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An Overview of Modification, Hybridization and Applications of Saponite

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26 **Abstract**

27 Modification of saponite (Sap) by surface engineering and intercalation chemistry introduces guest
28 species into the structure of Sap and enhances the functionalities of the resultant Sap-based hybrids or
29 composites. This review summarizes and evaluates latest scientific advances in the strategies for
30 surface engineering, intercalation and hybridization of Sap, the insights into the relevant mechanisms,
31 and the properties and applications of the resultant Sap-based materials. Studies have indicated that Sap
32 can be inorganically modified by acid activation, inorganic cation exchange, pillaring, and adsorption.
33 The methods of preparing organo-saponite (OSap) hybrids can be categorized as follows: 1)
34 exchanging the inorganic cations in the interlayer space of Sap with organic cations; 2) covalent
35 grafting of organic moieties or groups onto the surface of Sap; 3) intercalating polymer into the
36 interlayer space of Sap by solution intercalation, and melt mixing or *in situ* polymerization.
37 Organic-inorganic modified Sap can be made through the reactions between organic species and
38 inorganic-modified Sap, or by the combination of inorganic species with organic-modified Sap.
39 Modified Sap exhibits exceptional thermal stability, surface acidity, optical effects and adsorption. As
40 such, the modified Sap can be used for optical materials, adsorbents, catalysts and clay/polymer
41 nanocomposites (CPN). Literature survey suggests that future studies should place emphasis on
42 optimizing and scaling up the modification of Sap, probing the thermodynamics, kinetics and
43 mechanisms of the modification of Sap, endowing Sap with novel functionalities, and accordingly
44 advancing the practical applications of the resultant Sap-based materials.

45 **Keywords:** Saponite; Modification; Hybrid; Adsorbent; Catalyst; Saponite/polymer
46 nanocomposite.

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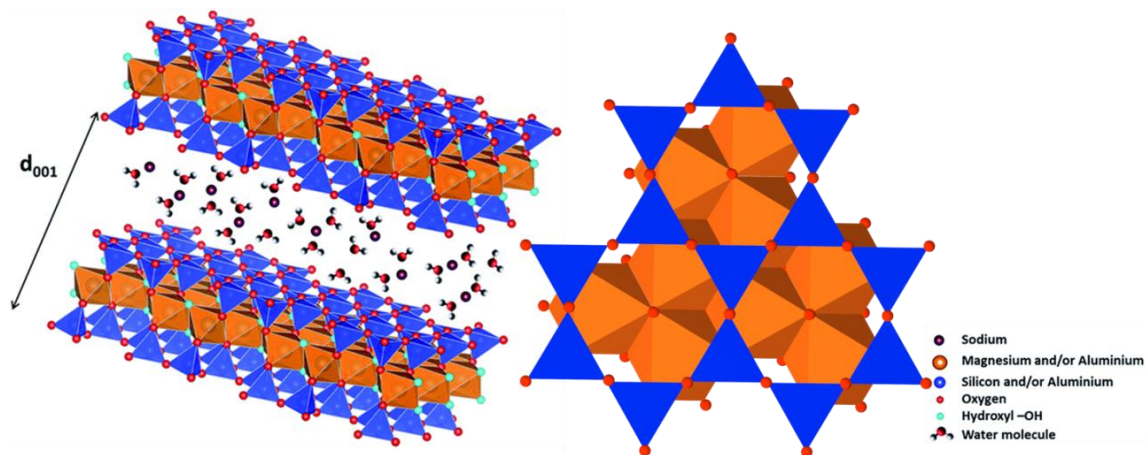
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56 1. Introduction

57 Saponite (Sap) is a 2:1 trioctahedral clay mineral and belongs to the smectite group. Typically, a layer
 58 of Sap is composed of two tetrahedral -O-Si-O- sheets sandwiching a central octahedral -O-Mg-O-
 59 sheet (**Fig. 1**). A small amount of isomorphous substitution of Si^{4+} by Al^{3+} (and possibly other trivalent
 60 cations such as Fe^{3+}) in the tetrahedral sheet causes the layer to be negatively charged. This charge is
 61 compensated by exchangeable interlayer cations including Na^+ , NH_4^+ , K^+ , Li^+ , and Mg^{2+} (M^{z+}). In this
 62 context, the ideal structural formula of Sap can be described as $\text{M}_{x/z}^{z+}[\text{Mg}_6][\text{Si}_{8-x}\text{Al}_x]\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$,
 63 where M^{z+} represents the interlayer cations and x can range from approximately 0.4 to 1.2. The
 64 majority or even all the layer charge of Sap is located on the tetrahedral sheet and this has an important
 65 influence in the properties of Sap. Nevertheless, some studies have suggested that Mg^{2+} in the
 66 octahedral sheet can be substituted by trivalent cations such as Al^{3+} . If Mg^{2+} cations are replaced by
 67 Al^{3+} cations at a ratio of $3\text{Mg}^{2+}/2\text{Al}^{3+}$, the substitution in the octahedral sheet does create additional
 68 positive charges in the layer; If at a ratio of $1\text{Mg}^{2+}/1\text{Al}^{3+}$, positive charges are created in the layer
 69 (Brigatti et al., 2013). The positive charges can partly compensate the negative charges of the
 70 tetrahedral sheet. Mg^{2+} in the octahedral sheet can also be substituted by other divalent cations (Ni^{2+} ,
 71 Co^{2+} , Fe^{2+} , etc.) with no consequence on the layer charge.



