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1 **Investigation of the interaction between adsorbed water and various morphologies of**
2 **boehmite nanoparticles prepared by continuous supercritical hydrothermal synthesis.**

3
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30 **Abstract**

31 Boehmite applications are often subject to specific characteristics in terms of morphologies
32 and surface properties. The versatile continuous supercritical hydrothermal method allows
33 synthesizing various boehmite morphologies from rhombic to hexagonal platelet-like
34 nanoparticles depending on the preferential adsorption of part of the precursor after
35 transformation species on the (020) surface resulting in a preferential growth along [001] and
36 mostly [100] directions. This adsorption on surface free sites plays the role of morphology
37 stabilizer and results in the reduction of adsorbed water.

38 The interaction between adsorbed water and the boehmite morphology depends on various
39 parameters; 1) the structure order of boehmite as exhibited by XPS analysis associated with
40 ^1H Solid-State NMR spectroscopy and, 2) the number of available free sites, which tend to be
41 filled by the adsorption of nitrates as observed by Raman spectroscopy.

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44 **Keywords:** Synthetic boehmite nanoparticles; Water and nitrate adsorption; pH-dependent
45 morphology; Continuous supercritical hydrothermal synthesis; Supercritical water.

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57 **1. Introduction**

58 An explosion of research works on nanotechnologies has marked the last decade. In
59 particular, inorganic nanoparticles are of interest in broad domains ranging from electronics to
60 pharmaceuticals. These fields require high performance crystallized materials with controlled
61 sizes and morphologies. Additionally, industrial scale applications need low-price,
62 reproducibility and environmentally friendly conditions to meet society challenges [1]. This
63 can be achieved through continuous supercritical hydrothermal synthesis [2].

64 Boehmite, an aluminium oxyhydroxide (γ -AlOOH), is widely used as catalyst [3], adsorbent
65 [4–6], coating [7], membrane [8] and fire-retardant [9]. Furthermore, it is an important
66 precursor for the preparation of aluminium oxides such as Υ -, θ -, χ -, κ - and α -Al₂O₃ [10].

67 Boehmite has an orthorhombic crystal structure (space group *Cmcm*), shown on Figure 1,
68 characterized by double sheets of distorted edge-sharing octahedra with oxygen atoms at the
69 top and aluminium ones at the centre. These double layers are linked together by hydrogen

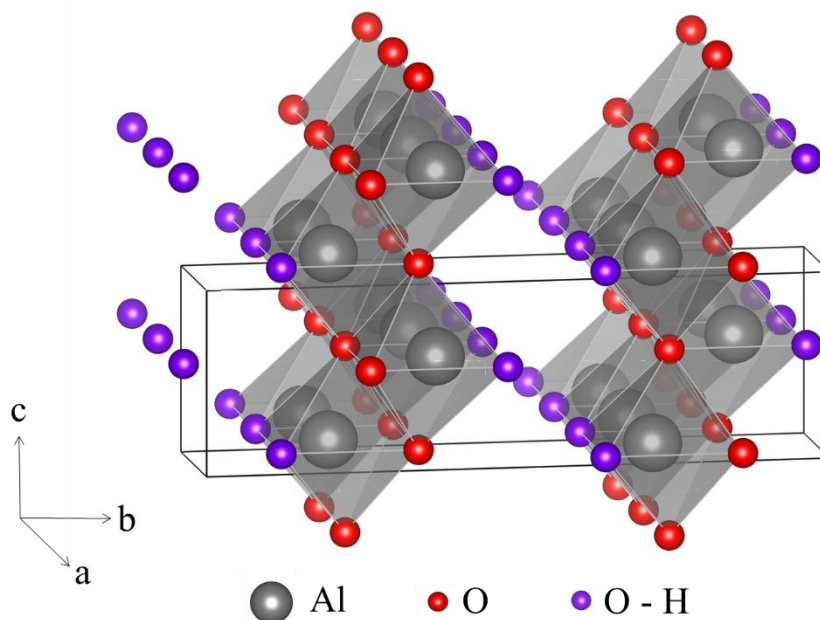


Figure 1: Schematic representation of two unit cells of orthorhombic crystal structure of boehmite.

70 bonds forming parallel rows of chains in zig-zag perpendicular to the b-axis.

71 Because of the weak interaction, the crystal surface ends in the interface between two double
72 layers. This produces surfaces full of hydroxyl groups [11,12]. Consequently, boehmite
73 nanoparticles tend to have a large excess of adsorbed water up to 30 wt.%, leading to the
74 name of “pseudo-boehmite” [13]. At first, the literature hypothesized that this adsorbed water
75 was incorporated in the sheet interlayer along the b-axis [14]. The lattice deformation along
76 this specific axis appears to be insufficient to insert water molecules which are considered to
77 be only adsorbed on the boehmite surfaces [15].

78 The structure tends to show platelet-like particles with a dominant (010) basal surface and less
79 stable (100), (101) and (001) edge facets. A Density Functional Theory (DFT) study of
80 boehmite surface properties exhibited the basal (010) surface forms about 50 % of the total
81 surface [16]. This surface is characterized by the smallest interfacial energy and a weak
82 chemical reactivity with water. That is why water is mainly physisorbed on it.

83 The relative surfaces of each facet can be modified through the synthesis route, which may
84 influence the adsorbed water content. The morphology of boehmite particles can be easily
85 tuned thanks to the versatility of the continuous supercritical hydrothermal synthesis method.

86 Adschiri *et al.* have reported for the first time the use of this technique for the preparation of
87 boehmite [17] which, was traditionally synthesized using sol-gel precipitation or
88 hydrothermal synthesis [18,19]. They showed the influence of various parameters such as
89 temperature, pressure, pH and precursor concentration on the particle characteristics. Hakuta
90 *et al.* were able, with a hydrothermal process, to modify the shape of boehmite particles from
91 hexagonal platelet-like to rhombic shaped by increasing the temperature from 350 °C to 400
92 °C [20]. More recently, Fujii *et al.* demonstrated the ability of alkylcarboxylic acids to change
93 the aspect ratio of boehmite particles up to 5-fold [21]. They suggested that carboxylic acid
94 inhibits crystal growth along the [001] and [010] axes relative to the [100] direction through

95 surface-capping, resulting in the formation of rodlike particles. The variation of the particle
96 morphology necessarily generates an evolution of the active surfaces, the surface properties
97 and thus of the potential quantity of adsorbed water. All of which play a crucial role in the
98 final material properties and thus performance for applications where boehmite is used and
99 need to be investigated.

100 This paper reports the ability of supercritical boehmite γ -AlOOH surfaces to interact with
101 water. Supercritical boehmite particles were synthesized using the continuous supercritical
102 hydrothermal process. Microstructures were determined by Rietveld analysis of Powder X-
103 Ray Diffraction (PXRD) data and Transmission Electron Microscopy (TEM). Adsorbed water
104 was investigated using X-Ray Photoelectron Spectroscopy (XPS), ^1H Solid-State Nuclear
105 Magnetic Resonance (NMR) and Raman Spectroscopy.

106

107 **2. Experimental**

108 *2.1 Materials*

109 Boehmite particles were prepared using the continuous supercritical hydrothermal synthesis.
110 Aluminium nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (> 98 % purity) was selected as precursor.
111 The metal salt was dissolved into distilled water (10-18 M Ω .cm). Sodium hydroxide NaOH (>
112 98 % purity) was used to increase the pH of the precursor solution from 3.9 up to 6.7. All the
113 chemicals were purchased from Sigma-Aldrich and used as received.

114

115 *2.2 Hydrothermal flow synthesis apparatus and procedure*

116 Continuous flow synthesis was carried out in a homemade reactor custom-designed to
117 minimize clogging problems. It is made of a 0.74 m long stainless steel pipe with an internal
118 diameter of 4.78 mm. The set-up consists of a HPLC pump, two ceramic band heaters and a

119 TESCO back pressure regulator. This equipment has been thoroughly described elsewhere
120 [22].

121 The reactor is first pressurized to 25 MPa at ambient temperature using distilled water and
122 then set to the process temperature of 400 °C. Precursor solution is fed at a flow rate of 3.5 or
123 6.6 mL.min⁻¹ corresponding to residence times of 60 s and 20 s, respectively. At the outlet of
124 the reactor, the chemical reaction is stopped by ice bath quenching. A stainless steel fritted
125 filter is placed inside the quenching system to collect the produced nanoparticles. The product
126 is recovered as a gel, which is washed several times with distilled water. Produced powders
127 were then dried in an oven at 60 °C overnight.

128

129 2.3 *Material characterization*

130 2.3.1 *Powder X-Ray Diffraction (PXRD)*

131 Powder X-Ray Diffraction (PXRD) patterns were collected at room temperature on a
132 PANalytical X'pert PRO MPD diffractometer with the Bragg–Brentano θ – 2θ geometry and
133 over a 2θ angular range from 10 ° to 130 ° (minimum step of 0.008 °). The diffractometer was
134 equipped with a Ge (111) monochromator, which generated a perfectly Cu K α_1 radiation
135 ($\lambda = 1.540598$ Å) at 45 kV and 40 mA. A multichannel X'Celerator detector was used to
136 collect the XRD patterns. Prior to measurement, samples were finely ground to break up the
137 aggregates and passed through a 50 μm mesh sieve. Afterward, powder was placed and
138 randomly distributed on a silicone sample holder.

139

140 2.3.2 *Rietveld refinement*

141 Data were analysed by Rietveld structural model refinements using the FullProf Suite
142 software package [23]. The Thompson–Cox–Hasting formulation of the pseudo-Voigt
143 function was used to fit the Bragg reflection. Refined parameters were the 8-coefficient

144 polynomial functions of background, instrumental zero, scale factor, unit cell parameters,
145 Gaussian and Lorentzian contributions and microstructural strain parameters. The model
146 included only the Al and O atom positions and isotropic thermal parameters. Crystallite shape
147 anisotropy, specific to boehmite particles, was taken into account through spherical harmonic
148 functions. Up to six harmonics were used to describe size broadening for the orthorhombic
149 structure [24]. Simulated X-ray diffractogram quality was measured with the weighted-profile
150 R -factor (R_{wp}).

