

Effect of LiCl aqueous solutions on the energetic performances of Silicalite-1

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Abstract

The energetic performances of different “Silicalite-1–LiCl aqueous solution” systems were evaluated under high pressure. Depending on the LiCl concentration in the aqueous medium (0 M, 5 M, 10 M, 20 M), an increase of the intrusion and extrusion pressures and therefore of the stored (~10, ~13, ~19, ~31 J/g) and restored (~10, ~13, ~18, ~27 J/g) energies are observed. Thus, compared to the “Silicalite-1–water” system, the stored energy is tripled in the case of “Silicalite-1–LiCl 20 M” system.

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. 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. Depending on the “zeosil–water” system, when the pressure is released (extrusion), the system is able to restore, dissipate or absorb the supplied mechanical energy during the compression step with a more or less significant hysteresis and therefore to display a spring, shock-absorber or bumper behaviour. Recently, this process was also extended to the use of other aqueous media such as highly concentrated electrolyte solutions (LiCl, 3H₂O, MgCl₂, 21H₂O and NaCl, 11H₂O) (Tzanis, 2014; Khay, 2014).

Experimental part

Synthesis of Silicalite-1 zeolite (MFI-structure type). Silicalite-1 was prepared in fluoride medium. This route allows the synthesis of material having a strong hydrophobic character. The synthesis requires the presence of tetrapropylammonium (TPA) cations as structure-directing agents (TPABr, Fluka, purum). Aerosil 130 (Degussa) was used as the silica source. The reaction gel had the following molar composition: 1 SiO₂ : 0.1 TPABr : 0.1 NH₄F : 20 H₂O. The mixture, transferred into PTFE-lined stainless-steel autoclaves, was heated at 100 °C for 7 days. After synthesis, the solid was calcined at 550 °C during 6 hours in order to remove the organic template.

Intrusion–Extrusion Experiments. The intrusion–extrusion experiments of aqueous solution in the zeosil sample in the form of compressed and preliminary degassed pellets were performed at room temperature using a modified mercury porosimeter (Micromeritics Model Autopore IV), as described in our previous works (Trzpit, 2007).

Results and discussion

The pressure–volume diagrams of the “Silicalite-1–water” and the “Silicalite-1–LiCl aqueous solutions” systems are illustrated in Figure 1. For each system, three intrusion–extrusion cycles were performed and the same results were obtained. For clarity only the third intrusion–extrusion cycles are reported in Figure 1. At low pressure (< 0.1 MPa), as it was shown in our previous works, the volume variation corresponds to the compression and the liquid filling in the interparticular porosity of the zeolitic pellet. Beyond this pressure (0.1 MPa), a steep step occurs at a higher pressure. Whatever the system, when the pressure is released down to 0.1 MPa all the liquid is expelled from the porosity of the material meaning that the intrusion–extrusion process is completely reversible. Nevertheless, if a perfect spring behavior is observed for the “Silicalite-1–water” system, the intrusion and extrusion curves being completely superimposable, for the “Silicalite-1–LiCl aqueous solution” systems, a slight hysteresis is observed; the latter increasing with the salt concentration. Therefore, the perfect spring behavior gradually moves slightly towards a shock absorber behavior. This hysteresis might reveal the presence of defect sites (silanol groups) created during the intrusion–extrusion steps. Indeed, these silanol groups interacting with water molecules, an increase of their number leads to longer extrusion step and, thus a larger hysteresis.

The main information of these pressure–volume diagrams is the considerable increase of the intrusion and extrusion pressures with the LiCl concentration. The pressure increases from 96 MPa (pure water) to 285 MPa for LiCl 20 M. This can be explained by a higher solid–liquid interfacial tension. Another way to explain the pressure increase

could be the ions desolvation phenomenon or the size of solvated ions. Indeed, in the LiCl solutions each lithium ion is solvated by a number of water molecules which depends on the LiCl concentration, consequently, the intrusion pressure could be influenced by this parameter.

For the “Silicalite-1–water”, the intruded volume, close to 0.10 mL/g, is lower than the one obtained from N₂ adsorption-desorption isotherms (see below, i.e., 0.17 mL/g). Such a difference was explained by Desbiens *et al.* by a lower density of water in the MFI structure (0.6 instead of 1g/mL) (Desbiens, 2005). For the “Silicalite-1–LiCl aqueous solution” systems, a similar intruded volume is obtained (0.10 to 0.11 mL/g).

Compared to the “Silicalite-1–water” system (yield = 99 %; stored energy \approx 10 J/g), the “Silicalite-1–LiCl aqueous solution” systems restore 96, 93 or 87 % of the stored energy corresponding to about 13, 19 or 31 J/g, respectively. Therefore, in the case of the LiCl 20 M, the energetic performances are tripled.

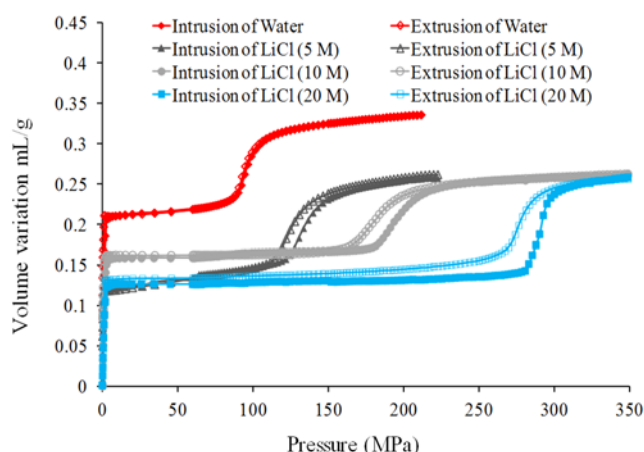


Figure 1: The third intrusion-extrusion cycle of the “Silicalite-1–water” and the different “Silicalite-1–LiCl aqueous solution” systems. For a better visibility, the diagrams are shifted along the Y-axis.

Conclusion

This work highlights the influence of LiCl aqueous solution concentration on the energetic performances of Silicalite-1 zeolite under high intrusion pressure. Compared to the perfect spring behavior observed for the “Silicalite-1–water” system, the “Silicalite-1–LiCl aqueous solution” systems move towards a shock absorber behavior which grows up with the increase of salt concentration. For these latter systems all the liquid is expelled from the solid when the pressure reaches to 0.1 MPa. However, the intrusion pressure increases with the concentration of the electrolyte from 96 MPa for pure water up to 285 MPa for LiCl 20 M. Therefore, compared to the “Silicalite-1–water” system, the stored energy is tripled for the “Silicalite-1–LiCl 20 M” system.

References

- L. Tzanis, H. Nouali, T.J. Daou, M. Soulard and J. Patarin, *Materials Letters*, 115 (2014) 229-232.
- I. Khay, H. Nouali, T.J. Daou, A. Ryzhikov, S. Rigolet and J. Patarin, *J. Phys. Chem. C*, 118 (2014) 3935-3941.
- M. Trzpit, M. Soulard, J. Patarin, *Chem. Lett.* 36 (2007) 980–981.
- N. Desbiens, I. Demachy, A. Fuchs, H. Kirsh-Rodeschini, M. Soulard, J. Patarin, *Angew. Chem., Int. Ed.*, 44 (2005) 5310–5313.