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High pressure intrusion–extrusion of electrolyte solutions in aluminosilicate FAU and *BEA-type zeolites

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ABSTRACT

The energetic performances of several FAU- and *BEA-type zeolites with different Si/Al molar ratios have been studied by high pressure intrusion–extrusion of water and LiCl aqueous solutions. It has been shown that FAU-type zeolites characterized by a low Si/Al molar ratio (up to 40) demonstrate hydrophilic properties and spontaneous intrusion of water and LiCl solutions. While dealuminated Y zeolite (DaY) with a Si/Al ratio of 110 displayed a shock-absorber behavior under intrusion of LiCl solutions with concentration ranging from 5 to 20 M; however the intrusion of water was spontaneous. The increase of the LiCl concentration leads to an increase of both the intrusion pressure and the intruded volume, but also a better efficiency of the shock-absorber. *BEA-type zeolite with a Si/Al ratio of 90 displayed a spring behavior under intrusion of 20 M LiCl solution with an intrusion pressure of 59 MPa and an intruded volume of 0.09 mL/g, whereas the intrusion of solutions with lower concentration was spontaneous. It has been shown that only zeolites with high Si/Al ratios can demonstrate high pressure intrusion of electrolyte solutions and that the presence of small traces of aluminum atoms changes considerably the behavior of the “zeolite–liquid” system. The characterization of the samples, before and after intrusion–extrusion experiments, by various physicochemical and structural methods has been performed.

1. Introduction

Zeolites are widely used for various applications in adsorption, separation, ion-exchange and heterogeneous catalysis [1]. In the past decade, thermodynamics of confined systems involving water as nonwetting liquid and hydrophobic microporous solids as all-silica zeolites (zeosils) have attracted considerable attention due to their potential application in the field of energetics. Since our pioneering work in 2001 [2], several “zeosil–water” systems have already been studied [3–19] and a summary of the energetic performances of these all silica zeolites was reported in our previous paper [19]. The use of “zeosil–water” system in energetic applications is based on the following principle. To penetrate water in the porous solid (intrusion), a certain pressure must be applied. Under intrusion liquid water is transformed into a multitude of molecular clusters in the pores. Thus, the supplied mechanical energy during the compression step is converted to interfacial energy. By reducing

the pressure, the system can induce an expulsion of the liquid out of the pores of the solid (extrusion). Depending on the zeosil, the “zeosil–water” system is able to restore, dissipate, or absorb energy and therefore, it displays a spring, shock-absorber, or bumper behavior, respectively. The behavior depends on various physical parameters related to the porous matrix such as pore size, pore system (cages or channels), dimensionality of the channels and the hydrophobic/hydrophilic character of the solids. This latter parameter depends on the number of defect sites in the zeolite material. Thus, the presence of silanol groups can considerably change the behavior of the “zeosil–water” system as it was observed for MFI-type zeolites [2]. It is well known that aluminosilicate zeolites demonstrate generally hydrophilic properties. However, at high Si/Al molar ratio their hydrophobic character increases. The intrusion–extrusion of different electrolyte solutions in hydrophobic porous solids can be a way to improve their energetic performances [20,21]. It has been found that highly concentrated aqueous solutions of salts such as LiCl, NaCl, MgCl₂ enhance the intrusion pressure up to 3 times (in the case of the “Silicalite-1–LiCl 20M” system) and that the pressure increases along with the salt concentration [20,22]. In the works of Qiao and coworkers, FAU

