

Supplementary information

Investigation of the structural and electrical conductivity properties in pure and cation exchanged rectorite

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Table S1. Line width lw and Gaussian broadening (dominated by a distribution of chemical shift) dCS in ppm obtained from the fit of the ^{23}Na MAS NMR spectra of pristine and cation-exchanged rectorite materials.

Sample		Na site			
		<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>
RT	lw	2.7	1.5	6.7	1.6
	dCS		1.5	5.5	
RT-Mg ²⁺	lw	-	6.2	11.5	1.1
	dCS		2.1	4.2	
RT-Li ⁺	lw	-	1.3	9.0	1.4
	dCS		1.6	5.1	
RT- Na ⁺	lw	3.2	8.9	17.8	3.5
	dCS		1.2	4.6	
RT-NH ₄ ⁺	lw	-	2.1	5.9	1.4
	dCS		1.5	5.5	

Assignment of ^1H MAS NMR spectra

The question arises what is the origin of the co-existence of two OH signals at 1.8 and 2.8 ppm. In our previous work, a high degree of Al substitution in the tetrahedral sheets has been found that is evidenced by a high fraction of the Si(3Al) component in ^{29}Si NMR and the presence of the tetrahedral signal in ^{27}Al NMR (Atanasova et al. 2016). Therefore, a frequent appearance of (-Si)₃OH and (-Al)₃OH groups is nearly possible. Instead, a co-existence of mixed (-Si_xAl_{3-x})OH aluminosilicate hydroxides can be suggested that should result in a distribution of OH spectral lines. The presence of only two distinct signals at 1.8 and 2.8 ppm requires alternative assignment. These two signals can originate from two kinds of OH-groups in the mica (dehydrated) layer: one involved in relatively strong hydrogen bonds between adjacent layers (-Si-O-H--), and the other one more mobile (-Si-O-H), perhaps located opposite tetrahedral cavities of the next layer. Indeed, the spectral parameters for the former support this assignment: the higher ^1H chemical shift (2.8 ppm vs. 1.8 ppm) indicates the

stronger hydrogen bonding, and its larger linewidth is a signature of lower mobility. Such assignment has been proposed for two types of OH groups determined by a combination of characterisation methods in H-exchanged layered silicate (Rojo et al. 1988).

We have assigned the ^1H NMR signals at 3.8 to 4.7 ppm to the hydration shell protons around the cations located in the hydrated smectitic interlayers. It is well known that ions in water affect the hydrogen-bonding network. That is the ions with high hydration energy enhance the formation of hydrogen bonds attracting a larger amount of water molecules. To confirm this assignment, we have performed the MAS NMR experiment at an increased MAS speed. An interesting observation is that the framework OH-signals remained invariant of the MAS speed, while the hydration shell ^1H signals showed upfield shift. This observation is explained by the temperature induced susceptibility change (due to faster spinning), which the water molecules are more sensitive to, than hydroxides. In addition, temperature enhancement would facilitate exchange between Na^+ and Ca^{2+} hydrating protons (if within the same interlayer) that would result in merging two water signals. Since this has not been observed in the experiment at a higher MAS, we assume that the water protons around Na and Ca are not exchangeable. There are two possible reasons for this: (1) water protons are strongly interacting with cations, around which they form the hydrating shells, and (2) they belong to different interlayers, and hence, non-exchangeable. The latter can be excluded based on the recent XRD data, which will be published in a separate paper.

