

1 **Structural, textural and thermal characterization of a confined**
2 **nanoreactor with phosphorylated catalytic sites grafted onto a**
3 **halloysite nanotube lumen**

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5 José González-Rivera,¹ Alessio Spepi,¹ Carlo Ferrari,² Iginio Longo,²
6 Jorge Tovar Rodriguez,³ Elvira Fantechi,¹ Claudia Innocenti,^{3,4}
7 Francesco Pineider,¹ Marco Antonio Vera-Ramírez,⁵ Maria Rosaria
8 Tiné^{1*} and Celia Duce¹

9 ¹Department of Chemistry and Industrial Chemistry, University of Pisa,
10 Via G. Moruzzi 13, 56124 Pisa, Italy.

11 ²National Research Council of Italy (C.N.R.), National Institute of
12 Optics, (INO) – UOS Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy.

13 ³Department of Chemistry “Ugo Schiff”, University of Florence, Via
14 della Lastruccia 3, 50019 Sesto Fiorentino, FI, Italy.

15 ⁴ICCOM-CNR, via Madonna del Piano 10, 50019 Sesto Fiorentino, FI,
16 Italy.

17 ⁵Department of Chemistry, UAM-I, 55534, México D.F, 09340,
18 México

19 *Email: mariarosaria.tine@unipi.it

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Abstract

21

22 Mesoporous materials are very attractive solids for the fabrication of
23 confined nanoreactors since they overcome the problems of
24 diffusion/deactivation shown by microporous structures. In this work,
25 we present the fabrication of a confined nanoreactor obtained by
26 functionalization with phosphoric acid of the empty lumen (diameter
27 10-15 nm) of halloysite nanotubes (Hal).

28 Two different halloysite nanoreactors with phosphorylated catalytic
29 sites were prepared by the wet impregnation method followed by
30 thermal activation: 1) phosphate modified Hal (starting with pristine
31 Hal), and 2) phosphate-modified etched Hal (starting with etched Hal
32 obtained by soft-etching pristine Hal using sulphuric acid). The
33 selective grafting of hydrogen phosphate groups onto the aluminol
34 active sites was characterized by solid-state nuclear magnetic resonance
35 (^1H , ^{27}Al , ^{29}Si HPDEC and ^{31}P) and Fourier transform-infrared
36 spectroscopies, and thermogravimetric and nitrogen physisorption
37 analyses.

38 Two different aluminium phosphate (Al-O-P) binding modes,
39 monodentate ($-\text{Al}-\text{O}-\text{P}=\text{O}(\text{OH})_2$) and bidentate ($-\text{Al}-\text{O})_2-\text{P}(\text{OH})_2$), with
40 different distributions were observed in both phosphorylated-Hal

41 nanoreactors. The selective functionalization of the internal lumen was
42 confirmed because no interaction (due to Si-O-P binding mode) was
43 detected between the outer surface of Hal and phosphoric acid.

44 The confined nanoreactors prepared here preserved the main chemical
45 structure and textural properties of Hal. The analysis of the specific
46 surface area and mesopore size showed that, depending on the starting
47 material, grafting the phosphate groups led to the formation of a
48 monolayer or a polycondensation of phosphate moieties inside the
49 tubular mesopore. However, in both prepared nanoreactors,
50 phosphorylation did not result in saturating the material or pore
51 blocking.

52 These mesoporous materials could be used in catalysis and in situ
53 nanoparticle synthesis.

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55 ***Keywords: Halloysite, Nanoreactor, Mesoporous materials,***
56 ***Phosphoric acid.***

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62 **1. Introduction**

63

64 Confined nanoreactors are unique architectures that promote a
65 localized and favorable chemical environment, enabling single
66 molecules to interact with specific catalytic active sites (De Martino et
67 al., 2018; Ye et al., 2020). The compartmentalization of the reactants
68 into the host nanoarchitecture can therefore lead to a higher reaction
69 rate and better selectivity, while preserving the advantages of
70 heterogeneous catalysts (easy recovery, re-use and regeneration) (De
71 Martino et al., 2018; Li and Zeng, 2019).

72 Porous materials are very attractive solid supports for the creation of
73 confined nanoreactors. The internal porous surface can be
74 functionalized with specific active phases, thus forming localized and
75 protected reactive sites in each individual pore or pore framework
76 (Corma, 1997; Eddaoudi et al., 2015). Confined active sites in
77 mesopores and microporous inorganic materials, such as naturally
78 occurring zeolites, halloysite nanotubes, diatomaceous earth, ceramic
79 nanostructures, rare earth metal oxides, and synthetic hexagonal
80 structures such as Mobile Crystalline Materials No. 41, 48 (MCM-41,

81 MCM-48) and Santa Barbara Amorphous-15 (SBA-15), have been
82 widely exploited as catalytic supports thanks to their thermal stability,
83 surface area, and surface chemistry (Corma, 1997; González-Rivera et
84 al., 2014b; Mortazavi-Derazkola et al., 2017; Rangel-Rivera et al.,
85 2018; Zinatloo-ajabshir et al., 2020b; Zinatloo-Ajabshir et al., 2020).
86 Applications have been reported in photocatalysis for environmental
87 remediation (Zinatloo-ajabshir et al., 2017, 2018b, 2018a; Massaro et
88 al., 2020a; Zinatloo-ajabshir et al., 2020a), esterification reactions,
89 (Rangel-Rivera et al., 2018) and cellulose decomposition for biomass
90 conversion (González-Rivera et al., 2014a).