72 **Fig. 1. (A) Structure of saponite, two TO_4 ($\text{T}=\text{Si}^{4+}$ and/or Al^{3+}) tetrahedral sheets on each side of an octahedral sheet**
 73 **occupied by magnesium and/or aluminium cations, forming 2D layers (Figure is made by using the VESTA software)**
 74 **(Adapted and Reprinted from Lainé, et al., 2017, Copyright 2017, with permission from Royal Society of Chemistry under the**
 75 **terms of Creative Commons CC By License; Momma and Izumi, 2011). Each TOT layer has a thickness of roughly 9\AA .**
 76 **Compensating cations (here sodium) are present in interlayer space and are surrounded by water molecules. The d_{001}**
 77 **value obtained from X-ray diffraction experiments enables determining the thickness of the interlayer space, and hence,**
 78 **the number of water layers in it (Lainé et al., 2017). (B) Top view of saponite structure (Figure is made by using the 3D**
 79 **Max software).**
 80

81
 82 Saponite has a large specific surface area (SSA), surface acidity and cation exchange capacity
 83 (CEC). In addition, it is distinct from dioctahedral smectites such as montmorillonite (Mt) and
 84 nontronite. For example, Sap has a higher thermal stability than Mt (Casagrande et al., 2005; Vogels et

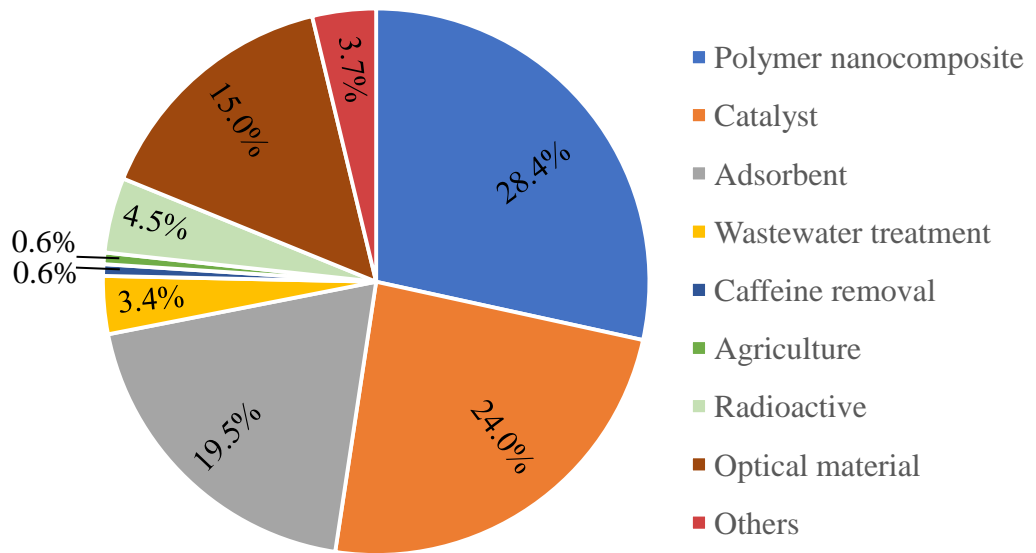
85 al., 2005; Tao et al., 2016); the size of Sap particles (~50 nm) is generally smaller than that of Mt (~300
86 nm) (Ebina and Mizukami, 2007; Paul and Robeson, 2008). In addition, Sap is easier to delaminate and
87 to be exfoliated into nanoplatelets, or even individual nanolayers in water (Takagi et al., 2013).
88 However, naturally occurring Sap is scarce. Due to the presence of impurities in the Sap deposits in
89 nature, laborious and time-consuming purification is required to obtain relatively pure Sap (Carrado et
90 al., 2006). Moreover, the chemical composition of natural Sap can be extremely variable, depending on
91 the geological genesis process (Utracki et al., 2007). This defects limits the use of natural Sap in
92 catalysis (Gómez-Sanz et al., 2017), adsorption (Franco et al., 2016a) and optics (Tsukamoto et al.,
93 2016b). Hence, Sap-like solids with well-controlled chemical composition are synthesized and such
94 solid products are often called synthetic Sap. Generally, typical approach to the synthesis of Sap are
95 hydrothermal synthesis (Suquet et al., 1977; Klopogge, 1999; Zhang, et al., 2009; Jaber et al., 2013;
96 Baldermann et al., 2014; Carniato et al., 2014; Zhang et al., 2017). The process can be modified to be
97 microwave-assisted synthesis (Trujillano et al., 2010; Gebretsadik et al., 2014), and sol-gel synthesis
98 (Garade et al., 2011; Garciano et al., 2014).

99 The synthesis of Sap is relatively mature, at least on a laboratory scale. However, either natural
100 Sap or synthetic Sap is rarely used directly. Under many circumstances the Sap needs modification,
101 including surface engineering, intercalation and hybridization of Sap. Taking advantage of the
102 swellability of Sap (Ferrage et al., 2010; Dzas et al., 2015; Ferrage, 2016), researchers can introduce
103 functional guest molecules into the structure of Sap and thus tune porosity, acidity and other physical
104 and chemical properties. Many types of Sap-based hybrids or composites have been successfully
105 prepared by the intercalation of bulky organic (Kurokawa et al., 2014; Marcal et al., 2015; Sas et al.,
106 2017) and inorganic (Franco et al., 2016b; Miyagawa et al., 2017) cationic species, neutral polar
107 molecules (Marcal et al., 2015) and polymers (Mishchenko et al., 2016; Eguchi et al., 2017) into the
108 interlayer space of Sap. Covalent grafting of a moiety of organic molecules onto the surface of Sap
109 proves feasible. Accordingly, the resultant Sap-based materials have been examined for a wide range of
110 applications. Increasing studies show that such materials can be used as adsorbents (Marcal et al., 2015;
111 Sato et al., 2016), catalysts and catalyst supports (Carniato et al., 2014; Fatimah et al., 2016). They can
112 also be used as a functional additive in clay/polymer nanocomposites (CPN) (Wu et al., 2014; Wang et
113 al., 2015) (**Fig. 2**). Strikingly, Sap has been used as a support for the immobilization of luminescent