151

152 2.3.3 *Transmission Electron Microscopy (TEM)*

153 The boehmite particle morphology was investigated using Transmission Electron Microscopy
154 (TEM) with a ThermoFisher Talos F200S G2 microscope. Micrographs were captured with
155 an electron beam voltage of 200 keV allowing an accessible range of magnification up to
156 $\times 1,050,000$ and a resolution of 0.1 \AA . Prior to the observation, less than 2 mg of powder were
157 put in ethanol ($\approx 1 \text{ mL}$) and dispersed with ultrasound during 5 min. Then, TEM thin foils
158 were prepared by drop casting the solution made beforehand onto a holey carbon-coated grid
159 and dried at room temperature.

160

161 2.3.4 *X-Ray Photoelectron Spectroscopy (XPS)*

162 XPS spectra of boehmite were collected with a ThermoFisher Scientific K-Alpha
163 spectrometer using a monochromatic Al $K\alpha$ X-radiation (1486.6 eV) and a hemispherical
164 electron energy analyser. Powder was pressed onto indium foil fixed on a metallic support.
165 This technique was used to characterize extreme surfaces of a set of grains (*i.e.* about 3 to 5
166 nm in depth) with a $400 \text{ }\mu\text{m}$ diameter X-Ray spot size. The binding energies reported were
167 referenced with the C_{1s} peak at 284.9 eV. Survey and the high-resolution spectra Al_{2p} , O_{1s} ,
168 and C_{1s} are reported. Elemental composition was calculated from areas of high-resolution

169 spectra acquired with a pass energy of 40 eV. Experimental data were curve fitted into
170 components with Gaussian-Lorentzian peaks using the ThermoFisher Scientific *Avantage*
171 software.

172

173 2.3.5 Raman Spectroscopy

174 The vibrational properties of boehmite were characterized by a Raman spectrometer Horiba
175 LaBRAM HR Evolution. Spectra were acquired with a 532 nm laser wavelength and a spot
176 size of 1 μm . Boehmite particles dispersed in ethanol were drop-casted onto a glass slide and
177 air dried during one day. Before each analysis, the spectrometer was calibrated using the
178 520.5 cm^{-1} peak of Si acquired on a silicon wafer. The measurements were performed with a
179 long working distance x100 objective lens, a 600 lines/mm grating and a CCD detector.
180 Acquisitions were done for an exposure time of 20 s. Each spectrum was accumulated 40
181 times to optimize the signal-to-noise ratio on the 200 – 1200 and 2900 – 3800 cm^{-1} ranges to
182 visualize the major bands of boehmite with the hydroxyl deformation modes located at 360,
183 495 and 674 cm^{-1} , the hydroxyl stretching bands at 3085 and 3220 cm^{-1} and any remaining
184 water beyond [25]. The aluminium nitrate band is mainly located at 1049 cm^{-1} [26].

185

186 2.3.6 Solid-State Nuclear Magnetic Resonance Spectroscopy

187 ^1H Solid-State Nuclear Magnetic Resonance (NMR) analyses were carried out on a Bruker
188 Avance III 300 WB spectrometer ($B_0 = 7.05\text{ T}$). Experiments were performed with a 2.5 mm
189 solid probe under Magic Angle Spinning (MAS) conditions (30 kHz) with a rotor-
190 synchronized Hahn-echo pulse sequence ($90^\circ - 180^\circ$) with a 90° pulse length of 2 μs and an
191 optimized recycle delay of 5 s. The chemical shift scale was calibrated using H_2O milliQ
192 ($\delta(^1\text{H}) = + 4.7\text{ ppm}$) as reference. Desummation of the ^1H MAS NMR spectra was performed
193 with *Dmfit* software [27].

194

195 3. Results

196 3.1 Influence of the process operating parameters on the grain morphologies

197 Influence of different operating parameters on the hydrothermal flow synthesis of boehmite
198 was widely reported in the literature [17,20,28]. pH is one of the major parameters to modify
199 the boehmite particle morphology without adding additives. Using aluminium nitrate as
200 precursor, pH variation can be achieved by: 1) adjusting the precursor concentration and, 2)
201 adding NaOH.

202 The syntheses were performed at 25 MPa, 400 °C and for different pH values 2.9, 3.5, 3.9 by
203 varying the nitrate concentration and at pH = 6.7 by adding NaOH. In this article, these
204 samples are labelled S2.9, S3.5, S3.9 and S6.7, respectively. Table 1 summarizes process
205 operating parameter variations we used. The residence time was fixed at 20 s except for S3.5

206 *Table 1: Process operating parameters for the boehmite syntheses performed at 25 MPa and 400 °C.*
with 60 s as residence time.

Sample name	S2.9	S3.5	S3.9	S6.7
Residence time (s)	20	60	20	20
Precursor concentration (mol.L ⁻¹)	1.10 ⁻¹	2.10 ⁻²	5.10 ⁻³	2.10 ⁻²
pH	2.9	3.5	3.9	6.7

207 Morphology of the as-synthesized particles was investigated using TEM analysis. As shown
208 in Figure 2, boehmite particles are anisotropic. S2.9 and S3.5 powders exhibit strongly
209 aggregated hexagonal particles of about a few hundred nanometers in length (Figure 2a) and
210 b)). The particles are very thin, less than 15 nm as observed on TEM images of S3.5 and S3.9
211 (Figure 2b) and c)). The increase of the residence time from 20 to 60 s does not seem to
212 favour the particle growth. This has already been observed by Hakuta *et al.* who assumed the

213 particles grow only at the very early stage of the reaction (< 2 s) at 25 MPa and 400 °C in
214 acidic conditions [20].

215

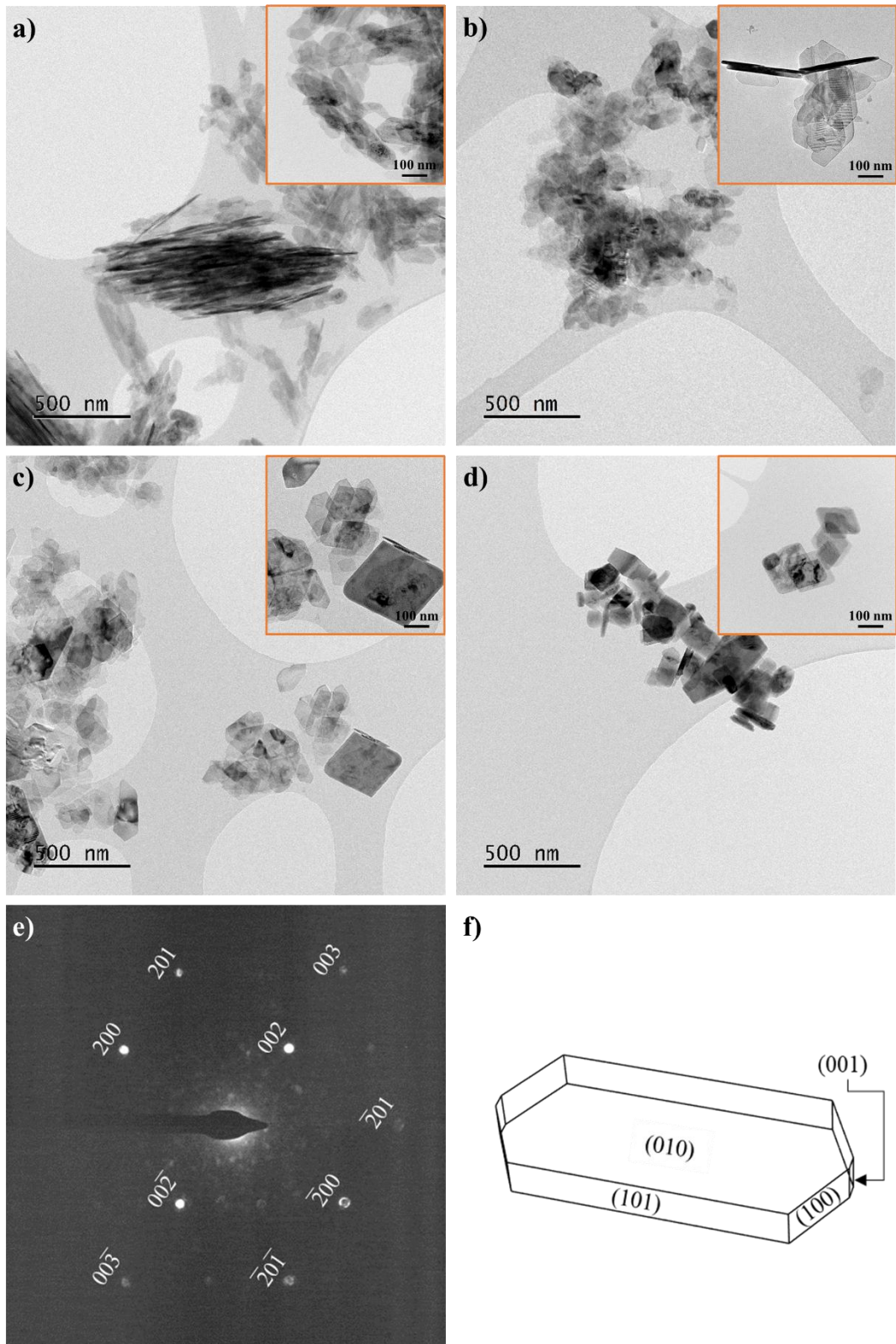


Figure 2: TEM images of boehmite particles: a) S2.9, b) S3.5, c) S3.9 and d) S6.7 associated with the electron diffraction pattern of a hexagonal particle of S3.9 on e) and a scheme of a hexagonal platelet grain on f).