91 The use of these inorganic porous materials, was initially explored
92 due to their intrinsic strong acidity (Lewis and Brønsted catalytic sites),
93 and their non-toxic and non-corrosive character (Verdoliva et al.,
94 2019).

95 However, these aluminosilicate clay minerals usually have a
96 microporous framework (micropore diameter < 2 nm) which have
97 several drawbacks, such as a decrease in the reaction rate, blockage of
98 the pores, or deactivation of the active catalytic sites, due to the slow
99 diffusion of the reactants from the reaction medium into the catalytic
100 support (Corma, 1997; Eddaoudi et al., 2015; Verdoliva et al., 2019).

101 Pore size, in fact, is an important factor in the design of a nanoreactor
102 as it affects the diffusion of the reactants/products towards the active
103 surface/reaction medium. The acid modification of some structures with
104 a large pore size, such as MCM-41, SBA-15 or halloysite nanotubes,
105 has thus been studied (Kawi et al., 2002; Xu et al., 2010; Zhang et al.,
106 2011; Santander et al., 2019). Mesoporous materials can in fact
107 overcome the diffusion/deactivation problems highlighted in
108 microporous structures.

109 Halloysite nanotubes (Hal) are characterised by an empty confined
110 space with a mesopore size of between 10-15 nm making them a very
111 attractive material for the fabrication of nanoreactors. In addition, Hal
112 is a naturally-occurring aluminosilicate with an ordered nanostructure
113 and a characteristically hollow tubular configuration. Over the last few
114 years it has been widely investigated (Zhang et al., 2016; Cavallaro et
115 al., 2018). The dimensions of Hal are at the nanoscale level with a
116 typical external diameter oscillating from 40 to 70 nm and with a length
117 ranging from 500 to 1000 nm. The tubular structure is generally built
118 up by 15 ~ 20 aluminosilicate layers with layer spacing of 10 Å for the
119 hydrated form, or 7 Å for the dehydrated form, respectively (Lvov et
120 al., 2016; Presti et al., 2016).

121 Halloysite has a specific set of physicochemical properties such as
122 biocompatibility (Naumenko et al., 2016), thermal stability (Duce et al.,
123 2015), and defined morphology (Yuan et al., 2015). In addition, given
124 its low cost, widespread availability, and the possibility of easily tuning
125 its surface while preserving its tubular structure, halloysite represents a
126 very promising class of mesoporous materials which is suitable for a
127 variety of applications such as reinforcing and flame retardant agents in
128 the fabrication of polymeric nanocomposites (Du et al., 2010; Lazzara
129 et al., 2018), adsorbent materials for the removal of heavy metals in
130 water (Cataldo et al., 2018), the synthesis of novel organic-inorganic
131 hybrid pigments (Zhuang et al., 2019), and nanocarriers for drug
132 delivery in biomedical applications (Massaro et al., 2019, 2020b; Saleh
133 et al., 2020).

134 Along with the tubular mesoporous shape of Hal, additional
135 interesting characteristics include the different chemical behavior of the
136 surfaces, with a negatively charged external surface (made up of
137 siloxane groups = -Si-O-Si) and a positively charged inner lumen
138 (made up of aluminol groups = -Al-OH). This chemical arrangement
139 and electrostatic behavior have been widely exploited to selectively
140 functionalize the internal or external surface of the Hal. Several active

141 phases, such as metal/metal oxide nanoparticles (Pt-Cu (Gao et al.,
142 2019), Ag (Zeng et al., 2017), Au (Rostamzadeh et al., 2017) Pd
143 (Dedzo et al., 2016; Sadjadi et al., 2019, 2020), Ru (Vinokurov et al.,
144 2017) and ZnO (Massaro et al., 2020a)), ionic liquids (1-(2-
145 hydroxyethyl)-3-methylimidazolium (Dedzo et al., 2016)), proteins
146 (Duce et al., 2017), organic acids (Salicylic acid (Ghezzi et al., 2018),
147 and octadecylphosphonic acid (Yah et al., 2012)), have been used to
148 functionalize the empty Hal tubular lumen and obtain a confined
149 mesoporous reactor. Of these, organic phosphonic acids have shown a
150 high selectivity to covalently bind the aluminol groups of the internal
151 surface (Yah et al., 2012).