114 entities, rendering the resultant nanocomposites with particularities in optical imaging (Tsukamoto et
 115 al., 2016b) and optoelectronic applications (Nanan et al., 2015).

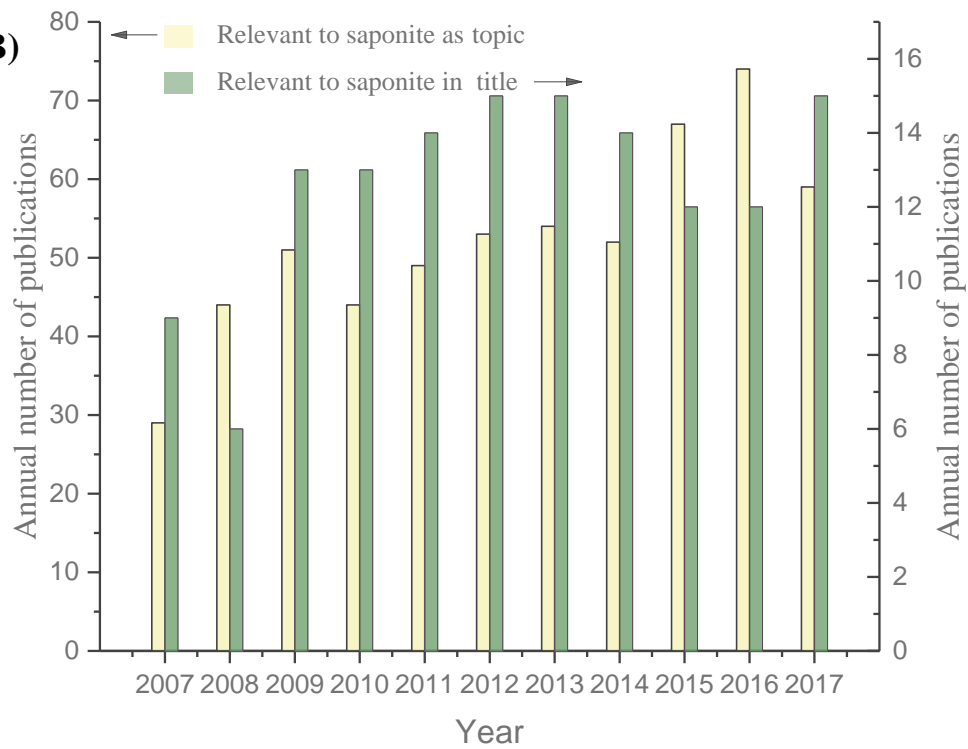
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117 (A)



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119 (B)



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Fig.2 (A) Application category distribution of saponite (by percentage) according to peer-reviewed scientific papers published (from 2007 to end of 2017). (Data from Web of ScinetCore Collection. Search terms: saponite, polymer

138 nanocomposite, catalyst, adsorbent, wastewater treatment, caffeine removal, agriculture, radioactive, optical material) (B)
139 Annual number of peer-reviewed papers published (from 2007 to 2017) relevant to the topics of saponite and the title
140 contain saponite. (Data from Web of SciencetCore Collection. Search terms: saponite).

141 2 Inorganic modification and hybridization of saponite

142 The inorganic modification of Sap is mainly achieved by the exchange of cations M^{Z+} in the
143 interlayer space of Sap with external inorganic cations or the generation of oxides in the form of pillars
144 in the interlayer space of Sap. The frequently-used methods include acid activation (M^{Z+} exchanges
145 with H^+), inorganic cation exchange (exchange with inorganic metal cations), pillaring (M^{Z+} first
146 exchanged with inorganic metal hydroxycations, followed usually by calcination to form oxide pillars),
147 and the hybridization of metal nanoparticles with Sap to form nanocomposite. After such inorganic
148 modifications, the interlayer spacing, the thermal stability and the surface acidity of Sap are usually
149 increased. Thus the resultant Sap-based materials are commonly used as catalysts and adsorbents.

150 2.1 Acid activation and inorganic cation exchange

151 Acid activation refers to the process treating Sap with mineral acids such as sulphuric acid or
152 hydrochloric acid. The final texture and structure of the treated Sap is dependent upon the
153 concentration of the acid used in the process. The product can be H^+ - Sap because merely M^{Z+} cations
154 in the interlayer space of Sap are exchanged by H^+ . It can also be smaller particulate H^+ -Sap if part of
155 Sap particles has been dissolved or damaged by the acid. It is worth noting that the dissolution of Sap is
156 much easier than that of Mt. Hence, the final product can even be an amorphous silica (Komadel and
157 Madejova, 2013). In the former two cases, the H^+ - Sap usually exhibits increased surface acidity, SSA
158 and pore volume (Komadel and Madejova, 2013; Franco et al., 2016b). A recent study shows that the
159 microwave irradiation as heating in the acid activation of Sap can remarkably reduce the time for acid
160 activation (Franco et al., 2016b). Similar to acid-activated Mt (also known as bleaching earth), such
161 acid-activated Sap can be used as adsorbents (Ugochukwu et al., 2014a; Ugochukwu and Fialips, 2017a)
162 and as catalysts (De Stefanis et al., 2013) or catalyst supports (Gebretsadik et al., 2016, 2017b).