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and MFI-type aluminosilicate zeolites with high Si/Al ratio have been studied under intrusion–extrusion of water and electrolyte solutions [21,23]. FAU-type zeolite with Si/Al ratio of 40 demonstrated a shock-absorber behavior under intrusion of NaCl, NaBr and KCl solutions, the higher the electrolyte concentration, the higher the intrusion pressure. Whereas, once this FAU-type sample is immersed in water, the latter is soaked up spontaneously [23–25]. However no characterizations were performed on the solids after the intrusion experiments. Recently, new effect was observed in the case of *BEA-type zeosil: the intrusion of highly concentrated LiCl solutions change drastically the system behavior – from bumper, with an irreversible intrusion of liquid (water and LiCl solutions up to 10 M), to shock-adsorber (with LiCl solution > 15M). The change of the system behavior was explained by a change in the nature of the intruded liquid – from water to highly concentrated LiCl solution with H₂O/Li⁺ molar ratio lower than Li⁺ coordination number [26]. That is why the intrusion of such highly concentrated solutions presents a particular interest. It should be noted that the solutions with very small H₂O/cation ratio were previously studied only in few works [20,22,26].

In this article the intrusion–extrusion experiments of water and highly concentrated LiCl solutions in FAU and *BEA-type zeolites with different Si/Al molar ratios were performed in order to study the influence of Si/Al ratio on intrusion–extrusion behavior of “zeolite – non-wetting liquid” system. The solids were fully characterized before and after intrusion–extrusion experiments by X-ray diffraction, N₂ adsorption desorption measurement, Scanning Electron Microscopy (SEM), TG analyses and solid state NMR spectroscopy. The influence of the electrolyte concentration on the energetic performances of the “zeolite-electrolyte” system is also discussed in order to demonstrate particular properties of highly concentrated electrolyte solutions.

2. Experimental

The following commercial and laboratory-made FAU and *BEA-type zeolite samples with various Si/Al ratios were studied: FAU-type zeolite – NaX (Sigma Aldrich, Si/Al = 1.3), EMC-1 (home made, Si/Al = 3.8) [27], dealuminated HY zeolites (Zeolyst CBV720, Si/Al = 15, CBV780, Si/Al = 40) and DaY zeolite (Degussa Si/Al = 110), *BEA-type zeolite – Zeolyst CBV 811C (Si/Al = 150) and Clariant H-BEA-150 (Si/Al = 90).

The Si/Al molar ratio of the different samples was determined by X-ray Fluorescence spectrometry on a Philips PW spectrometer.

Intrusion–extrusion experiments of aqueous solutions in the zeolite sample in the form of compressed and preliminary degassed (at 300 °C under vacuum) pellets were performed at room temperature using a modified mercury porosimeter (Micromeritics Model Autopore IV), as described in our previous works [19]. The liquid phase was either pure water or aqueous solution of lithium chloride with various concentrations (5, 10, 15 or 20 M). The compressibility curve of pure water or LiCl aqueous solution was subtracted from experimental intrusion–extrusion curves. The values of the intrusion (P_{int}) and extrusion (P_{ext}) pressures correspond to that of the half volume total variation. The pressure is expressed in megapascals (MPa) and the volume variation in milliliters (mL) per gram of calcined samples. The experimental error is estimated to 1% on the pressure and on the volume.

After intrusion–extrusion experiments, the volume intruded with LiCl were washed with water to remove traces of LiCl. The absence of chloride anions in the filtrate was controlled by adding few drops of 1 M silver nitrate aqueous solution (no silver chloride precipitate). Then the samples were dried at 70 °C overnight, and hydrated in a 80% relative humidity atmosphere during 24 h.

X-ray powder diffraction patterns of the different samples were recorded in a Debye–Scherrer geometry on a STOE STADI-P diffractometer equipped with a curved germanium (111) primary monochromator, and a linear position-sensitive detector (6° 2 θ) using Cu K α_1 radiation (λ = 0.15406 nm). Measurements were achieved for 2 θ angle values in the 3–50 range, step 0.15° 2 θ , and time/step = 120 s. The unit-cell parameters were determined using Louër's DICVOL91 indexing routine [28] of the STOE WinXPOW program package [29].

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 –196 °C using a Micromeritics ASAP 2420 apparatus. Prior to the adsorption measurements, the samples were outgassed at 90 °C overnight under vacuum to eliminate physisorbed water. Low degassing temperature was chosen 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.

