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Energetic performances of FER-type zeolite in the presence of electrolyte solutions under high pressure

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The influence of the synthesis procedure and therefore of the morphology (elongated crystals and plate-like crystals) and crystal size on the energetic performances of pure silica Ferrierite was studied by high pressure intrusion-extrusion of water and LiCl aqueous solutions (nonwetting liquid) at different concentrations. The results indicate that the morphology does affect neither the intrusion pressure nor the intruded volume. High intrusion pressure values were found (150, 189, 243 MPa for water, 5 M and 10 M LiCl aqueous solution, respectively) probably due to the channel pore system and to the small pore openings (8 and 10 MR) characteristic of this zeolite. A similar spring behavior of the "zeosil-nonwetting liquid" system is observed whatever the LiCl concentration. The zeolite samples were characterized by XRD, TG, ^{29}Si solid-state NMR spectroscopy, N_2 adsorption-desorption and SEM analysis before and after the intrusion-extrusion process.

1. Introduction

One of the most important global challenges is low cost, efficient and sustainable energy production and storage. Heterogeneous lyophobic systems (HLS) based on high pressure intrusion of non-wetting liquid in a porous lyophobic matrix are one of the promising technologies for mechanical energy absorption and storage [1–8].

During the intrusion step (intrusion process), the bulk phase is transformed into a multitude of molecular clusters that interact with the porous matrix converting the supplied mechanical energy into interfacial one. The absorbed mechanical energy corresponds to a work (W) which can be expressed as $W = \int_{V_1}^{V_2} -P \cdot dV$, where P , V_1 and V_2 are the intrusion pressure, the initial and the final volume, respectively.

Heterogeneous lyophobic systems can be used for various applications in absorption, storage and generation of mechanical energy. They can be applied for highly comfortable shock absorbers for automotive industry with very low damping coefficient

[2,9–12]. The HLS can be also used in highly effective shock and blast resistant materials [13]. From the point of view of mechanical energy storage the HLSs demonstrate the volumetric energy density considerably higher than ones for hydro pumped energy storage and for conventional springs, whereas they are similar to the ones for compressed air [14]. The HLS-based self-contained actuator for space applications proposed by V. Eroshenko can be cited as an example of energy storage application [1,15]. It showed not only considerably higher energy density in comparison with conventional springs, but also provided very high and constant force. The systems can be also used for the generation of energy from low temperature heat. HLS-based thermomolecular engines for the conversion of heat energy to mechanical one and new thermodynamic cycles were proposed in the works [14,16].

Zeolites are crystalline microporous materials which are involved in many industrial applications such as ion exchange, adsorption, catalysis and molecular sieving [17]. In 2001 our group used hydrophobic pure silica zeolites, called zeosils, for potential mechanical energy storage or dissipation applications by the forced intrusion-extrusion of water [18,19].

Several intrusion-extrusion experiments were performed on "zeosil-water" systems [18–29]. Depending on various structural and physicochemical parameters of the zeosil, such as the pore system (cages or channel), the pore dimensionality (1, 2, or 3D), the pore size or the framework stability, the "zeosil-water" system can

expulse the whole amount of the intruded liquid showing a spring ("MFI-type and MTT-type zeosil-water" systems for instance) [18,30] or a shock absorber ("RRO-type zeosil-water" system) [24] behavior. Otherwise if water is not expelled after the pressure release, the system acts like a bumper ("BEA-type zeosil-water" system) [18]. Therefore, according to the reversible or irreversible character of the intrusion-extrusion cycle, "pure silica zeolite-water" systems can restore, dissipate or absorb the supplied mechanical energy.

In recent years further experiments were conducted on "zeosil-electrolyte aqueous solution" systems [31–38]. An increase of the intrusion pressure and therefore of the energetic performances was observed replacing water with electrolyte aqueous solutions. For instance, the intrusion pressure could be enhanced up to 74 times for the LTA-type zeosil when a 20 M LiCl aqueous solution was used as nonwetting liquid instead of water [37].

The nonwetting liquid intrusion-extrusion process under high pressure was also extended to hierarchical zeolites [39,40] and to another family of hydrophobic microporous materials, the metal organic framework materials (MOFs) such as ZIF-8 [41,42], ZIF-71 [43], ZIF-67 [44,45] and Cu₂(tebpz) [46].