217 A further increase of the pH value results in the formation of rhombic particles. S3.9 powder
218 shows both aggregated hexagonal and rhombic particles. Moving to a near neutral pH allows
219 the synthesis of perfectly rhombic boehmite particles. Alkaline pH of 9.3 and 12.0 were also
220 tested, but are not presented here. Slightly basic conditions gave a mix of boehmite and
221 bayerite, an aluminium hydroxide $\alpha\text{-Al(OH)}_3$ whereas strong basic ones did not produce any
222 particles. This is in agreement with Hakuta *et al.* observations [20]. They explained the
223 particle disappearance by a redissolution of very small particles during cooling. However,
224 recent research brings new hypotheses with the discovery of Hydrothermal Molten Salts
225 (HyMOS) [29]. The precipitation at a higher temperature than their melting point *i.e.* between
226 318 and 323 °C for NaOH is instantaneously followed by the fusion of the salts. It produces a
227 unique system composed of supercritical water at low density with a fraction of dissolved salt
228 and a molten salt phase with a fraction of water [30]. The high polarity and density of molten
229 salts results in dissolving a large amount of inorganic particles that could be the case of
230 boehmite. Voisin *et al.* [29] demonstrated the formation of NaOH molten salts in supercritical
231 water at 400 °C and 25 MPa. One of the conditions for observing molten salt is the prior
232 NaOH precipitation (before melting) meaning that a salt concentration above its solubility
233 (133 ppm at 400 °C and 25 MPa) is necessary. In this study, this condition is achieved with a
234 NaOH concentration of 400 ppm approximately at a pH of 12. Although molten salts have
235 never been observed under these specific conditions, all conditions required to obtain them
236 are met and could also explain the redissolution of boehmite nanoparticles. Zhang *et al.*
237 discussed the effect of pH on the growth of boehmite using traditional hydrothermal synthesis
238 based on sol-gel process. In their study, a pH higher than 12 is required to obtain rhombic
239 grains [31]. The [010] zone axis electron diffraction pattern in Figure 2e) reveals diffraction
240 spots of (100), (001) and (101) planes. Such a result is consistent with a hexagonal grain with

241 a dominant (020) surface and (100), (001) and (101) edge surfaces as represented on the
242 scheme shown in Figure 2f).

243 The aggregation makes particle size determination complex. To overcome this issue,

244 boehmite particles are then defined by their Average Crystallite Size (A.C.S). X-ray

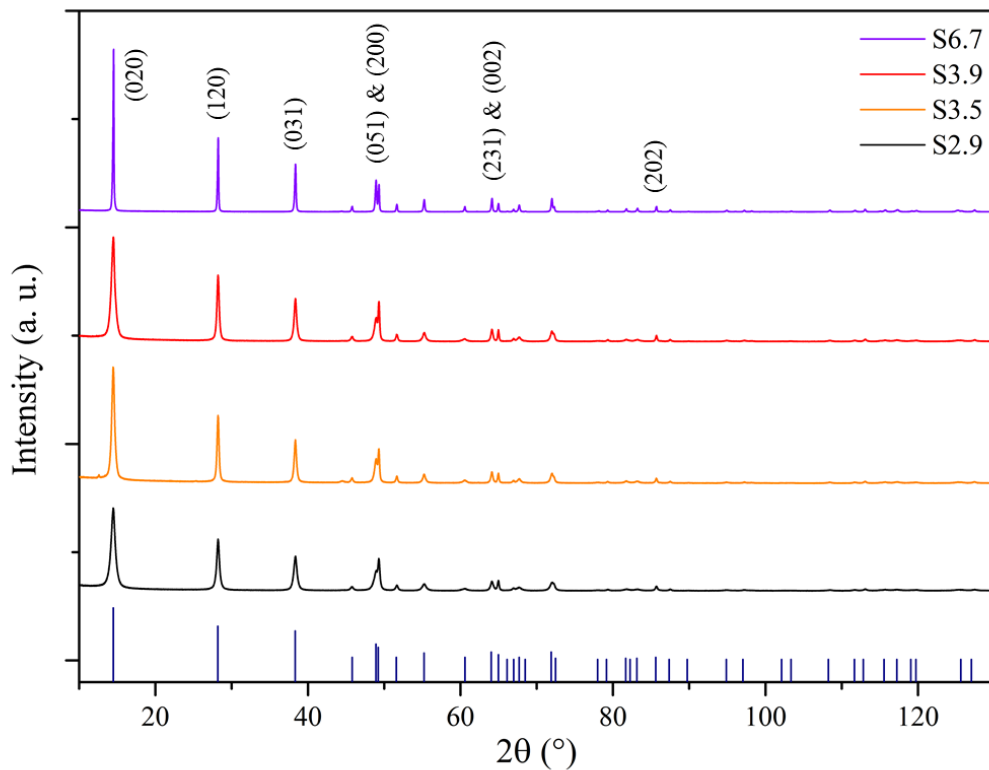


Figure 3: X-ray diffraction patterns of the four studied samples. In blue, boehmite peak positions and their theoretical intensities from the PDF file # 00-021-1307.

245 diffraction patterns of the as-synthesized powder are shown in Figure 3. They confirmed the

246 synthesis of well-crystallized boehmite powders independently of the pH value. Using the

247 PDF # 00-021-1307 file for an orthorhombic boehmite (space group *Cmcm*), plan

248 identification of boehmite is assigned in Figure 3. Crystallized boehmite is described by a

249 most intense (020) peak ($2\theta = 14.5^\circ$) followed by (021) ($2\theta = 28.2^\circ$) and (130) ($2\theta = 38.4^\circ$)

250 peaks of half the intensity.

251 A deep study of the crystal structure is proposed by simulating the experimental X-ray
252 diffraction patterns thanks to the Rietveld refinement method. An example for the S2.9
253 sample is displayed in Figure 4. The accuracy of the Rietveld refinement presented is
254 relatively good with a weighted-profile R-factor of 9%. Refined crystal parameters for all the
255 studied powders are reported in Table 2.

256 Refined lattice parameters, and especially along the b-axis, do not show significant
257 discrepancies showing that no atom or water molecule could be inserted within the structure.
258 Guzmán-Castillo *et al.* have also made this observation [15]. As expected for anisotropic
259 particles, peak broadening varies from peak to peak. In agreement with the scheme of a
260 hexagonal grain and the electron diffraction pattern (Figure 2e) and f)), boehmite particles can
261 be characterized by the (200), (020), (002) and (202) diffraction peaks observed at 49.3°,
262 14.5°, 65.0° and 85.7°, respectively.

263 The assumption of a parallelepipedic grain is done by taking into account the crystallite
264 dimensions only along the [100], [010] and [001] directions to facilitate the study. Table 2

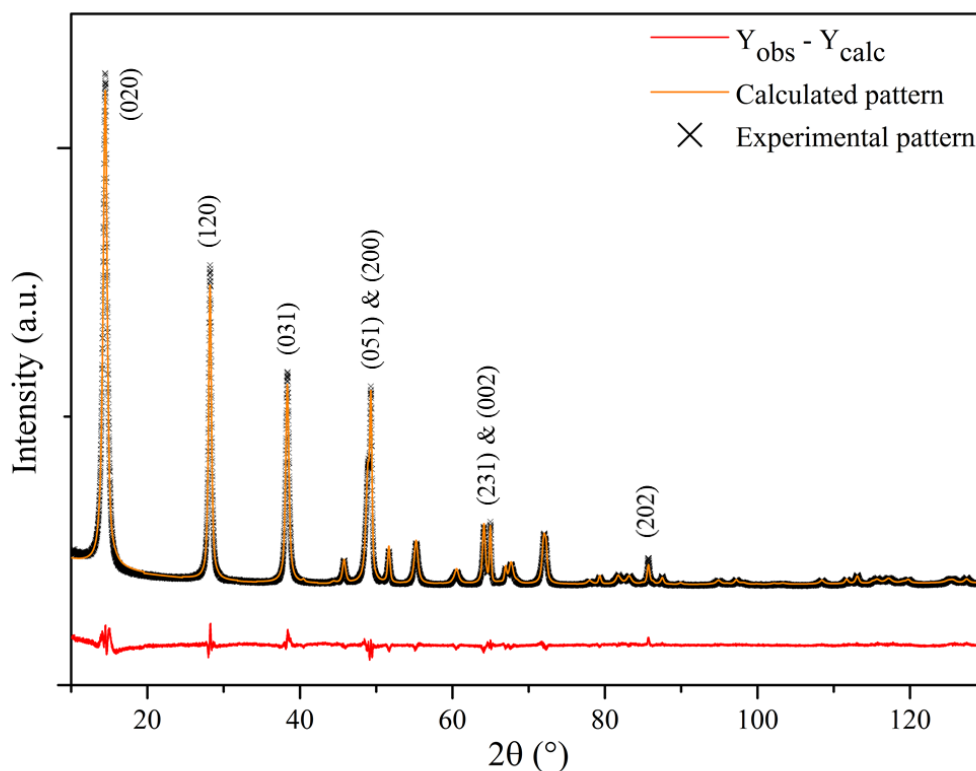


Figure 4: Rietveld refinement plot performed for the S2.9 X-ray diffraction pattern.

265 discloses estimated average crystallite dimensions using full width at half maximum (FWHM)
266 from refinement output labelled l_{200} , l_{020} and l_{002} along the [100], [010] and [001] directions.
267 A.C.S. reported through Rietveld refinement are smaller than qualitative observations
268 performed on the TEM images, which confirmed the polycrystalline nature of the powders. In
269 contrast, the l_{020} length corresponds approximately to the measurements done on the
270 crystallite thicknesses shown in Figure 2b) and c) for S3.5 and S3.9, respectively. These
271 particles oriented parallel to the b-axis exhibit thicknesses less than 15 nm fitting with the 12
272 and 10 nm values estimated from Rietveld refinement. It suggests that polycrystalline
273 particles are made of a unique layer of crystallites perpendicularly aligned to the b-axis.
274 S6.7 powder presents relatively large crystallites compared to the three others (at least twice
275 the size along all crystallographic directions). For instance, S2.9 has l_{200} , l_{020} and l_{002} of 28 ± 5
276 nm, 10 ± 2 nm and 23 ± 6 nm while those of S6.7 are 47 ± 4 nm, 39 ± 4 nm and 47 ± 4 nm,
277 respectively. The ratios between these particular distances report on specific growth rate.
278 From acidic to near neutral conditions at a constant residence time, the ratio l_{200} / l_{020} is
279 reduced from 2.8 to 1.2, l_{002} / l_{020} from 2.3 to 1.2 whereas l_{200} / l_{002} shows a slight decrease

Table 2: Refined parameters and residuals from the Rietveld refinement using spherical harmonic peak shape functions. Calculation error values are mentioned in brackets.

280 from 1.2 to 1.0.

