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Influence of LiCl aqueous solution concentration on the energetic performances of pure silica chabazite

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In order to study the energetic performances of different "pure silica chabazite-LiCl aqueous solution" systems, intrusion-extrusion experiments were performed under high pressure. Depending on the LiCl concentration in the aqueous medium (0 M, 5 M, 10 M, 20 M), an increase of the stored (4.4, 9.9, 13.5, 24.3 J g⁻¹) and restored (2.6, 8.1, 11.8, 20.5 J g⁻¹) energies are observed. Therefore, compared to the "pure silica CHA-H₂O" system, the stored energy is increased by 5.5 times for the "pure silica CHA-20 M LiCl" one. The zeolite samples were characterized (XRD, TG, NMR spectroscopy, N₂ adsorption and SEM) before and after the intrusion-extrusion process in order to better understand the influence of the LiCl concentration on the system behavior.

Introduction

Zeolites are aluminosilicate molecular sieves that present very interesting adsorption, separation and catalytic properties.¹⁻⁷ Originally found as a natural fossil,⁸ zeolites were then synthesized and used in the petroleum and chemical industries.² Increasing their silica to aluminum ratio (Si/Al) led to hydrophobic properties, and pure silica zeolites (zeosils) were therefore examined toward Volatile Organic Compound (VOC) adsorption^{9,10} and energy storage.¹¹⁻¹³ Zeosils offer notably higher thermal and chemical stability than their aluminosilicate zeolite counterparts.¹⁴ Zeosil materials are expected to be a key pillar of 21st century technology in the areas of sustainable energy and environmental applications.

In 2001 zeosils were used for the first time for potential energy storage or adsorption applications.¹¹⁻¹³ Since, several intrusion-extrusion experiments were conducted by our research team on different zeosils using water as non-wetting liquid.¹⁵⁻²⁶ Other hydrophobic materials have been tested for water intrusion-extrusion: Metal Organic Framework (MOF) materials,²⁷⁻²⁹ carbon nanotubes and nanoporous carbon³⁰ and hydrophobic mesoporous materials.³¹ The thermal effects of water intrusion in silicalite-1 zeosil were also quantified by high pressure calorimetry.³²

Since the stored and restored energies (E) depend on the intrusion/extrusion pressures (P) and the intruded/extruded

volumes (V) " $E = P \times V$ ", two routes were followed in order to improve the energetic performances: (1) increasing the pore volume by creating additional meso- and macropores in the starting material^{33,34} but it was observed that meso- and macropores do not really contribute to the increase of the stored energy since the intrusion-extrusion of solution in these pores occurs at very low pressure, and therefore only a small increment of the stored energy was obtained (~20%). (2) Otherwise, the intrusion pressure can be increased by replacing water by electrolyte aqueous solutions.

Various experiments and atomistic simulations were performed testing different zeosils and various solutions³⁵⁻⁴³ observing an enhanced intrusion pressure up to 7.4 times when using aqueous electrolyte solutions compared to the one obtained with pure water.⁴⁴ The same trends were observed with high silica FAU and MFI (ZSM-5) zeolites.⁴⁵⁻⁴⁷

In this work a pure silica chabazite (CHA) was chosen because of its 3D structure characterized by rhombohedral cages that can enhance the available volume and the small 8 MR (diameter of 3.8 nm) pore opening. Our previous works on the intrusion-extrusion of water in pure silica CHA-type zeolite^{16,19} revealed a spring behavior with an intrusion pressure of $P_{\text{int}} = 41.6$ MPa and an intruded volume of $V_{\text{int}} = 0.158$ mL g⁻¹ for the first cycle and $P_{\text{int}} = 37.0$ MPa and $V_{\text{int}} = 0.148$ mL g⁻¹ for the following cycles. A little amount of water molecules is not extruded after the first cycle because of the interaction with the defect sites or because they are trapped inside the cages.¹⁹ Therefore, the real behavior of the first cycle is a combination of the bumper and the spring.