The influence of the downsizing of the crystal sizes (from micrometer to nanometer scale) of the MFI-type zeosil [47] and ZIF-8 [48] on the energetic performances were also investigated. For MFI-type zeosil no real influence has been observed on the intrusion pressure, whereas for ZIF-8 this pressure decreases by decreasing the crystal size.

Pure silica Ferrierite was already chosen for intrusion-extrusion tests with different liquids by Arletti et al. in order to study the nature and the influence of the intruded species or the phase transitions that occur during the high pressure process [49,50]. In this work the energetic performances of "pure silica FER-type zeolite (zeosil Ferrierite)-nonwetting liquid" systems are investigated by water or aqueous electrolyte solutions intrusion-extrusion experiments under high pressure. The water intrusion was already studied in a previous work [22], "Ferrierite-water" system demonstrated a spring behavior with very high intrusion pressure (150 MPa). In this paper we show that the intrusion pressure can be enhanced by using LiCl aqueous solutions instead of pure water. The influence of the morphology and the size of Ferrierite crystals synthesized by different methods on the energetic performances is also studied. The zeosil samples were obtained by two synthesis methods [51,52]: from a Layered Zeolite Precursor named LZP [53] or by direct hydrothermal synthesis. The synthesis of zeosils from LZP was previously used for the synthesis for instance of RRO-type zeosil (RUB-41) [54] and it was shown after water intrusion-extrusion experiments [24] that the breaking of the siloxane bonds occurred preferentially at the level of the condensation of the layers of the RUB-39 layered precursor. Therefore it is interesting to see if such a behavior will be reproduced for the Ferrierite sample prepared by this synthesis route.

All the samples were fully characterized before and after water intrusion-extrusion experiments mainly by powder X-ray diffraction (XRD), N₂ adsorption-desorption measurements at 77 K, thermal analysis (TG), Scanning Electron Microscopy (SEM) and ²⁹Si solid-state NMR spectroscopy in order to study the influence of the experiments on Ferrierite structural and physicochemical parameters.

2. Experimental

2.1. Synthesis of the samples

The samples of FER-type zeosil were obtained following two different protocols: i) the sample derived from the Schreyeck et al.

[51] procedure (hereafter, FER-P sample), where the LZP named PREFER is firstly synthesized and after calcination the FER-type zeolite is obtained; ii) the sample from the Kuperman et al. [52] procedure (hereafter, FER-K sample) using a non-aqueous medium and leading to giant crystals of Ferrierite in only one step.

2.1.1. Synthesis of FER-P

The pure silica FER-type zeolite derived from the PREFER precursor was synthesized according to the procedure published by Schreyeck et al. [51]. The reaction gel had the following composition: 1 SiO₂: 1 4-amino-2,2,6,6-tetramethylpiperidine: 1.5 NH₄F: 0.5 HF: 10 H₂O, where precipitated silica (Rhodia Z1175 MP) is used as silica source. The fluorinated compounds (NH₄F, Sigma-Aldrich, ≥98%; HF, Sigma-Aldrich, ≥40 wt%) were added to a mixture of SiO₂ and water, at the end the organic template was mixed too. The starting gel was introduced in a Teflon-lined stainless-steel autoclave and heated at 170 °C during 15 days. After the synthesis, the product was filtered, washed with distilled water and ethanol, then dried at 70 °C overnight. This layered precursor was then calcined at 600 °C to remove the organic template and to get the FER-type zeosil by topotactic condensation of the silicate layers.

2.1.2. Synthesis of FER-K

This FER sample was obtained following the Kuperman et al. [52] procedure. The reaction gel had the following molar composition: 1.5 SiO₂: 2 HF-py: 4 PrNH₂: 16 py: 8 H₂O. The reactants used were fumed silica (Aerosil 130, Degussa), hydrogen fluoride-pyridine (HF-py, 70 wt% HF in pyridine, Sigma-Aldrich), pyridine (py, SDS, 99.5 wt%), propylamine (PrNH₂, Fluka, 99 wt%) and distilled water. After homogenization (slight stirring), the mixture was introduced in a Teflon-lined stainless-steel autoclave and heated at 180 °C during 5 days. After the synthesis, the product was filtered, washed with distilled water and ethanol, then dried at 70 °C overnight. The solid was then calcined at 880 °C to completely remove the organic template.