152 Phosphoric acid (acting as additive or catalysts) has been used to
153 prepare halloysite-based geopolymers (Zhang et al., 2020), Hal-
154 polyurethane (Gaaz et al., 2018), Hal-polyvinyl alcohols (Qiu and
155 Netravali, 2013), and Hal-polyvinyl alcohol-polyvinyl pyrrolidone
156 (Gaaz et al., 2017) nanocomposites. However, to the best of our
157 knowledge, the use of phosphoric acid to functionalize the internal
158 lumen of Hal has not yet been explored.

159 In this paper, we investigate the preparation of a confined nanoreactor
160 by the phosphorylation of Hal. Under controlled reaction conditions,

161 phosphoric acid covalently binds the aluminol groups of the internal
162 surface of Hal, yielding a phosphorylated nanoreactor.

163 A Hal confined nanoreactor with phosphorylated catalytic sites could
164 lead to new applications of Hal similar to those already reported for
165 phosphorylated aluminosilicate clay materials. Just to give a few
166 examples, H₃PO₄-modified-diatomaceous earth has been used for
167 propene oligomerization to produce environmentally friendly synthetic
168 liquid fuels (Zhang et al., 2015); H₃PO₄/Al₂O₃ to catalyse the
169 decarboxylation reaction in the conversion of oleic acid to biofuels
170 (Raddi de Araujo et al., 2006); H₃PO₄-modified-Si-MCM-41 for the
171 dehydration of isopropanol to propylene (Kawi et al., 2002). H₃PO₄-
172 modified-Al-Si-MCM-41 for the vapor-phase Beckmann rearrangement
173 reaction (Zhang et al., 2011), and H₃PO₄-modified-Si-SBA-15 in the
174 condensation of o-tert-butylaniline with paraformaldehyde (Xu et al.,
175 2010). Lastly H₃PO₄-modified-Al/SBA-15 has been used in the
176 cellulose fast pyrolysis for the production of levoglucosenone
177 (Santander et al., 2019).

178 Together with catalytic applications, due to their confined active
179 lumen, Hal phosphorylated nanoreactors are very attractive materials

180 for the in-situ synthesis of nanoparticles with a controlled shape and
181 size, as they act as nano-templating for particle formation. They are
182 also suitable for the preparation of bifunctional materials (i.e. magnetic
183 catalysts) since they expose an external surface area available for
184 further functionalization.

185 In this work H₃PO₄-grafted-Hal were prepared by a wet impregnation
186 method with H₃PO₄ followed by a thermal activation treatment. We
187 thus exploited both the strong affinity of phosphate groups to
188 covalently bind the internal aluminol groups, and the large pore size
189 (diameter of about 15 nm) of Hal, to obtain a selective functionalized
190 mesoporous material that can be used as a confined nanoreactor.

191 The structural, textural, and thermal properties of H₃PO₄-grafted-Hal
192 were then investigated by solid-state nuclear magnetic resonance (¹H,
193 ²⁷Al, ²⁹Si HPDEC and ³¹P MAS-NMR) and FTIR spectroscopies, N₂
194 physisorption and thermogravimetric analyses, respectively. The
195 different binding modes of hydrogen phosphate groups onto the
196 aluminol active sites of Hal were determined and fully explored.

197 **2. Experimental section**

198 *Materials*

199 Pristine halloysite nanotubes (Hal), sulfuric acid (H₂SO₄, 98%) and
200 phosphoric acid (H₃PO₄, 85%) were purchased from Sigma-Aldrich and
201 used without further purification. Deionized water obtained with a
202 Milli-Q system (Millipore, Bedford, MA, USA) was used as solvent.

203 *Hal acid etching and phosphate functionalization*

204 Hal were initially modified by lumen etching following a procedure
205 already described in detail (Spepi et al., 2016). Briefly, 5 g of Hal were
206 dispersed in 500 mL of a 2 M H₂SO₄ solution. The suspensions were
207 magnetically stirred for 48 h at room conditions (25°C, atmospheric
208 pressure). Hal were then filtrated and washed several times with
209 deionized water (until the pH of the supernatant from the washing stage
210 was in the range 6–7) and finally dried at 70°C leading to acid etched
211 Hal-(H⁺). The phosphoric acid reaction with both: pristine Hal and Hal-
212 (H⁺) was performed by dispersing the substrate materials into a H₃PO₄
213 saturated aqueous solution. The Hal-H₃PO₄ suspensions were evacuated

214 in a vacuum jar for 3 h, and then cycled back to atmospheric pressure.
215 This process was repeated three times in order to increase the H₃PO₄
216 loading efficiency. Finally, H₃PO₄ impregnated Hal were separated
217 from the H₃PO₄ saturated aqueous solution by centrifugation, washed
218 with water and dried in an oven at 70°C for 12 h. The dried H₃PO₄
219 impregnated Hal were activated by a thermal treatment in an oven at
220 320°C for 2 h under static air conditions in order to produce the
221 phosphoric acid modified Hal (Hal-(PO₄)) or etched phosphate
222 modified HNT (Hal-(H⁺-PO₄)) materials. Pristine Hal, Hal-(H⁺), Hal-
223 (PO₄) and Hal-(H⁺-PO₄) were characterized by multinuclear MAS
224 NMR, FTIR, TGA, and N₂ physisorption.