Sample name	S2.9	S3.5	S3.9	S6.7
a (nm)	0.2868 (1)	0.2869 (1)	0.2868(1)	0.2868 (1)
b (nm)	1.2225 (1)	1.2221 (2)	1.2222 (1)	1.2219 (1)
c (nm)	0.3693 (1)	0.3694 (1)	0.3693 (1)	0.3694 (1)
R_{wp} (%)	9	8	10	11
l_{200} (nm)	28 (5)	19 (4)	17 (3)	47 (4)
l_{020} (nm)	10 (2)	12 (2)	10 (2)	39 (4)
l_{002} (nm)	23 (6)	18 (4)	17 (3)	47 (4)
l_{200} / l_{020}	2.8	1.6	1.8	1.2

I_{200}/I_{002}	1.2	1.1	1.0	1.0
I_{002}/I_{020}	2.3	1.5	1.8	1.2

281 Considering only a decrease of the pH, a preferential growth may be underlined along the
 282 [100] and [001] directions compared to the [010] one. In addition, crystallite dimensions,
 283 measured on TEM images (figure 2), of S3.5 powder with l_{200} , l_{020} and l_{002} of 19 ± 4 nm, $12 \pm$
 284 2 nm and 18 ± 4 nm, respectively, agreed with a non-significant impact of the residence time
 285 on particle growth.

286 Acidic conditions have led to hexagonal platelets whereas rhombic grains are produced in
 287 near neutral solutions. Morphology modification is correlated to pH and so is the variation of
 288 nitrates in the solution.

289

290 3.2 Adsorption of nitrates

291 Modification of boehmite morphology can be obtained through anisotropic adsorption of
 292 chemical species, nitrates for instance. He *et al.* characterized sulfates adsorption on boehmite
 293 particles using Raman spectroscopy [32]. In the case of a sulfate H-bonded complex, a sulfate
 294 would not form a direct chemical bond with the surface and the vibrational spectrum is very
 295 similar to the spectra of sulfate in solution. Raman spectroscopy appears to be a suitable
 296 technique to analyse chemical bonds of adsorbed species thanks to its high sensitivity to
 297 molecule vibration. The low wavenumber region Raman spectra of the different boehmite
 298 samples is reported in Figure 5. The $400 - 800 \text{ cm}^{-1}$ region consists of the hydroxyl
 299 translation modes. In particular, the most intense peak at 359 cm^{-1} corresponds to the A_g fully
 300 symmetric mode due to the movement of aluminium and oxygen atoms parallel to the [010]
 301 direction [33]. The AlO_6 octahedron structure causes two peaks at 494 and 674 cm^{-1} [34,35].
 302 The small and sharp peak at 1049 cm^{-1} which is slightly intense for S2.9 and S3.9 and almost
 303 extinct for S6.7 is attributed to NO_3^- vibrations [26,33]. Although Raman spectroscopy gives

304 qualitative information, this peak confirmed the presence of nitrates at the boehmite surfaces,
 305 especially on S2.9 and S3.9.
 306 A further study at high wavenumber was performed. Results are presented in Figure 6. This

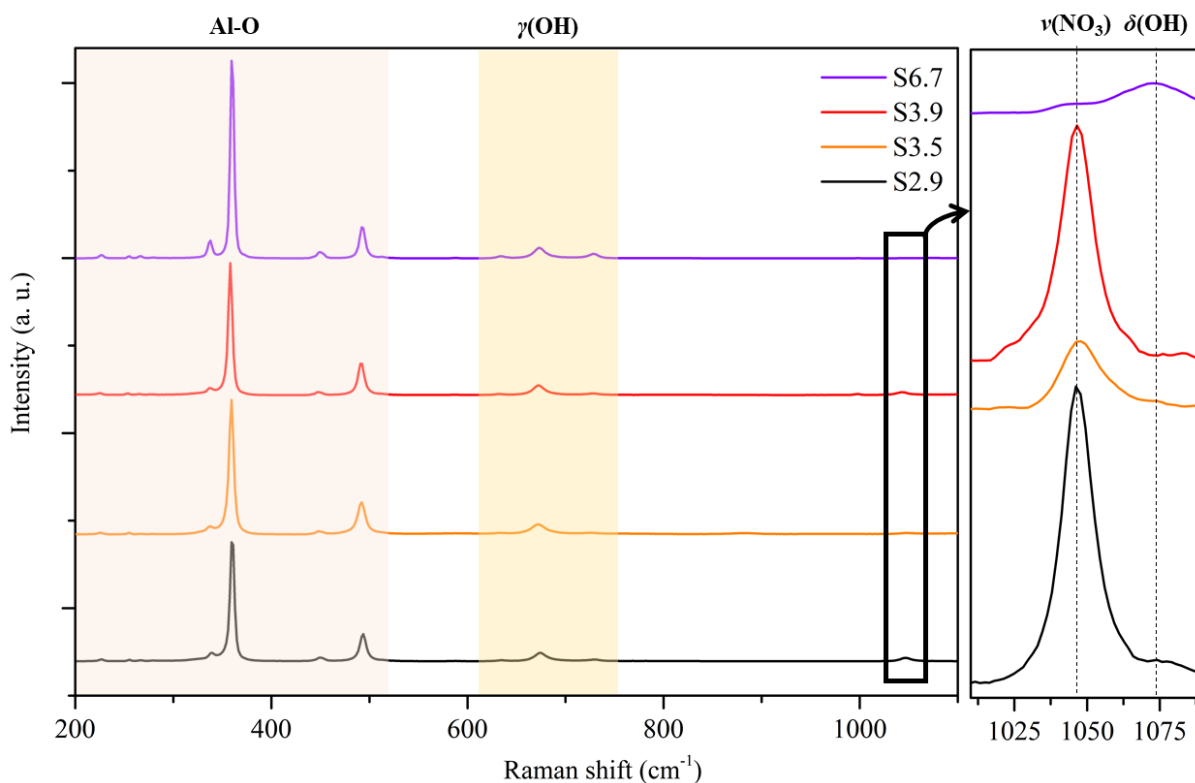


Figure 5: Raman spectra of the low wavenumber region of S2.9, S3.5, S3.9 and S6.7; on the left, from 200 to 1200 cm^{-1} ; on the right, a focus on the 1020 - 1080 cm^{-1} region. Each part of the spectra is described with its corresponding assignment.

307 region exhibited up to four bands at 3078, 3219, 3340, 3515 cm^{-1} and eventually a shoulder at
 308 3561 cm^{-1} . The two first peaks characterized the hydroxyl stretching vibrations within
 309 boehmite structure and are observable for all the samples [25,34,35].

310 The assignment above 3300 cm^{-1} is extremely complex because of the intricate hydrogen
 311 bonding network [36]. This region is associated with the stretching vibrations of surface OH
 312 groups or residual water on the surfaces [25,37]. Bands at 3340, 3515 and 3561 cm^{-1} are
 313 displayed for S2.9 and more particularly for S3.5. On the top of Figure 6, a spectrum of a
 314 boehmite sample synthesized in a batch reactor using gibbsite $\text{Al}(\text{OH})_3$ as a precursor and so

315 without nitrates is depicted. This spectrum shows the structural hydroxyl stretching vibrations
 316 between 3000 and 3300 cm^{-1} but does not display any bands at higher frequency.
 317 Consequently, bands above 3300 cm^{-1} may have a link with surface hydroxynitrates.
 318 Observations done by Herzog-Cance *et al.* who studied the nitric acid autoprotolysis using
 319 Raman spectroscopy confirmed the substantial correlation between these bands and nitrates
 320 [38]. Thus, the band at 3340 cm^{-1} may correspond to the stretching contribution of weakly
 321 bonded HNO_3 also named as “free” nitric acid. The greatest band at 3515 cm^{-1} could be
 322 attributed to the stretching vibration of water associated with nitric acid molecules through the

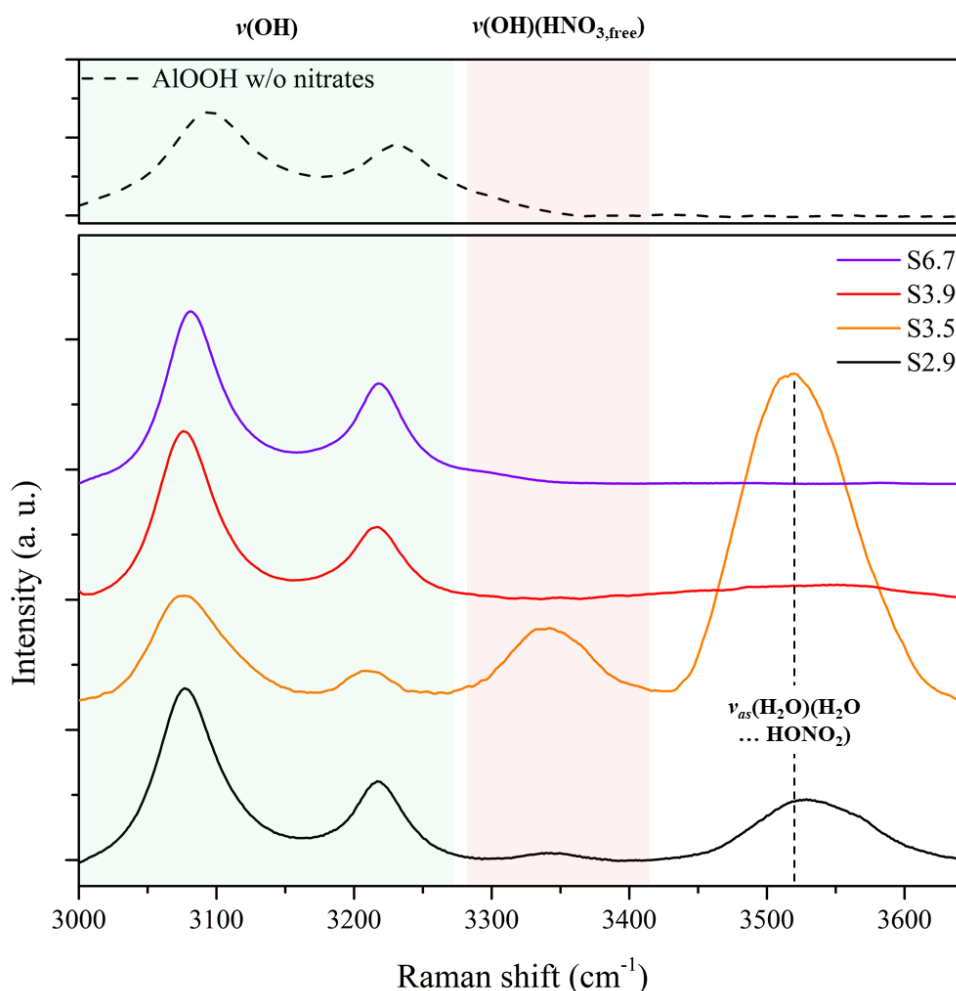


Figure 6: Raman spectra of the high wavenumber region from 3000 to 3650 cm^{-1} of; on the top, a boehmite sample synthesized without nitrates; on the bottom, S2.9, S3.5, S3.9 and S6.7. Each part of the spectra is described with its corresponding assignment.