163 The inherent nature of acid activation of Sap is a cation exchange reaction. As such, the
164 exchangeable cations M^{Z+} in the interlayer space of Sap are replaced by H^+ ions. Nevertheless, under
165 many circumstances, the dissolution of part of the octahedral and tetrahedral sheets often occurs

166 simultaneously (Kaviratna and Pinnavaia, 1994; Komadel and Madejová, 2013). The dissolution of the
167 whole layer is also possible if the acid is strong enough. As a result, due to the attack by the proton H^+
168 the structural cations are released from the layers, leading the breakage of the layers (Kaviratna and
169 Pinnavaia, 1994; Komadel and Madejová, 2013). Such attack prefers to be at the edge of the layer
170 which is the broken-bond plane, but it can also take place on the oxygen plane.

171 When Sap is treated by mild acid and harsh conditions usually caused by the acid and temperature,
172 the morphology, structure, and texture of the resultant acid-treated Sap appears different (Bisio et al.,
173 2008; Guidotti et al., 2009). When Sap is treated under mild conditions, usually the amount of Brønsted
174 acid sites increases without little alteration of the structure of Sap. In contrast, when Sap is treated
175 under harsh conditions, the cation exchange reaction is also accompanied by progressive dealumination
176 of the framework (layer) of Sap. Accordingly, a significant amount of porous amorphous silica can be
177 produced. Though microporosity and SSA are largely increased, the number of Brønsted acid sites
178 significantly decreases.

179 In addition to acid activation, the original cations M^{z+} in the interlayer space of Sap can also be
180 exchanged with other inorganic cations, such as Li^+ , Cu^{2+} , Ni^+ (Vicente et al., 2011), Zn^{2+} (Intachai et
181 al., 2017), and Fe^{3+} (Franco et al., 2016a). In particular, Cu^{2+} , Ni^+ and Fe^{3+} can be converted into
182 zero-valent metal nanoparticles by appropriate reduction reaction. In this context, two-dimensional Sap
183 acts as a nanoreactor with limited space for generating metal nanoparticles and such metal
184 nanoparticles are -free of organic protectants (Miyagawa et al., 2017).

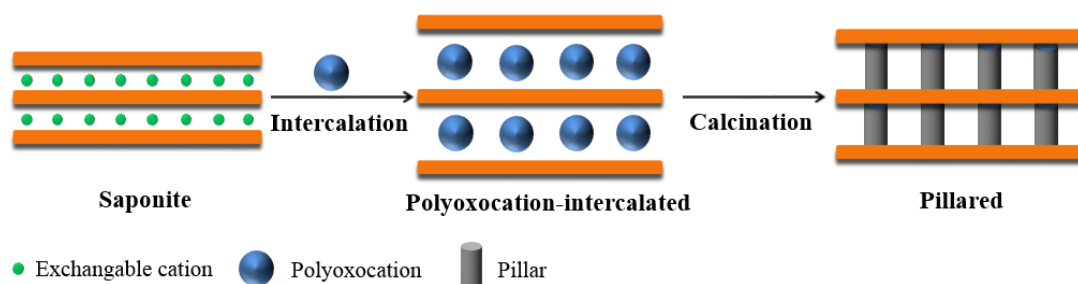
185 **2.1 Pillaring, supporting and hybridization**

186 A typical pillaring procedure of Sap involves the introduction of pre-prepared bulky inorganic
187 metal polyhydroxycations or polyoxocation into the interlayer space of Sap by a cation exchange
188 reaction or the electrostatic attraction, following by calcination, which usually cause dehydration,
189 dehydroxylation and oxidation of the intercalated species (**Fig. 3A**) Hence, the polyoxocations are
190 converted to metal oxide clusters called pillars commonly (Gil et al., 2000). If the solid is calcined
191 under a flow of H_2 , a reduction reaction occurs. Namely, the layered structure of Sap is pillared by the
192 metal oxide clusters. The pillars stably expand the 2:1 layers of Sap, prevent its collapse, expose their
193 internal surface and make the pillared Sap with micro- to mesoporosity (Ding et al., 2001; Vicente et al.,

194 2013). In addition, the pillars bring additional acid sites or redox sites and thus provide catalytic active
 195 species for specific catalysis and adsorption (**Table 1**). Upon the pillaring procedures, the precursors
 196 and the chemical compositions of pillars, the interlayer spacing and the porosity of the pillared Sap
 197 vary.