225 *Characterization*

226 *Multinuclear magic angle solid-state magnetic nuclear resonance* 227 *(MAS NMR)*

228 ¹H, ²⁷Al, ²⁹Si HPDEC and ³¹P MAS NMR spectroscopy studies were
229 recorded using a Bruker Avance II 300 spectrometer. All multinuclear
230 MAS NMR measurements were performed at a resonance frequency of

231 300 MHz using a 4 mm ZrO₂ rotor spun at 9 kHz (¹H and ²⁷Al MAS
232 NMR) and 6 kHz (²⁹Si HPDEC and ³¹P MAS NMR). A 4 μs flip angle
233 was used (90°), and the recycling time was 3 s ((¹H and ²⁷Al MAS
234 NMR) and 10 s (²⁹Si HPDEC and ³¹P MAS NMR) with an acquisition
235 time of 10 ms.

236 *Fourier-transform infrared spectroscopy*

237 Infrared spectra were recorded using an FT-IR Agilent Technologies
238 Spectrophotometer model Cary 640, equipped with a universal
239 attenuated total reflectance (ATR) accessory. A few micrograms of dry
240 and purified Hal powder sample were used with the following
241 spectrometer parameters; resolution: 4 cm⁻¹, spectral range: 600–4000
242 cm⁻¹, number of scans: 16. Agilent spectrum software was used to
243 process FTIR spectra.

244 *Nitrogen physisorption*

245 Nitrogen adsorption and desorption isotherms were recorded at 77 K
246 using a Beckman Coulter SA 3100 surface area analyser. All the
247 samples (pristine Hal, acid treated-Hal and phosphate functionalized)

248 were outgassed for 120 min at 50°C under vacuum conditions ($P=10^{-3}$
249 mmHg). The isotherm was measured over the relative pressure range
250 (P_s/P_0) from 0.01 to 0.991. The specific surface area (S_{BET}) was
251 calculated using the Brunauer–Emmett–Teller (BET) equation in the
252 low relative pressure interval from 0.05 to 0.2. The Langmuir model
253 and the t-plot method were used to obtain further information on the
254 size of the monolayer and micropore volume at lower relative pressures
255 ($P_s/P_0 < 0.05$). Total pore volume was determined at the relative
256 adsorption pressure of 0.9814. The pore size distribution was calculated
257 with the adsorption branch of the isotherm using the
258 Barrett–Joyner–Halenda (BJH) method.

259 *Thermogravimetric Analysis*

260 A TA Instruments Thermobalance model Q5000IR equipped with an
261 FTIR (Agilent Technologies) spectrophotometer Cary 640 model for
262 evolved gas analysis (EGA) was used. Thermogravimetric
263 measurements were performed at a rate of 10°C/min, from 25°C to
264 800°C under nitrogen flow (25 mL/min) using Pt crucibles. TG-FTIR
265 measurements were performed at a rate of 20°C/min, from 30°C to

266 900°C under nitrogen flow (70 mL/min), from 500 to 3000 cm^{-1} with a
267 4 cm^{-1} width slit. A background spectrum was taken before each
268 analysis in order to zero the signal in the gas cell and to eliminate the
269 contribution due to the amount of ambient water and carbon dioxide.
270 The amount of sample in each experiment varied between 4 and 8 mg.
271 Mass calibration was performed using certified mass standards, in the
272 range from 0 to 100 mg, supplied by TA Instruments. Temperature
273 calibration was based on the Curie point of paramagnetic metals.

274

275 **3. Results and discussion**

276 Confined nanoreactors with phosphorylated catalytic sites were
277 prepared by reacting the halloysite nanotubes with phosphoric acid to
278 functionalize the Hal hollow lumen by selective grafting of hydrogen
279 phosphate groups onto the aluminol active sites (see Scheme 1). Since
280 etching can increase the loading capacity of Hal by enhancing their
281 textural properties (Abdullayev et al., 2012), we prepared two different
282 confined nanoreactors: 1) phosphate modified Hal (referred to as Hal-
283 PO_4), starting with pristine Hal, and 2) phosphate-modified etched
284 Hal (referred to as Hal- (H^+-PO_4)), starting with etched Hal- (H^+) . Etched
285 Hal- (H^+) were obtained by soft acidic treatment of pristine Hal, as

286 described in the experimental section. The structural, textural and
287 thermal properties of both Hal-(PO₄) and Hal-(H⁺-PO₄) were then
288 investigated by several techniques (multinuclear MAS NMR, FTIR,
289 TGA, and N₂ physisorption) and the results are fully discussed in the
290 following sections. The characterization of parent starting materials
291 (Hal and acid etched Hal-(H⁺)) is also presented for comparison.

292

293 **Scheme 1 above here**

294 **Scheme 1.** Acid treatment of pristine Hal and grafting of the inner
295 surfaces with phosphoric acid.