2.2. Intrusion-extrusion experiments

The intrusion-extrusion of water and LiCl aqueous solutions in Ferrierite samples in the form of compressed pellets was performed at room temperature using a modified mercury porosimeter (Micromeritics Model Autopore IV) as described in our previous works [20]. Before the experiments the pellets were outgassed at 300 °C under vacuum. The experimental intrusion-extrusion curves were 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 megapascals (MPa) and volume variation in millilitres (mL) per gram of anhydrous calcined zeosil. The experimental error is estimated to 1% on the pressure and on the volume.

After intrusion-extrusion experiments, the samples intruded with LiCl aqueous solutions were washed with water to remove all traces of LiCl. Then the samples were dried at 70 °C overnight.

Prior to the analyses, all the intruded-extruded samples were hydrated in a 80% relative humidity atmosphere for 24 h in order to set the hydration state.

2.3. Powder X-ray diffraction

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° 2 θ) using Cu K α_1 radiation ($\lambda = 0.15406$ nm). Measurements were achieved for

2θ angle values in the 3–50 range, step 0.2° 2θ , and time/step = 10 s.

2.4. Scanning electron microscopy

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

2.5. Nitrogen adsorption–desorption measurements

Nitrogen adsorption–desorption isotherms were performed at 77 K using a Micromeritics ASAP 2420 apparatus. Prior to the adsorption measurements, the nonintruded samples were outgassed at 300 °C overnight under vacuum. The intruded–extruded samples were outgassed at 90 °C overnight to eliminate physisorbed water and to avoid the dehydroxylation process. The specific surface area (S_{BET}) and microporous volume (V_{micro}) were calculated using the BET and t-plot methods, respectively.

2.6. Thermogravimetric (TG) analysis

The analyses were carried out on a METTLER-TOLEDO TG/DSC1 STARE System apparatus, under air flow, with a heating rate of 5 °C/min from 30 to 800 °C.

2.7. Solid-state NMR spectroscopy

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

3. Results and discussion

3.1. Intrusion–extrusion isotherms

The pressure–volume diagrams of the “Ferrierite–water” and “Ferrierite–LiCl aqueous solutions” systems are shown in Fig. 1. For each studied system, three intrusion–extrusion cycles were performed, but for clarity only the first and the second intrusion–extrusion cycles are reported. The corresponding data are listed in Table 2. The 0–5 MPa pressure range on the pressure axis is not shown, since the observed volume variation is due to the intrusion of the liquid in the interparticular porosity of the pellet, as already mentioned in our previous work (see Fig. S1) [27]. The intrusion–extrusion of three different liquids was performed: water, 5 M and 10 M lithium chloride aqueous solutions. The intrusion curves on one side and the extrusion curves on the other side are superimposable and the intrusion–extrusion process is completely reversible. Whatever the LiCl solution concentration, a spring

Table 1
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)	2.1	5.0
Flip angle	$\pi/6$	$\pi/2$
Contact time (ms)	/	1
Recycle time (s)	80	7 ^b
Spinning rate (kHz)	4	4
Scans number	1000	10,000

^a Tetramethylsilane.

^b The relaxation time t_1 was optimized.

Fig. 1. Pressure–volume diagrams (first and second intrusion–extrusion cycles) of the “Ferrierite–water” and “Ferrierite–LiCl aqueous solutions” systems for the FER-P (a) and FER-K (b) samples. For clarity the intrusion–extrusion isotherms are shifted along the Y-axis. The 0–5 MPa range is not shown.

behavior with a slight hysteresis is observed; the extrusion pressure being slightly lower to the one observed for the intrusion.

