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High pressure intrusion of water and LiCl aqueous solutions in hydrophobic KIT-6 mesoporous silica : influence of the grafted group nature

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ABSTRACT. High pressure intrusion-extrusion of water and LiCl aqueous solutions in KIT-6 mesoporous silica grafted with alkyl or perfluoroalkyl groups have been studied for absorption of mechanical energy. The “grafted KIT-6 – LiCl solution” systems demonstrate a shock absorber behavior with a large hysteresis between intrusion and extrusion curves and partially irreversible intrusion in the first intrusion-extrusion cycle. The samples of KIT-6 with perfluoroalkyl grafting demonstrate higher values of intrusion pressure in comparison with ones grafted with alkyl groups, but lower intruded volume. It has been found that the intrusion of LiCl solutions leads to a considerable increase of intrusion pressure, particularly pronounced in the case of the samples

grafted with perfluoroalkyl groups. This increase is higher than one expected from the Laplace-Washburn equation. When salt concentration increases, the intrusion becomes more reversible in the case of alkyl grafting, but slightly less in the case of perfluoroalkyl one.

1. Introduction

Heterogeneous Lyophobic Systems (HLS) are one of the promising technologies for absorption, storage and generation of mechanical energy [1-10]. Their operational principle is based on the following phenomenon. To penetrate a non-wetting liquid into a porous matrix an external pressure equal or higher than the capillary one should be applied. The capillary pressure value is determined by the Laplace-Washburn equation: $P = 2\gamma \cos \theta / r$, where γ – vapor-liquid surface tension, r – pore radius and θ – solid-liquid contact angle. The liquid is intruded into the pores of the solid with a large increase of the solid-liquid interface and the absorbed mechanical energy transformed to the energy of the interface is determined by the equation: $W = \int_{V_1}^{V_2} P dV$, where P – intrusion pressure, V_1 and V_2 – volume of the system before and after the intrusion step. When the pressure is reduced, in some cases, the system can induce an expulsion of the liquid out of the pores (extrusion) with recovering of mechanical energy. Depending on the properties of porous materials and the nature of non-wetting liquid, HLS are able to absorb, dissipate or restore the supplied mechanical energy with a more or less significant hysteresis and, as a consequence, they display a bumper (irreversible intrusion, the energy is not restored), shock-absorber (reversible intrusion with large hysteresis between intrusion and extrusion curves) or spring behavior (reversible intrusion with no or narrow hysteresis), respectively.

The first heterogeneous lyophobic systems developed by V. Eroshenko were based on porous silica and liquid metals [2], then on hydrophobized porous silicas and water as light and environmentally friendly non-wetting liquid [11,12]. Later, other hydrophobic materials such as pure-silica zeolites [13-15] and metal-organic frameworks [16-19] were studied as porous matrix. Generally, the HLS based on porous silicas demonstrate a shock-absorber behavior with relatively low intrusion pressure with water (up to several tens megapascals), however high intruded volume allows to achieve relatively high values of specific absorbed energy. Silicas with irregular nanopores of various **shape** and diameter, such as silica gels, were studied in most cases, but several works were performed on ordered mesoporous silicas and organosilicas [20-29]. Such materials are of high interest because of their regular structure and pore size tunable by controlling synthesis conditions. The most part of these works were performed on MCM-41 [20-25], SBA-15 [22,27] and other [22,26] organized mesoporous silica with regular hexagonal arrangement of cylindrical mesopores forming a one-dimensional pore system (with interconnections in the last two cases). Among other mesoporous structures, only SBA-1 silica with cubic structure and tridimensional pore system was tested [28]

In the majority of cases, the internal surface of porous silicas should be functionalized with hydrophobic groups in order to confer non-wettability by water. The most used grafting molecules are chloroalkylsilanes, particularly, chlorodimethyloctylsilane [21,22,30,31]. It is known that the functionalization with perfluoroalkylsilane groups can also make the surface of porous silica highly hydrophobic [32], however HLS based on silica grafted with perfluoroalkyl chains are poorly studied.

It has been found that the use of electrolyte aqueous solution (LiCl, NaCl, KCl, MgCl₂...) is an effective way to improve the energetic performance of HLS due to a considerable increase of the

intrusion pressure. A particularly high increase of intrusion pressure is observed for microporous materials such as hydrophobic zeolites [33-36] and metal-organic frameworks [37], where the pressure can rise in several times, whereas the increase is considerably lower for mesoporous silicas [38-41]. In some cases, highly concentrated electrolyte solutions (ones with H_2O/M^+ molar ratio close or higher than ions coordination number) can also change the behavior of HLS [36,42,43]. The intrusion-extrusion of such solutions has never been studied for mesoporous silicas.

In this work we present the experiments on high pressure intrusion-extrusion of water and highly concentrated LiCl aqueous solutions in KIT-6 mesoporous silica with cubic structure (Ia3d symmetry) and tridimensional system of interconnected channels. The influence of the grafted group nature (alkyl or perfluoroalkyl chains) on the behavior and the energetic performance of the corresponding HLS has been studied.

2. Experimental

2.1. Synthesis

Mesoporous silica KIT-6 has been obtained according the following procedure adapted from the work of Kim *et al.* [44]. The triblock copolymer Pluronic P123 [(EO)₂₀-(PO)₇₀-(EO)₂₀, BASF] (6 g) was used as a pore templating agent. In a polypropylene bottle, P123 was dissolved in an acidic medium of concentrated hydrochloric acid and water (11.25 g of HCl 37% (SigmaAldrich) in 217 mL of demineralized water). The bottle was placed in a water bath at 35°C, then 6 g of n-butanol (SigmaAldrich) and 13.11 g of tetraethylorthosilicate (TEOS, 98%, SigmaAldrich) were added. The molar composition of the synthesis mixture was 1 SiO₂ : 0.017 P123 : 1.84 HCl : 1.32 BuOH: 194.5 H₂O. The mixture was stirred at 35°C during 24 h, then heated at 90°C for 24 h under static

conditions. The white powder was collected by filtration and washed with deionized water on a Buchner funnel, then dried at 70°C overnight. In order to remove the organic template, the sample was calcined at 500°C for 6 hours under air.