296 *Structural, textural and thermal characterization of confined*
297 *nanoreactors: Hal-(PO₄) and Hal-(H⁺-PO₄)*

298 The covalent bond formed by the phosphoric acid on the aluminol
299 sites located on the internal surface layer of Hal was confirmed by
300 multinuclear (¹H, ²⁷Al, ³¹P and ²⁹Si) solid-state magic angle spinning
301 nuclear magnetic resonance (MAS-NMR), FTIR spectroscopy, TG, and
302 N₂ physisorption analyses.

303 Table 1 summarizes the main signals which enabled us to identify the
304 main chemical species detected in pristine Hal and Hal-(H⁺), and in
305 phosphate-modified Hal-(PO₄) and Hal-(H⁺-PO₄) in accordance with
306 the literature (Zhao et al., 2002; Zhang and Eckert, 2004; Raddi de
307 Araujo et al., 2006; Abdullayev et al., 2012; Yah et al., 2012; Yuan et
308 al., 2012; González-Rivera et al., 2014b; Huang et al., 2015; Paul et al.,
309 2018). The single chemical shifts detected at -2.2 in the ²⁷Al spectra
310 (Fig. 1-a) and at -93.8 ppm in the ²⁹Si MAS NMR spectra (Fig. 1-b)
311 confirmed that pristine Hal are only built up by octahedral aluminum
312 sites (-AlO₆), while Si atoms are mainly found as Q₃ silicon groups (-
313 Si(OSi)₃OAl₂) (Abdullayev et al., 2012). These structural chemical
314 features were also confirmed by FTIR spectroscopy. In fact, the
315 absorption peaks at 463, 530, 907, 1026 and 1123 cm⁻¹, shown in Fig.
316 2-a, correspond to the vibration modes for the Si-O (deformation), Al-O
317 (vibration), Si-O-Si (in plane stretching) and Si-O (perpendicular
318 stretching), respectively (see Table 1 for the corresponding literature
319 references). Hal-(H⁺), Hal-(PO₄) and Hal-(H⁺-PO₄) showed the same
320 chemical shifts, but with a lower intensity, at -2.2 ppm (²⁷Al) and at -
321 93.8 ppm (²⁹Si) MAS NMR, and the same vibration bands at 463, 530,
322 907, 1026 and 1123 cm⁻¹ in the FTIR spectra (see Figs. 1, 2 and Table

323 1). The main chemical structure of Hal was then preserved after the
324 acidic treatment and phosphoric acid grafting process.

325

326

Table 1 above here

327

328 A new silicon environment (chemical shift at -103.6 ppm in ^{29}Si
329 MAS NMR spectra, Fig. 1-b), with a lower intensity than the main Q^3
330 groups, was identified in Hal-(H^+), Hal-(PO_4) and Hal-(H^+ - PO_4). This
331 signal is related to external surface defects ($-\text{Si}(\text{OSi})_3\text{OH}$) caused by the
332 acidic treatment (slightly stronger signal for Hal-(PO_4) and Hal-(H^+ -
333 PO_4)) (Abdullayev et al., 2012; González-Rivera et al., 2014b).

334 Tetrahedral Si (Q^4 silicon groups ($-\text{Si}(\text{OSi})_4$)) were also detected (at -
335 113 ppm ^{29}Si) in the Hal-(PO_4) and Hal-(H^+ - PO_4) materials. Q^4 Silicon
336 groups may be related to the formation of SiO_2 nanoparticles by the
337 possible partial external surface damage during the phosphoric acid
338 treatment (Abdullayev et al., 2012).

339 Regarding the aluminum species, a new coordination environment of
340 Al atoms was detected (chemical shift at 38 ppm) for the Hal-(PO_4) and
341 Hal-(H^+ - PO_4). This chemical shift corresponds to tetrahedral aluminum
342 bonded to the phosphate group (AlPO_4) (Zhang and Eckert, 2004)

343 which is complemented by the Al-O vibration at 910 cm^{-1} in the FTIR
344 spectra (Fig. 2) (Yuan et al., 2012).

345 The ^{31}P MAS NMR spectra (Fig. 1-c) confirmed the successful
346 binding of Al-O-P and highlighted the nature of the interaction between
347 phosphoric acid and the aluminol groups of the Hal internal surface
348 (Al-OH) in Hal-(PO_4) and Hal-($\text{H}^+\text{-PO}_4$). Signals at -10, -18, and -28
349 ppm were detected and assigned to monodentate ($-\text{AlO-P}=\text{O}(\text{OH})_2$) and
350 bidentate ($-\text{AlO})_2\text{-P}(\text{OH})_2$ arrangements (Raddi de Araujo et al., 2006).