Thermogravimetric (TG) analyses were carried out on a TG Mettler Toledo STARE apparatus, under air flow, with a heating rate of 5 °C/min from 30 to 800 °C. As mentioned above, all samples were hydrated in 80% relative humidity atmosphere during 24 h in order to set the hydration state.

²⁹Si MAS and ¹H–²⁹Si CP/MAS NMR spectra were recorded 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

Firstly the experiments of intrusion of water and the most concentrated LiCl solution (20 M) were performed for all the samples. It was observed that almost all the faujasite zeolites (Si/Al ratio: 1.3; 3.8; 15; 40) demonstrate hydrophilic properties: the intrusion of H₂O and 20 M LiCl solution takes place spontaneously (the samples soak up the liquid at atmospheric pressure). Only DaY zeolite, with the highest Si/Al molar ratio (110) among all the FAU-type zeolites showed a shock-absorber behavior under intrusion of 20 M LiCl (Fig. 1), whereas the intrusion of water was spontaneous as observed for the other studied faujasite zeolites. Hydrophilic properties of faujasite zeolites with low Si/Al ratio (≤ 15) are not surprising since the adsorption of water and other polar molecules are well known for these materials. However, it was quite surprising that the commercial dealuminated Y zeolite with a Si/Al ratio of 40 (CBV 780) demonstrates spontaneous intrusion of water

Table 1
Recording Conditions of the ²⁹Si MAS and ¹H–²⁹Si CP/MAS NMR Spectra.

	²⁹ Si	
	MAS	CP MAS
Chemical shift standard	TMS ^a	TMS ^a
Frequency (MHz)	59.6	59.6
Pulse width (μs)	1.87	4
Flip angle	$\pi/6$	$\pi/2$
Contact time (ms)	–	8
Recycle time (s)	80	10 ^b
Spinning rate (kHz)	4	4
Scans number	1000	8000

^a TMS: Tetramethylsilane.

^b The relaxation time t_1 was optimized.

Fig. 1. The first intrusion-extrusion cycle of the "DaY-LiCl aqueous solution" systems. For a better visibility, the diagrams are shifted along the Y-axis.

and 20 M LiCl solution. Indeed, in the works of Qiao and coworkers, the faujasite CBV901 from Zeolyst (Si/Al ratio = 40) displayed a shock-absorber behavior under intrusion-extrusion of concentrated NaCl, NaCl + NaBr and KCl solutions with an intrusion pressure up to 20 MPa [23–25]. It can be supposed that the number of hydrophilic defect sites (silanol sites, since both zeolites are in protonated form) is higher in the CBV 780 faujasite sample compared to the CBV901 one.

In order to study the influence of the electrolyte concentration on the energetic performances of DaY zeolite, intrusion/extrusion experiments were also performed with 5, 10 and 15 M LiCl solutions. For each system, three intrusion-extrusion cycles were performed and reproducible results were obtained. Since the cycles are extremely close one to another, for clarity, only the first intrusion-extrusion cycles are reported for each experiment. The corresponding intrusion-extrusion curves are shown in Fig. 1. In the case of 20 M LiCl solution the systems demonstrate a shock-absorber behavior. The energetic performances of system are summarized in Table 2. It is observed that the intrusion and extrusion pressures increase considerably with the LiCl concentration. The obtained intruded volume when using 15 and 20 M LiCl solution was about 0.23 mL/g which corresponds to the one obtained by Qiao and coworkers while using other electrolyte solutions [25]. However, this volume is lower than the one determined from N₂ adsorption-desorption experiment (0.28 mL/g). As already mentioned by Desbiers et al. [5], for the "Silicalite-1 water" system such a difference can be due to a density of the intruded liquid lower than that of the bulk liquid. At lower concentrations, for instance for the 5 M LiCl solution, the intruded volume decreases

Fig. 2. Intrusion-extrusion cycle of the "H-BEA-150-20 M LiCl" system. For comparison, the "pure-silica*BEA zeolite - water" and "pure-silica*BEA zeolite - 20 M LiCl" systems adapted from Ref. [26] are also reported.

up to 0.13 mL/g with an energy yield (restored energy to absorbed energy ratio) of 71%. At this low concentration, the solution or free water molecules (nonsolvated molecules) spontaneously fill in the most hydrophilic parts of the pores. Similar energy yields (48–51%) were observed for higher concentrations of LiCl solutions (10, 15 and 20 M). Such yields are expected for a shock-absorber.