323 molecular association $\text{H}_2\text{O} \dots \text{HONO}_2$ produced from the dissociation of the HNO_3 molecule
 324 [38]. The shoulder at 3561 cm^{-1} may assimilate to differently bonded water molecules.
 325 Assignments of the Raman spectra indicated a strong adsorption of nitrate species, especially
 326 in acidic conditions. Bands correlated to nitrate signatures almost disappear for S3.9 and are
 327 inexistent for S6.7. Raman spectroscopy of S3.5 at a longer residence time has demonstrated
 328 many signatures of nitrates under various forms.
 329 Nitrate adsorption occurred more under acidic conditions as shown in Raman spectroscopy
 330 results, leading to the formation of hexagonal particles. The next part will deal with the
 331 interaction between these specific morphologies and the adsorption of water molecules.

332

333 3.3 Adsorbed water determination

334 Nguetack *et al.* developed a model to investigate adsorbed water content on boehmite
 335 crystallites based on free sites available on each facet [39]. They obtained the maximum
 336 adsorption capability by expanding the coordination number of surface aluminium atoms to
 337 six and surface oxygen atoms to four. Stoichiometric water content adsorption x is calculated
 338 by dividing the number of free sites by the total number of atoms in the crystal. To estimate
 339 the free site number, the model uses the A.C.S. and lattice parameters refined from the

Table 3: Determination of the relative facet areas of the three mains faces (100), (010) and (001) and of the overall adsorbed water calculated using the model of Nguetack et al. [38].

340 Rietveld method. The corresponding results are summarized in Table 3.

Sample name	S2.9	S3.5	S3.9	S6.7
$S_{(100)}$ (%)	20	26	30	31
$S_{(010)}$ (%)	56	45	41	38
$S_{(001)}$ (%)	24	28	29	31
$\text{AlOOH} \cdot x\text{H}_2\text{O}$	0.16	0.18	0.21	0.07

341 As stated above, the (010) facet is dominant with a relative surface area between 56 % and 38
 342 % for S2.9 and S6.7, respectively. However, the basal surface decreases when the pH

343 becomes more neutral to the benefit of the (100) and (001) facets. This is in agreement with
344 the observation of the Rietveld refinement with the inhibition of (100) and (001) facets in
345 acidic conditions. Stoichiometric water content increased from 0.16 to 0.21 following the
346 inverse of the (010) relative facet area.

347 S3.5 sample follows the same tendency and does not show a significant effect of residence
348 time. Bigger crystallites obtained for S6.7 have less adsorption sites in proportion to the total
349 number of atoms in the crystal and so less water is adsorbed following this model.

350 To sum up, a raise of the pH from 2.9 to 3.9 is followed by a slight increase of water content
351 whereas a further increase of the pH to 6.7 generated a drastic reduction of water content.

352 As explained in the introduction, two possibilities have been suggested for the location of
353 water. The first assumption was inside the structure along the b-axis. However, the Rietveld
354 refinement revealed a restricted variation of the crystal dimension along the b-axis,
355 insufficient to insert any atoms within the structure. Consequently, the excess of water is
356 probably adsorbed on the crystal surfaces.

357 *3.4 Investigation of surface species and their chemical environment*

358 XPS survey scans, shown in Figure 7, exhibit very clean samples with mostly Al and O atoms

Table 4: Summary of the C_{1s} , Al_{2p} and O_{1s} spectra description with the full width at half maximum (FWHM), the atomic proportions of each environment and the ratio between

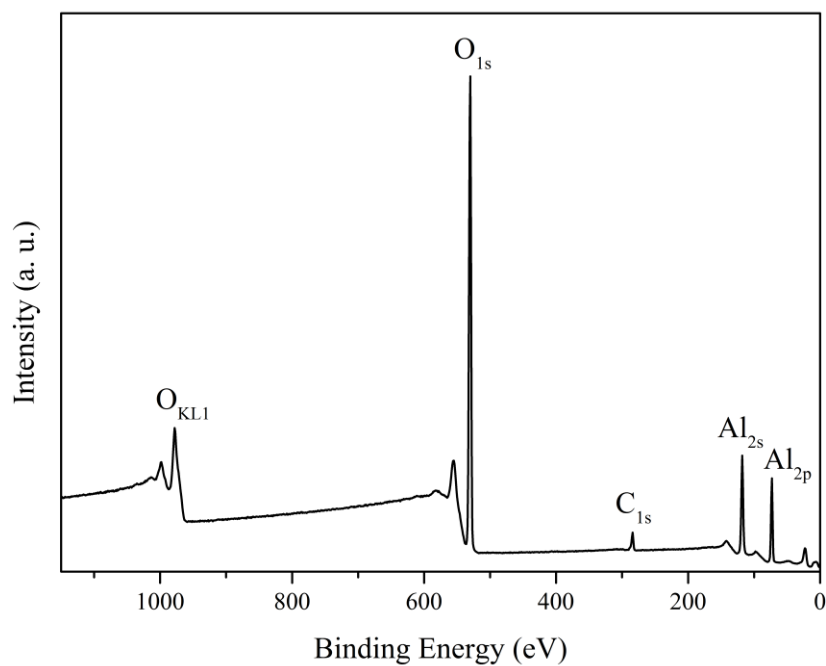


Figure 7: XPS survey spectrum of the boehmite S2.9 sample.

359 and the adventitious C between 4.2 and 9.7 at. %. This is confirmed by the Al/O ratio equal to
 360 0.5. In addition, no significant shift of the Al_{2p} binding energies is observed with a position at
 361 approximately 74.0 and 74.1 eV meaning that the oxidation state of Al atoms is stable for all
 362 the samples.

Sample name	S2.9	S3.5	S3.9	S6.7
FWHM (± 0.1 eV)				
Al_{2p}	1.8	1.4	1.5	1.5
<i>Al-O-Al</i>	1.6	1.4	1.5	1.5
O_{1s}				
<i>Al-OH</i>	1.9	1.6	1.7	1.8
<i>Ads. H₂O</i>	1.9	1.4	1.7	1.8
Atomic proportions (± 0.1 %)				
C_{1s}	6.2	4.2	6.5	9.7

Al_{2p}		31.3	33.3	31.3	29.9
	<i>Al-O-Al</i>	18.3	25.7	19.8	20.5
O_{1s}	<i>Al-OH</i>	26.6	30.7	22.1	24.8
	<i>Ads. H₂O</i>	17.7	6.1	20.4	15.1

Ratio					
Al_{2p}/O_{1s}		0.5	0.5	0.5	0.5
O_{1s}	<i>(Ads. H₂O/Al-O-Al)</i>	1.0	0.2	1.0	0.7
O_{1s}	<i>(Al-OH/Al-O-Al)</i>	1.5	1.2	1.1	1.2

363 Figure 8 exhibits the high-resolution O_{1s} spectra of the four samples fitted into three

364 components. The first contribution at 530.4 ± 0.1 eV is attributed to the Al-O-Al structure, the

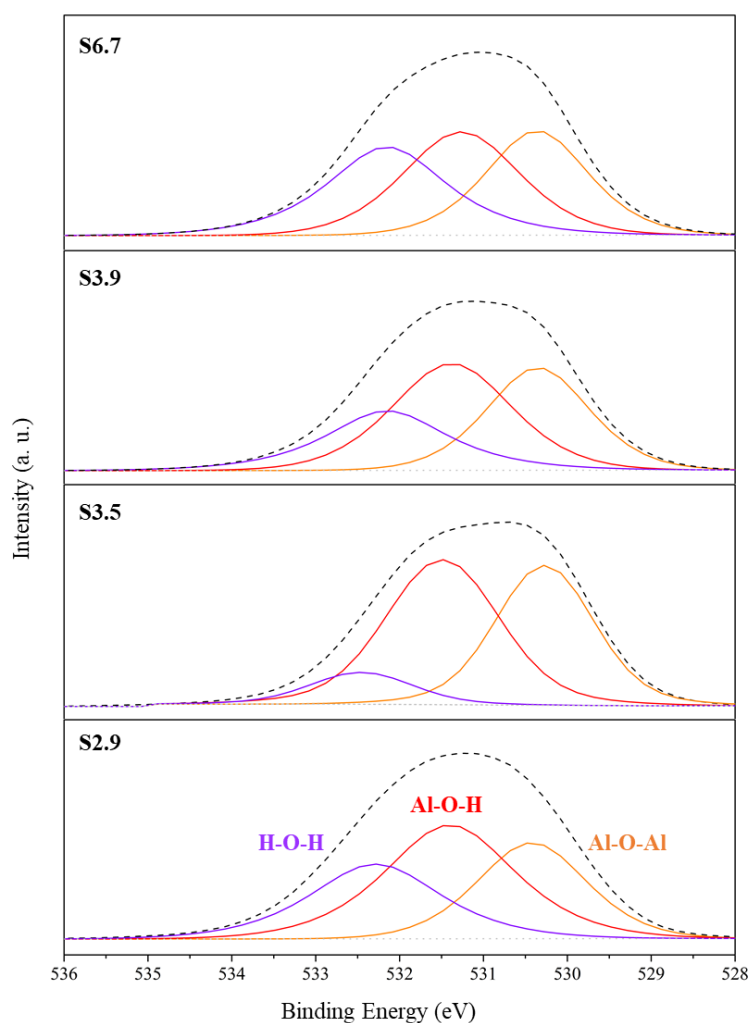


Figure 8: Fitted XPS O_{1s} spectra of S2.9, S3.5, S3.9 and S6.7 into three contributions: Al-O-Al structure in orange, structural hydroxyls in red and adsorbed water in purple.