351 FTIR spectra (Fig. 2-a) only showed a broad band in the range of
352 1290 to 1150 cm^{-1} , under which the P=O stretching (1228 cm^{-1}) (Yah et
353 al., 2012), P-O stretching (1186 cm^{-1}) (Huang et al., 2015), and Al-OP
354 stretching (1143 cm^{-1}) (Huang et al., 2015) vibration bands overlapped.
355 The distribution of the Al-O-P binding modes was different for the two
356 modified materials. Hal-(PO_4) showed a higher amount of bidentate ($-\text{AlO})_2\text{-P}(\text{OH})_2$
357 sites, while the monodentate $\text{AlO-P}=\text{O}(\text{OH})_2$ species is
358 more likely formed in the Hal-($\text{H}^+\text{-PO}_4$). Moreover, the lack of any
359 chemical shift at around -35 to -45 ppm in the ^{31}P MAS NMR spectra
360 (see Fig. 1-c), which is associated with Si-O-P binding mode,
361 confirmed that there was no interaction between the outer surface of
362 Hal and phosphoric acid. These results highlight the selective

363 functionalization of the internal lumen of Hal and Hal-(H⁺) with
364 phosphoric acid.

365

366 **Figure 1 above here**

367 **Figure 1.** ²⁷Al (a), ²⁹Si HPDEC (b), ³¹P HPDEC (c) and ultrafast ¹H
368 (d) MAS NMR spectra of Hal, Hal-(H⁺), Hal-(PO₄) and Hal-(H⁺-
369 PO₄).

370

371 Other structural surface changes can be seen by studying the surface
372 groups of Hal, Hal-(H⁺), Hal-(PO₄) and Hal-(H⁺-PO₄) by ¹H MAS
373 NMR. The ¹H MAS spectrum of pristine Hal, shows a broad signal
374 ranging from 1 to 10 ppm (fig. 1-d) with some resolved peaks at 6.9,
375 4.7 and 3.3 ppm. The signals at 4.7 and 3.3 ppm can also be seen in the
376 ¹H MAS spectrum of etched Hal-(H⁺), while there is no longer a peak at
377 6.9 ppm. The chemical shifts at 6.9 ppm and 4.7 ppm are due to the
378 hydration of the internal surface of halloysite nanotubes (physisorbed
379 and interlayer water molecules respectively), while the chemical shift at
380 3.3 ppm may be related to the aluminol groups (Zhao et al., 2002; Paul
381 et al., 2018). Hal and Hal-(H⁺), in fact do not show any signal related to
382 the presence of silanol groups (-Si-OH) (chemical shift at 103 ppm in

383 the ^{29}Si MAS spectrum and at 1.8 ppm in the ^1H MAS spectrum)
384 (Abdullayev et al., 2012; González-Rivera et al., 2014b).
385 FTIR spectroscopy also revealed the presence of Al-OH groups (O-H
386 stretching at 3695 and 3625 cm^{-1}) (Yah et al., 2012; Yuan et al., 2012)
387 and physisorbed water (O-H deformation at 1648 cm^{-1}) (Yah et al.,
388 2012); see Fig. 2-b and Table 1.

389

390 **Figure 2 above here**

391 **Figure 2.** FTIR spectra of Hal and Hal-(H^+), Hal-(PO_4) and Hal-
392 ($\text{H}^+\text{-PO}_4$): (a) wavenumber from 1800-600 cm^{-1} and (b)
393 wavenumber in the -OH group region (3800-3500 cm^{-1}).

394

395 Hal-(PO_4) and Hal-($\text{H}^+\text{-PO}_4$) showed different proton sites and
396 distribution. A broad band with a main peak around 6.9 ppm (due to
397 physisorbed water) was detected for Hal-(PO_4) which probably hid the
398 signals at 4.7 ppm (interlayer water) and at 3.3 ppm (corresponding to
399 the hydroxyl group of phosphates (-P-OH) (Paul et al., 2018). ^1H MAS
400 spectrum of Hal-($\text{H}^+\text{-PO}_4$) showed no signal at 6.9 ppm. Instead, there
401 was a broad band centred at 4.7 ppm, which also hid the signal at 3.3
402 ppm due to the phosphate hydroxyl group of (-P-OH). A small band

403 centred at 1.8 ppm corresponding to Si-OH was detected for both Hal-
404 (PO₄) and Hal-(H⁺-PO₄).

405

406 **Figure 3 above here**

407 **Figure 3.** N₂ adsorption/desorption isotherms for (a) pristine and
408 PO₄ loaded Hal and b) Acid modified and PO₄ loaded Hal-(H⁺),
409 Hal-(H⁺-PO₄) (inset, pore volume distribution)

410

411 This finding suggests that the sulphuric acidic treatment modifies the
412 external surface of these samples, making them more hydrophilic as
413 already found in a pervious work (Spepi et al., 2016), and was also
414 highlighted by the results of the thermal analysis, which will be
415 discussed later.

416 The FTIR spectra of Hal-(PO₄) and Hal-(H⁺-PO₄) still showed peaks at
417 3695 and 3625 cm⁻¹ however their intensity was clearly lower than for
418 Hal and Hal-(H⁺), supporting the idea of Al-O-P bond formation (see
419 Fig. 2-b). The NMR signals were thus likely due, at least in part, to the
420 protons of the mono- or bidentate phosphate group, although it is
421 difficult to associate them with a specific proton, due to the high
422 similarity of the proton chemical environment.