For the *BEA-type zeolites, the two commercial samples (CBV 811C and H-BEA-150) show hydrophilic properties with spontaneous intrusion of water and LiCl solutions in the case of CBV 811C. However, the system "H-BEA-150-20 M LiCl solution" displays a spring behavior with an intrusion pressure of 59 MPa (Fig. 2) which is not the case for the CBV 811C sample, where the intrusion of the 20 M LiCl solution occurs at atmospheric pressure, revealing thus, despite a higher Si/Al molar ratio more hydrophilic defect sites in this sample. It is worthy to note that the intruded volume is quite low (0.09 mL/g) and about half of the one determined from N₂ adsorption-desorption experiment (0.20 mL/g). This might indicate, as already seen for FAU-type zeolites, that a part of the pore volume is filled at atmospheric pressure.

A strong difference can be observed in the water and 20 M LiCl solution intrusion-extrusion curves of the H-BEA-150 sample (Si/Al ratio of 90) with those of a pure silica *BEA-type zeolite [26]. The corresponding curves are reported in Fig. 2. Pure silica *BEA zeolite (zeosil) shows a bumper behavior under intrusion of water and LiCl solutions up to the concentration of 10 M with an intrusion pressure of 53 MPa, whereas H-BEA-150 sample is hydrophilic under these conditions and intrusion occurs at atmospheric pressure. With the 20 M LiCl solution, both samples demonstrate a similar behavior (spring for H-BEA-150 and shock-absorber with a narrow

Table 2

Energetic properties of "DaY-LiCl solution" and "H-BEA-150-LiCl solution" systems: intrusion (P_{int}) and extrusion (P_{ext}) pressure, intruded (V_{int}) and extruded (V_{ext}) volumes, absorbed (E_a) and restored (E_r) energies and energy yield ($E_r/E_a \times 100\%$).

Sample	P_{int} MPa	P_{ext} MPa	V_{int} mL/g	V_{ext} mL/g	E_a J/g	E_r J/g	Yield %	Behavior
DaY-5 M LiCl	8.5	6	0.13	0.13	1.1	0.8	71	Shock-absorber
DaY-10 M LiCl	14.5	7	0.17	0.17	2.5	1.2	48	Shock-absorber
DaY-15 M LiCl	25.5	13.5	0.23	0.23	5.9	3.1	51	Shock-absorber
DaY-20 M LiCl	34	17	0.23	0.23	7.8	3.5	50	Shock-absorber
H-BEA-150-20 M LiCl	59	57	0.09	0.09	5.3	5.1	97	Spring

hysteresis for *BEA zeosil), but the intrusion pressure and the intrusion volume in the H-BEA-150 sample are considerably lower than the ones in *BEA zeosil (59 MPa, 0.09 mL/g and 115 MPa, 0.16 mL/g, respectively). Thus we can conclude that the presence of a small amount of aluminum in the zeolite framework increases the hydrophilic character of the material and leads to a considerable change in the intrusion–extrusion behavior.