In all cases, the intrusion–extrusion cycle exhibits one main step with an intrusion pressure (P_{int}) between 150 and 243 MPa (150, 189, 243 MPa for water, 5 M, and 10 M LiCl aqueous solutions, respectively). The intrusion pressures of the “FER-P and FER-K–water” systems are comparable to the one determined in a previous work [22]. The intruded volumes (V_{int}) are in the range 0.052–0.056 mL/g and 0.060–0.064 mL/g for “FER-P–nonwetting liquid” and “FER-K–nonwetting liquid” systems, respectively. This volume is lower than the microporous volume obtained from nitrogen adsorption–desorption isotherms (see Table 3; i.e., FER-P = 0.13 cm³/g, FER-K = 0.15 cm³/g). Such a difference was already observed for other “zeosil–water” systems and explained by a confined water density lower than 1 [55]. For the FER-P sample, experiments with 13 M, 15 M and 20 M LiCl aqueous solutions were also performed (not shown). With 13 M LiCl aqueous solution, the intrusion pressure (321 MPa) was doubled compared to the one with water and no intrusion was observed for 15 M and 20 M LiCl aqueous solutions. For these two concentrations, the intrusion probably occurs at a pressure higher than 400 MPa that our instrument cannot provide. According to the literature, the rise of the intrusion pressure can be explained by: i) a higher surface tension

Table 2

Characteristics of the FER-P and FER-K 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 after water and LiCl aqueous solution intrusion-extrusion experiments at two different salt concentrations (5, 10 and 13 M).

System	P_{int} [MPa] ^a	P_{ext} [MPa] ^a	V_{int} [mL/g] ^a	V_{ext} [mL/g] ^a	E_s [J/g] ^b	E_r [J/g] ^c	Energy Yield (%) ^d
FER-P-H ₂ O	150	143	0.056	0.056	8.4	8.2	97
FER-P-5 M LiCl	189	184	0.052	0.052	9.8	9.6	96
FER-P-10 M LiCl	243	231	0.052	0.052	13.2	12.0	91
FER-P-13 M LiCl	321	300	0.055	0.055	17.7	16.5	93
FER-K-H ₂ O	150	143	0.064	0.064	9.6	9.1	97
FER-K-5 M LiCl	189	184	0.060	0.060	11.3	11.0	97
FER-K-10 M LiCl	243	231	0.060	0.060	14.6	13.9	95

^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 = $E_r/E_s \times 100$.

Table 3

Values of the BET surface area and microporous volume obtained by N₂ adsorption-desorption isotherms at 77 K of the FER-P and FER-K samples before and after three intrusion-extrusion cycles in water, 5 M and 10 M LiCl aqueous solutions.

System	S_{BET} [m ² /g]	V_{microp} [cm ³ /g]
FER-P	322	0.13
FER-P-H ₂ O	295	0.12
FER-P-5 M LiCl	304	0.12
FER-P-10 M LiCl	293	0.12
FER-K	367	0.15
FER-K-H ₂ O	352	0.15
FER-K-5 M LiCl	364	0.14
FER-K-10 M LiCl	359	0.14

of electrolyte aqueous solution in comparison with water [56,57], ii) osmotic phenomena [58,59], iii) a confinement effect of nanopore walls [33] or iv) a ion desolvation [34,60,61]. In a recent study, we showed by Rietveld refinement of *in situ* high pressure synchrotron X-ray powder diffraction data that during intrusion-

extrusion experiments in the "FER-K-MgCl₂·21 H₂O aqueous solution" system, solvated ions are intruded into the zeosil porosity, but the solvation degree of the intruded ions (MgCl₂·10 H₂O) differs from the initial solution, revealing a partial desolvation of both magnesium and chloride ions [50]. Thus, this result seems to support the ion desolvation hypothesis.

As a general trend whatever the FER-P-aqueous electrolyte solution system, the intrusion and extrusion pressures increase with the salt concentration (Fig. S2), which leads to an increase of the stored energy as shown in Table 2.