Herein, we present the study of the influence of electrolyte concentration on the energetic performances of the "CHA-type

zeosil (Si-CHA here below)–LiCl aqueous solution'' system using high pressure intrusion–extrusion experiments with a thorough investigation on the structural and physicochemical properties of the zeosil.

Results and discussion

Energetic performances of CHA-type zeosil

The intrusion–extrusion data are reported in Table 1 and the corresponding isotherms (P – V diagrams) of ''Si-CHA–water'' and ''Si-CHA–LiCl aqueous solution'' systems are shown in Fig. 1.

For all the samples, three intrusion–extrusion cycles were performed. For clarity only the first two cycles are presented in Fig. 1, because the II and III cycles for all the samples are superimposable. The 0–3 MPa range on the X -axis is not shown, since the observed volume variation is due to the intrusion of liquid in the interparticular porosity of the pellet.²⁴

In the first cycle the ''Si-CHA–water'' system shows a combination of the bumper (a part of water is not extruded, as was shown in our previous work¹⁹) and spring behavior with small hysteresis as mentioned in our previous study.¹⁹ In contrast, in the following cycles the system demonstrates spring behavior. The intruded volumes correspond to the one extruded in the first cycle, no additional irreversible intrusion is observed. The NMR spectroscopy results (see below) show the presence of silanol defects in the nonintruded sample. Thus, partial bumper behavior in the first intrusion–extrusion cycle can be explained by the irreversible adsorption of some water molecules on the defects. In the case of ''Si-CHA–LiCl aqueous solution'' systems the intrusion is reversible: the liquid is always completely extruded. The systems demonstrate a shock-absorber behavior with a small hysteresis between intrusion and extrusion curves.

A change in the system behavior related to the salt concentration was already observed by our team in ''*BEA or LTA-type zeosil–LiCl aqueous solution'' systems^{37,44} even if the effect was more pronounced in these cases. This change can be related to the nature of the liquid intruded into the pores that could be water or solvated ions in the case of concentrated LiCl aqueous solutions.

Moreover, by increasing the salt concentration, a greater hysteresis between intrusion and extrusion curves is also observed.

It has been found that the intrusion pressure grows with LiCl aqueous solution concentration. The pressure increases from 29 MPa for pure water up to 162 MPa for 20 M LiCl

Fig. 1 The first and the second intrusion–extrusion cycles of ''Si-CHA–water'' and ''Si-CHA–LiCl aqueous solution'' systems. For better visibility, the diagrams are shifted along the Y -axis and the X -axis is not entirely (350 MPa) shown.

aqueous solution. Thus it is enhanced by a factor of 5.6. This increase is much more important than the results obtained for *BEA-type zeosil³⁷ and for silicalite-1 (MFI-type zeosil),³⁶ where the intrusion pressure was only doubled and tripled, respectively.

This phenomenon can be related to the smaller pore openings (8 MR) in the chabazite framework compared to the ones for MFI (10 MR) and *BEA (12 MR) frameworks. To penetrate into the pores the solvated ions should pass through the pore openings. For smaller pore openings, the deformation of a coordination sphere of solvated ions is expected to be more important, and thus, an additional pressure should be applied.

Comparing our results with the ones obtained for LTA-type zeosil,⁴⁴ two similar trends can be noted for these two zeosils with similar structural features (3D cages, 8 MR): a low value of the intrusion pressure of the ''zeosil–water'' system due to the cage-type pore systems²⁶ and a large increase of intrusion pressure for 20 M LiCl aqueous solution: 5.6 and 7.4 times for CHA and LTA-type zeosils, respectively. According to the literature, the increase of the intrusion pressure can be explained by a higher surface tension of aqueous electrolyte solution in comparison with water,^{48,49} osmotic phenomena,^{50,51} a confinement effect of nanopore walls^{13,46} or ion desolvation.^{36,39,52,53}

Recent studies⁵⁴ demonstrated that during intrusion–extrusion experiments in pure silica ferrierite (FER-type zeolite) using

Table 1 Characteristics of the samples: intrusion (P_{int}) and extrusion (P_{ext}) pressures, intruded (V_{int}) and extruded (V_{ext}) volumes, stored (E_s) and restored (E_r) energies