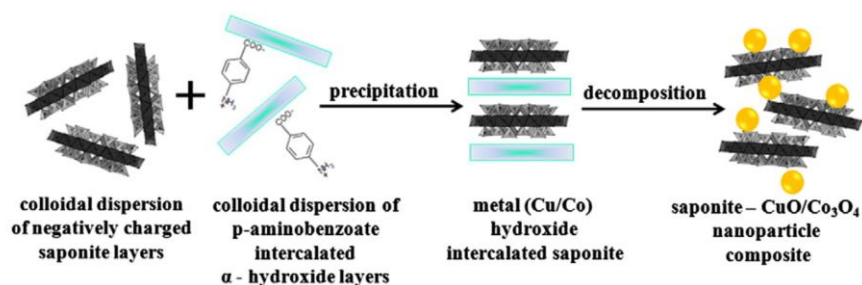
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199 (A)



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201 (B)



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204 Fig. 3 Schematic representation of (A) A typical pillaring process. (B) A process to prepare metal oxide nanoparticle

205 /saponite nanocomposite (Reprinted from Nityashree et al., 2014, Copyright 2014, with permission from Elsevier). The

206 steps mainly include the synthesis of metal hydroxide intercalated saponite and their decomposition to metal oxide

207 nanoparticle /saponite–nanocomposite. Layered α -hydroxide and hydroxysalt [or basic salt] are obtained by intercalating

208 p-aminobenzoic acid (PABA) into the interlayer space.

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210

211 **Table 1. Basal spacing (d_{001}), pore volume, surface area and applications of metal pillared saponite.**

Pillaring agent	Amount	d_{001} [*] (Å)	V_p [*] (cm ³ /g)	S_{BET} [*] (m ² /g)	Applications	Ref.
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Al ₁₃	5mmol/g	17.8	0.188	177		
Cs- Al ₁₃	0.25 wt% ^{a)}	18.0	0.167	95	Catalyst for the synthesis of N-alkyl pyrazoles.	Velasco et al. (2011)
Cs- Al ₁₃	1.25 wt%		0.156	111		
Al ₁₃	5mmol/g	18.0	-	274	Catalyst for acetalation of pentaerithritol	Kannan et al. (2011)
Al	-	17.6	0.120	134		
Fe/Al	Al: 12 mmol/g Fe: 1 mmol/g	18.2	0.130	162	Catalyst for the cracking of polyethylene	De Stefanis et al. (2013)
Zr	-	14.3	0.053	233	Catalyst for the isopulegol hydrogenation	Fatimah et al. (2015)
Ni/Zr	1 wt%	17.0	0.042	199		
Al	10mmol/g	16.6 ^{b)}	0.042 ¹	191. ¹	Photocatalytic phenol photo-oxidation in aqueous solution	Fatimah and Wijaya (2015)
Al-Ti	1.2 wt%	-	0.019 0.019 ¹	132 276 ¹		
Fe	2 mmol/g	12.8	0.160	127	Adsorption of heavy metal cations from water	Franco et al. (2016a)
Al	20 mmol/g		0.180	178		
Magnetite	2 wt%		0.1441	53		
	4 wt%		0.1455	56	Adsorption of dyes from aqueous solution	Makarchuk et al. (2016)
	7 wt%	-	0.1464	53		
	10 wt%		0.3058	69		
Zr	5 wt%	13.4	0.0054	177	Catalyst for the conversion of citronellal into menthol	Fatimah et al. (2016)
S-Zr		15.7	0.0016	190		

212 *For clarity, consistency, and easy comparison, some original data have been rounded off.

213 a) Saponite pillared with Al and then the pillared solid doped with Cs. b) Samples prepared by using microwave irradiation as
214 calcination procedure instead of conventional calcination method. S_{BET}: specific surface area calculated according to the BET
215 equation; V_p = total pore volume; S-Zr: sulphated zirconium pillared saponite.

216

217

218 As the precursors of the pillars, also called pillaring agents, can be metallic cations, metallic oxide
219 sol, polyhydroxycations or polyoxocations (**Table 1**). [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺ usually abbreviated as
220 Al₁₃ is the most widely studied (Trujillano et al., 2009; Kannan et al., 2011; Velasco et al. , 2011).
221 Accordingly, the Al-pillared saponite is well-documented. This is mainly because the preparation of
222 Al₁₃ is very mature and its structure is better understood than that of other cations. In addition, Al₂O₃

223 pillars is thought to possess solid acidity. Particularly, thermal resistance of Al-pillared Sap is higher
224 than that of Al-pillared Mt (Chevalier et al., 1994; Lambert et al., 1994; Bergaoui et al., 1995a,b).
225 Pillars made from polycations which formed by the hydrolysis of Zr^{4+} , Ti^{4+} , Fe^{3+} , or Ga^{3+} (Malla and
226 Komarneni, 1993; Vicente et al., 2008; Fatimah et al., 2015; Fatimah and Wijaya, 2015; Franco et al.,
227 2016a; Makarchuk et al., 2016; Gebretsadik et al., 2017b) has also been reported. It is worth mentioned
228 that Ni^{2+} cation does not form polycations upon hydrolysis. In general, the basal spacing and the pore size of
229 the resultant pillared Sap are inherently decided by the size of the oligomers and accordingly the
230 products after calcination (Vicente et al., 2008; Franco et al., 2016a). In the two-dimensional network
231 of pillared Sap, interlayer spacing is controlled by the height of the pillars, whereas both the distance
232 between the pillars and the height of the pillars known as inter-pillar distance, determines the pore size.
233 The inter-pillar distance also reflects the density of pillars in the interlayer space of Sap. Of great
234 challenge is the interactions between guest pillars and the layers of the Sap. For Al-pillared Sap, the
235 -O-Al-O- on the Al_2O_3 pillars could form covalent bonds with -Al-O and -Si-O on the layer of Sap.
236 However, for many other elements with 4f/5f orbitals, the interactions remain unclear. Possibly
237 theoretical modeling can be conducive to getting more insights into this issue (Bian et al., 2015; Dong
238 et al., 2016). Besides, it has not yet to find an effective way to measure the size and charge of each
239 individual pillar accurately.