The energetic performances of the "FER-zeosil-nonwetting liquid" systems can be compared with the ones of the "MFI-zeosil-nonwetting liquid" systems, since these zeosils have relatively close structure (Ferrierite - 2D channel system with 10 and 8 MR pore openings, MFI-type zeosil - 3D channel pore system with 10 MR openings) and the intrusion-extrusion of different liquids in MFI-type zeosil is well studied. In both cases a similar spring behavior with a slight hysteresis that increases with the LiCl concentration is observed. The high reversibility of the intrusion could be ascribed

Fig. 2. The FER-P and FER-K samples before (a and b, respectively) and after three intrusion-extrusion cycles in water (c and d, respectively).

to the low content of defect sites ($-\text{OH}$ groups) in the framework as confirmed by ^{29}Si solid-state NMR spectroscopy (see below). However, lower intrusion pressure values are found for the MFI-based system (96, 133 and 193 MPa for water, 5 M and 10 M LiCl aqueous solution, respectively) [36]. The higher pressure values for FER-based systems can be explained by a smaller pore opening (8 and 10 MR instead of 10 MR) and, possibly, by the smaller dimensionality of the channel system (2D instead of 3D) of the FER structure that subject the solvated ions to a stronger distortion to enter inside the small pores. The energetic performances of all the FER-based studied systems are close to 8, 10 and 13 J/g in the case of "FER-P- H_2O ", "FER-P-5 M LiCl" and "FER-P-10 M LiCl" systems, respectively (see Table 2).

The same trend is observed for the "FER-K-nonwetting liquid" systems which have slightly better energetic performances than "FER-P-nonwetting liquid" ones thanks to a higher intruded volume (see Table 2). The smaller intruded volume for the FER-P samples, expressed per gram of adsorbent, can be due to the presence of traces of amorphous impurities as shown by SEM (see Fig. 2a). Thus, for both FER-zeosil samples, the energetic performances are quite similar. Therefore, the synthesis procedure used, the shape and size of the ferrierite crystals do not play a crucial role.

3.2. SEM analysis

The Ferrierite samples were examined by scanning electron microscopy before and after intrusion-extrusion experiments. After synthesis the FER-P samples consist of elongated crystals with dimensions mostly of $\sim 100\text{ }\mu\text{m} \times \sim 10\text{ }\mu\text{m}$, (Fig. 2a), while the FER-K crystals display a well defined plate-like morphology (Fig. 2b) with a uniform size of $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$. In both cases, the thickness of the crystallites is small ($\sim 1\text{ }\mu\text{m}$). Small particles are clearly visible on the surface of FER-P crystals and might be assigned to the presence of amorphous impurities (Fig. 2a). After water (Fig. 2c and d) or LiCl aqueous solutions (not shown) intrusion-extrusion experiments the crystals of FER-P and FER-K zeosils are broken and damaged.

3.3. XRD analysis

The XRD patterns of the Ferrierite samples are reported in Fig. 3. The diffractograms of the starting materials (before intrusion-extrusion experiments) and intruded ones correspond to well crystallized FER-type solids. The patterns can be indexed in the orthorhombic symmetry (space group $Pmnn$) [62]. However, as it will be confirmed by NMR analysis, it should be noted that the FER-K sample displays a better crystallization rate. Furthermore, whatever the nature of the nonwetting liquid and of the FER-type sample, the XRD patterns before and after intrusion-extrusion experiments are quite similar, which means that at the long-range order, the Ferrierite structure is not affected.

3.4. N_2 adsorption-desorption isotherms

Whatever the intruded liquid, all the isotherms of the materials before and after intrusion-extrusion experiments are quite superimposable. Therefore only the isotherms of the nonintruded and 10 M LiCl aqueous solution intruded samples are shown in Fig. 4. They are mainly of type I characteristic of microporous solid. At a relative pressure higher than 0.9 a slight increase of the adsorbed volume is observed mainly for the intruded samples, this can be ascribed to the interparticular porosity and to the mesoporosity due to the breaking of the crystals that occurs during the intrusion-extrusion process (see SEM micrographs). The specific surface area (S_{BET}) and the microporous volume (V_{micro}) of the nonintruded

samples is equal to $322\text{ m}^2/\text{g}$ and $0.13\text{ cm}^3/\text{g}$, respectively for the FER-P sample, while they are equal to $367\text{ m}^2/\text{g}$ and $0.15\text{ cm}^3/\text{g}$ for the FER-K one. The difference between the microporous volume of the two nonintruded samples could be due to the higher number of defect sites in the FER-P sample as shown by TG analysis (see Fig. 5a) and to the presence of the amorphous impurities on the surface sample (see SEM micrographs) that reduces the microporous volume value expressed per gram of adsorbent.

