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1 INFLUENCE OF THE PRECURSOR AND THE TEMPERATURE OF
2 SYNTHESIS ON THE STRUCTURE OF SAPONITE

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10 ABSTRACT

11 Several procedures of hydrothermal synthesis of saponite can be found in the literature.
12 They differ in terms of the preparation conditions of the precursor and of the synthesis
13 temperature. The objective of this study was to investigate how these two parameters
14 influence the structure of the final synthesis product. The precursor was prepared from
15 $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$ and Na_4SiO_4 in three different ways: as a gel, a dried gel and a
16 calcined gel. The influence of the synthesis temperature on the structure of saponite was
17 investigated in 90 – 200 °C range. The results showed that the use of calcined precursor
18 yields a single mineral phase, saponite with up to 90% aluminum in tetrahedral
19 configuration. In comparison, the use of gel precursor, resulted in a product with only
20 60% of aluminum in the tetrahedral configuration. The synthesis temperature did not
21 have a significant effect on saponite structure. The reported synthesis method showed

22 the possibility to obtain saponite with superior characteristics, in terms of crystallinity,
23 surface acidity and thermal stability compared to natural mineral, even at 90 °C and
24 then with a higher potential for industrial applications.

25 **Keywords:** Synthesis, Minerals, Nanoclay, Saponite, precursor

26 INTRODUCTION

27 For solid state catalysts, the surface and pore characteristics play a decisive role and
28 are investigated with many different approaches. Mesophase templating allows to
29 synthesise amorphous silica with defined mesoporosity of up to 10 nm (Gleiter 2000).
30 Limitations in this approach are difficulties in large-scale production and the possibility
31 to functionalise the surface to create catalytic active sites. Zeolites are easy to
32 synthesise, but the access to the sites positioned inside the pores, which constitutes the
33 biggest part due to the high internal surface area, is restricted due to the presence of
34 micropores with a dimension < 0.8 nm and therefore not reachable by larger molecules.
35 However, a partial inhibition of crystallization using an excess of grafted organic
36 species can lead to intracrystalline mesoporosity with increased accessibility for active
37 sites (Xue et al. 2012). Saponite clay minerals with an important anisotropy due to their
38 layered structure allow a better adsorption of more complex molecules onto their
39 surface. This makes saponite clay minerals suitable for a wide range of catalytic
40 applications for organic molecules from cracking, isomerisation (Vogels et al. 2005)
41 and oxydation (Trujillano et al. 2009) to the Mannich reaction (Gómez-Sanz et al.
42 2017). In polymer composite materials saponite nanoparticles are used to give origin to
43 novel properties not shown before by one of the components at the macro or micro scale
44 (Nathani et al. 2004). Improvements in the mechanical properties and hindrance to
45 diffusion were observed. The particular properties of saponites, as the high cation

46 exchange capacity and important specific surface area, make them also attractive for
47 such applications as adsorbents and in wastewater treatment (Marchesi et al. 2020).
48 Their high surface area, thermal stability, large availability and resource friendly
49 characteristics make the use of synthetic and natural saponites increasingly attractive in
50 research and industry (Zhou et al. 2019; Carniato et al. 2020).

51 Saponites are part of the smectite group and belong to the 2:1 clay minerals, which
52 consist of layers composed of two tetrahedral silica sheets sandwiching an octahedral
53 sheet. For synthetic saponites, the octahedral sheet can contain various divalent metals,
54 like Mg^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , and Fe^{2+} (Decarreau 1981; Trujillano et al. 2011). One of
55 the requirements of the materials intended for the catalytic use, is their thermal stability.
56 The thermal stability is found to be higher in smectites like saponites (with Mg^{2+} as the
57 major cation in the octahedral sheet) that are stable up to 750 °C, when compared to
58 smectites like montmorillonites (with Al^{3+} as a major cation in the octahedral sheet)
59 with a maximum stability temperature of 480 °C (Ames and Sand 1958).

60 In the tetrahedral silica sheet functional ions like Al^{3+} can isomorphously substitute
61 Si^{4+} to create active sites. Si-O-Al groups have shown strong acidic properties as a
62 Lewis site (Aquino et al. 2004; Zhou et al. 2019). In addition, it has been suggested in
63 the literature that the acid activity of clay minerals could be correlated to the tetrahedral
64 surface charge density (Davidtz 1976). Thus, a product with the most of Lewis sites and
65 with high thermal stability at the same time, could be a structure with a high amount of
66 Al^{3+} substitution in tetrahedral sheet, i.e. having Al/Si molar ratio equal to 0.33. The
67 possibility to synthesize saponite clay mineral with such high amount of Al^{3+} has been
68 previously demonstrated (Suquet et al. 1977).

69 In general, the formation of saponites is possible under vastly different hydrothermal
70 conditions. Moderate conditions with temperatures between 100 and 575 °C and
71 pressures to several kbars are most promising in terms of growth rate, yield and purity
72 (Kloprogge et al. 1999). In the 125 – 280 °C hydrothermal temperature range, a higher
73 temperature results in an increase of the crystalline phases for ammonium saponites,
74 shown by Fourier-transform Infrared (FTIR) spectroscopy (Kloprogge and Frost 2000).
75 However, the chemical composition, and thus to some extent saponite crystal structure,
76 would not be expected to significantly change by increasing the temperature. To test
77 this hypothesis, saponite synthesis was performed from 90 to 220 °C and a detailed
78 characterization of the chemical composition and structure of final synthesis product
79 was performed.

80 While in nature the formation of smectites is determined by the availability of
81 elements and their speciation (Christidis and Dunham 1997), in hydrothermal synthesis
82 the most common starting materials are solid phases, such as other aluminosilicates,
83 glasses and gels, whose composition is close to the that of the desired clay mineral
84 (Kloprogge et al. 1999). The effect of precursor treatments on the structure of the final
85 synthesis products is not well investigated and therefore investigated in this work.

86 EXPERIMENTAL

87 *Synthesis*

88 0.2 M solutions of magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) from Sigma Aldrich (India),
89 aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) from Carlo Erba (Val de Reuil, France) and sodium
90 orthosilicate (Na_4SiO_4) from Alfa Aesar (Karlsruhe, Germany) in distilled water
91 ($18.2 \text{ M}\Omega \cdot \text{cm}$) were prepared. The solutions were mixed in a beaker to form a precursor
92 that contained a Mg/Al/Si molar ratio of 1/0.33/1. The precursor was then stirred at

93 room conditions for 3 h to achieve a homogeneous suspension. For the precursor
94 experiments the suspension was put into the autoclave directly at this stage (sample
95 labeled “Gel”) followed by the hydrothermal treatment. To reduce the water content, the
96 suspension was dried in an oven at 200 °C (sample labeled “Dried gel”). For the rest of
97 the experiments the dried gel was put into a crucible and calcined at 450 °C (sample
98 labeled “Calcined gel”). At maximum temperature the holding time was 1 h after a
99 heating rate of 5 °C/min and a cooling time of less than 10 °C/min afterwards.