In the case of *BEA-type zeosil the difference between the system behavior under intrusion of low and highly concentrated LiCl solutions was explained by a change of the intruded liquid. At low LiCl concentrations, only water molecules are intruded into the pores, whereas at high LiCl concentrations there are no free water molecules and solvated Li^+ and Cl^- ions are intruded [26]. In the case of H-BEA and DaY samples we also observe a change of the system behavior with the electrolyte concentration. The zeolites demonstrate hydrophilic properties under intrusion of water (for both zeolites) and low concentrated (≤ 15 M) LiCl solutions (for H-BEA only). However they display a shock-absorber behavior in the case of DaY for all LiCl solutions and a spring behavior for the H-BEA sample with 20 M LiCl solution. A similar phenomenon was observed by Qiao and coworkers for “high-silica faujasite – NaCl, NaBr and KCl solution” systems [23–25]. A threshold concentration exists in all cases. However, it is difficult to determine the nature of the intruded liquid in the case of DaY zeolite, since it demonstrates a shock-absorber behavior even in the case of a 5 M LiCl solution which is characterized by a high amount of free water molecules. Generally, the increase of the intrusion pressure with the LiCl concentration can be related to a higher solid–liquid interfacial tension and/or the ions desolvation phenomenon [20,24], and at high LiCl concentration, the change of intruded liquid is also possible [26]. The change of intruded liquid can be an explanation for the increase of the intruded volume in DaY zeolite with a rise of LiCl concentration. Solvated Li^+ and Cl^- species of the nonwetting liquid fill the pore volume only at high pressure; the latter being close to 0.23 mL/g. Whereas, at low LiCl concentration free water molecules already fill in a part of the pore volume at atmospheric pressure; consequently, the intruded volume of nonwetting solution in high pressure range is lower (about 0.13 mL/g).

Since only DaY and H-BEA-150 zeolites demonstrate interesting energetic performances under intrusion–extrusion of LiCl solution, only their characterization by structural and physicochemical methods is presented below.

3.2. XRD and SEM characterization

The XRD patterns of DaY and H-BEA-150 zeolites before and after intrusion–extrusion of 20 M LiCl aqueous solution are shown in Fig. 3. The XRD patterns of the H-BEA-150 samples show a sequence of large and narrow diffraction peaks typical for the *BEA zeolite which is a disordered structure. They were indexed in the tetragonal symmetry (polymorph A) and the corresponding unit-cell parameters are reported in Table 3. No significant change of the unit-cell parameters (cubic symmetry) is observed after intrusion–extrusion experiments in the case of DaY sample, which means that at the long-range order, the FAU structure is not affected. In the case of H-BEA-150 sample a slight shift of the XRD peaks to lower angle values is observed after intrusion–extrusion experiments leading to an expansion of the crystalline lattice. An increase of the unit-cell volume (from 4010 to 4039 Å³) is observed after 20 M LiCl intrusion–extrusion experiments. The lattice expansion is also observed after intrusion of water (XRD pattern not reported). Therefore, the slight lattice change is probably caused by the high pressure treatment and the creation of additional hydrophilic defect sites which stick water molecules after rehydration. It should be noticed that a contraction of the

Fig. 3. X-ray diffraction patterns of the H-BEA-150 and DaY samples before and after three intrusion–extrusion cycles in 20 M LiCl aqueous solution.

Table 3
Unit-cell parameters of H-BEA-150 (polymorph A) and DaY samples before and after three intrusion–extrusion cycles in 20 M LiCl aqueous solution.

Sample	a (Å)	c (Å)	V (Å ³)
H-BEA-150	12.395 (8)	26.189 (19)	4009.8 (30)
H-BEA-150 -20 M LiCl	12.411 (9)	26.221 (23)	4038.7 (43)
DaY	24.272 (20)	–	14,300.4 (20)
DaY –20 M LiCl	24.269 (23)	–	14,296.5 (24)

crystalline lattice was observed in the case of water and 20M LiCl intrusion–extrusion experiment with pure silica *BEA zeolite [26].

The crystal morphology of the H-BEA-150 and DaY samples was examined by scanning electron microscopy. No difference between non-intruded and water-intruded samples was found. SEM images are presented in Fig. 4. For the H-BEA sample, agglomerates with a size ranging from 150 to 300 nm, composed from grains with a size of several tens nm, are observed (Fig. 4A and B). The DaY sample is composed from large agglomerates of crystals with irregular shape and a size ranging from several tens to several hundreds nm. (Fig. 4C and D).