240 Though the chemical composition and structure of the metallic cation or its polycation used in the
241 pillaring process play a pivotal role in the characteristics and properties of the pillars in the pillared Sap,
242 other important factors such as the concentration of the pillaring agent (Khumchoo et al., 2016;
243 Makarchuk et al., 2016), the drying method and the calcination temperature (Vicente et al., 2008) have
244 significant effect on the pillars. For instance, recently, Fatimah and Wijaya (2015) found that during
245 the calcination procedure, when microwave irradiation for 15min was used, the Al-pillared Sap with a
246 higher SSA was obtained, compared with the Al-pillared Sap by conventional slow heating for 4h.
247 Inherently, under the two different calcination methods, the conversion of polycations would be
248 different. As conventionally to prepare pillared Sap need a long procedure, rapid microwave irradiation
249 for heating or calcination can shorten the process and much increase productivity.

250 Saponite can also be used as a matrix or support for adsorption of metallic nanoparticles or oxides
251 to produce nanocomposite. To this end, there are such ways as impregnation and deposition. Also the
252 Sap can be pre-modified judiciously if necessary. For example, in the case of Zn, it is deposited as

253 oxide on a cetyltrimethylammonium cation (CTA⁺)-intercalated Sap (Khumchoo et al.,2016) while in
254 the case of Ni, this metal is supported on Sap (Gebretsadik et al.,2017b). Notably, Sap easily
255 delaminates or can be exfoliated in water. By spontaneous flocculation of delaminated Sap, the
256 delaminated or exfoliated Sap can then be used to host other layered nanomaterials (e.g. Co, Cu
257 hydroxide) to form composites (Nityashree et al., 2014). Upon calcination, the metal hydroxide therein
258 decomposes to form metal oxide nanoparticle/Sap nanocomposite in which the nanoparticles get
259 uniformly distributed in Sap matrix (**Fig. 3B**). The particle size of the metal oxide nanoparticles formed
260 in the nanocomposite could be altered by varying factors such as the temperature, atmosphere and
261 duration of decomposition. If the nanoparticles are chosen to be nanosized magnetite, then a magnetic
262 nanocomposite can be achieved (Makarchuk et al., 2016).

263 **3 Organic modification of saponite**

264 Positively charged organic cations can be intercalated into the interlayer space of Sap by cation
265 exchange or adsorption to produce OSap (Zhen and Wang, 2016; Tominaga et al., 2017). The inorganic
266 cations in the interlayer space of Sap, that compensate the negatively charged layer, can be exchanged
267 with positively charged organic cations. Such cations can be formed from surfactants, dye or
268 organometallic complexes in water (Kurokawa et al., 2014; Seki et al., 2015; Sas et al., 2017). The
269 organic cations are not only intercalated in the interlayer space of Sap, but also adsorbed on the surface
270 of Sap to form an electric double layer. Such organic modification of Sap is easily achieved. Studies
271 have demonstrated that during the synthesis process of Sap, OSap can be synthesized in a one-pot way
272 by the direct adding organic cations into the inorganic gel for synthesizing Sap (Bisio et al., 2011;
273 Kurokawa et al., 2014). The surface of Sap is usually hydrophilic and the inorganic cations in the
274 interlayer space tend to be hydrated (Ferrage, 2016). When such places are occupied by organic species
275 after organic modification, the surface is then covered by organic carbon chains or groups, thus the
276 hydrophilic Sap are changed into hydrophobic OSap. Accordingly, the polarity is altered (de Paiva et al.,
277 2008). Besides, a wide range of organic cations, groups or molecules can be used and can perform a
278 variety of functions such as in optical properties (Wu et al., 2015), adsorption (Seki et al., 2010, 2015)
279 and catalysis (Goto et al., 2016). In addition, the inorganic layers of Sap play an active role in
280 stabilizing and protecting the intercalated organic species. Typically, their thermal stability or

281 heat-resistance remarkably increased (Bisio et al., 2011).

282 **3.1 Organic cations**

283 By taking advantage of cation exchangeability of Sap, organic cations can be incorporated into the
284 interlayer space of Sap by a cation exchange reaction. Consequently, organic cations replace the
285 original inorganic cation in the interlayer space of Sap to compensate the negative electric charge in the
286 layer of Sap. Such organic cations are commonly moieties of cationic surfactants such as
287 cetyltrimethylammonium (CTA), benzylammonium (BA), and didecyldimethylammonium (DDDMA)
288 cations. In particular, cationic surfactants have been successfully used as organic modifiers of Mt to
289 produce organo- Mt in industry (Lagaly and Weiss, 1969; Lagaly, 1981, 1986; Yu et al., 2014). In
290 addition, over the last decade, quaternary fulvic acid (QFA), and aminopropyl isobutyl
291 titanosisilsesquioxane (Ti-NH₃POSS) have also been used to modify Sap (**Table 2**).