2.2. Grafting

Two different grafting molecules with alkyl and perfluoroalkyl chains of similar length (C8) were used in order to study the impact of the nature of grafting on the intrusion-extrusion of water and electrolyte solutions in KIT-6 mesoporous silica: n-octyldimethylchlorosilane ($\text{C}_8\text{H}_{17}(\text{CH}_3)_2\text{SiCl}$, 97%, AlfaAesar) and 1H,1H,2H,2H-perfluorooctylchlorosilane ($\text{C}_6\text{F}_{13}\text{C}_2\text{H}_4(\text{CH}_3)_2\text{SiCl}$, 97%, AlfaAesar). KIT-6 samples with alkyl and perfluoroalkyl grafting will be named hereafter as KIT-6CH and KIT-6CF, respectively. The grafting protocol was adapted from the work of Martin and Lefebvre *et al.* [45,46]. The grafting molecules were put in excess - 5 molecules per nm^2 (7.3 mmol per 1 g of KIT-6). 1 g of KIT-6 silica placed into a three-neck flask was dried at 150°C for 4 hours under vacuum. After cooling under nitrogen atmosphere 50 ml anhydrous toluene were added, followed by anhydrous pyridine in equimolar quantity to grafting molecules (7.3 mmol). Then, grafting molecules were added dropwise. The silanisation reaction was carried out at 120°C for 15 hours under stirring. After reaction, the silica powder was filtered on a Buchner funnel, washed successively with anhydrous toluene, acetone, acetone/water mixture, acetone and ether, and then dried at 70°C overnight. In the case of KIT-6CH sample, an additional hydrophobic grafting with trimethylchlorosilane ($(\text{CH}_3)_3\text{SiCl}$, 98%, AlfaAesar) (2 molecules per nm^2) was performed in the same conditions in order to functionalize residual silanol groups, since the preliminary tests showed too low intrusion reversibility without this grafting.

2.3. Intrusion-extrusion experiments and characterization

The intrusion-extrusion of water and LiCl aqueous solutions in powder KIT-6 samples was performed at room temperature using a Micromeritics mercury porosimeter (Model Autopore IV), in the range of 0.2-150 MPa. The materials were preliminary outgassed at 90°C under vacuum overnight, then the sample with the added liquid were placed into a special polymer cell sealed by a mobile piston. Then, the cell was introduced in the porosimeter one. The experimental intrusion-extrusion curves were obtained after subtraction of the ones corresponding to the compressibility of pure water or the corresponding LiCl aqueous solution.

X-ray diffraction patterns were collected on a PANalytical MPD X'Pert Pro diffractometer operating with Cu K α radiation ($\lambda = 1.5418\text{\AA}$) equipped with an X'Celerator real-time multiple strip detector (active length = $2.122^\circ 2\theta$). The powder pattern was collected at 293 K in the range $0.6^\circ < 2\theta < 5^\circ$, step = $0.017^\circ 2\theta$, time/step = 7 s, the total collecting time was about 30 minutes.

Nitrogen adsorption-desorption isotherms were performed at 77 K using a Micromeritics Tristar apparatus. Prior to the adsorption measurements, the samples were outgassed at 90 °C overnight to eliminate physisorbed molecules, but to avoid the dehydroxylation process and the degradation of grafted groups. The specific surface area (S_{BET}) and pore volume (V_{pores}) were calculated using the BET and BdB methods, respectively.

Thermogravimetric (TG) analyses were carried out on a Mettler Toledo STARE apparatus, under air flow, with a heating rate of 5 °C/min from 30 to 700 °C.

3 Results and Discussion

3.1. Intrusion-extrusion experiments

The intrusion-extrusion curves (P-V diagrams) for both KIT-6 samples with water and LiCl aqueous solutions are shown in Figure 1 and 2, respectively. The corresponding data are reported in Table 1. The volume variation observed at low pressure (< 0.5 MPa) corresponds to the

compression and the liquid filling in the interparticular porosity of KIT-6 powder. The curves are shifted along the Y-axis for better visibility, only 1st and 2nd intrusion-extrusion cycles are shown, since 2nd and 3^d cycles are superimposable for all the systems except “KIT-6CH – H₂O” one (see corresponding values in Table 2). The latter system demonstrates a combination of bumper (irreversible water intrusion) and shock-absorber behavior (reversible intrusion) with a very large hysteresis between intrusion and extrusion isotherms. The intruded volume in the first cycle is 0.40 mL/g, whereas only 0.29 mL/g is extruded meaning that 0.1 mL/g of water is still trapped in the porosity. The intruded volumes in the 2nd and 3^d cycles decrease to 0.29 and 0.23 mL/g, respectively, therefore we can conclude that the system displays again a combination of bumper and shock-absorber behavior. The intrusion pressure is 26 MPa which is in the range of intrusion pressure values observed for hydrophobized mesoporous silicas and silica gels in the literature [20-28]. The extrusion pressure (1 MPa) is much lower than the intrusion one, thus, almost the totality of supplied mechanical energy is absorbed (energy yield = 3 %).

When the LiCl aqueous solutions are intruded, significant differences are observed in comparison with water. The irreversibility of intrusion is drastically diminished. The “KIT-6CH – LiCl solution” systems demonstrate a combination of bumper and shock-absorber behavior, but only in the first cycle, whereas in following cycles the intrusion is fully reversible that corresponds to shock absorber behavior. In the first cycle, the non-extruded volume becomes significantly lower in comparison with water (0.03-0.05 mL/g against 0.11 mL/g, respectively) of total intruded volume. It should be noticed that a similar phenomenon of the increase of intrusion reversibility using electrolyte solutions was previously observed for porous silica [39] and hydrophobic zeolites [35,36,42]. Such a change of systems behavior is probably related with different nature of intruded liquid: in such highly concentrated LiCl aqueous solutions, the water molecules are involved in

the solvation of the ions (1st and 2nd solvation shells). We suppose that the solvated ions interact less with the pore surface leading to lower irreversibility. The irreversible interactions of intruded water molecules with the residual silanol defects of the surface are also possible. It can be supposed that water molecules penetrate easier through eventual irregularities of grafting layer to the silica surface and interact stronger with residual silanols in comparison with the solvated ions.