3.3. Thermal analysis and N₂ adsorption–desorption isotherms

The experimental results issued from the thermogravimetric (TG) analysis of H-BEA-150 and DaY samples before and after intrusion–extrusion experiments are shown in Fig. 5. The total weight loss of H-BEA-150 sample before and after intrusion/extrusion of 20 M LiCl solution is high – 13.2 and 14.9 wt.%, respectively. Thus, the zeolite demonstrates its hydrophilic character. Two steps are clearly observed. The first one between 30° and 200 °C (11.1 and 12.3 wt.%, respectively) is ascribed to the desorption of physisorbed water molecules. The second step, located between 260° and 700 °C, can be attributed to the removal of water molecules arising from dehydroxylation reactions. The weight loss is close to 2.1 wt.% and 2.6 wt.% for the nonintruded and intruded–extruded H-BEA-150 samples, respectively, that corresponds to about 9 and 11 OH-group per unit-cell. Thus, the intrusion of 20 M LiCl solution leads to a weak increase of silanol defects in the zeolite, which is in agreement with the XRD result (see above).

The thermogravimetric curves of the DaY sample show its higher hydrophobicity. Two badly pronounced steps can be

Fig. 4. SEM micrographs of the H-BEA-150 and DaY samples before (A and C, respectively) and after (B and D) intrusion–extrusion experiments.

distinguished. The first one ranging from 30° to 150 °C is ascribed to the desorption of physisorbed water molecules. The weight loss is slightly higher in the case of the nonintruded sample (2.2 wt.% against 1.7 wt.%). This loss is followed by a continuous weight loss up to 800 °C without clear step, probably ascribed to the removal of water molecules adsorbed on silanol groups and to the removal of water molecules arising from dehydroxylation reactions. In both cases, the values of weight loss are very close (1.2 wt.%). Thus no additional defects seem to be formed in the DaY zeolite after the 20 M LiCl intrusion–extrusion experiment.

The N_2 adsorption–desorption isotherms of the nonintruded and intruded DaY and H-BEA-150 samples are shown in Fig. 6. The isotherms are mainly of type I characteristic of microporous solids for DaY sample and of type I + type IIb for H-BEA-150. The BET surface area and microporous volume of the nonintruded H-BEA-150 sample is equal to 535 m²/g and 0.20 cm³/g. For the intruded–extruded sample with 20 M LiCl solution the surface area and pore volume are slightly lower: S_{BET} = 492 m² g^{−1} and

V_{micro} = 0.18 cm³ g^{−1}. Such a result is quite surprising since defect sites after intrusion–extrusion experiment are expected from the TG analysis. In the case of DaY zeolite the BET surface area and microporous volume values before and after intrusion–extrusion are very close: 821 m²/g and 0.30 cm³/g and 804 m²/g and 0.29 cm³/g for the nonintruded and the 20 M LiCl solution intruded samples, respectively, which is in agreement with the TG analysis.

3.4. ²⁹Si MAS NMR spectroscopy

The ²⁹Si MAS NMR spectra of the DaY and H-BEA-150 zeolites before and after 20 M LiCl solution intrusion–extrusion experiments are shown in Fig. 7. The spectrum of the DaY zeolite exhibits a unique resonance signal located at −108 ppm which corresponds to Q₄ groups (Si(−OSi)₄) associated to the one crystallographic silicon site in FAU-type structure. After 20 M LiCl

Fig. 5. TG curves of the H-BEA-150 and DaY samples before and after three intrusion–extrusion cycles in 20 M LiCl solution.

Fig. 6. N_2 adsorption–desorption isotherms at −196 °C of the DaY and H-BEA-150 samples before and after three intrusion–extrusion cycles in 20 M LiCl solution.