100 For the hydrothermal synthesis a 0.01 M NaOH solution was prepared using NaOH
101 powder from Sigma Aldrich (St Louis, USA) and then added to the grinded calcined
102 precursor gel. The autoclave with the suspension was securely closed and placed into an
103 oven for 120 hours. The synthesis was conducted at 90, 120, 150, 180 and 200 °C. In
104 the autoclave a pressure corresponded to a water pressure at those temperatures. The pH
105 was measured with Hi2211 pH ORP Meter by Hanna Instruments (Tanneries, France)
106 with two point calibration at pH = 7 and pH = 10 after the precipitation of the precursor
107 and after the synthesis.

108 After the synthesis, samples were recovered by centrifugation at 8000 rpm for
109 10 min, which was followed by washing with distilled water two times and ion
110 exchange with Ca²⁺ using 1 M CaCl₂ solution (Carrado et al. 2006). The choice to
111 saturate the samples with Ca²⁺, was driven by a practical conveniency. As Ca²⁺-
112 saturated smectites have two water layer hydrate structure over a large relative humidity
113 range (Suquet et al. 1975), such material is then less sensitive to relative humidity
114 changes and more practical to handle during the different characterization experiments.
115 After the ion-exchange and washing, the suspension was dried in an oven at 60 °C and
116 ground in a mortar.

117 *X-ray diffraction of powder and oriented preparations*

118 The ground saponite powder was placed into a backloading sample holder and
119 compacted. The prepared sample was measured by X'Pert Pro from PANalytical
120 (Malvern, United Kingdom) equipped with an X'Celerator real-time multiple strip
121 detector operating with an angular aperture of $2.12^\circ 2\theta$ in 3° to $70^\circ 2\theta$ range using $\text{CuK}\alpha$
122 radiation with the wavelength of 0.15406 nm. Diffractogrammes were recorded at room
123 temperature with step size of $0.017^\circ 2\theta$ and scan time of 4 s per step. The divergence
124 slit, the anti-scatter slit and the two Soller slits were 0.0625° , 0.125° and 2.3° ,
125 respectively.

126 The oriented slides were prepared by placing a droplet of the diluted suspension on a
127 glass slide to evaporate with time. Particles settled by gravity and adopted a preferable
128 orientation parallel to the substrate. For optimal measurement results 3 to 20 mg of
129 powder were used. The dried slides were then recorded in 3° to $35^\circ 2\theta$ range with the
130 same scanning parameters as before. To saturate the samples with ethylene glycol, the
131 glass slides were put into a desiccator with ethylene glycol for 2 days.

132 *Fourier-transform infrared spectroscopy*

133 The synthesized saponite was mixed with potassium bromide in the weight ratio
134 1:100 and ground with a mortar by hand. The powder was given into a mold and
135 pressed isostatically at 5 bar for 3 minutes. The resulting pellets were put into an oven at
136 150°C overnight to reduce the water content. FTIR spectroscopy measurements were
137 conducted with the device Equinox 55 from Bruker (Karlsruhe, Germany). The obtained
138 spectrum was the average of 32 measurements with a resolution of 4 cm^{-1} . The software
139 OPUS was used to record the spectra and to subtract the reference with CO_2 and H_2O
140 contributions.

141 *Nuclear magnetic resonance spectroscopy*

142 The ^{27}Al MAS NMR spectra were recorded at room temperature with a Bruker
143 Avance II 400 MHz spectrometer (Wissembourg, France) operating at $B_0 = 9.4$ Tesla
144 giving a ^{27}Al Larmor frequency of 104.23 MHz, equipped with a Bruker 4 mm double
145 channels probe. All experiments were performed at room temperature in ZrO_2 rotors,
146 with a $\pi/12$ radio frequency pulse length of 0.5 μs , a recycle delay of 1 s, at a spinning
147 rate of 12 kHz. The chemical shifts were referred to external $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ in AlCl_3
148 aqueous solution. The decompositions of the spectra were performed using the DMFit
149 software (Massiot et al. 2002).

150 *X-ray fluorescence spectroscopy*

151 The sample pellet was prepared by applying an isostatic pressure of 5 bar on 200 mg
152 of sample. The spectrometer Zetium from PANalytical (Malvern, United Kingdom) was
153 used to record the spectra that were analysed towards the composition of oxides in
154 weight percent. The atomic weight percent was then calculated.

155 *Nitrogen adsorption*

156 A Micromerics ASAP 2420 (Verneuil en Halatte, France) was used to adsorb
157 nitrogen at the temperature of liquid nitrogen (-196 °C). Prior to adsorption, 100 to
158 200 mg of the sample were outgassed in vacuum at 120 °C to remove the water
159 adsorbed on the surface of the particles. The sample mass after pretreatment was
160 measured, then the sample flask was connected to the device to be cooled down to -
161 196 °C during the whole measurement. Specific surface area of the sample was derived
162 with the BET method using the software MicroActive version 1.01. The average
163 mesopore size was derived from the adsorption branch of the isotherm using the

164 Barrett–Joyner–Halenda (BJH) method. The micro and mesopore size distribution was
165 derived using the density function theory (DFT). Slit and cylinder shape for oxide
166 surfaces were tested and evaluated by their RMS (Root mean square) error of the
167 isotherm fit and by the correct fit between the experimental isotherm and the different
168 modelizations (step-like fits were avoided and the fits were tested in log and linear
169 scales).