System	P_{int}^a [MPa]	P_{ext}^a [MPa]	V_{int}^a [mL g ^{−1}]	V_{ext}^a [mL g ^{−1}]	E_s^b [J g ^{−1}]	E_r^c [J g ^{−1}]	Energy yield ^d (%)
Si-CHA–H ₂ O	29 ^e /22 ^f	20 ^e /20 ^f	0.15 ^e /0.13 ^f	0.13 ^e /0.13 ^f	4.4 ^e /2.9 ^f	2.6 ^e /2.6 ^f	60 ^e /91 ^f
Si-CHA–5 M LiCl	66 ^e /63 ^f	54 ^e /54 ^f	0.15 ^e /0.15 ^f	0.15 ^e /0.15 ^f	9.9 ^e /9.4 ^f	8.1 ^e /8.1 ^f	82 ^e /86 ^f
Si-CHA–10 M LiCl	90 ^e /86 ^f	79 ^e /79 ^f	0.15 ^e /0.15 ^f	0.15 ^e /0.15 ^f	13.5 ^e /12.9 ^f	11.8 ^e /11.8 ^f	88 ^e /92 ^f
Si-CHA–20 M LiCl	162 ^e /153 ^f	137 ^e /137 ^f	0.15 ^e /0.15 ^f	0.15 ^e /0.15 ^f	24.3 ^e /22.9 ^f	20.5 ^e /20.5 ^f	85 ^e /89 ^f

^a Determined from intrusion–extrusion isotherms. ^b Stored energy $E_s = V_{\text{int}} \times P_{\text{int}}$. ^c Restored energy $E_r = V_{\text{ext}} \times P_{\text{ext}}$. ^d Energy yield = $E_r/E_s \times 100$. ^e First cycle. ^f Second and third cycles.

MgCl₂·21H₂O aqueous solution, the ions are intruded into zeosil pores. Surprisingly, it was found that the solution intruded into the pores (MgCl₂·10H₂O) was more concentrated than the initial one. The decrease of the water content and, thus, the higher concentration of the intruded solution could be reasonably the result of the hydrophobic nature of the host zeolite matrix. Therefore, the ion desolvation hypothesis seems to be confirmed. The increase of intrusion pressure is probably related to the hypothesis that the solvated ions are subjected to a strong distortion to enter inside the small pores.⁴⁴

Our values of water intrusion pressure are lower than the ones obtained in a previous work¹⁹ (I cycle: 29 instead of 42 MPa; II cycle: 22 instead of 37 MPa, respectively), probably because of the higher amount of silanol defects in this Si-CHA sample. The latter was shown by NMR spectroscopy. Besides, the higher amount of non-extruded water after the first cycle in our chabazite sample corroborates with a higher number of defects in our sample.

Since the behavior of the “zeosil–LiCl solution” systems is fully reversible and almost the same for all the salt concentrations, no great textural and structural differences are expected between these samples after the intrusion–extrusion experiments.

Influence of the intrusion–extrusion process on the morphology and the structure of chabazite on the long-range order

The obtained patterns of the samples before and after intrusion–extrusion experiments are very similar and correspond to a pure chabazite phase (Fig. 2). It means that at the long-range order, the structure of chabazite is not affected. The XRD patterns can be indexed with a hexagonal cell (space group *R3m*). The cell parameters of the nonintruded sample are: $a = 13.5516(12)$ Å, $c = 14.7692(15)$ Å. The cell volume is not affected by the intrusion–extrusion experiments as is shown in Table 2.

The size and the morphology of chabazite crystals were studied before and after intrusion–extrusion cycles by scanning

Fig. 2 X-ray patterns of Si-CHA samples (a) before and after three intrusion–extrusion cycles in (b) water and in (c) 5 M, (d) 10 M and (e) 20 M LiCl aqueous solutions.