Fig. 7. ^{29}Si -MAS NMR spectra of DaY and H-BEA-150 zeolites before and after three intrusion–extrusion cycles in 20 M LiCl aqueous solution.

intrusion–extrusion experiments no significant change of the spectrum is observed. The spectrum of H-BEA-150 sample exhibits two main broad resonances with maxima at -111 and -114 ppm ascribed to the non equivalent crystallographic Q_4 silicon sites and two broad resonances at -101.5 and -105 ppm corresponding to Q_3 sites (silanol ($\text{Si}(\text{OSi})_3\text{OH}$) groups or ($\text{Si}(\text{OSi})_3\text{O}^-$) groups). After intrusion–extrusion experiments a decrease of the resonance at -114 ppm and the broadening of Q_3 components is observed. The Q_3/Q_4 area ratios determined from these spectra are equal to 0.41 and 0.39 for the intruded and nonintruded samples, respectively, revealing thus the creation of defect sites (about 5%) after 20 M LiCl intrusion–extrusion experiment.

3.5. ^1H – ^{29}Si CPMAS NMR spectroscopy

The ^1H – ^{29}Si CPMAS NMR spectra of the DaY and H-BEA-150 samples before and after 20 M LiCl solution intrusion–extrusion are reported in Fig. 8. These spectra were performed to enhance the silicon atoms that bear protons and thus to get evidence of the presence of silanol groups. The ^1H – ^{29}Si CPMAS technique does not provide quantitative results; however, it allows a relative comparison of the spectra if they were registered under the same conditions. On the spectrum of the nonintruded DaY zeolite, a very broad

Fig. 8. ^1H – ^{29}Si CPMAS NMR spectra of DaY and H-BEA-150 zeolites before and after three intrusion–extrusion cycles in 20 M LiCl aqueous solution.

signal is observed in the Q_4 range with a well pronounced resonance at -108 ppm, a broader one in the Q_3 range and very small broad resonance in the Q_2 range. After intrusion of 20 M LiCl solution no considerable change is observed, only the resonance of Q_3 groups at -101 ppm becomes more pronounced.

On the spectrum of H-BEA-150 zeolite three broad resonances at -92 , -102 and -112 ppm are observed. The first one of weak intensity is ascribed to Q_2 groups ($\text{Si}(\text{OSi})_2(\text{OH})_2$). The other resonances correspond to the Q_3 and Q_4 groups, respectively. Although a slight increase of defect sites (about 5%) was evidenced by ^{29}Si MAS NMR after intrusion–extrusion of 20 M LiCl solution (see above), no significant change is observed on the CP MAS NMR spectra of the H-BEA-150 samples.

4. Conclusions

A study of energetic performances of several FAU-type and *BEA-type zeolites with different Si/Al molar ratio has been performed by high pressure intrusion–extrusion of water and LiCl aqueous solutions. It has been shown that most of FAU-type zeolites demonstrate hydrophilic properties and spontaneous intrusion of water and LiCl solutions. Only high-silica Y zeolite (DaY sample) with a Si/Al ratio of 110 displays a shock-absorber behavior under intrusion of LiCl solutions. The increase of the LiCl concentration leads to a rise of the intrusion pressure from 8.5 to 34 MPa for 5 M and 20 M LiCl solutions, respectively. An increase of the intruded volume was also observed – from 0.13 to 0.23 mL/g. It can be related with a change of the intruded liquid from water to solvated Li^+ and Cl^- ions in the case of highly concentrated solutions. The latter nonwetting liquid fill the pore volume at high pressure, whereas at low LiCl concentration a part of the pore volume is already filled spontaneously at atmospheric pressure by free water molecules.

*BEA zeolite characterized by a Si/Al molar ratio of 90 displayed a spring behavior under intrusion of 20 M LiCl solution with an intrusion pressure of 59 MPa and an intruded volume of 0.09 mL/g, whereas at lower LiCl concentrations the intrusion is spontaneous. In the same conditions pure-silica *BEA zeolite shows a shock-absorber behavior with an intrusion pressure of 115 MPa and an intruded volume of 0.16 mL/g and a bumper behavior under intrusion of water and LiCl solutions up to the concentration of 10 M. Thus, the presence of small traces of aluminum atoms changes considerably the behavior of the “*BEA-type zeolite – solution” system.

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