292 After organic modification, the surface of the Sap becomes hydrophobic from hydrophilic
293 (Ugochukwu et al., 2014b; Ugochukwu and Fialips, 2017b). Depending on the layer charge density
294 (LCD) of Sap, and the chain length or the stereoscopic structure and geometric size of organic cations,
295 the extent to which the inorganic cations are replaced by the organic cations, the organic moieties
296 appear to have several types of arrangements in the interlayer space of Sap. In the interlayer space of
297 Sap, the organic cations may lie flat as a monolayer (Okada et al., 2014) or bilayer (Marcal et al., 2015)
298 pseudo-trilayers or multilayers (Yu et al., 2014). Clearly, the arrangements of organic cations, along
299 with the length of their carbon chains, decide the degree of expansion of the Sap. For example, for
300 BA-intercalated Sap, when BA⁺ cations occur in the form of a monomolecular layer, the cations should
301 be aligned parallel to the oxygen plane of the Sap layer. As a result, the interlayer spacing of BA-Sap can
302 be increased a little by a few Angstroms from the basal spacing 1.26 nm of original Sap (Okada et al.,
303 2014). By contrast, for CTA-intercalated Sap, when an arrangement of bilayer CTA⁺ ions is achieved,
304 the interlayer spacing of Sap increases remarkably by several Angstroms to a few nanometers
305 (Marcal et al., 2015). In this case, the ammonium groups occur like being tethered to the surface Sap
306 layer, and the alkyl chains lay almost vertical to the layers. Moreover, the intercalated organic cations
307 may undergo a conformational change when the thickness of the intercalated molecule is larger than
308 the interlayer spacing of Sap. This conformational change depends on the extent of loadings of organic
309 species and the layer charge density of Sap (Tominaga et al., 2017).

310

311 **Table 2. Characteristics of some organic modified saponite (Sap).**

Modifier	Amounts (modifier/Sap)	Basal spacing (nm)	$S_{BET}^{\#,*}$ (m ² /g)	Interlayer* space (Δd) (nm)	Ref.
Ti-NH ₃ POSS	-	-	-	2.60	Carniato et al. (2009,2011)
CONH	110% CEC	1.51	144	0.55	Seki et al. (2010, 2015)
CTAB	200% CEC	1.43 ^{a)} 1.35 ^{b)}	-	-	Bisio et al. (2011)
BA	50,100% CEC,	1.31, 1.30	-	0.35, 0.34	Okada et al. (2014)
CONH	200% CEC	1.51	-	-	
Arquad 2HT-75	500% CEC	3.60	-	-	Albeniz et al. (2014)
Octadecylamine	50% CEC	1.42	-	-	
OTAB	200% CEC	1.92	-	-	Ugochukwu et al. (2014b, 2017b)
DDDMA	35% CEC	1.40	330(EGME) ♀	-	
CTAB	-	1.84	0.1	0.88	Marçal et al. (2015)
QFA	50 wt%	1.57	-	-	Zhen and Wang, (2016)
BP	10-27% CEC	-	-	0.51-0.55	Tominaga et al. (2017)

312 # The specific surface area (SSA) of the samples was determined by BET equation. ♀ The SSA of the samples was determined
 313 by the EGME (Ethylene glycol monoethyl ether) method (Carter et al., 1965) * For clarity, consistency, and easy comparison,
 314 some original data have been rounded off.

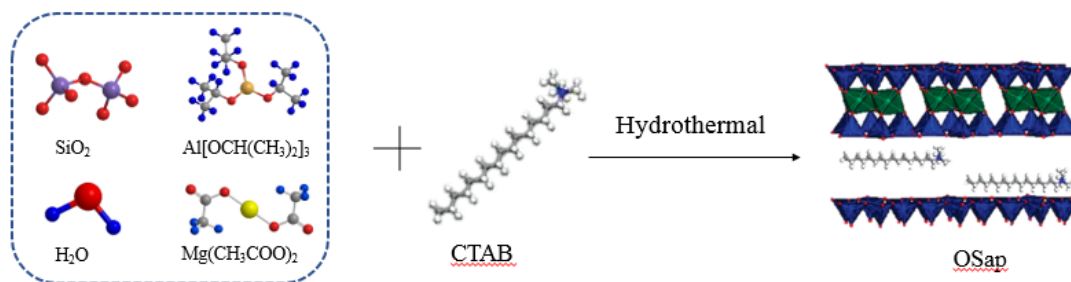
315 ^{a)} One-pot synthesized CTA-Sap. ^{b)} Post synthesized CTA-Sap.

316 Ti-NH₃POSS: aminopropyl isobutyl titanosilsesquioxane; CONH: neostigmine; CTAB: cetyltrimethylammonium bromide; BA:
 317 benzylammonium; OTAB: trimethyloctadecylammonium bromide; DDDMA: didecyldimethylammonium; QFA: quaternary
 318 fulvic acid; BP: biphenyl derivative.

319

320 A one-pot strategy for producing OSap has been developed as an alternative to the
 321 post-modification method of Sap (Roelofs and Berben, 2006; Bisio et al., 2011). This new method can
 322 intercalate organic cations into the interlayer space of Sap by the direct introduction of organic cations
 323 in the gel used for synthesizing Sap during the process (**Fig. 4**). By this methodology the procedure of
 324 producing OSap is significantly simplified and no longer time-consuming. Moreover, a low amount of
 325 surfactant is needed in such a method that thereby lowers the costs of producing OSap. Besides, the
 326 distribution of surfactant molecules could be more homogeneous in the OSap (Bisio et al., 2011)

327



328

329 **Fig. 4 Schematic drawing showing one-pot synthesis of organo-saponite (OSap) (Bisio et al., 2011). CTAB:**