Table 2 Unit-cell parameters of Si-CHA samples before and after three intrusion–extrusion cycles in water and in LiCl aqueous solutions at different concentrations

Sample	a [Å]	c [Å]	V [Å ³]
Si-CHA	13.5516(12)	14.7692(15)	2348.9(3)
Si-CHA–H ₂ O	13.5497(18)	14.7757(23)	2349.3(4)
Si-CHA–5 M LiCl	13.5487(25)	14.772(3)	2348.4(6)
Si-CHA–10 M LiCl	13.5460(23)	14.764(3)	2346.1(6)
Si-CHA–20 M LiCl	13.5477(15)	14.770(22)	2347.7(4)

Fig. 3 SEM micrographs of Si-CHA samples before (a) and after (b) three intrusion–extrusion cycles in water.

electron microscopy (SEM). The samples exhibit cubic-shaped morphology with an average size of $1 \times 1 \times 1 \mu\text{m}^3$ (Fig. 3a).

After three intrusion–extrusion cycles, the crystals are partially damaged as is shown in Fig. 3b.

Textural properties

The N₂ adsorption–desorption isotherms of the nonintruded sample and the one intruded in 20 M LiCl aqueous solution are shown in Fig. 4. Only the isotherms of Si-CHA before and after 20 M LiCl aqueous solution intrusion–extrusion are shown, because all the curves obtained for the intruded samples are almost superimposable. In all cases the isotherms are mainly of type I characteristic of microporous solids. The BET surface area and microporous volume of the nonintruded sample are 844 m² g^{−1} and 0.30 cm³ g^{−1} respectively. The values obtained for the intruded samples are slightly lower, but very close

Fig. 4 N₂ adsorption–desorption isotherms at 77 K of Si-CHA samples before and after three intrusion–extrusion cycles in 20 M LiCl aqueous solution.

Table 3 Values of the BET surface area and the micropore volume obtained by N₂ adsorption-desorption isotherms at 77 K for Si-CHA samples before and after three intrusion-extrusion cycles in water, 5 M, 10 M, and 20 M LiCl aqueous solutions

System	S_{BET} [m ² g ⁻¹]	V_{micro} [cm ³ g ⁻¹]
Si-CHA	835	0.30
Si-CHA-H ₂ O	761	0.28
Si-CHA-5 M LiCl	748	0.27
Si-CHA-10 M LiCl	755	0.28
Si-CHA-20 M LiCl	755	0.28

between them (see Table 3). This may indicate that some defect sites have been created after three intrusion-extrusion cycles or that some traces of liquid remain inside the zeolite cages. The slight hysteresis observed in the desorption isotherm for the intruded sample is probably due to the interparticular porosity and to the mesoporosity created by the breaking of the crystals that occurs during the intrusion-extrusion process as shown from the SEM image of the intruded-extruded sample.

Detection of water loss and OH-groups

The experimental results issued from thermogravimetric (TG) analysis of the Si-CHA samples before and after intrusion-extrusion experiments are depicted in Fig. 5. The total weight loss ranges from 3.4 wt% for the nonintruded sample to 4.3 wt% for 10 M and 20 M LiCl intruded samples. The weight losses occur in two steps: the first one, situated between 30 °C and 180 °C, is ascribed to the desorption of the adsorbed water molecules.

The second one, in the temperature range of 180–700 °C, can be assigned to water arising from dehydroxylation reactions. The weight loss due to the adsorbed water is 2.6 wt% for the nonintruded chabazite and 3.1–3.7 wt% for the intruded samples. The weight loss of the Si-CHA and Si-CHA intruded-extruded samples due to the dehydroxylation reaction is 0.7 wt% and ~1.1 wt% respectively that corresponds to ~2 and ~3 OH-groups per chabazite unit cell (Si₃₆O₇₂).

The thermogravimetric analysis shows that the nonintruded sample, even if it is hydrophobic, presents some defect sites.

Fig. 5 TG curves of the Si-CHA samples before and after three intrusion-extrusion cycles in water, 5 M, 10 M and 20 M LiCl aqueous solutions.

Fig. 6 ²⁹Si-MAS NMR spectra of the Si-CHA samples (a) before and after three intrusion-extrusion cycles in (b) water, (c) 5 M, (d) 10 M and (e) 20 M LiCl aqueous solutions.