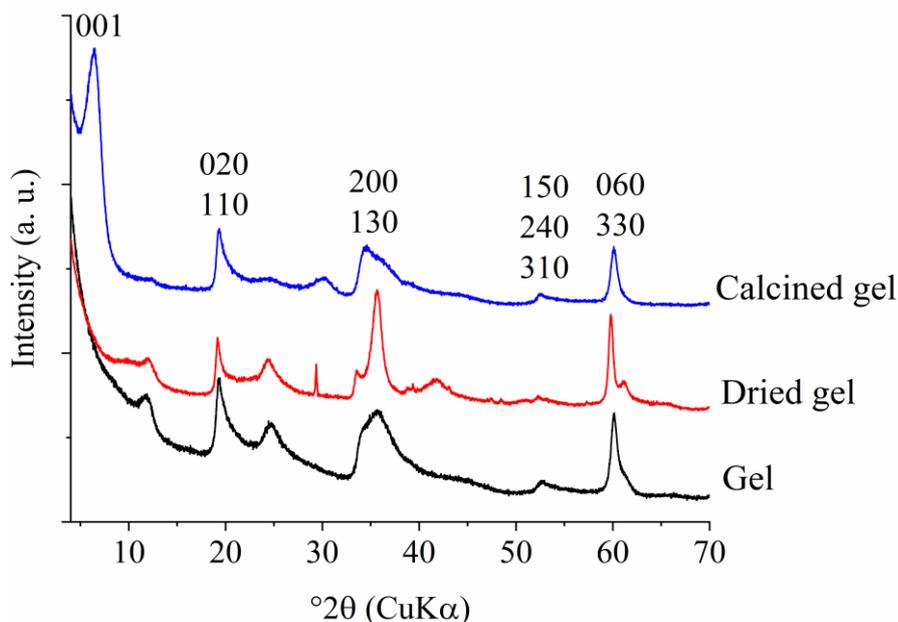
170 *Transmission electron microscopy*

171 Samples were prepared by dispersing the synthesized saponite powder with
172 ultrasound in chloroform. The resulting suspension was evaporated on a carbon coated
173 copper grid at room temperature leaving homogeneously distributed particles. The
174 device ARM200F from JEOL (Tokyo, Japan) with an acceleration voltage of 200 kV
175 was used to record the images. The software Digital Micrograph allowed to measure the
176 average basal spacing by calculating the mean over 6 to 10 clay mineral layers in a
177 selected area.

178 RESULTS AND DISCUSSION

179 *Influence of precursor preparation on structure formation*

180 The pH was 12.7 after 3 hours of the gel aging and 12.5 after the hydrothermal
181 synthesis. The X-ray powder diffractograms (Fig. 1) of synthesis products using
182 different precursors revealed that typical 2:1 tri-octahedral clay mineral planes (020),
183 (200), (150) and (060) could be identified in all three samples. The basal reflection
184 (001) at $5.9^\circ 2\theta$ was only well-defined and symmetrical for the sample prepared from the
185 calcined gel. It indicated an ordered structure with layer-to-layer distances of around
186 1.5 nm.

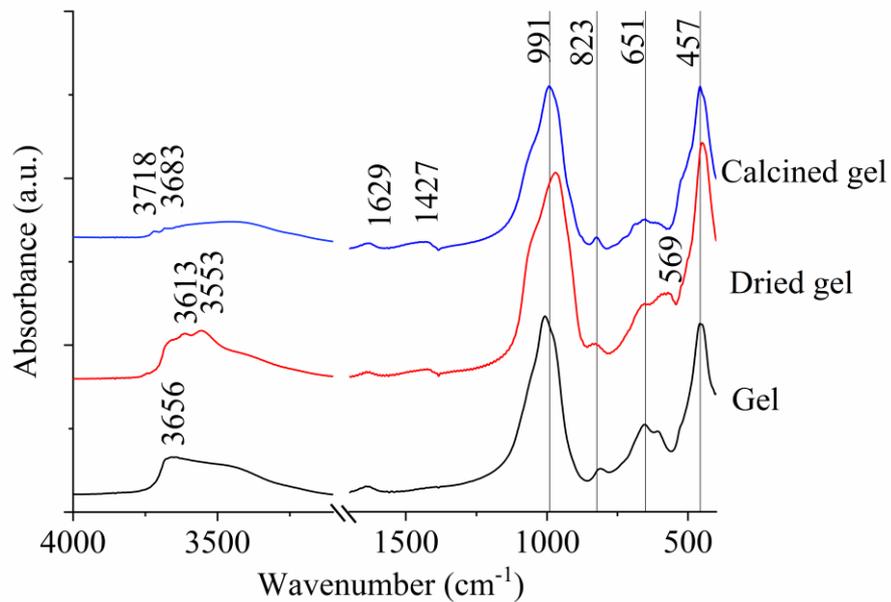


187

188 **Fig. 1** Powder XRD patterns after hydrothermal synthesis at 200 °C using different
 189 precursors.

190 For the samples prepared from gel and dried gel precursors, XRD peaks at 12°
 191 (0.75 nm) and 24°2θ (0.36 nm) were observed that corresponded to heterogeneous
 192 formations of polymorphs of the kaolinite-serpentine group and chlorites. The peak at
 193 35.7°2θ (2.51 nm) and the two peaks at 59.8°2θ (0.154 nm) and 61.1°2θ (0.151 nm)
 194 suggested the presence of lizardite-like structure. Other phases like chlorites could
 195 contribute to a higher amount of octahedral Al, especially for the sample prepared from
 196 dried gel precursor. The XRD patterns showed crystalline and single clay mineral
 197 saponite formation using the precursor of calcined gel. The product after hydrothermal
 198 synthesis then contained a higher purity crystalline saponite. No characteristic peaks of
 199 other aluminum phases such as alumina, gibbsite or boehmite, neither hydroxalite-like
 200 phases were identified in X-ray diffractograms. The small sharp peak at 29.5°2θ
 201 (0.303 nm) corresponded to calcite, an impurity arising from an incomplete washing
 202 prior to the sample saturation with Ca²⁺.

203 FTIR spectroscopy was used to compare the results from XRD, regarding the sample
 204 crystallinity, and to obtain the information on the presence of amorphous aggregates and
 205 the type of bonds present in the samples. For all three samples, O-H and Si-O vibration
 206 modes, characteristic of clay minerals, could be identified (Fig. 2) (Petit 2006). The
 207 large band at $\sim 3400\text{ cm}^{-1}$ and at 1629 cm^{-1} corresponded to the vibration modes of H_2O
 208 molecules. The band at 1427 cm^{-1} corresponded to carbonates, an impurity identified
 209 also by XRD. The O-H bending mode identified at 651 cm^{-1} was characteristic for tri-
 210 octahedral clay minerals (Russell and Fraser 1994).



211
 212 **Fig. 2** FTIR spectra of saponite obtained after hydrothermal synthesis at $200\text{ }^{\circ}\text{C}$ using
 213 different precursors.