The increase of intrusion pressure is observed, when LiCl concentration rises, that is conformed to our previsions. For the first cycle, the pressure increases from 26 MPa when using pure water to 32.5, 35 and 38 MPa for 5, 10 and 20 M LiCl solutions, respectively. For the following cycles the values are ~1 MPa lower. The extrusion pressure rises more drastically – from 1 MPa for pure water to 6 MPa for 20 M LiCl solution that leads to an increase of energy yield – from 3 to 16 %, however the systems still remain good shock absorbers, where at least 84% of supplied mechanical energy is dissipated.

The increase of intrusion pressure can be mostly explained by the rise of vapor-liquid surface tension with LiCl concentration. The surface tension is about 98 mN/m for 20 M LiCl solution and 72.8 mN/m for pure water [47]. According to the Laplace – Washburn equation ($P = 2\gamma \cos \theta / r$), this corresponds to an increase of 35 % of the intrusion pressure, that is slightly lower than observed in our experiments (increase 46 % – from 26 to 38 MPa). It can be supposed that the additional intrusion pressure increase is related to higher contact angle of LiCl solutions with grafted pore surface. The calculated liquid-solid contact angle values are 127° and 131° for water and 20 M LiCl solutions, respectively. Comparing to the literature on intrusion-extrusion of electrolyte solutions in mesoporous silica [38-41], the increase of intrusion pressure obtained in our case is found among the highest ones that is probably related to the use of highly concentrated solutions. However, for hydrophobic microporous materials such as pure silica zeolites and Metal-

Organic Frameworks, the intrusion pressure rises much more drastically when using 20 M LiCl solution, in 2.1 – 7.4 times in comparison with pure water [35-37,42]. More pronounced effect in the case of microporous materials can be explained by different mechanisms of intrusion in sub-nanometer pores which have lower diameter than the one of solvated ions: osmotic phenomena and desolvation or distortion of solvated ions during the penetration into the pores [48,49]. In the case of mesoporous materials, the pores are considerably larger than the diameter of solvated ions, thus, the intrusion pressure is determined mostly by the parameters of the Laplace-Washburn equation, such as the vapor-liquid surface tension and contact angle.

The increase of intruded volume from 0.40 mL/g (water) to 0.42-0.47 mL/g is also observed for all the LiCl aqueous solutions. It can be supposed that the saline solutions fill better the pore volume or that the molecular clusters of the solutions have more compact (dense) organization inside the pores in comparison with water. A similar effect was observed for the intrusion of concentrated saline solutions in zeosils [36,50].

The change of the nature of the grafting molecules – from alkyl to perfluoroalkyl chains leads to the changes in the behavior and the intrusion-extrusion characteristics of the systems (Figure 2). The system « KIT-6CF – H₂O » demonstrates a shock-absorber behavior with slightly irreversible intrusion in the 1st cycle only, whereas in the case of “KIT-6CH – H₂O” system the intrusion irreversibility is more pronounced in every cycle (see corresponding values in Table 2) The grafting with perfluoroalkyl chains leads also to the increase of intrusion pressure – 31.5 and 26 MPa for « KIT-6CF – H₂O » and « KIT-6CH – H₂O » systems, respectively. This effect cannot be explained only by a lower pore diameter for the KIT-6CF sample (6.3 against 6.7 nm, respectively, see N₂ adsorption-desorption section), it is also related to a higher hydrophobic character of perfluoroalkyl-grafted surface that corresponds to a higher water-surface contact angle (127° and

134°C for KIT-6CH and CF, respectively). An increase of contact angle for such surfaces was previously observed in the work of Fadeev and Eroshenko [32]. The extrusion pressure changes more considerably – from 1 (KIT-6CH) to 6.5 MPa (KIT-6CF) that corresponds to a more narrow hysteresis between intrusion and extrusion curves with the increase of energy yield from 3 to 19-22 %, respectively. It has been also observed that for KIT-6 grafted with perfluoroalkyl chains the intruded volume is considerably lower than the one for KIT-6CH (0.27 against 0.40 mL/g, respectively). This difference of specific intruded volume is mainly explained by higher impact of perfluoroalkyl grafting in the mass of the sample in comparison with alkyl one (see TG and N₂ adsorption-desorption sections).

The “KIT-6CF – LiCl solution” systems demonstrate a combination of shock absorber and bumper behaviors with a small intrusion irreversibility in the first cycle. In contrast to the KIT-6CH samples, the intrusion of LiCl solutions becomes slightly less reversible: when LiCl concentration increases, the non-extruded volume increases from 0.02 for water to 0.06 mL/g for 20 M LiCl solution. To explain this unusual tendency, it can be supposed that the solvated ions from salt solution interact stronger with perfluoroalkyl groups than with alkyl-grafted ones because of their higher polarity. The intruded volume increases with salt concentration up to 0.33 mL/g for 20 M LiCl solution.

As in the case of other HLS, the increase of LiCl concentration leads to the rise of intrusion pressure and the effect is more pronounced than in the case of KIT-6CH sample. The pressure increases from 31.5 for pure water to 52.5 MPa for 20 M LiCl solution that corresponds to a rise of 67 % (against 46 % increase for KIT-6CH) that cannot be explained by only the increase of surface tension. The contact angle between the solution and KIT-6CF perfluoroalkyl-grafted pore

walls increases stronger with LiCl concentration than in the case of alkyl-grafted one: from 134° for water to 148° for 20 M LiCl solution (a rise of 14° against 4° for KIT-6CH).

The values of absorbed energy in the case of KIT-6CF sample are generally lower than the one observed for KIT-6CH one, because of lower intruded volume. However, the maximal values of absorbed energy for the first cycle are very close - 17.3 and 17.9 J/g for “KIT-6CF - 20 M LiCl solution” and “KIT-6CH - 20 M LiCl solution” systems, respectively. Nevertheless, the latter system seems to be more effective as a shock absorber due to lower restored energy.

Thus, the shock absorber behavior and the energetic performance of KIT-6 based systems is similar to the ones obtained for other systems based on mesoporous silicas [20-28, 38-41]. The cubic pore structure of KIT-6 seems to not have a significant influence on the behavior and energetic performances. Compared to the microporous hydrophobic materials (zeosils, metal-organic frameworks), the mesoporous silicas demonstrates more pronounced shock absorber behavior, with more than 66-97% of the supplied mechanical energy dissipated (yield of 3-34 %), whereas the metal-organic frameworks with a shock absorber behavior do not show a yield lower than 42% [18,19] and the zeosils show generally a spring one (yield > 90%) [14].