The quantity of defects is increased by the intrusion-extrusion experiments. As was already observed by Khay *et al.*³⁶ the increase of the salt concentration leads to an increase of the weight loss and therefore to a higher number of defect sites.

These results are different from what was obtained by Trzpit *et al.*,¹⁹ indeed they found a lower weight loss for the non-intruded sample (2%) but a higher value (5.8%) for the water-intruded one. Such differences are quite difficult to explain. However, in our sample the number of defect sites is larger.

Detection of structural defects on the short-range order

In order to evaluate the changes in the zeolite framework and the formation of the defects after the intrusion-extrusion experiments, the samples were characterized by ²⁹Si MAS NMR spectroscopy. The ²⁹Si MAS NMR spectra of the Si-CHA samples before and after intrusion-extrusion experiments in water, 5 M, 10 M and 20 M LiCl aqueous solutions are shown in Fig. 6. The spectra of the starting material and the intruded samples are very close and exhibit a well-defined resonance at -111.6 ppm attributed to Q₄ groups (Si(OSi)₄). This sharp peak corresponds to the unique crystallographic site of the chabazite framework. A very small broad component is also detected at around -102 ppm. The latter can be assigned to Q₃ groups (HO-Si-(OSi)₃ or ⁻O-Si-(OSi)₃).

Comparing the spectra of this work to the one obtained by Trzpit *et al.*,¹⁹ the difference between the Q₃ site amount of the samples of CHA-type zeosil before intrusion-extrusion experiments is clearly observed (7.7% and 4.3%, respectively). Thus, our sample contains a higher amount of Q₃ defects, which is also confirmed by comparison of the corresponding TG curves. The silanol groups confer hydrophilicity to the zeosil that facilitates the transfer of water into the pores. This fact can

Fig. 7 ^1H - ^{29}Si CPMAS NMR spectra of the Si-CHA samples (a) before and after three intrusion-extrusion cycles in (b) water, (c) 5 M, (d) 10 M and (e) 20 M LiCl aqueous solutions.

explain the higher value of the nonextruded volume after the first intrusion-extrusion cycle in the “Si-CHA-water” system and the lower intrusion pressure obtained for our sample.

The ^1H - ^{29}Si CPMAS NMR spectra of the Si-CHA samples before and after intrusion-extrusion experiments (Fig. 7) were recorded with a short contact time (1 ms) in order to enhance the silicon atoms that bear protons and get evidence of the presence of silanol groups. The spectra of all samples show the presence of a resonance at -91.8 ppm corresponding to Q_2 species. Two resonances corresponding to Q_3 groups are observed at -101.2 and -102.1 ppm. ^1H - ^{29}Si CPMAS NMR does not provide quantitative results; however, it allows a relative comparison of the spectra if they were registered under the same conditions. Thus, it can be said that the Q_3 and Q_4 resonances in all spectra have similar intensities and no significant differences are observed that is in agreement with ^{29}Si MAS data.

Conclusions

The intrusion of electrolyte solutions in CHA-type zeosil has been performed for the first time. The influence of LiCl aqueous solution concentration on the energetic performances of the “Si-CHA-solution” system has been studied. In the case of water intrusion the system demonstrates a combination of bumper and spring behavior in the first cycle with partially irreversible water intrusion, while in the second and in the third cycles a spring behavior is observed. In the case of LiCl aqueous solution intrusion, the systems show a shock-absorber behavior with a low hysteresis between intrusion and extrusion isotherms in all cycles. The intrusion pressure increases with the increase of LiCl concentration, and at the same time the hysteresis between the intrusion and extrusion isotherms is slightly enhanced. The intrusion pressure increases from 29 MPa for pure water up to 162 MPa for 20 M LiCl aqueous solution. Thus, compared to the “Si-CHA-water” system, the stored energy is increased by a factor of 5.5 for the “Si-CHA-20 M aqueous LiCl”

system and reaches the value of 24 J g^{-1} . This value is one of the highest obtained for the zeosil-based systems. This increase in the energetic performances of Si-CHA when using LiCl aqueous solution instead of water is promising for technological uses in mechanical energy storage.