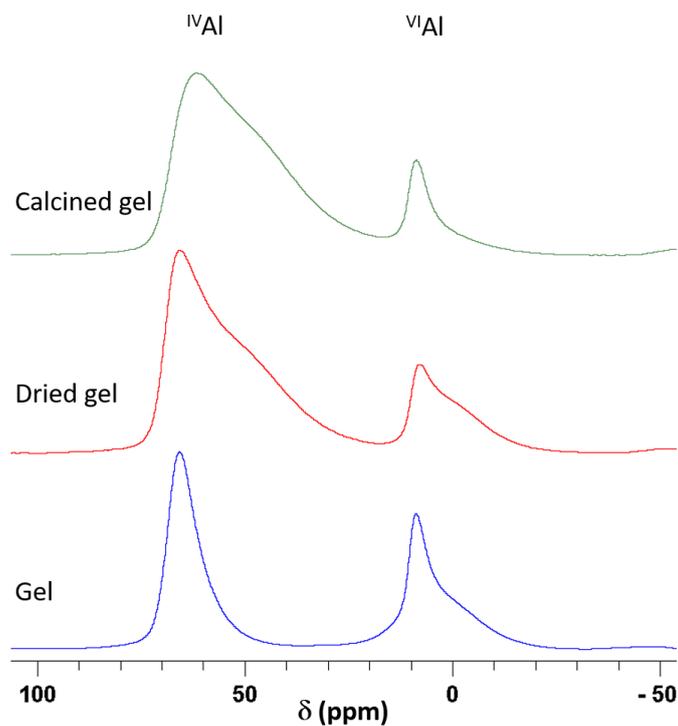
214 The region of O-H stretching vibration mode was rather broad for samples prepared
 215 from the gel and dried gel precursors. Two bands of 3718 and 3683 cm^{-1} could be
 216 clearly identified for the sample prepared from calcined precursor. The bands
 217 corresponded to $\text{Mg}_3\text{O-H}$ stretching mode. It was shown by Pelletier et al. (2003) that
 218 the bands corresponding to the hydroxyl groups were influenced by the saponite layer

219 charge. The Mg₃O-H peak shifted from 3676 to 3692 cm⁻¹ due to bond stretching with
220 increasing tetrahedral Al³⁺ substitutions and the compensating cation. The peak visible
221 at 3683 cm⁻¹ and additionally at 3716 cm⁻¹ in our reorded spectra was then an additional
222 evidence for Al³⁺ substitutions in the tetrahedral sheet. For the sample prepared from the
223 gel precursor a band at 3656 cm⁻¹ could be identified corresponding to Mg₂AlO-H
224 stretching mode (Petit et al. 2004). It indicated an important substitution of Al³⁺ for
225 Mg²⁺ in the octahedral sheet. Among the broad zone of O-H stretching mode, two bands
226 could be distinguished for the sample prepared from the dried gel precursor: 3613 and
227 3553 cm⁻¹. These bands were charateristic of Al₂O-H stretching modes. In particular,
228 3553 cm⁻¹ band was characteristic of chlorites, which was in agreement with phases
229 identified in XRD pattern (Russell and Fraser 1994).

230 In all three samples, bands at 991 and 457 cm⁻¹ could be clearly identified
231 corresponding to Si-O vibration modes. In addition, a band at 692 cm⁻¹ could be
232 identified for the calcined gel sample corresponding to Si-O vibration mode as well.
233 The substitution of Al³⁺-for-Si⁴⁺ in the tetrahedral sheet is known to shift Si-O
234 stretching mode band value from 1000 cm⁻¹ towards lower values, which corresponds to
235 the present case (991 cm⁻¹). Klopproge and Frost (2000) had attributed 457 cm⁻¹ to the
236 Si-O bending mode of amorphous silica. In the present case, as no other Si-O modes in
237 this region could be clearly identified and considering XRD results, this could then
238 correspond to Si-O vibration mode belonging to clay minerals. However, the presence
239 of amorphous silica cannot be discarded. Indeed, a band ~569 cm⁻¹ could be identified
240 for the samples prepared from the gel and dried gel precursors, reported as belonging to
241 amorphous SiO₂. Finally, all samples contain a band at 823 cm⁻¹ attributed to Al-O₄

242 band vibration, affirming the presence of tetrahedral aluminum. The characteristic bands
243 of alumina were not identified.

244 The NMR results (Fig. 3) revealed the aluminum resonances for the tetrahedral (^{IV}Al)
245 and octahedral (^{VI}Al) configuration of all precursor types after synthesis. Signals
246 observed around 60 and 8 ppm were attributed to ^{IV}Al and ^{VI}Al respectively. Using the
247 gel precursor, the Al content was nearly evenly distributed between the octahedral and
248 the two tetrahedral sheets in the final product with ^{IV}Al = 55%. The NMR spectroscopy
249 results were in agreement with the FTIR spectroscopy results, where Mg₂AlO-H
250 stretching mode was identified suggesting an important substitution of Al³⁺ for Mg²⁺ in
251 the octahedral sheet. Using the dried and calcinated gel precursors the content of
252 tetrahedral aluminum increased with ^{IV}Al = 80% and ^{IV}Al = 85%, respectively. NMR
253 results showed a higher amount of octahedral Al in the samples prepared from the gel
254 and dried gel precursors. In agreement with XRD results, the structure with maximum
255 Al in the tetrahedral position was obtained using the calcined gel as precursor.



256

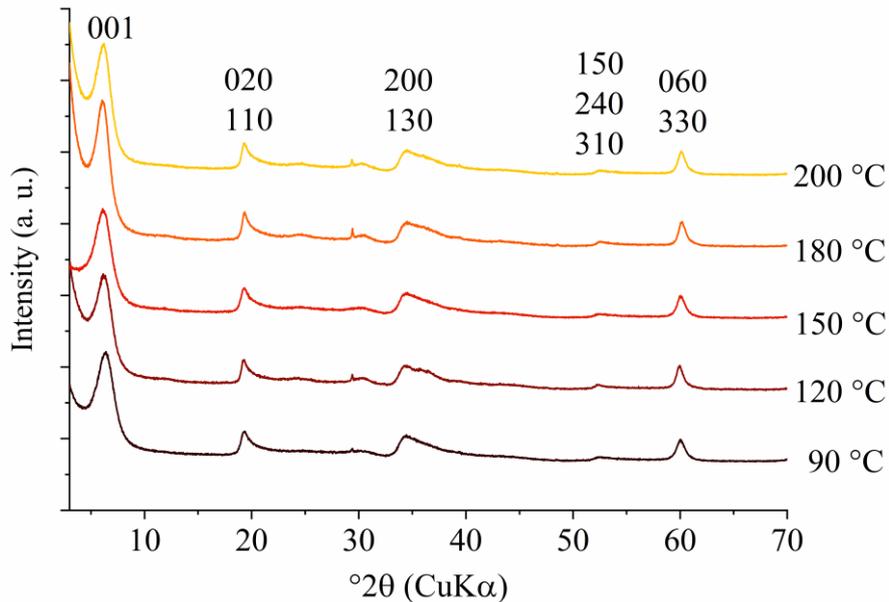
257 **Fig. 3** ^{27}Al MAS NMR spectra of samples synthesized at 200 °C with different
258 precursor preparation methods. ^{VI}Al and ^{IV}Al corresponds to the chemical shift (δ) of
259 octahedrally and tetrahedrally coordinated aluminum respectively.