3.2. X-ray diffraction

The XRD patterns of initial calcined KIT-6 sample and grafted ones before and after intrusion-extrusion experiments are shown in Figure 3. Typical peaks of cubic KIT-6 structure (Ia3d symmetry) at 1.0° (211), 1.15° (220) and two large ones at 1.45° and 1.84° (2 θ) are visible on the diffractogram of the calcined sample. After grafting and intrusion-extrusion tests the peak positions do not change, but their intensity varies considerably, in particular for the peaks at 1.45° and 1.84°, which disappear completely for the grafted samples (the second one only for KIT-6CF). It can be concluded that the intrusion-extrusion experiments do not change the organisation of the

material, whereas the intensity of peaks varies with the filling of the pores by the grafting molecules.

3.3. Thermogravimetric analysis

Thermogravimetric curves of KIT-6CH and KIT-6CF samples before and after intrusion-extrusion experiments and also of the sample before grafting are presented in Figure 4. The non-grafted sample demonstrates total weight loss of 12.4 wt% the most part (9.5 wt%) of which is observed at low temperature (30°-80°C) that corresponds to the removal of physisorbed water molecules. After both graftings with alkyl and perfluoroalkyl groups the material becomes hydrophobic: almost no weight loss (0.5-1.0 wt%) is observed below 200°C. For the KIT-6CH sample, a weight loss of 16.2 wt% starting at 210°C corresponds to the removal of grafted molecules. In the case of KIT-6CF, the grafting is more thermally stable, the step corresponding to the removal of grafting groups starts from 400°C and the weight loss is considerably higher (38 wt%) than in the case of alkyl grafting groups. The silane grafting density calculated from these weight losses is ~1.0 and ~1.1 groups/nm² for octyl- and perfluorooctyl groups, respectively. The intrusion-extrusion experiments change slightly the thermogravimetric curves. The most visible change is observed for the curve corresponding to KIT-6CH sample after water intrusion-extrusion experiments. An additional weight loss step of 5.2 % is observed between 130° and 230°C which could be attributed to water molecules strongly physisorbed on residual silanol groups in the pores. This result is in correlation with the partially irreversible character of water intrusion in KIT-6CH sample. Slightly higher total weight loss observed for KIT-6CF samples after intrusion-extrusion experiments in comparison with non-intruded one is related to higher content of adsorbed water molecules.

3.4. N₂ adsorption-desorption

The nitrogen adsorption–desorption isotherms of the KIT-6CH and KIT-6CF samples are shown in Figure 5A and B, respectively. The corresponding data are reported in Table 2. The isotherms are of type IVa that is typical for mesoporous silicas. The calcined KIT-6 sample demonstrates BET surface area of 875 m²/g and the total pore volume of 1.07 mL/g. The pore diameter (BdB) ranges between 7.2 to 8.5 nm with an average value of 7.8 nm. After the grafting step, the hysteresis shape changes slightly, but the type H1 of the hysteresis loop is maintained which means that the pore shape is not modified. Indeed, whatever the grafted material, the adsorption and desorption isotherm branches are still quite parallel. After the functionalization with n-octyldimethylchlorosilane and trimethylchlorosilane (KIT-6CH) BET surface area drops to 305 m²/g, the total pore volume - to 0.55 mL/g and the average pore diameter – to 6.7 nm. In spite of the same number of carbon atoms in the chain, in the case of the grafting of 1H,1H,2H,2H-perfluorooctylchlorosilane (KIT-6CF) the decrease of pore size is more pronounced (average pore diameter of 6.3 nm and $V_{\text{pores}} = 0.42$ mL/g) that is probably related to the rigidity of perfluoroalkyl chains. Thus, the decrease of KIT-6CF pore diameter is too low to explain the difference in intrusion pressure values, in comparison with KIT-6CH ones, according to Laplace-Washburn equation. It should be also noticed that the values of pore volume for the grafted samples are very close when calculated for pure SiO₂ (see column 4, Table 2), since, according to TG results, the impact of the grafting groups in the sample mass is considerably different (16 and 38 % of sample weight for alkyl and perfluoroalkyl grafting, respectively). This explains mainly the difference between the intruded volume values for KIT-6CH and KIT-6CF samples. It should be noticed that after the grafting step, the microporous volume of the parent material decreases drastically from 0.26 mL/g to 0.07 mL/g. The decrease should be due to the filling of the micropores or the blocking of the micropores by the grafted group or to a micropore collapse upon the grafting process. It can

be supposed that the microporosity is partially responsible for the intrusion irreversibility. The irreversibly intruded water and LiCl molecules can be trapped inside the micropores, where no hydrophobic grafting is present. The intrusion-extrusion experiments lead to a decrease of pore volume – to 0.46-0.48 mL/g for KIT-6CH samples, 0.36-0.38 mL/g for KIT-6CF ones.

4. Conclusions

High pressure intrusion-extrusion of highly concentrated LiCl aqueous solutions in KIT-6 mesoporous silica with different hydrophobic grafting groups (alkyl and perfluoroalkyl chains) has been studied. Under high pressure intrusion-extrusion, the systems demonstrate generally a shock absorber behavior with partially irreversible intrusion in the first cycle. The hysteresis between intrusion and extrusion curves is very large (energy yield = 3-34 %), thus, the most part of supplied mechanical energy is dissipated, that makes the systems promising for shock absorber applications. The influence of the nature of grafted groups is clearly observed. In the case of water intrusion-extrusion, the grafting with perfluorinated chains makes the system much more reversible in comparison with alkyl-grafted silica. The samples with perfluorinated grafting groups demonstrate higher values of intrusion pressure. The use of electrolyte aqueous solutions leads to the increase of intrusion pressure and, thus, of absorbed energy. The effect is more pronounced for KIT-6 with perfluorinated grafting, where the pressure increases by 67 % against 46 % for alkyl-grafted silica. It should be noticed that the increase of intrusion pressure with the rise of salt concentration is considerably less pronounced than in the case of the systems based on hydrophobic microporous materials (zeosils, MOFs). In the case of mesoporous silica, the increase of intrusion pressure seems to be mostly related to the variation of the parameters of Laplace-Washburn equation. It can not be explained by only the rise of LiCl solution surface tension and

