to the one proposed by Desbiens et al. [5] for the “Silicalite-1 – water” system where a bulk water density lower than 1 (*i.e.* 0.6 g mL^{-1}) was observed. At low pressure ($<$ 0.1 MPa), the intruded volume corresponds to the interparticular porosity of the zeolitic pellet. Fig. 1 shows that the water intrusion – extrusion process is completely reversible with a slight hysteresis since the extrusion of water occurs at a lower pressure than the one observed for the intrusion (P_{ext}=275 MPa). The second and third intrusion – extrusion cycles are nearly identical to the first one revealing the excellent reversibility of the phenomenon (Fig. 1 and Table 1).

Compared to the “Silicalite-1 – water” system, the intruded volume remains equal to 0.11 mL/g, while the extruded volume is lower (0.095 mL/g at 260 MPa). However, at the end of the process (complete release of the pressure), the liquid is completely expelled from the solid and the extruded volume is close to 0.11 mL/g. The “Silicalite-1 – LiCl, $3H_2O$” system displays mainly a spring behavior; 84% of the stored energy being restored at 260 MPa (see Table 1). The intrusion and extrusion pressures are strongly higher to those found in the case of pure water (*i.e.*, 100 MPa, see Fig. 2). Therefore, the energetic performances are almost tripled in comparison to the “Silicalite-1 – water” system,

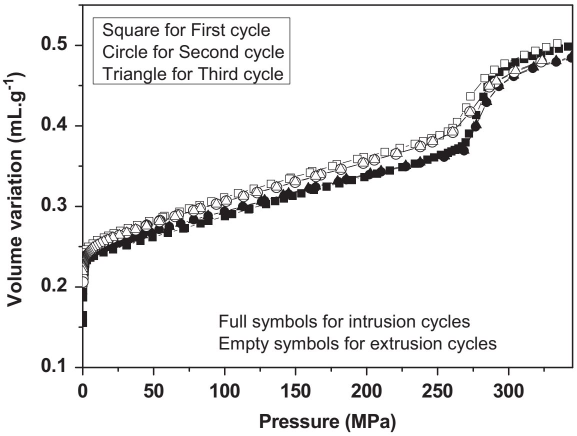

Fig. 1. Pressure–Volume diagrams of the “Silicalite-1 – LiCl, $3H_2O$” system.

Table 1
Characteristics of the “Silicalite-1 – LiCl, $3H_2O$” system: intrusion (P_{int}) and extrusion (P_{ext}) pressures, intruded (V_{int}) and extruded (V_{ext}) volumes, stored (E_{int}) and restored (E_{ext}) energies.

	P_{int} [a] (MPa)	V_{int} [a] (mL g^{-1})	P_{ext} [a] (MPa)	V_{ext} [a] (mL g^{-1})	E_{int} [b] (J g^{-1})	E_{ext} [b] (J g^{-1})	Energy yield [c] (%)
Cycle 1	280	0.11	275	0.095	~31	~26	84
Cycle 2	280	0.11	275	0.095	~31	~26	84
Cycle 3	280	0.11	275	0.095	~31	~26	84

[a] Determined from the Pressure–Volume diagrams. $V_{ext.}$ was determined at 260 MPa.

[b] Stored (E_{int}) or restored (E_{ext}) energy, corresponding to the area located between the relevant curve of intrusion or extrusion, respectively, and the volume axis (Fig. 1) is given by: $E=\int_{V_0}^{V_f} PdV$, where V_0 is the initial volume and V_f is the final volume.

[c] bb% Energy yield=E_{ext}/E_{int}*100.

The powder X-ray diffraction patterns (Fig. S1) of the nonintruded and intruded – extruded samples are very similar; which means that at the long range order, the MFI structure is not affected. However, from SEM analysis, probably due to the high intrusion pressure, the crystals of the intruded – extruded sample are broken (Fig. 3). Such a result, might explain the particular shape of the extrusion curve (Fig. 1).

The thermogravimetric analyses achieved under air are depicted in Fig. S2. For the nonintruded samples, the total weight loss is quite low (close to 0.7 wt%); whereas the later reaches 2.8 wt% for the intruded samples. The weight losses occur in two steps. The first one between 20 and 200 °C, is ascribed to the desorption of the physisorbed water molecules (0.4 wt% before and 1.6 wt% after intrusion. The second weight loss, in the temperature range 200–500 °C, can be attributed to the removal of the trapped water in the micropores or arising from dehydroxylation reactions (0.3 wt% before and 1.2 wt% after intrusion). After water intrusion – extrusion experiments the total weight loss increases by 2.1% revealing, as shown by solid-state NMR, the creation of few defect sites.

N_2 adsorption – desorption isotherms (Fig. 4) of the intruded and nonintruded samples are mainly of type I characteristic of microporous solids. For both solids, the corresponding textural characteristics (BET surface areas and micropore volumes) are quite similar and equal to 367 and 359 m² g^{-1} and 0.18 and 0.17 $cm^3\ g^{-1}$, respectively.

The ^{29}Si MAS NMR spectra of the nonintruded and intruded samples (Fig. 5) exhibit eight resonances in the -108 to 118 ppm range ascribed to the 24 inequivalent crystallographic silicon sites. On both spectra, no signals assigned to Q_3 groups corresponding to defects such as Si–OH groups (silanol) and expected at about -100 ppm are observed. After the intrusion – extrusion step, the peak resolution of Q_4 sites is similar indicating no significant modification of the local structural order in the inorganic framework. The ^1H–^{29}Si CP MAS NMR spectra of the corresponding samples (Fig. S3) recorded under the same conditions (see Table S1) did not reveal the presence of Q_3 sites on the nonintruded sample (the detection limit is around 2% of Si sites). After intrusion – extrusion experiments, a very small component appears at

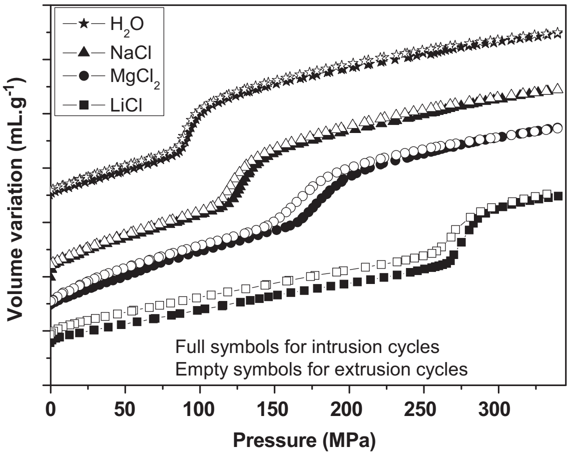

Fig. 2. Pressure–Volume diagrams of the “Silicalite-1 – aqueous medium” systems: (stars) H_2O, (triangles) NaCl, $11H_2O$, (circles) $MgCl_2$, $21H_2O$, (squares) LiCl, $3H_2O$. For a better visibility, the diagrams are shifted along the Y-axis.