260 In summary, three different characterization techniques: XRD, FTIR and NMR
261 spectroscopies, indicated that the sample prepared from calcined gel precursor gave
262 better defined structure of saponite with a maximum substitution in the tetrahedral sheet
263 compared to samples prepared with the gel and dried gel precursors. The initial
264 precipitation of precursor was expected to create a homogenous gel from its constituents
265 (Hamilton and Henderson 1968). The calcination of precursor removed water, and it
266 was then expected that more amorphous regions with a large number of defects were
267 created. Moreover, amorphous and crystalline $\text{Al}(\text{OH})_3$ containing compounds could
268 undergo phase transitions at temperatures between 130 and 450 °C and were more likely
269 to disappear during the calcination of the precursor (Walker 1993; Földvári 2011). Also,
270 during drying, water was gradually evaporated and a very basic environment could be
271 locally created thus favoring the formation of tetrahedral Al^{3+} . The obtained powder
272 from calcined precursor was amorphous and very reactive upon dissolution and
273 subsequent forming of crystalline phase in hydrothermal synthesis experiments.

274 *Influence of synthesis temperature on structure formation*

275 The increase of temperature could be expected to enhance the sample crystallinity, as
276 shown by Kloprogge and Frost (2000). The calcined gel precursor was used to
277 synthesize saponites at five different temperatures from 90 to 200 °C. The powder XRD
278 pattern (Fig. 4) showed the regular saponite structure nearly independent from the
279 synthesis temperature, without crystalline secondary phases. The layer-to-layer
280 distances were between 1.43 and 1.48 nm with a slight trend to increase with synthesis

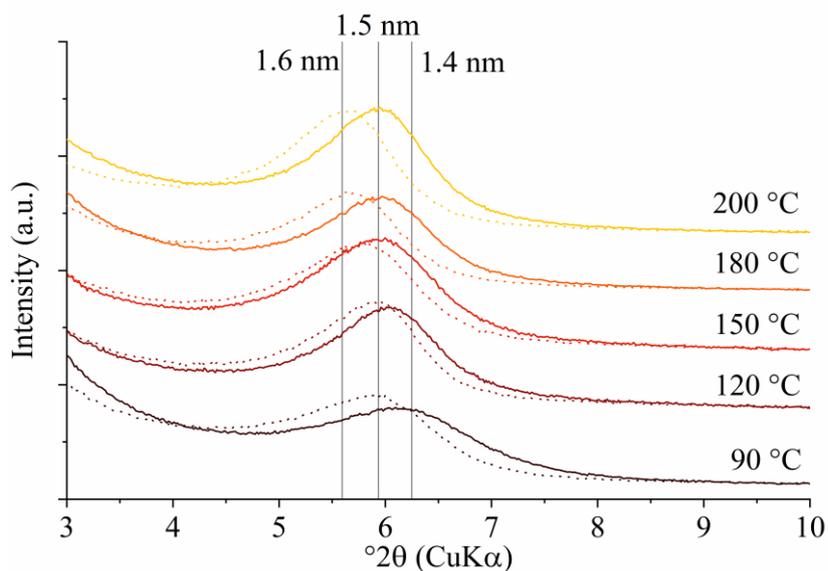
281 temperature. Such layer-to-layer distance corresponds to Ca^{2+} -saturated saponite with
282 two layers of the water in the interlayer (Suquet et al. 1977).



283
284 **Fig. 4** Powder XRD pattern of synthetic saponite with indexed diffraction planes at
285 different temperatures. $d_{001}=1.5$ nm and $d_{060}= 0.154$ nm.

286 The swelling property (typical of smectite clay minerals) was assessed using the
287 saturation of oriented preparations with ethylene glycol (Fig. 5). For such preparations,
288 the 001 reflection was pronounced because of the alignment of particles, and shifted its
289 position when saturated with ethylene glycol due to the increase of the layer-to-layer
290 distance. Only a slight shift of around 0.05 to 0.1 nm was observable and indicated a
291 high charge of the layers as expected. Substitution of Al^{3+} -for- Si^{4+} in the silicate sheets
292 resulted in a more localized charge that had to be compensated by interlayer cations
293 compared to the aluminum substitution in the octahedral sheet, which was compensated
294 over a larger volume by slightly more negatively charged oxygen atoms (Kloprogge et
295 al. 1999). The analysis of oriented slides indicated smaller layer-to-layer distances for
296 the lower synthesis temperatures (90 and 120 °C) suggesting a stronger interaction

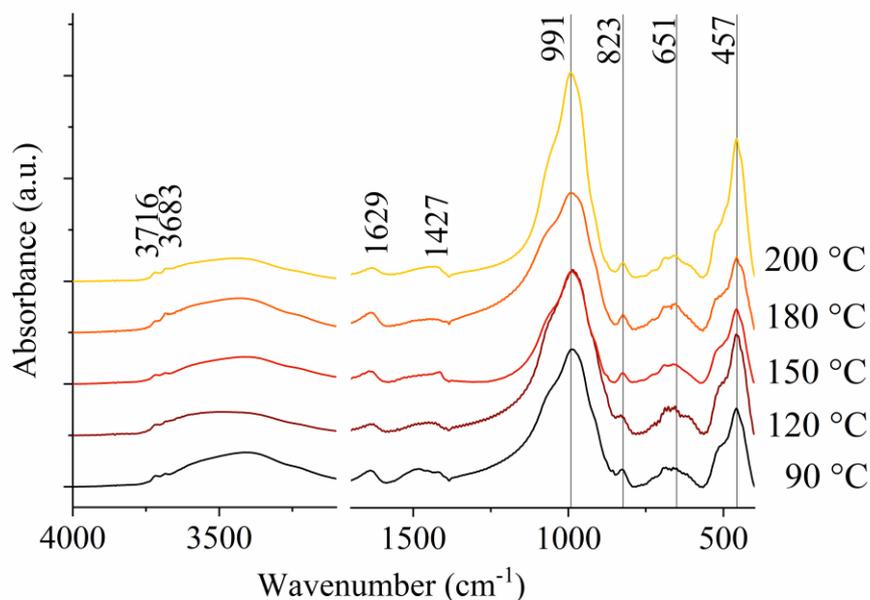
297 between the layers and more pronounced localization of the charge in the tetrahedral
298 sheets. Moreover, the diffraction peak was broadened with the decrease of the
299 temperature, suggesting a smaller particle size and/or more heterogeneous structure.