seems to be also related to the variation of solution-pore contact angle. Moreover, in the case of KIT-6CH samples, the intrusion of LiCl aqueous solutions leads to the change of HLS behavior by the increase of intrusion reversibility in comparison with pure water, whereas in the case of perfluoroalkyl grafting (KIT-6CF samples) a slight increase of irreversibility of the first intrusion is observed. The values of absorbed energy in the case of KIT-6CH sample are generally higher than ones for KIT-6CF, because of its higher intruded volume. However, the maximal values of absorbed energy for the first cycle are very close - 17.3 and 17.9 J/g for “KIT-6CF - 20 M LiCl solution” and “KIT-6CH - 20 M LiCl solution” systems, respectively. It can be concluded that the use of highly concentrated electrolyte solutions is a promising way to improve the absorbed energy and the intrusion reversibility of heterogeneous lyophobic systems based on mesoporous silica.

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TABLES.

Table 1. Energetic performance of “KIT-6CH – H₂O”, “KIT-6CF – H₂O”, “KIT-6CH – LiCl aqueous solution” and “KIT-6CH – LiCl aqueous solution” systems.

Sample	P _{int} ^a (MPa)	P _{ext} ^a (MPa)	V _{int} ^a (mL/g)	V _{ext} ^a (mL/g)	E _s ^b (J/g)	E _r ^b (J/g)	Yield ^c (%)
KIT-6CH based systems							
H ₂ O	26 ^d /25 ^{e,f}	1	0.40 ^d /0.29 ^e /0.23 ^f	0.29 ^d /0.23 ^e /0.2 ^f	10.4 ^d /7.3 ^e /5.8 ^f	0.3 ^d /0.2 ^e /0.2 ^f	3 ^{d,e,f}
5M LiCl	32.5 ^d /31 ^{e,f}	3	0.42 ^d /0.39 ^{e,f}	0.39	13.7 ^d /12.1 ^{e,f}	1.2	9 ^d /10 ^{e,f}
10M LiCl	35 ^d /34 ^{e,f}	5	0.45 ^d /0.40 ^{e,f}	0.40	15.8 ^d /13.6 ^{e,f}	2.0	13 ^d /15 ^{e,f}
20M LiCl	38 ^d /37 ^{e,f}	6	0.47 ^d /0.42 ^{e,f}	0.42	17.9 ^d /15.6 ^{e,f}	2.5	14 ^d /16 ^{e,f}
KIT-6CF based systems							
H ₂ O	31.5 ^d /29.5 ^{e,f}	6.5	0.27 ^d /0.25 ^{e,f}	0.25	8.5 ^d /7.4 ^{e,f}	1.6	19 ^d /22 ^{e,f}
5M LiCl	38.5 ^d /37.5 ^{e,f}	10.5	0.29 ^d /0.26 ^{e,f}	0.26	11.2 ^d /9.8 ^{e,f}	2.7	24 ^d /28 ^{e,f}
10M LiCl	42.5 ^d /41 ^{e,f}	12	0.31 ^d /0.28 ^{e,f}	0.28	13.2 ^d /11.5 ^{e,f}	3.4	26 ^d /29 ^{e,f}
20M LiCl	52.5 ^d /52 ^{e,f}	17.5	0.33 ^d /0.27 ^{e,f}	0.27	17.3 ^d /14.0 ^{e,f}	4.7	27 ^d /34 ^{e,f}

^a P_{int} and P_{ext} - intrusion and extrusion pressures, V_{int} and V_{ext} - intruded and extruded volumes, respectively.

^b Stored (absorbed) energy E_s=P_{int}V_{int} , restored energy E_r=P_{ext}V_{ext}.

^c Yield = (E_r/E_s)×100%.

^d 1st intrusion-extrusion cycle.

^e 2nd intrusion-extrusion cycle.

^f 3^d intrusion-extrusion cycle.

Table 2. BET surface area, pore volume and average pore diameter obtained from N₂ adsorption-desorption isotherms at 77 K for calcined KIT-6 sample and KIT-6CH and KIT-6CF ones before and after intrusion-extrusion experiments.

	BET surface area (m ² /g)	Total pore volume (mL/g)	Total pore volume (mL/g of SiO ₂)	Average pore diameter (BdB), nm
KIT-6 calcined	875	1.07	1.07	7.8
KIT-6CH	305	0.55	0.65	6.7
KIT-6CF	307	0.42	0.67	6.3
KIT-6CH after H ₂ O intrusion	254	0.48	0.58	6.9
KIT-6CH after 20M LiCl solution intr.	262	0.46	0.55	6.7
KIT-6CF after H ₂ O intrusion	266	0.38	0.61	6.2
KIT-6CF after 20M LiCl solution intr.	252	0.36	0.58	6.2

FIGURE CAPTIONS:

Figure 1. Intrusion-extrusion curves of the « KIT-6CH – H₂O » and « KIT-6CH – LiCl solution » systems. The curves are shifted along the Y-axis for better visibility.

Figure 2. Intrusion-extrusion curves of the « KIT-6CF – H₂O » and « KIT-6CF – LiCl solution » systems. The curves are shifted along the Y-axis for better visibility.

Figure 3. X-ray diffraction patterns of KIT-6 samples before grafting (calcined), after grafting with alkyl and perfluoroalkyl chains (KIT-6CH and KIT-6CF) and after three intrusion–extrusion cycles in water and 20 M LiCl aqueous solution.

Figure 4. TG curves of KIT-6 samples before grafting (calcined), after grafting with alkyl and perfluoroalkyl chains (KIT-6CH and KIT-6CF) and of grafted samples after three intrusion–extrusion cycles in water and 20 M LiCl aqueous solution.

Figure 5. N₂ adsorption-desorption isotherms at 77 K of KIT-6 samples before grafting (calcined), after grafting with alkyl (A) and perfluoroalkyl chains (B) and after three intrusion–extrusion cycles in water and 20 M LiCl aqueous solution.

FIGURES.