365 second one at 531.4 ± 0.1 eV to the Al-O-H within the crystal and the third one between 532.2
 366 ± 0.1 eV and 532.5 ± 0.1 eV to the adsorbed water on the surface [40]. Peak broadening
 367 provides information on the structure disorder. The wider is the peak broadening, the more
 368 disordered the local atom environment is. Al_{2p} and O_{1s} peak broadenings follow the same
 369 trend and decrease with pH. For instance, Al_{2p} peak broadening changes from 1.8 eV to 1.5
 370 eV for S2.9 and S6.7, respectively. S3.5 sample exhibits the more ordered structure with the
 371 lowest peak broadening for aluminium. This means that an increase in the residence time to
 372 60 s does not promote the particle growth but improves the local structure order. The
 373 contribution of ads. H_2O revealed some variations of the adsorbed water on the boehmite

374 surfaces. Indeed, S3.9 has the highest adsorbed water contribution with 20.4 at.%. In
375 comparison, the lowest is contained on S3.5 surfaces with only 6.1 at.%. The study of the
376 ratios between these contributions makes it possible to get rid of the impurity effects such as
377 carbon. The adsorbed water content is quite similar for both S2.9 and S3.9 with a ratio
378 $\frac{O_{1s}(Ads. H_2O)}{O_{1s}(Al-O-Al)}$ close to 1 and is reduced down to 0.7 for S6.7 at high pH.

379 However, an increase in the residence time with S3.5 proposed to reduce significantly this
380 ratio and so the adsorbed water content to 0.2. These observations are almost in agreement
381 with the adsorption site calculation (Table 3) except for S3.5. The ratio $\frac{O_{1s}(Al-OH)}{O_{1s}(Al-O-Al)}$ is
382 expected to be nearly 1 according the AlOOH chemical formula [40]. This ratio is about 1.2
383 for S3.5, S3.9 and S6.7 and raised to 1.5 for S2.9, highlighting an excess of surface hydroxyls
384 in these conditions. The depth probed by XPS (≈ 3 to 5 nm) coupled with crystallite thickness
385 near 10 nm for S2.9, S3.5 and S3.9 likely might overestimate the adsorbed water and surface
386 hydroxyl compared to thicker crystallites of S6.7.

387 Even if the assignment of 1H resonance lines is very challenging, 1H Solid-State NMR spectra
388 of the S2.9 and S3.5 samples confirmed the observations done using XPS and summarized in
389 Figure 8.

390 In Figure 9, the 1H MAS NMR spectrum of S3.5 can be described as the sum of four main
391 resonance lines centered at 1.2, 3.5, 7.1 and 10.4 ppm. Peaks at 7.1 and 10.4 ppm are
392 tentatively assigned to structural octahedral Al_2OH sites which involve different strength of
393 bonds while the one located at 3.5 ppm is attributed to octahedral AlOH sites [41]. The
394 narrow resonance line at 1.2 ppm is often referred as another contribution of octahedral AlOH
395 sites. The slight variation in 1H NMR shifts between different authors is likely due to
396 difference in morphology of boehmite particles [42]. In comparison, an additional peak at 4.7
397 ppm is exhibited for the sample S2.9. This contribution counting for 25 % of the overall

398 resonance area coincides undoubtedly to the protons of “physisorbed” water on boehmite
399 particles [41,42].

400 As stated previously, A.C.S. plays an important role but are insufficient to explain all the
401 involved surface reactions. Especially, the local environment order would appear to have a
402 major impact.

403

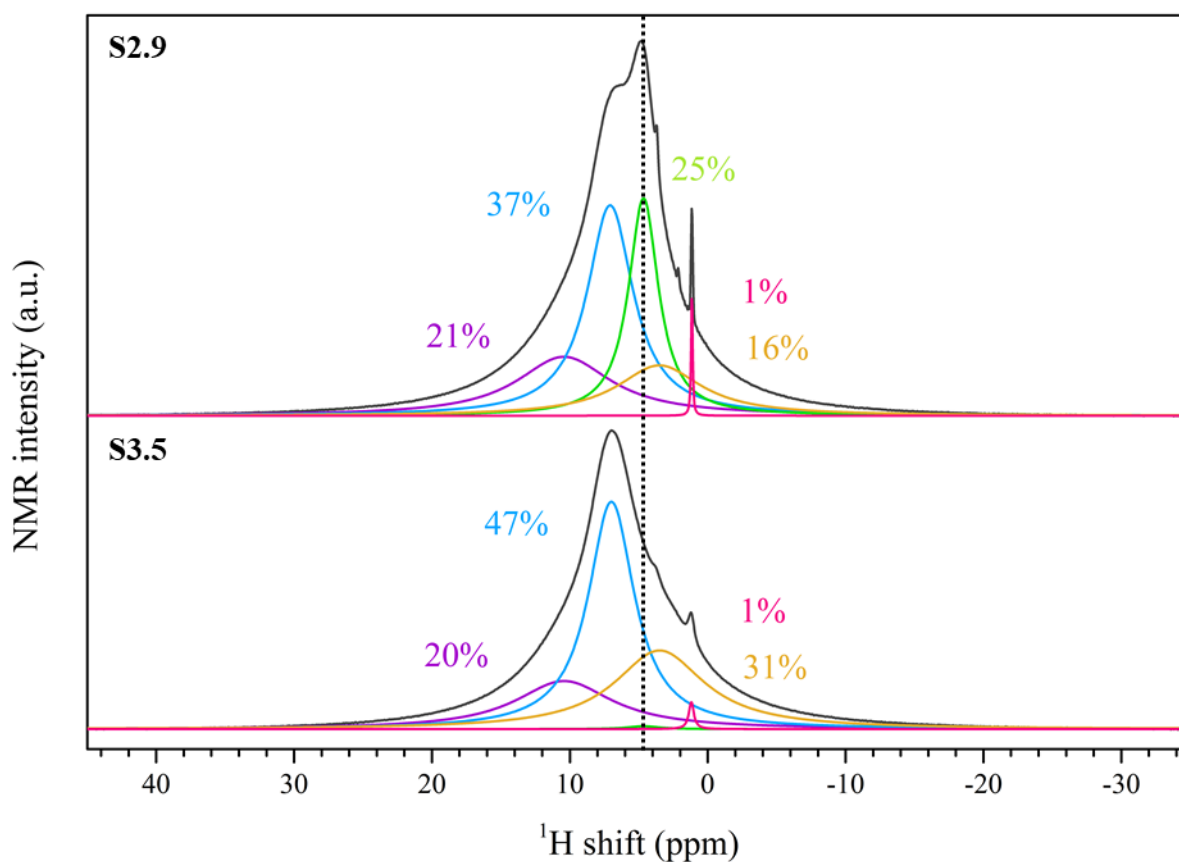


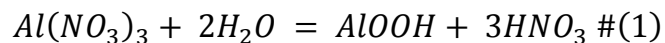
Figure 9: ^1H MAS NMR spectra of boehmite samples S2.9 and S3.5. Fitted curves with the respective contributions in percentage are presented. The dashed line corresponds to the weakly bonded water.

404

405 4. Discussion

406 Firstly, the discussion is focused on the effect of pH considering the samples S2.9, S3.9 and
407 S6.7. pH has a great impact on the fluctuation of the boehmite particle morphology

408 synthesized using the continuous supercritical hydrothermal process. Indeed, a highly acidic
409 pH or a neutral one will give anisotropic hexagonal-plate and rhombic particles, respectively.
410 Boehmite synthesis, described by the chemical reaction below, produces also HNO₃ [43].



411 These HNO₃ molecules may adsorb on boehmite particle surfaces. Raman spectroscopy
412 underlined the strong presence of nitrates on the hexagonal-plate boehmite powders (Figure 5
413 and Figure 6). In acidic conditions, the anion adsorption is favored due to the positive charges
414 at the boehmite surface determined with a zeta potential study considering an isoelectric point
415 of boehmite between 7 and 9.2 depending on the morphology and the particle size [44,45].
416 On the contrary, at near neutral pH, there is no adsorbed anions leading to no or a little
417 preferential growth and so to large rhombic particles. The less acidic the solution is, the less
418 anion adsorption will occur. Furthermore, the anion adsorption may be surface-dependent.
419 Nitrates seem to adsorb preferentially on (020) surface resulting in a preferential growth along
420 the [001] and mostly [100] directions. Consequently, the relative (020) surface is increased
421 compared to the edge surfaces (Table 3).

422 According to the model developed by Nguéfack *et al.*, the less prominent the (020) relative
423 surface is, the less water is adsorbed on the boehmite surfaces. The XPS results tend to this
424 conclusion too with a strong reduction of the adsorbed water content for pH from 2.9 to 6.7.
425 This is directly linked to the crystal structure of boehmite. As the octahedral double layer
426 interactions are weak in the boehmite structure, the crystal is easily cleaved between these
427 layers causing (010) surfaces to be covered by hydroxyl groups [11,12]. However, the
428 difference is not significant between pH values equal to 2.9 and 3.9, which could be explained
429 by a reduction of the available sites for water adsorption. Even if the sample S2.9 has more
430 adsorption sites, they are probably mostly filled with nitrate species. In addition, a very low

431 pH seems to promote a dissociative adsorption of water resulting in more surface hydroxyl
432 groups.

433 Secondly, the residence time does not significantly influence the morphology. In acidic
434 conditions, hexagonal-plate particles with the same range of size were synthesized at longer
435 residence time (60 s instead of 20 s). Surprisingly, this sample exhibits a very small adsorbed
436 water content, lower than the one of sample done at pH 6.7, which is totally at odds with the
437 model of Table 3. The increase of the residence time implies a real improvement of the local
438 structure environment (Table 4, see FWHM). In this case, oxygen with a free orbital will form
439 a ligand between an aluminium atom and the non-reacted nitrates in solution. Thus, nitrate
440 hydroxyls such as $\text{Al}_2\text{O}_2(\text{OH})\text{NO}_3$ can be formed at the surfaces preventing further adsorption
441 of water [46]. These species may have the time to be stabilized and so to reduce the local
442 disorder.