Whatever the nonwetting liquid, the N_2 adsorption-desorption data for the intruded samples are only slightly lower than those of the starting materials but similar between them as shown in Table 3.

3.5. Thermogravimetric analysis

The experimental results issued from the thermogravimetric (TG) analysis before and after intrusion-extrusion experiments are depicted in Fig. 5. For the FER-P and FER-K samples, the total weight

Fig. 3. XRD patterns of the FER-P (a) and FER-K (b) samples before and after three intrusion-extrusion cycles in water, 5 M and 10 M LiCl aqueous solutions.

Fig. 4. N₂ adsorption-desorption isotherms at 77 K of the FER-P (a) and FER-K (b) samples before and after three cycles of intrusion-extrusion in 10 M LiCl aqueous solution.

loss ranges from 2.2 to 2.6 wt% and 1.3 to 2.1 wt%, respectively. The weight losses occur in two main steps. The first one, between 30 and 250 °C, is ascribed to the desorption of the physisorbed water molecules. The second weight loss, in the temperature range of 250–800 °C, can be assigned to water arising from dehydroxylation reactions. More detailed values are shown in Table 4.

The total weight loss (1.3 wt%) found for the nonintruded FER-K sample is lower than the one of the FER-P sample (2.2 wt%). Indeed, in the first range of temperature (30–250 °C) the weight loss for the FER-K sample is almost negligible unlike the FER-P one (0.5 and 1.6 wt%, respectively). This difference indicates that the hydrophilic character is slightly more pronounced for the FER-P sample. This higher weight loss might be due to the presence of Q₂ ((HO)₂-Si-(OSi)₂) groups as shown by NMR (see below) and therefore, for the FER-P sample, also to some dehydroxylation reactions. Surprisingly, the second weight loss (dehydroxylation reactions) for the non-intruded FER-K sample is well pronounced and steeply sharp which is not the case for the other FER samples. However, for all the samples, this second weight loss leads to a similar number of –OH groups per unit cell (Si₃₆O₇₂), i.e., from 1.5 to 2 –OH groups. From these results, it appears that after intrusion-extrusion experiments, the number of –OH groups does not increase significantly.

Fig. 5. TG curves of the FER-P (a) and FER-K (b) samples before and after three intrusion-extrusion cycles in water and in LiCl aqueous solution at different concentrations.

3.6. ²⁹Si MAS NMR spectroscopy

The ²⁹Si MAS NMR spectra of the FER-P and FER-K samples before and after intrusion-extrusion experiments are shown in Fig. 6. The spectra of the nonintruded FER-P and FER-K samples reported in Fig. 6a and b, respectively, display three (FER-P: –112.1, –116.1, –116.9 ppm) and five (FER-K: –111.7, –112.1, –116.0, –116.3 and –116.9 ppm) components ascribed to the five distinct crystallographic silicon sites of the structure and corresponding to Q₄ groups (Si–(OSi)₄). From this

Table 4

Weight variation (%) of the FER-P and FER-K samples before and after three intrusion-extrusion cycles in water and in LiCl aqueous solution at different concentrations.

System	Weight loss (30–250 °C) wt%	Weight loss (250–800 °C) wt%	Number of –OH per unit cell
FER-P	1.6	0.60	~1.5
FER-P-H ₂ O	1.7	0.65	~1.5
FER-P-5 M LiCl	1.8	0.88	~2.0
FER-P-10 M LiCl	1.6	0.69	~1.5
FER-K	0.5	0.78	~2.0
FER-K-H ₂ O	1.4	0.75	~2.0
FER-K-5 M LiCl	1.2	0.66	~1.5
FER-K-10 M LiCl	1.1	0.54	~1.3

Fig. 6. ^{29}Si -MAS NMR spectra of the FER-P (a) and FER-K (b) samples before and after three intrusion-extrusion cycles in water and LiCl aqueous solutions at different concentrations.