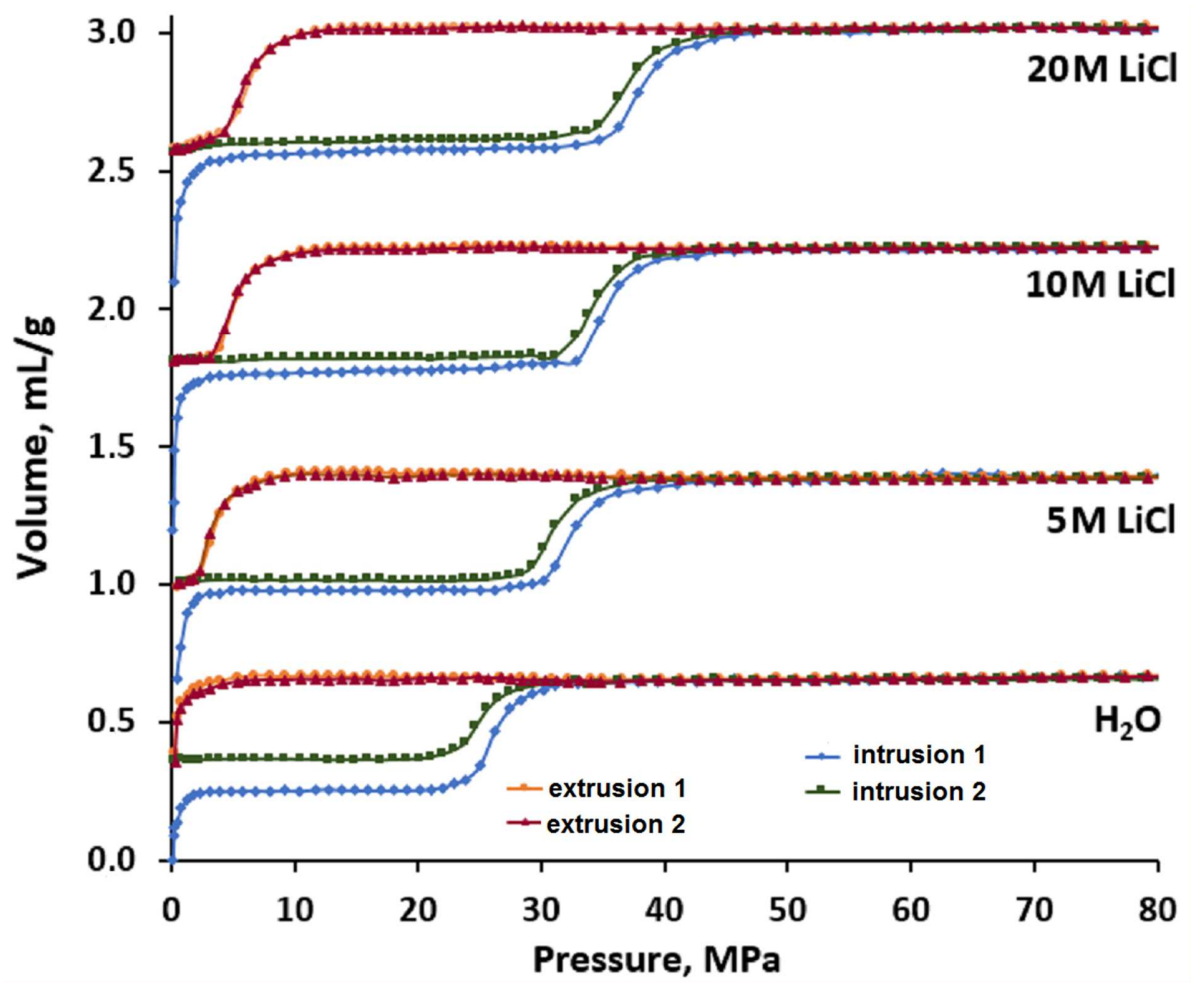


Figure 1.