443 Surfaces may be fully adsorbed by H-bonded liquid HNO_3 . During the synthesis, produced
444 nitric acid in the fluid will react with the surface of the particles and especially at low pH. The
445 strong peak at 3515 cm^{-1} in Figure 6 may prove that the molecular association $\text{H}_2\text{O} \dots$
446 HONO_2 is weakly bonded at the surface of boehmite. The intensity of this peak differs from
447 the small content of adsorbed water observed using XPS and ^1H MAS NMR spectroscopy. As
448 a result, the residence time increase may promote the adsorption of hydroxynitrates combined
449 with the one of liquid HNO_3 leading to the full filling of the free adsorption sites of boehmite.

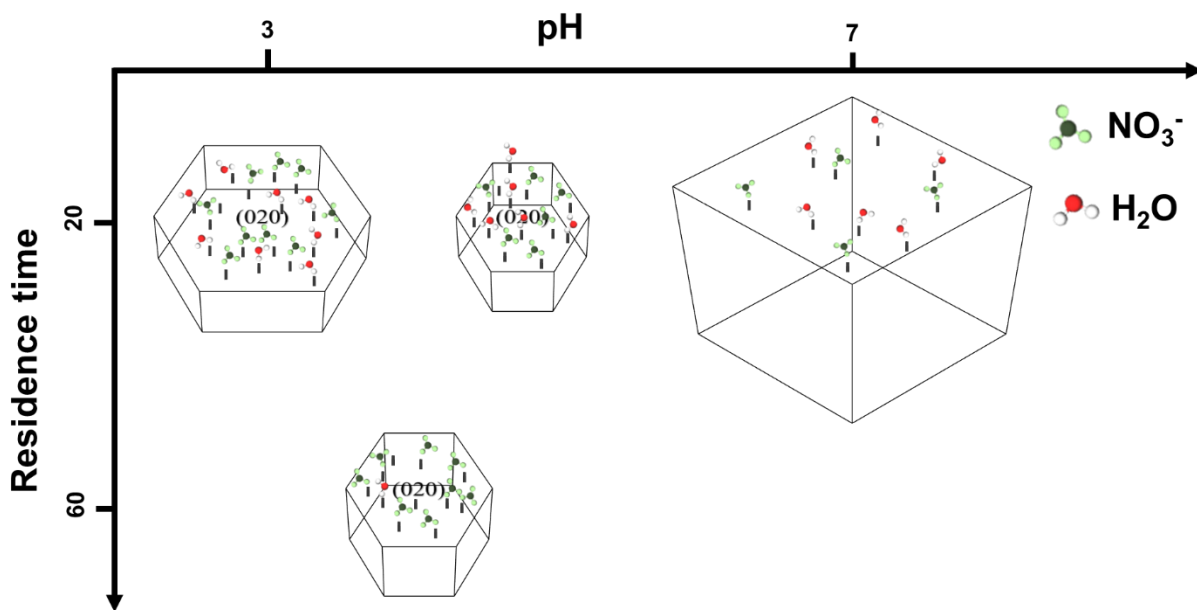


Figure 10: Schematic representation of the adsorption phenomena on different morphologies of boehmite.

450 The scheme displayed in Figure 10 summarizes the discussion.

451 From the pH variation, two factors are pointed out on the adsorbed water modification. A
 452 weakly alkaline pH will give rhombic grains with a little relative (020) surface. This will lead
 453 to a reduced adsorbed water content validated by XPS results (Figure 8).

454 In the case of an acidic environment, it is more complex. The decrease of the pH will allow
 455 the production of hexagonal-plate grains associated with an increase of the relative (020)
 456 surface area (Table 3). Nevertheless, the more acid the environment is, the more nitrates will
 457 be adsorbed (Figure 5). These molecules may block the further adsorption of water at the
 458 surface of boehmite particles.

459 Decrease of the available adsorption sites at high residence time is due to the improvement of
 460 the intricate structure with the hydroxynitrates and of the HNO₃ content at the surface.

461 Finally, the prediction of the adsorbed water quantity is very tricky. Indeed, it involves
 462 complex interdependent phenomena linking the growth along specific directions, anisotropic
 463 surface reactions of chemical species such as anions and available adsorption free sites.

464

465 **5. Conclusion**

466 This study investigated the adsorption of water on various morphologies of boehmite particles
467 synthesized using the continuous supercritical hydrothermal synthesis. The use of this process
468 allowed to synthesize pure and crystalline submicrometer boehmite particles. pH modification
469 from 2.9 to 6.7 offered a way to tune the particle morphologies from hexagonal platelets to
470 rhombic grains and the sizes of the particles. In fact, the anisotropic nature of boehmite results
471 in a surface-dependent anion adsorption. Nitrates were adsorbed preferentially on the (020)
472 surface leading to a preferential growth along [001] and mostly [100] directions.

473 Our results showed that the adsorption of water cannot be characterized only by a
474 morphological analysis. It depends substantially on two phenomena. First, the more ordered
475 the crystal structure is, the less the adsorbed water will be. XPS analysis combined with ^1H
476 Solid-State NMR experiments have effectively highlighted the very small amount of adsorbed
477 water on well-ordered boehmite particles. Secondly, in acidic conditions, anions such NO_3^-
478 are attracted to the boehmite surfaces leading to the diminution of the adsorption sites as
479 shown by Raman spectroscopy.

480 Then interaction between the boehmite morphology and the adsorption of water is very
481 difficult to be predicted because it is correlated with different parameters such as crystallite
482 size, structural order and other adsorbed species such as nitrates.

483

484 **Declaration of Competing Interest**

485 The authors declare that they have no known competing financial interests or personal
486 relationships that could have appeared to influence the work reported in this paper.

487

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493

494 **References**

- 495 [1] C. Aymonier, A. Loppinet-Serani, H. Reverón, Y. Garrabos, F. Cansell, Review of
496 supercritical fluids in inorganic materials science, *J. Supercrit. Fluids.* 38 (2006) 242–251.
497 <https://doi.org/10.1016/j.supflu.2006.03.019>.
- 498 [2] C. Aymonier, G. Philippot, A. Erriguible, S. Marre, Playing with chemistry in
499 supercritical solvents and the associated technologies for advanced materials by design, *J.*
500 *Supercrit. Fluids.* 134 (2018) 184–196. <https://doi.org/10.1016/j.supflu.2017.12.021>.
- 501 [3] A. Takagaki, J. Chul Jung, S. Hayashi, Solid Lewis acidity of boehmite γ -AlO(OH) and
502 its catalytic activity for transformation of sugars in water, *RSC Adv.* 4 (2014) 43785–
503 43791. <https://doi.org/10.1039/C4RA08061K>.
- 504 [4] F. Granados-Correa, J. Jiménez-Becerril, Chromium (VI) adsorption on boehmite, *J.*
505 *Hazard. Mater.* 162 (2009) 1178–1184. <https://doi.org/10.1016/j.jhazmat.2008.06.002>.
- 506 [5] P. Li, S. Zheng, P. Qing, Y. Chen, L. Tian, X. Zheng, Y. Zhang, The vanadate adsorption
507 on a mesoporous boehmite and its cleaner production application of chromate, *Green*
508 *Chem.* 16 (2014) 4214–4222. <https://doi.org/10.1039/C4GC00897A>.
- 509 [6] H. Zhang, P. Li, Z. Wang, X. Zhang, S. Zheng, Y. Zhang, *In Situ* Synthesis of γ -AlOOH
510 and Synchronous Adsorption Separation of V(V) from Highly Concentrated Cr(VI)
511 Multiplex Complex solutions, *ACS Sustain. Chem. Eng.* 5 (2017) 6674–6681.
512 <https://doi.org/10.1021/acssuschemeng.7b00918>.
- 513 [7] Z. Wang, J. Gong, J. Ma, J. Xu, In situ growth of hierarchical boehmite on 2024
514 aluminum alloy surface as superhydrophobic materials, *RSC Adv.* 4 (2014) 14708–14714.
515 <https://doi.org/10.1039/C4RA00160E>.
- 516 [8] V. Vatanpour, S.S. Madaeni, L. Rajabi, S. Zinadini, A.A. Derakhshan, Boehmite
517 nanoparticles as a new nanofiller for preparation of antifouling mixed matrix membranes,
518 *J. Membr. Sci.* 401–402 (2012) 132–143. <https://doi.org/10.1016/j.memsci.2012.01.040>.
- 519 [9] J. Zhang, Q. Ji, P. Zhang, Y. Xia, Q. Kong, Thermal stability and flame-retardancy
520 mechanism of poly(ethylene terephthalate)/boehmite nanocomposites, *Polym. Degrad.*
521 *Stab.* 95 (2010) 1211–1218. <https://doi.org/10.1016/j.polymdegradstab.2010.04.001>.
- 522 [10] A. Boumaza, L. Favaro, J. Lédion, G. Sattonnay, J.B. Brubach, P. Berthet, A.M.
523 Huntz, P. Roy, R. Tétot, Transition alumina phases induced by heat treatment of
524 boehmite: An X-ray diffraction and infrared spectroscopy study, *J. Solid State Chem.* 182
525 (2009) 1171–1176. <https://doi.org/10.1016/j.jssc.2009.02.006>.
- 526 [11] X. Bokhimi, J.A. Toledo-Antonio, M.L. Guzmán-Castillo, B. Mar-Mar, F. Hernández-
527 Beltrán, J. Navarrete, Dependence of Boehmite Thermal Evolution on Its Atom Bond
528 Lengths and Crystallite Size, *J. Solid State Chem.* 161 (2001) 319–326.
529 <https://doi.org/10.1006/jssc.2001.9320>.