Experimental

The Si-CHA sample was synthesized in fluoride medium according to the procedure published by Díaz-Cabañas *et al.*⁵⁵ using N,N,N -trimethyladamantammonium (TMAda⁺) as a structure-directing agent. The starting gel (molar composition: $1\text{SiO}_2:0.5\text{TMAdaOH}:0.5\text{HF}:4.7\text{H}_2\text{O}$) was introduced in a Teflon-lined stainless-steel autoclave and heated at 150°C for 5 days. After synthesis, the product was filtered, washed with distilled water and ethanol, and then dried at 70°C overnight. At the end the solid was calcined at 600°C for 8 hours to completely remove the organic template. The intrusion-extrusion of water and LiCl aqueous solutions in Si-CHA samples was performed at room temperature using a Micromeritics mercury porosimeter (Model Autopore IV).

The zeolite powder was compressed in a pellet. The cell containing zeosil and water/aqueous solution consists in a polypropylene cylinder of 2 mL capacity sealed using a mobile piston. This cell is introduced in the 15 mL glass cell of the porosimeter which is filled with mercury. The volume variation is determined from the capacity measurement which depends on the height of mercury in the capillary tube of the glass cell. The experimental intrusion-extrusion curve is obtained after subtraction of the curve corresponding to the compressibility of the medium. The values of the intrusion (P_{int}) and extrusion (P_{ext}) pressures correspond to that of the half volume total variation. Pressure is expressed in MPa, and volume variation in mL per gram of anhydrous calcined zeolite. The experimental error is of the order of 1% on the pressure and on the volume.

After the intrusion-extrusion experiments, the samples intruded with LiCl were washed with water to remove traces of LiCl (if there any). Then the samples were dried at 70°C overnight and hydrated in an 80% relative humidity atmosphere in order to set the hydration state.

Powder X-ray diffraction patterns of the different samples were recorded on a STOE STADI-P diffractometer in the transmission scan mode equipped with a curved germanium(111) primary monochromator and a linear position-sensitive detector ($6^\circ 2\theta$) using $\text{CuK}\alpha 1$ radiation ($\lambda = 0.15406 \text{ nm}$). Measurements were achieved for 2θ values in the 3 – 50° range, step $0.2^\circ 2\theta$, and time per step = 10 s.

The size and the morphology of the crystals were determined by scanning electron microscopy (SEM) using a Philips XL 30 FEG microscope.

Nitrogen adsorption-desorption isotherms were performed at 77 K using a Micromeritics ASAP 2420 apparatus. Prior to the adsorption measurements, the intruded-extruded samples were outgassed at 90°C overnight to eliminate physisorbed water and to avoid the dehydroxylation process. For comparison

Table 4 Recording conditions of the ^{29}Si MAS and ^1H - ^{29}Si CPMAS NMR spectra

	^{29}Si MAS	^1H - ^{29}Si CPMAS
Chemical shift standard	TMS ^a	TMS ^a
Frequency (MHz)	59.6	59.6
Pulse width (μs)	2.3	5.00
Flip angle	$\pi/6$	$\pi/2$
Contact time (ms)	—	1
Recycle time (s)	80	7; ^{b,c} 5; ^c 10 ^d
Spinning rate (kHz)	4	4
Scan number	1000	10 000

^a Tetramethylsilane. ^b Si-CHA. ^c Si-CHA-H₂O; Si-CHA-5 M LiCl; Si-CHA-10 M LiCl. ^d Si-CHA-20 M LiCl. ^e The relaxation time t_1 was optimized.

the nonintruded sample was activated under the same conditions. The specific surface area (S_{BET}) and microporous volume (V_{micro}) were calculated using the BET and t -plot methods, respectively.

Thermogravimetric (TG) analyses were carried out on a Mettler Toledo STARE apparatus, under air flow, with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ from 30 to $700\text{ }^\circ\text{C}$.

^{29}Si MAS and ^1H - ^{29}Si CPMAS NMR spectra were recorded at room temperature on a Bruker Avance II 300 MHz spectrometer equipped with a double-channel 7 mm Bruker MAS probe. The recording conditions are given in Table 4.

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