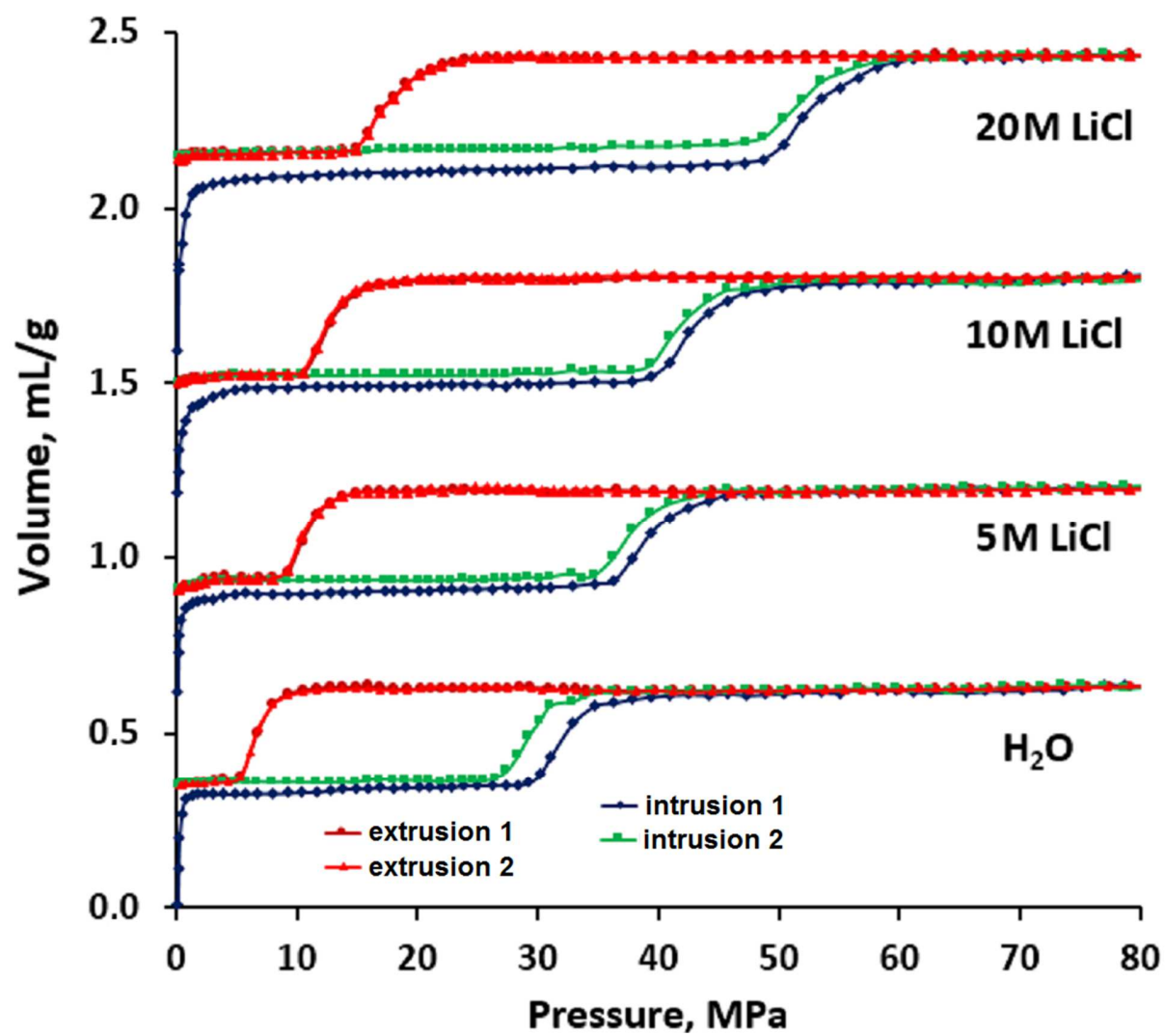


Figure 2.

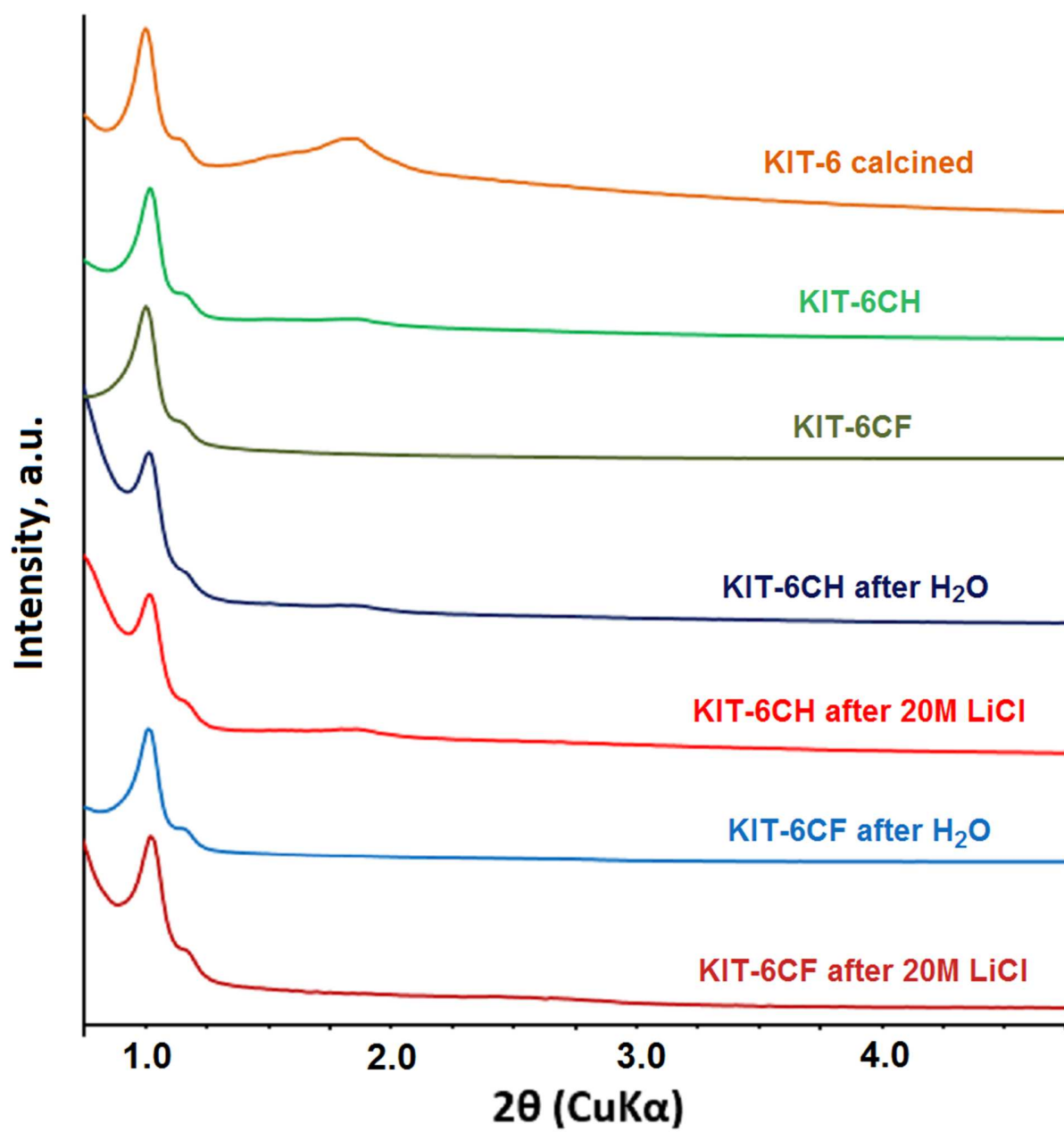


Figure 3.