- 530 [12] X. Bokhimi, J.A. Toledo-Antonio, M.L. Guzmán-Castillo, F. Hernández-Beltrán,
531 Relationship between Crystallite Size and Bond Lengths in Boehmite, *J. Solid State*
532 *Chem.* 159 (2001) 32–40. <https://doi.org/10.1006/jssc.2001.9124>.
- 533 [13] B.R. Baker, R.M. Pearson, Water content of pseudoboehmite: A new model for its
534 structure, *J. Catal.* 33 (1974) 265–278. [https://doi.org/10.1016/0021-9517\(74\)90270-X](https://doi.org/10.1016/0021-9517(74)90270-X).
- 535 [14] B.C. Lippens, Structure and texture of aluminas, Technical University of Delft, 1961.
- 536 [15] M.L. Guzmán-Castillo, X. Bokhimi, A. Toledo-Antonio, J. Salmones-Blásquez, F.
537 Hernández-Beltrán, Effect of Boehmite Crystallite Size and Steaming on Alumina
538 Properties, *J. Phys. Chem. B.* 105 (2001) 2099–2106. <https://doi.org/10.1021/jp001024v>.
- 539 [16] P. Raybaud, M. Digne, R. Iftimie, W. Wellens, P. Euzen, H. Toulhoat, Morphology
540 and Surface Properties of Boehmite (γ -AlOOH): A Density Functional Theory Study, *J.*
541 *Catal.* 201 (2001) 236–246. <https://doi.org/10.1006/jcat.2001.3246>.
- 542 [17] T. Adschiri, K. Kanazawa, K. Arai, Rapid and Continuous Hydrothermal Synthesis of
543 Boehmite Particles in Subcritical and Supercritical Water, *J. Am. Ceram. Soc.* 75 (1992)
544 2615–2618. <https://doi.org/10.1111/j.1151-2916.1992.tb05625.x>.
- 545 [18] P.H. Hsu, Effect of salts on the formation of bayerite versus pseudo-boehmite, *Soil*
546 *Sci.* 103 (1967) 101–110.
- 547 [19] R. Tettenhorst, Crystal Chemistry of Boehmite, *Clays Clay Miner.* 28 (1980) 373–380.
548 <https://doi.org/10.1346/CCMN.1980.0280507>.
- 549 [20] Y. Hakuta, H. Ura, H. Hayashi, K. Arai, Effects of hydrothermal synthetic conditions
550 on the particle size of γ -AlO(OH) in sub and supercritical water using a flow reaction
551 system, *Mater. Chem. Phys.* 93 (2005) 466–472.
552 <https://doi.org/10.1016/j.matchemphys.2005.03.047>.
- 553 [21] T. Fujii, S. Kawasaki, A. Suzuki, T. Adschiri, High-Speed Morphology Control of
554 Boehmite Nanoparticles by Supercritical Hydrothermal Treatment with Carboxylic Acids,
555 *Cryst. Growth Des.* 16 (2016) 1996–2001. <https://doi.org/10.1021/acs.cgd.5b01584>.
- 556 [22] V. Musumeci, P.S. Camacho, K. Xu, P.J.M. Monteiro, J.S. Dolado, C. Aymonier, Sub-
557 and supercritical hydrothermal route for the synthesis of xonotlite nanofibers for
558 application to green concrete materials, *J. Supercrit. Fluids.* 184 (2022) 105583.
559 <https://doi.org/10.1016/j.supflu.2022.105583>.
- 560 [23] J. Rodríguez-Carvajal, FullProf Suite, (2005).
- 561 [24] J. Rodríguez-Carvajal, Study of Micro-Structural Effects by Powder Diffraction Using
562 the Program FULLPROF, *Lab. Léon Brillouin CEA-CNRS.* 91191 (2003) 11.
- 563 [25] H.D. Ruan, R.L. Frost, J.T. Kloprogge, Comparison of Raman spectra in
564 characterizing gibbsite, bayerite, diasporite and boehmite, *J. Raman Spectrosc.* 32 (2001)
565 745–750. <https://doi.org/10.1002/jrs.736>.
- 566 [26] J.T. Kloprogge, R.L. Frost, Raman microscopy study of basic aluminium nitrate,
567 *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* 55 (1998) 163–169.
568 [https://doi.org/10.1016/S1386-1425\(98\)00178-4](https://doi.org/10.1016/S1386-1425(98)00178-4).
- 569 [27] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B.
570 Bujoli, Z. Gan, G. Hoatson, Modelling one- and two-dimensional solid-state NMR
571 spectra, *Magn. Reson. Chem.* 40 (2002) 70–76. <https://doi.org/10.1002/mrc.984>.
- 572 [28] N. Lock, P. Hald, M. Christensen, H. Birkedal, B.B. Iversen, Continuous flow
573 supercritical water synthesis and crystallographic characterization of anisotropic boehmite
574 nanoparticles, *J. Appl. Crystallogr.* 43 (2010) 858–866.
575 <https://doi.org/10.1107/S0021889810019187>.
- 576 [29] T. Voisin, A. Erriguible, C. Aymonier, A new solvent system: Hydrothermal molten
577 salt, *Sci. Adv.* 6 (2020). <https://doi.org/10.1126/sciadv.aaz7770>.

- 578 [30] E. Duverger-Nédellec, T. Voisin, A. Erriguible, C. Aymonier, Unveiling the
579 complexity of salt(s) in water under transcritical conditions, *J. Supercrit. Fluids.* 165
580 (2020) 104977. <https://doi.org/10.1016/j.supflu.2020.104977>.
- 581 [31] X. Zhang, P.L. Huestis, C.I. Pearce, J.Z. Hu, K. Page, L.M. Anovitz, A.B.
582 Aleksandrov, M.P. Prange, S. Kerisit, M.E. Bowden, W. Cui, Z. Wang, N.R. Jaegers, T.R.
583 Graham, M. Dembowski, H.-W. Wang, J. Liu, A.T. N'Diaye, M. Bleuel, D.F.R. Mildner,
584 T.M. Orlando, G.A. Kimmel, J.A. La Verne, S.B. Clark, K.M. Rosso, Boehmite and
585 Gibbsite Nanoplates for the Synthesis of Advanced Alumina Products, *ACS Appl. Nano*
586 *Mater.* 1 (2018) 7115–7128. <https://doi.org/10.1021/acsanm.8b01969>.
- 587 [32] T. He, L. Xiang, S. Zhu, Hydrothermal Preparation of Boehmite Nanorods by
588 Selective Adsorption of Sulfate, *Langmuir.* 24 (2008) 8284–8289.
589 <https://doi.org/10.1021/la8008514>.
- 590 [33] C.J. Doss, R. Zallen, Raman studies of sol-gel alumina: Finite-size effects in
591 nanocrystalline AlO(OH), *Phys. Rev. B.* 48 (1993) 15626–15637.
592 <https://doi.org/10.1103/PhysRevB.48.15626>.
- 593 [34] A.B. Kiss, G. Keresztury, L. Farkas, Raman and i.r. spectra and structure of boehmite
594 (γ -AlOOH). Evidence for the recently discarded D172h space group, *Spectrochim. Acta*
595 *Part Mol. Spectrosc.* 36 (1980) 653–658. [https://doi.org/10.1016/0584-8539\(80\)80024-9](https://doi.org/10.1016/0584-8539(80)80024-9).
- 596 [35] J. Yang, R.L. Frost, Synthesis and Characterization of Boehmite Nanofibers, *Res. Lett.*
597 *Inorg. Chem.* 2008 (2008) 1–4. <https://doi.org/10.1155/2008/602198>.
- 598 [36] A.J. Casella, T.G. Levitskaia, J.M. Peterson, S.A. Bryan, Water O–H Stretching
599 Raman Signature for Strong Acid Monitoring via Multivariate Analysis, *Anal. Chem.* 85
600 (2013) 4120–4128. <https://doi.org/10.1021/ac4001628>.
- 601 [37] D. Tunega, H. Pašalić, M.H. Gerzabek, H. Lischka, Theoretical study of structural,
602 mechanical and spectroscopic properties of boehmite (γ -AlOOH), *J. Phys. Condens.*
603 *Matter.* 23 (2011) 404201. <https://doi.org/10.1088/0953-8984/23/40/404201>.
- 604 [38] M.-H. Herzog-Cance, A. Potier, J. Potier, Étude, par spectroscopie de vibration, de
605 l'autoprotolyse de l'acide nitrique absolu. Nouvelle interprétation, *Can. J. Chem.* 63
606 (1985) 1492–1501. <https://doi.org/10.1139/v85-256>.
- 607 [39] M. Nguéfac, A.F. Popa, S. Rossignol, C. Kappenstein, Preparation of alumina
608 through a sol-gel process. Synthesis, characterization, thermal evolution and model of
609 intermediate boehmite, *Phys Chem Chem Phys.* 5 (2003) 4279–4289.
610 <https://doi.org/10.1039/B306170A>.
- 611 [40] J.T. Klopogge, L.V. Duong, B.J. Wood, R.L. Frost, XPS study of the major minerals
612 in bauxite: Gibbsite, bayerite and (pseudo-)boehmite, *J. Colloid Interface Sci.* 296 (2006)
613 572–576. <https://doi.org/10.1016/j.jcis.2005.09.054>.
- 614 [41] J.J. Fitzgerald, G. Piedra, S.F. Dec, M. Seger, G.E. Maciel, Dehydration Studies of a
615 High-Surface-Area Alumina (Pseudo-boehmite) Using Solid-State ^1H and ^{27}Al
616 NMR, *J. Am. Chem. Soc.* 119 (1997) 7832–7842. <https://doi.org/10.1021/ja970788u>.
- 617 [42] P. Paluch, N. Potrzebowska, A.M. Ruppert, M.J. Potrzebowski, Application of ^1H and
618 ^{27}Al magic angle spinning solid state NMR at 60kHz for studies of Au and Au-Ni
619 catalysts supported on boehmite/alumina, *Solid State Nucl. Magn. Reson.* 84 (2017) 111–
620 117. <https://doi.org/10.1016/j.ssnmr.2017.01.005>.
- 621 [43] T. Adschiri, Y. Hakuta, K. Sue, K. Arai, Hydrothermal Synthesis of Metal Oxide
622 Nanoparticles at Supercritical Conditions, *J. Nanoparticle Res.* 3 (2001) 227–235.
- 623 [44] T. He, L. Xiang, S. Zhu, Different nanostructures of boehmite fabricated by
624 hydrothermal process: effects of pH and anions, *CrystEngComm.* 11 (2009) 1338.
625 <https://doi.org/10.1039/b900447p>.
- 626 [45] M. Pandey, P. Mishra, D. Saha, K. Sengupta, s. S. Islam, Development of
627 Commercial Trace Moisture Sensor: A Detailed Comparative Study on Microstructural

628 and Impedance Measurements of Two Phases of Alumina, *Electron. Mater. Lett.* 10
629 (2014). <https://doi.org/10.1007/s13391-013-2196-1>.
630 [46] M.W. Ross, T.C. DeVore, Desorption of Nitric Acid From Boehmite and Gibbsite, *J.*
631 *Phys. Chem. A.* 112 (2008) 6609–6620. <https://doi.org/10.1021/jp7110555>.
632