result, it appears clearly that the FER-K sample with its 5 narrow components (intensity ratio 2:2:2:1:2) [62] is very well crystallized and displays a higher local structural order than the FER-P sample. Whatever the nature of the intruded liquid, it is worthy to note that the spectra of the FER-K samples after intrusion experiments (Fig. 6b) show a lower resolution since only 3 or 4 broader components are evidenced revealing thus some local structural disorder after intrusion-extrusion experiments. Surprisingly, for the intruded FER-P samples (Fig. 6a), an opposite behavior seems to be observed. Compared to the nonintruded sample, the 3 components are slightly thinner. It might be explained by a higher condensation degree of the silicate layers after intrusion-extrusion experiments (see below, ^1H - ^{29}Si CPMAS NMR spectroscopy). In all cases, no signal is observed at about -100 ppm corresponding to Q_3 groups ($\text{HO-Si}-(\text{OSi})_3$ or $^-\text{O-Si}-(\text{OSi})_3$) which indicates that the amount of defect sites is very low (around 2 $-\text{OH}$ groups) as confirmed by thermal analysis.

3.7. ^1H - ^{29}Si CPMAS NMR spectroscopy

The ^1H - ^{29}Si CPMAS NMR spectra of the calcined FER-P and FER-K samples before and after water and LiCl aqueous solutions

intrusion (Fig. 7) were recorded with a short contact time (1 ms) in order to enhance the silicon atoms that bear protons and to get evidence of the presence of silanol groups. The ^1H - ^{29}Si CPMAS NMR technique does not provide quantitative results, however, it allows a relative comparison of the spectra if they were registered under the same conditions. The resonances are observed between -85.9 and -119.4 ppm. However, the first component at around -100 ppm is broader for the nonintruded FER-P sample (from -85.9 to -110 ppm) revealing the presence of Q_3 ($\text{HO-Si}-(\text{OSi})_3$), but might be also Q_2 ($(\text{HO})_2\text{-Si}-(\text{OSi})_2$) groups. The latter could result from a lower condensation degree of the silicate layers of the PREFER precursor during the topotatic dehydration-condensation reaction. For the intruded-extruded FER-P samples, this component is slightly narrower (absence of Q_2 groups) which could indicate a higher condensation degree after intrusion-extrusion experiments. This result is quite surprising, since for the RRO-type zeosil prepared from the layered RUB-39 precursor,

Fig. 7. ^1H - ^{29}Si -CPMAS NMR spectra of the FER-P (a) and FER-K (b) samples before and after three intrusion-extrusion cycles in water and LiCl aqueous solutions at different concentrations.

an opposite phenomenon was observed. Indeed, after water intrusion-extrusion experiments, the ^{29}Si MAS NMR spectrum of the intruded RRO sample was quite similar to that of its precursor suggesting a breaking of the siloxane bonds preferentially at the level of the condensation of the RUB-39 layers.

With the exception to what is mentioned above, whatever the FER sample (FER-P or FER-K) and the nonwetting liquid, the CP/MAS NMR spectra are quite similar. Therefore, as already observed by TG analysis, the high pressure intrusion-extrusion experiments do not increase significantly the amount of defect sites in the FER-type structure.

4. Conclusion

The influence of LiCl aqueous solution concentration, the synthesis procedure (from a layered precursor or by direct hydrothermal synthesis) and therefore the shape and size of the Ferrierite crystals on the energetic performances of pure-silica Ferrierite were evaluated using intrusion-extrusion experiments under high pressure. Whatever the intruded nonwetting liquid and the shape of materials, all "FER-type zeosil-nonwetting liquid" systems display a spring behavior and no significant difference on the energetic performances is observed for both Ferrierite crystal morphology. As expected, the intrusion pressure rises when the concentration of LiCl aqueous solution increases. Compared to the MFI-type zeosil, the intrusion pressures are higher: for water 150 MPa vs 100 MPa and for 10 M LiCl aqueous solution 243 MPa vs 193 MPa. These higher values should be related to a lower pore opening (8 and 10 MR vs 10 MR).

For the sample prepared from a layered precursor by topotactic condensation of silicate layers, a higher condensation degree seems to be observed after intrusion-extrusion experiments. Therefore, and contrary to what was observed with the RRO-type zeosil prepared by a similar route, no significant breaking of siloxane bonds occurs at the level of the condensation of the silicate layers for the FER-type zeosil. Whatever the synthesis procedure, high pressure intrusion-extrusion experiments do not increase significantly the amount of defect sites in the FER-type structure.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.energy.2017.04.128>.

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