X-ray photoelectron spectroscopy results

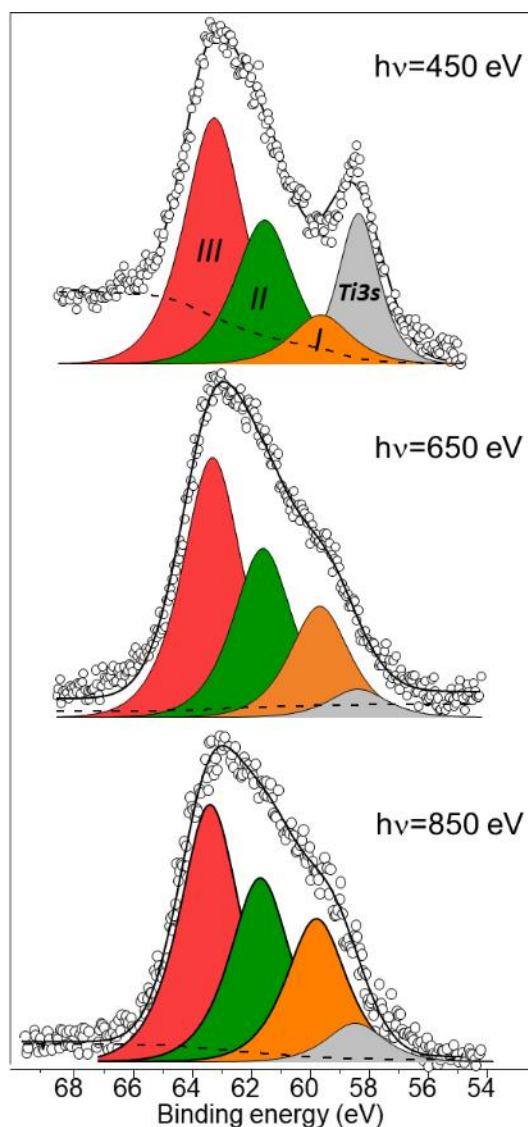


Figure S1. XPS Na 2s spectra of RT-Na at a photon energy of 450, 650 and 850 eV.

The chemical state of sodium in RT-Na is studied with the XPS Na 2s spectra, as shown in Figure S1. The spectra at three photon energy values of 450, 650 and 850 eV are fitted with 4 peaks. The fit parameters are given in Table S1. The fit component at 58.5 eV is attributed to Ti3s arising from conducting coating of the rectorite films. The decrease of its concentration from 450 eV to 650 eV and 850 eV proves its location on a surface. The other three components arise from Na species in the pores and interlayers of rectorite. In Ref. (Tissot et al. 2015) the Na 2s at 63.2 eV is found for sodium halide solutions and not affected by the photon energy change and by the nature of the anion. Based on literature we assign the component *III* at 63.4 eV to the Na⁺ cations surrounded by water molecules in hydrated interlayers. This component shows the highest intensity as compared to other Na-fractions that is in a good agreement to the NMR data. The components *I* and *II* correspond to Na in dehydrated mica

interlayers and exchangeable Na^+ in pores. Analysis of the XPS data shows that the number of the Na structural environments agrees well with the number of Na fit component in the NMR spectra of RT-Na.

Table S1. Fit parameters of the XPS Na 2s spectra at photon energy values of 450, 650 and 850 eV.

Peak position, eV, Assignment		63.4 (III)	61.7 (II)	59.8 (I)	58.5 (Ti3s)
Concentration, %	450 eV	45	27	9	19
	650 eV	46	30	19	5
	850 eV	41	30	23	6