300

301 **Fig. 5** XRD patterns of 001 reflection of oriented slides at ambient conditions (solid
302 line) and after ethylene glycol saturation (dotted line) with d_{001} indicated above.

303 For a better insight into the amorphous phases and their bond structure, FTIR spectra
304 were acquired for sample prepared at each synthesis temperature. The identified bands
305 corresponded to bonds in saponite structure, as previously discussed in section 3.1
306 (Fig.6). The peak shapes at 991 and 457 cm^{-1} corresponding to Si-O vibration modes
307 expressed a higher crystallinity for the synthesis at 200 °C. At lower synthesis
308 temperatures the reduced and broader peaks indicated smaller particle size and/or more
309 heterogenous structures. Apart from the Si-O vibration bands, the rest of the spectrum
310 seemed nearly unaffected by the synthesis temperature.

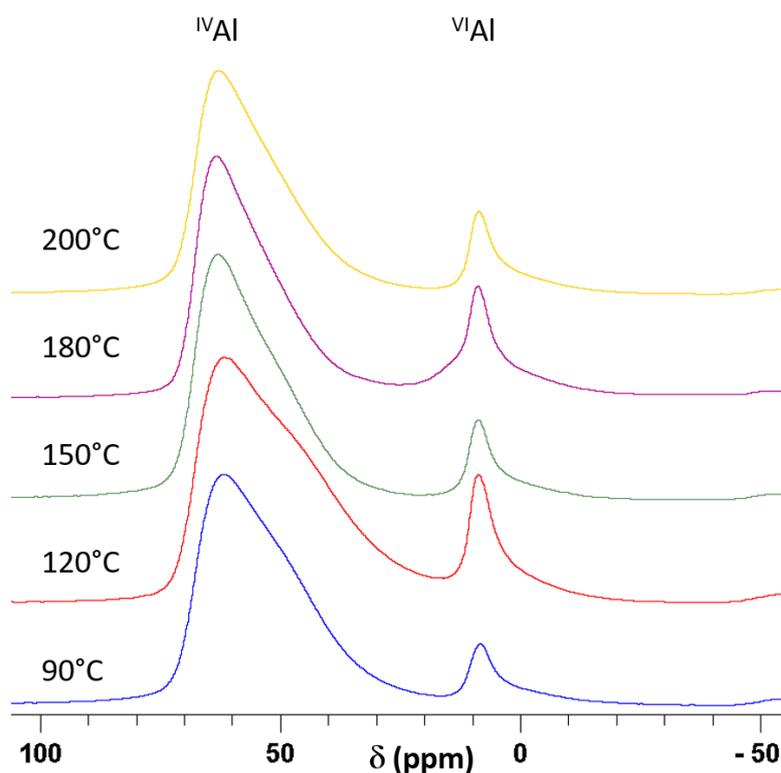


311

312 **Fig. 6** FTIR spectra of saponite synthesized at different temperatures.

313 To obtain structural information about the location of aluminum in the structure,
314 NMR spectroscopy measurements were performed (Fig. 7). With the synthesis
315 procedure used, the aluminum content in the tetrahedral sheet was about 80 to 90%,
316 while the octahedral sheet only contained the small remaining amount. There was a
317 slight trend towards a higher amount of octahedral Al at high synthesis temperatures
318 (Table 1). This result was in agreement with the trend observed by the XRD experiment

319 performed on oriented slides, which suggested the localization of the charge in the
320 tetrahedral sheet with the decrease of the synthesis temperature. But because the
321 quantification of the NMR data is rather approximate and a deviation of 5 to 10%
322 should be assumed for interpretation, this trend had to be handled with care.
323 Nevertheless, it can be stated that even at low synthesis temperatures the vast majority
324 of the substitution by Al happened in the tetrahedral sheet.



325

326 **Fig. 7** ^{27}Al MAS NMR spectra of saponite synthesized at different temperatures
327 indicating aluminum in octahedral ($^{\text{VI}}\text{Al}$) and tetrahedral sheet ($^{\text{IV}}\text{Al}$).

328 The chemical composition of synthesized products was analyzed by XRF
329 spectroscopy. The highest Al/Si and Ca/Si molar ratios were obtained for samples
330 synthesized at 90 and 120 °C (Table 1). The higher amount of interlayer Ca^{2+} correlated
331 with the increased amount of Al substitutions in the structure. Assuming that no other
332 phases were present in significant amounts, and that probably a slightly higher amount

333 of Al was located in the tetrahedral sheets compared to octahedral sheets for samples
 334 prepared at a lower synthesis temperature, these results could then also be correlated to
 335 the XRD experiments on oriented slides. The analysis of oriented slides lead to the
 336 hypothesis that for the lowest synthesis temperatures (90 and 120 °C) the charge was
 337 mainly localized in the tetrahedral sheets. These results were then in good agreement
 338 with the chemical composition and NMR results.

339 **Table 1.** Element molar ratios obtained by XRF and calculated ratio of tetrahedral
 340 aluminum obtained by NMR spectroscopy. Surface area and average pore size
 341 calculated from N₂ adsorption measurement.