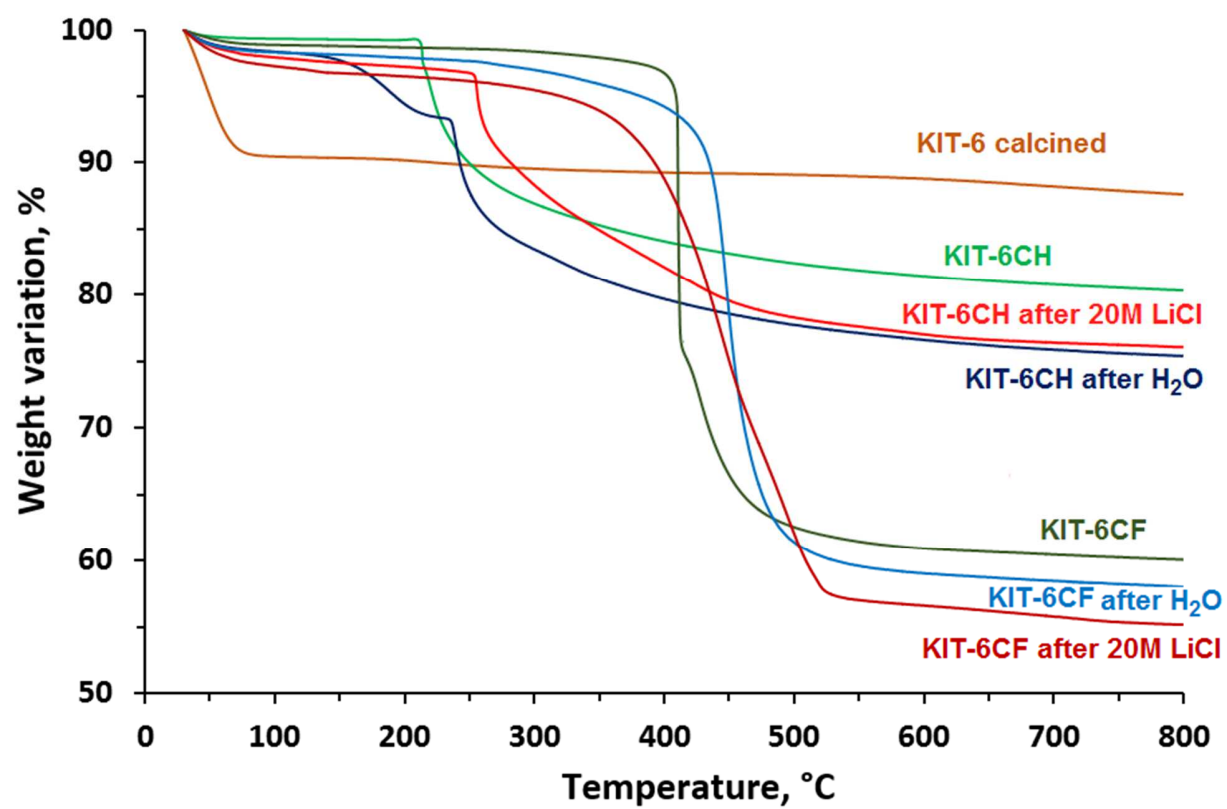


Figure 4.

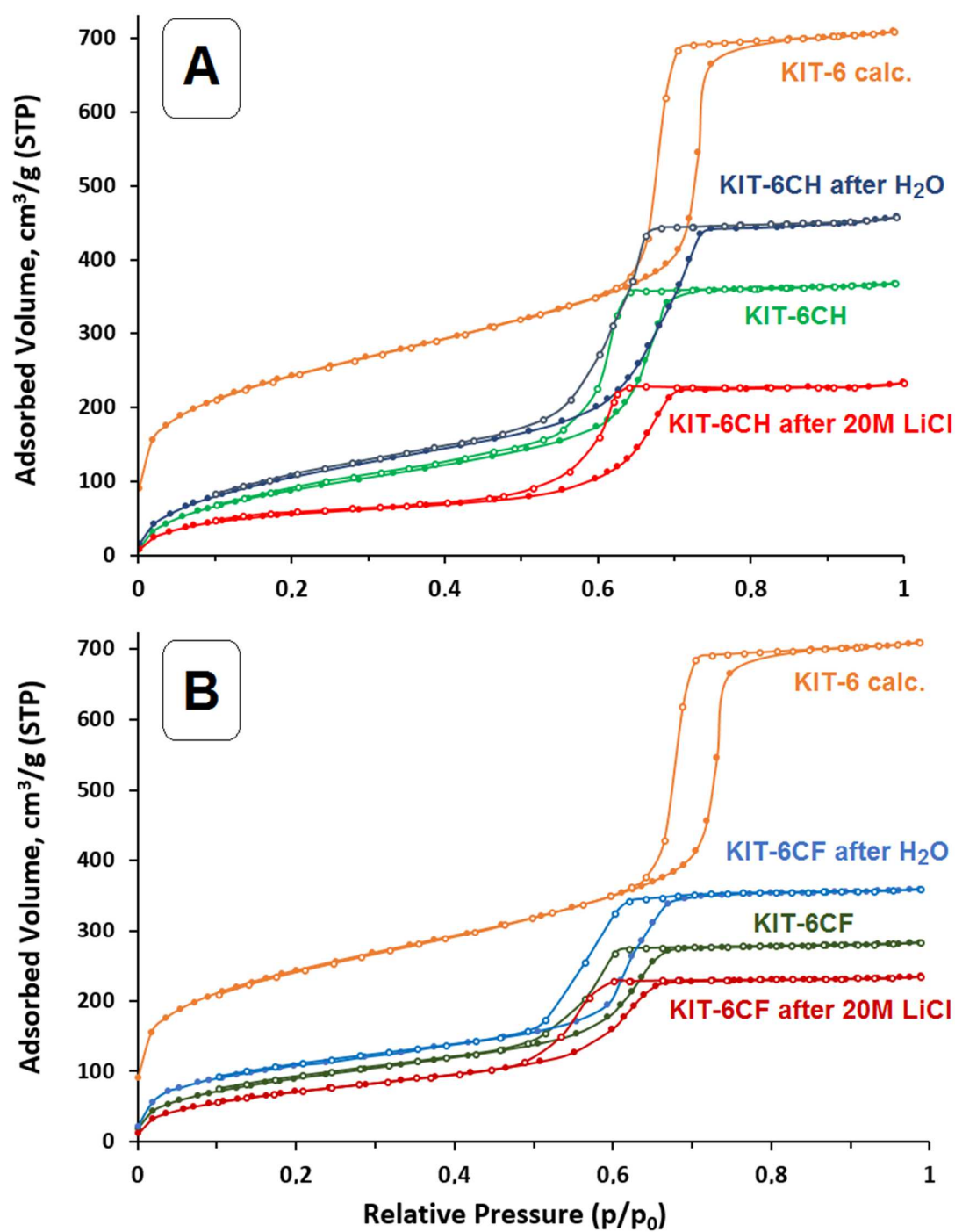


Figure 5.

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