Powder XRD measurements

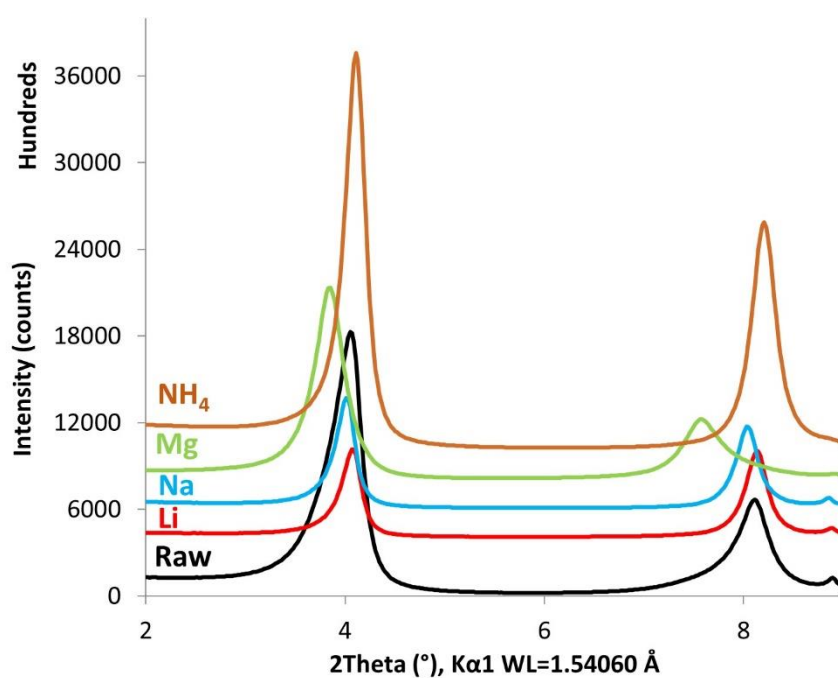


Figure S2. XRD data from oriented specimens of RT-Raw, RT-Li⁺, RT-Na⁺, RT-Mg²⁺ and RT-NH₄⁺.

Electrical impedance spectra for the samples RT, RT-Na⁺, RT-Mg²⁺ and RT-NH₄⁺.

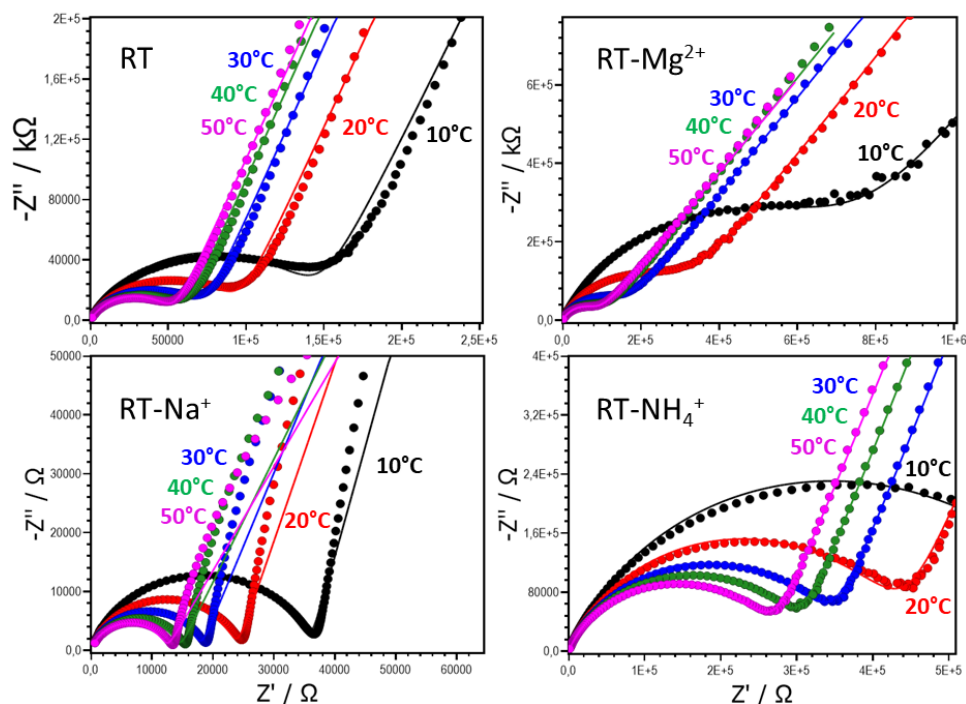


Figure S3. Impedance spectra at different temperatures for pure and cation-exchanged rectorite samples. The spectra are cut for a better visibility of the bulk process.

Comment on near-Arrhenius behavior for RT-NH₄ at ΔT_1 and ΔT_2

Commonly, independence of $\ln(\sigma T)$ on temperature (or $\tan(\alpha) = \text{const}$) is an indication of Arrhenius-like thermal activation expected for glass forming materials above the glass transition temperature. Also, the constant activation energy for RT-NH₄ above 30°C agrees well with the VFT fit parameter $T_0 + 50 = 33 \pm 3$ [°C] associated with glass transition temperature.

References

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