423 Table 2 summarizes the textural properties of Hal, Hal-(H⁺), Hal-
424 (PO₄), and Hal-(H⁺-PO₄) samples. Pristine Hal have a BET surface area
425 of 71 m²/g. The acidic treatment, using a 2 M solution of H₂SO₄,
426 produces an aluminum etching effect that modifies the textural features
427 of the material, increasing the surface area to 114 m²/g. These values
428 are in good agreement with those obtained, in the same conditions, in a
429 previous paper, in which we reported the halloysite etching and lumen
430 modification as a result of acidic treatment at different temperatures
431 (Spepi et al., 2016).

432 Figure 3 shows the N₂ adsorption/desorption isotherms and pore size
433 distributions for both a) Hal and Hal-(PO₄) and b) acid modified Hal-
434 (H⁺) and Hal-(H⁺-PO₄). In line with the classification by IUPAC
435 (Thommes et al., 2015), all samples exhibited a type IV-a isotherm with
436 an H-3 hysteresis loop. All samples showed three well defined regions
437 in the isotherm: a) an initial rapid increase in the nitrogen volume
438 adsorbed, denoting micropore filling and monolayer formation at very
439 low relative pressures, below P_s/P₀=0.02, until an inflexion point can be
440 observed; b) a rectilinear, slowly increasing, section of the isotherm
441 curve, indicative of unrestricted multilayer adsorption, and again c) a
442 rapid increase in the curve, which is a large nitrogen uptake after a

443 second inflexion point, suggesting capillary condensation in the
444 mesopore region. The value of the second inflexion point, at around
445 $P_s/P_0=0.76$ for pristine Hal and Hal-(PO_4) and 0.80 for the acid-treated
446 samples Hal-(H^+) and Hal-($\text{H}^+\text{-PO}_4$) may be related to the higher
447 average mesopore diameter size in the acid-modified samples
448 (Thommes et al., 2015).

449 Concerning the pore volume, the Hal-(H^+) material showed a larger
450 total pore volume than the pristine sample ($0.25 \text{ cm}^3/\text{g}$ compared to
451 $0.16 \text{ cm}^3/\text{g}$ for Hal), which may also be attributed to the acid-promoted
452 metal leaching. The insets to Figures 3a) and 3b) show the desorption
453 pore volume distribution graphs for these materials. The chemical
454 changes induced by the soft acidic treatment may also be responsible
455 for the changes observed in the pore size distribution. The acid-
456 modified samples showed a different pore size distribution, with a
457 higher average diameter (around 24 nm, and 14 nm for the unmodified
458 sample). This could also be due to the partial dealumination of the inner
459 nanotube walls.

460

461

Table 2 above here

462

463 Non-phosphorylated samples showed an H-3 hysteresis loop that
464 is characteristic of plate-like or pillared particles in accordance
465 with the classification by IUPAC (Thommes et al., 2015).
466 Interestingly, after $-\text{PO}_4$ grafting, the isotherm shape did not
467 change, whereas there was a reduction in the width of the
468 hysteresis loop.

469 After phosphate functionalization, Hal-(PO_4) underwent a surface
470 area reduction of over 50% up to a final value of $33 \text{ m}^2/\text{g}$, while
471 the etched Hal-(H^+-PO_4) had a final BET area of $98 \text{ m}^2/\text{g}$, with a
472 surface area reduction of around 15%. This suggests that the loss
473 of aluminol sites in Hal-(H^+), as a consequence of aluminium
474 leaching, may have reduced the amount of reactive sites available
475 for $-\text{PO}_4$ binding. The pore volume of the Hal-(PO_4) material
476 decreased (from $0.16 \text{ cm}^3/\text{g}$ of Hal to $0.12 \text{ cm}^3/\text{g}$ of Hal-(PO_4)),
477 but remained unchanged for the acid treated Hal-(H^+-PO_4). After
478 surface grafting, the pore size distribution of both the materials
479 had a smoother curve.

480

481

Figure 4 above here

482 **Figure 4.** Thermogravimetric curves (a) and their derivatives (b) of
483 halloysite samples performed under N₂ flow at 10 °C/min heating
484 rate.

485

486 The values of the monolayer capacity and surface area S_{BET} ,
487 reported in Table 2, and the phosphate and aluminum site
488 distribution established by ²⁷Al and ³¹P MAS NMR, suggest that
489 Hal-(H⁺-PO₄) grafting may thus be obtained through the formation
490 of a covalently attached monolayer of -PO₄ moieties anchored
491 onto the internal surface of Hal-(H⁺). For Hal-(PO₄), a
492 polycondensation of phosphate groups on the cavity walls of the
493 Hal may have been responsible for the greater reduction in surface
494 area and pore volume, and for the modification in the textural
495 properties of Hal. In both cases, -PO₄ functionalization did not
496 result in saturation of the material or pore blocking.