Synthesis temperature	Al/Si molar ratio	Mg/Si molar ratio	Ca/Si molar ratio	^{IV} Al by NMR (%)	S _{BET} (m ² /g)	Average pore size (nm)
90 °C	0.42	1.13	0.21	90	172	6.0
120 °C	0.41	0.96	0.20	85	131	8.7
150 °C	0.35	0.99	0.17	90	173	6.2
180 °C	0.36	1.01	0.16	80	113	7.0
200 °C	0.35	0.98	0.17	80	179	6.7

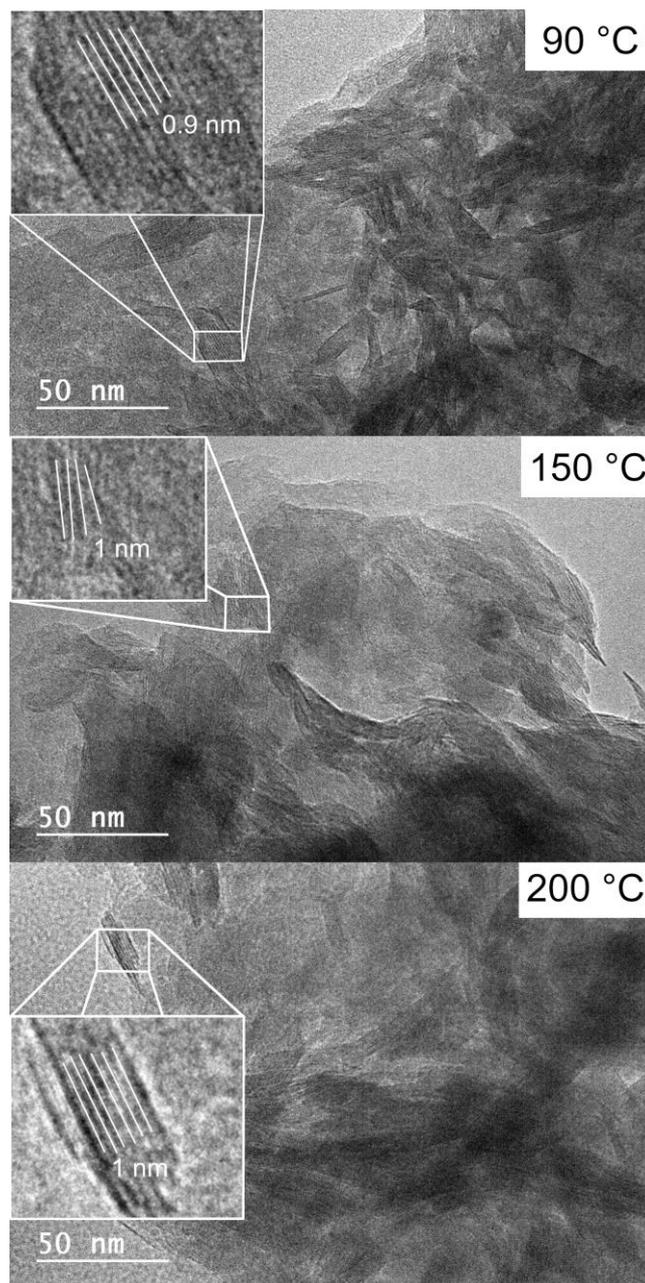
342

343 The creation of functional groups, as the Lewis acid groups, requires a maximum
 344 tetrahedral substitution. Here, the sample synthesized at 90 °C, using calcined
 345 precursors, showed that a high amount of functional groups could be created even at
 346 low temperature. In comparison with the study of Kloprogge and Frost (2000), where a
 347 shorter synthesis time (3 days instead of 5 days) and a temperature of 280 °C were used,
 348 well defined saponite structure could be obtained even at lower temperature.

349 *Nanostructure and porosity*

350 Although the synthesis at 90 °C seemed to be the most promising, the FTIR
 351 spectroscopy results suggested a higher homogeneity and/or better crystallinity for the

352 sample synthesized at 200 °C. Thus, with XRD and FTIR spectroscopy results alone, it
353 remained unclear how amorphous constituents might be distributed. The observations of
354 samples synthesized at three different temperatures (90, 150 and 200 °C) under TEM
355 were undertaken to obtain an overview of particle size and shape (Fig. 8). The particle
356 size was visually estimated to be between 50 and 100 nm. The TEM images showed a
357 majority of crystalline regions, which was in agreement with the XRD and FTIR
358 spectroscopy results. No particular difference, in terms of particle size and presence of
359 amorphous aggregates, was observed among the samples synthesized at different
360 temperatures. Thus, the slight differences observed by the XRD and FTIR spectroscopy
361 analysis of oriented slides among the various samples could be due to the
362 inhomogeneity of structure in terms of Al distribution in the structure, which increased
363 with decreasing the temperature. In the TEM pictures the layer fringe contrast was used
364 to approximate the basal spacing. In all locations chosen, the values were found
365 between 0.9 to 1.1 nm. This was considerably smaller than the 1.4 to 1.5 nm obtained
366 by powder XRD. This was due to the removal of interlayer water in the ultra-high
367 vacuum. It has to be noted that the estimation of basal spacing was only approximate
368 due to the unknown exact orientation angle of the layers.

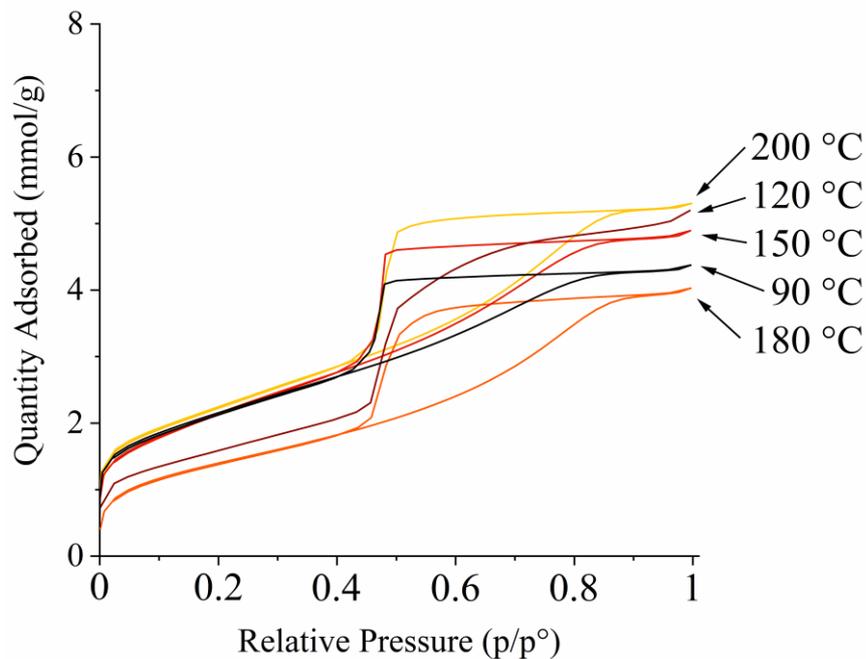


369

370 **Fig. 8** TEM images of saponite synthesized at different temperatures. Basal spacings
371 derived by lattice fringe contrast.