497 Figure 4 shows the TG (a) and DTG curves (b) of pristine Hal and acid
498 modified Hal-(H⁺), and of phosphorylated Hal-(PO₄), and Hal-(H⁺-PO₄)
499 materials. Hal and Hal-(H⁺) are characterized by the typical four
500 degradation steps reported in the literature (Duce et al., 2015), where
501 the first three mass losses are due to the loss of water (adsorbed,

502 interlayered, and chemically bound, respectively). On the other hand
503 the mass loss at higher temperatures (at around 750°C) can be attributed
504 to the degradation of sulphate impurities, such as alunite or jarosite
505 (Duce et al., 2015; Spepi et al., 2016). The figure shows that Hal-(H⁺)
506 have a lower content of interlayered water than pristine Hal (1.5%
507 compared with 3.1%). In addition the mass loss at about 470°C, related
508 to chemically-bound water, shifts to a lower temperature, suggesting a
509 destabilization of the tubular structure (Spepi et al., 2016).

510 Phosphorylation led to the same effect in both Hal and Hal-(H⁺):

511 i) Hal-(PO₄) and Hal-(H⁺-PO₄), were more hydrophilic than Hal and
512 Hal-(H⁺) (higher mass loss of absorbed water of about 2%, see Fig. 4-
513 a).

514 ii) the mass loss due to interlayered water, at about 250°C, was no
515 longer observed (see Fig. 4-b). This suggests that the phosphate groups
516 bind not only in the inner lumen but also in the interlayer space, by
517 replacing interlayered water molecules.

518 iii) the mass loss at about 470°C, related to chemically bound water,
519 shifted to lower temperatures. This suggests that the PO₄ groups,
520 grafted onto the inner lumen of the nanotubes, also promote a
521 destabilization of the tubular structure (Spepi et al., 2016).

522 iv) the mass loss at about 740°C, related to the sulphate impurities,
523 was no longer observed. This could be due to the action of phosphoric
524 acid. In fact, iron ions have a high affinity for phosphate. This suggests
525 that impurities consist mainly of jarosite (Duce et al., 2015).

526 **4. Conclusions**

527 The selective functionalization with phosphoric acid of the aluminol
528 groups of the positively charged internal surface of Hal led to the
529 successful formation of two confined nanoreactors (Hal-(PO₄) and Hal-
530 (H⁺-PO₄)) with phosphorylated catalytic active sites inside the hollow
531 lumen. The main chemical structure of pristine Hal is maintained after
532 the soft sulphuric acid treatment and phosphoric acid impregnation.

533 Multinuclear MAS NMR enabled us to determine the nature of the
534 interaction between phosphoric acid and the aluminol groups, revealing
535 the presence of two different Al-O-P binding modes with a different
536 distribution in the two modified nanotubes.

537 We believe that our results demonstrate the following:

538 Hal-(PO₄) show a higher amount of bidentate (-AlO)₂-P(OH)₂ sites,
539 while the monodentate AlO-P=O(OH)₂ species is more likely to be

540 formed in the Hal-(H⁺-PO₄). In addition, the lack of NMR signals
541 associated with the presence of Si-O-P bonds, shows that phosphoric
542 acid does not interact with the external surface of Hal, thus confirming
543 the selective functionalization of the internal lumen.

544 Thermogravimetric analysis showed that phosphorylated halloysite
545 nanotubes are more hydrophilic than Hal and Hal-(H⁺). In addition, the
546 disappearance of the mass loss due to interlayered water, suggests that
547 the phosphate groups also bind in the interlayer space, by replacing
548 interlayered water molecules.

549 Lastly, the analysis of the textural properties highlighted that the
550 grafting of the phosphate groups leads to the formation of a monolayer
551 of -PO₄ moieties anchored onto the internal surface of Hal-(H⁺-PO₄),
552 while Hal-(PO₄) nanoreactors are subjected to polycondensation. In
553 both cases, -PO₄ functionalization does not result in the saturation of
554 the material or pore blocking.

555 The phosphorylated confined Hal nanoreactors prepared here could
556 be used in catalysis, nanoparticles synthesis, and composite material
557 preparation. Due to the selective functionalization of the internal
558 surface, they also show great potential for the preparation of

559 bifunctional materials, since they have an external surface area
560 available for further functionalization.

561

562 **CRedit authorship contribution statement**

563 **Jose González-Rivera:** Conceptualization, Investigation, Writing-
564 original draft. **Alessio Spepi:** Investigation. **Carlo Ferrari:** Writing -
565 review & editing.

566 **Iginio Longo:** Writing-review & editing. **Jorge Tovar Rodriguez:**
567 Investigation. **Elvira Fantechi:** Investigation. **Claudia Innocenti:**
568 Writing-review & editing. **Francesco Pineider:** Writing - review &
569 editing. **Marco Antonio Vera-Ramirez:** Investigation. **Celia Duce:**
570 Writing-original draft, Funding acquisition, Writing - review & editing.
571 **Maria Rosaria Tiné:** Conceptualization, Supervision, Funding
572 acquisition, Writing-original draft, Writing - review & editing.

573 **Declaration of competing interest**

574 The authors declare no conflict of interest.

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