372 N₂ adsorption measurements (Fig. 9) provided additional insight about the
373 microstructure of the samples giving information about the accessible surface area, pore
374 volume, and pore size distribution and shape. Adsorption at low relative pressure
375 corresponded to the filling of the microporosity and at higher pressure to the

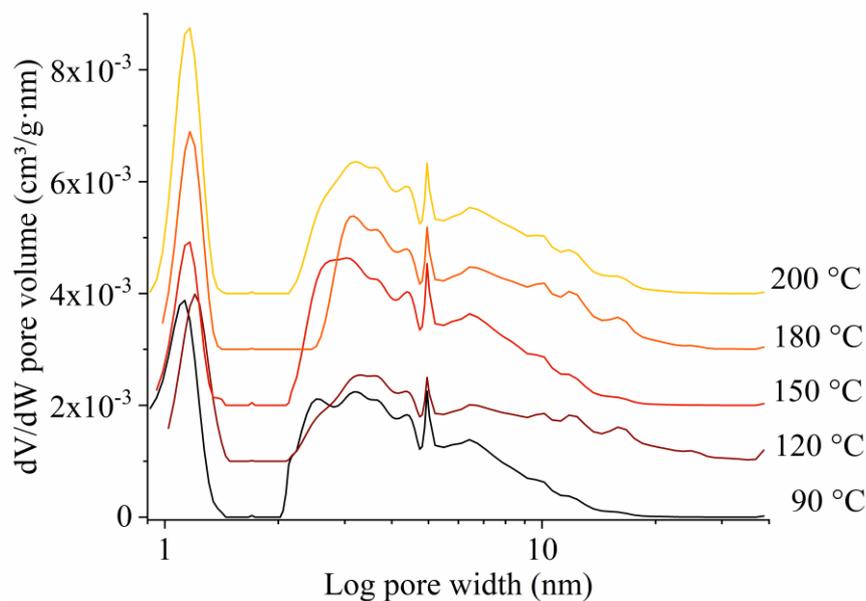
376 mesoporosity. The specific surface area for each synthesis temperature, determined by
377 the BET method, was up to 179 m²/g (Table 1). The samples prepared at 120 and
378 180 °C presented the lowest specific surface area. This did not correlate to the
379 microstructural features investigated earlier and might therefore be connected to the
380 sample preparation previous to the isotherm acquisition. The analysis of the shape of the
381 isotherms (and of the hysteresis) gave information about the pore shape. The adsorption
382 curve was a type IV and hysteresis was of H2 type, according to IUPAC classification.
383 The hysteresis shape corresponded to ink bottle shape cavities, which needed to reach a
384 critical pressure (quite lower than during adsorption) in order to desorb nitrogen.
385 Applying the BJH method, average pore sizes of 6 to 8.7 nm was obtained (Table 1).



386
387 **Fig. 9** Isotherms of nitrogen adsorption and desorption for saponites synthesized at
388 different temperatures.

389 With the t-plot technique, a small amount of micropores could be identified. Occelli
390 et al. (2002) found micropores with the diameter of 1.5 nm using the DFT model. The
391 derivative of the pore volume over the pore width calculated by the DFT model was

392 then also applied in this study. Clay minerals are known for their layered structure,
393 which means that a slit-like pore shape with constant height but larger and varying
394 width and length could be expected. However, the overall RMS error of the isotherm fit
395 was significantly lower assuming a cylindrical pore shape than a slit one. The
396 distribution showed two pore domains (Fig. 10).



397

398 **Fig. 10** Pore size distribution derived from the adsorption isotherm with the DFT
399 method assuming cylindrical pores on oxide surface with regularization of 0.1 .

400 The micropores were narrowly distributed around 1.1 nm. For the samples obtained at
401 120 and 180 °C nearly no micropores could be found by DFT. No clear trend in the pore
402 size was observable for increasing synthesis temperature. Instead, the pore distribution
403 seemed to remain the same. The mesoporous domain above 2 nm was at the origin of
404 the most part of the pore volume. On the other hand, micropores contributed to the
405 increase of surface area and their absence in these two samples explained the lower BET
406 specific surface area measured. If existing, pillars in between the layers could result in
407 more cylindrical shapes, but such structures were not revealed by XRD, FTIR
408 spectroscopy or TEM, and they could be then excluded. However, applying a

409 cylindrical pore shape a better fit with the presence of mesopores could be obtained,
410 which contributed largely to the total volume. These observations showed the
411 discrepancy on the application of the various models, since it is not easy to differentiate
412 among different pore shapes for a certain pore dimension. Cylindrical mesopores could
413 be more likely created in the intercrystallite spaces formed during aggregation.
414 Therefore, the pore size distribution and shape did not correlate (or only partially) to the
415 materials intrinsic properties, as the charge, but to the preparation unitary steps, as
416 grinding, sieving and outgassing.

417 CONCLUSIONS

418 In this study, saponites were synthesized and the influence of the heat treatment of
419 the precursor was shown. The characterization of the synthesized products by XRD and
420 FTIR spectroscopy indicated that a homogenous powder of saponite (in terms of
421 structure and chemical composition) could be obtained using a precursor calcined at
422 450 °C. Additionally, a higher quantity of aluminum in tetrahedral configuration was
423 measured for this sample, which might bring to a higher thermal stability and a higher
424 amount of acidic groups useful in catalysis. By using the calcined precursor,
425 hydrothermal synthesis performed at low temperature (90 °C) allowed to obtain a high
426 purity saponite. A synthesis temperature of 200 °C resulted in a very similar product,
427 probably presenting a slightly improved homogeneity, but with lower layer charge and
428 consequently less tetrahedral aluminum.

429 The distribution of mesopores was found to be in the 2 to 11 nm range, promising for
430 the accessibility of large organic molecules. Additionally, it was shown that pillaring or
431 acidic activation could further increase the accessible surface area (Kloprogge 1998;
432 Michot et al. 1998; Trombetta et al. 2000). In contrast to montmorillonite, saponite can

433 be more easily modified by acidic leaching due to of the presence of octahedral
434 magnesium. Such acidic treatments could greatly enhance the microporosity and
435 specific surface area (up to 510 m²/g) (Vicente et al. 1996; Bisio et al. 2008).

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441

442 On behalf of all authors, the corresponding author states that there is no conflict of
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