330 **cetyltrimethylammonium bromide.**

331

332 **3.2 Dye molecule**

333 Compared with Mt, Sap is more easily delaminated completely in water to form a transparent
 334 dispersion. Such optical transparency, together with high absorption capacity of Sap, make it a very
 335 good two-dimensional inorganic host for many organic dye molecules with optical functions
 336 (Tsukamoto et al., 2016b), in particular fluorescence. The interlayer space and the layer charge can
 337 provide a static confinement to the fluorescent dyes and is conducive to better distribution and
 338 assembly of the dye molecules, thereby preventing fluorescence from quenching. A variety of dye
 339 molecules, including porphyrin dyes (Takagi et al., 2013; Konno et al., 2014), cyanine dyes (Takagi et
 340 al., 2013; Czímerová et al., 2017; Matejdes et al., 2017), acetylene derivatives (Suzuki et al., 2014),
 341 methylene blue (MB) (Donauerová et al., 2015), triphenylbenzene derivatives (Tokieda et al., 2017),
 342 biphenyl derivative (BP) (Tominaga et al., 2017), laser dyes rhodamine 6G (R6G), oxazine 4 (Ox4)
 343 (Belušáková et al., 2017), and anthocyanin (Ogawa et al., 2017) have been successfully introduced onto
 344 the surface or into the interlayer space of Sap. The driving forces involve cation exchange reactions,
 345 electrostatic attraction, hydrophobic interaction, van der Waals force, physical adsorption and
 346 chemisorption between dye and Sap.

347 Organic dye cations generally tend to aggregate on the surface of Sap, due largely to the
 348 hydrophobic interaction and van der Waals force between organic species (Konno et al., 2014;
 349 Donauerová et al., 2015; Matejdes et al., 2017; Sas et al., 2017; Tokieda et al., 2017). The aggregates
 350 are categorized into two types: H-aggregates and J-aggregates. The former more frequently occurs and
 351 is based on a sandwich-type intermolecular association and absorbs the light of higher energy; the latter
 352 appears less frequent and are formed by a head-to-tail intermolecular association. The types of the

353 aggregates are related to the amount of adsorbed dye cations. At higher ratio of dye/Sap, a large amount
354 of H-aggregates tends to form whereas at the lower ratio of dye/Sap, J-aggregates are preferentially
355 formed (Boháč et al., 2016). The amount of the J-aggregates also increased with the aging of hybrid
356 colloids and is influenced by the solvents (Czímerová et al., 2017). In reverse, segregation of dye
357 cations on the surface of Sap often occurs (Konno et al., 2014). Segregation behavior depends
358 primarily on the chemical structure of the dye cations. Such aggregation drastically reduces the
359 efficiency of the intermolecular photochemical reactions because the functional dye cations are
360 separated from each other in the interlayer space of Sap or on the surface of Sap.

361 The structure of dye assembly on Sap can be effectively controlled by the electrostatic host-guest
362 interaction (Takagi et al., 2013). It includes the intermolecular distance, the molecular orientation, the
363 segregation, aggregation and integration, and the strength of the immobilization. In this context, a
364 size-matching effect have been proposed. In addition, the arrangement of organic fluorescent dyes can
365 be also affected by the layer charge density of Sap (Wu et al., 2015). Hence, it can be tuned by
366 changing the layer charge of Sap. According to a recent study by molecular dynamic simulation, (Wu et
367 al., 2015) as to bis-N-methylacridinium (BNMA)-intercalated Sap, when the layer charge density
368 increased, the electrostatic attraction between the layer of Sap and BNMA became stronger, and
369 BNMA in the interlayer space of Sap tended to arrange in a monolayer parallel to the layer. The parallel
370 orientation suppressed remarkably the molecular aggregation, preserving the photoactivity of dye
371 molecules.

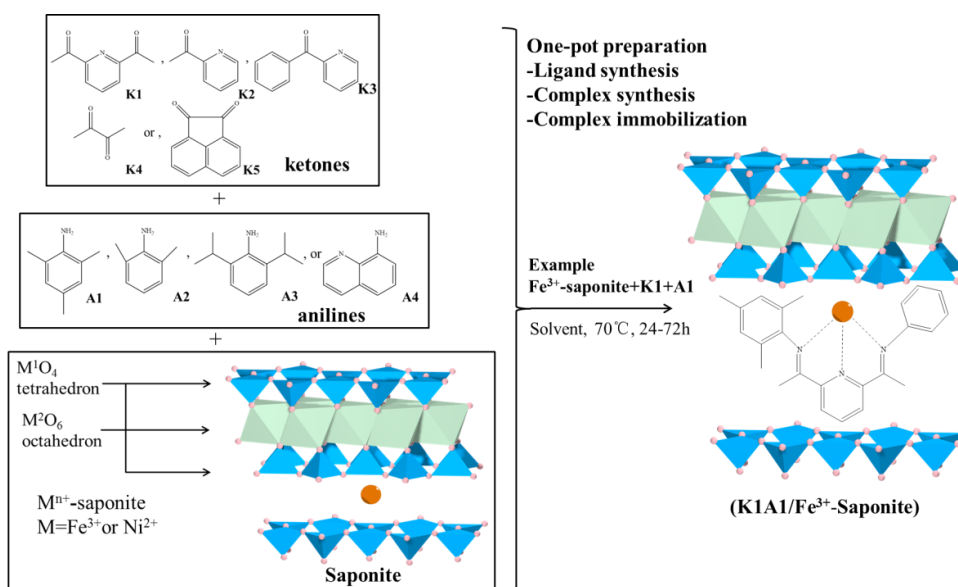
372 **3.3 Organometallic complex**

373 Some organometallic complexes can be introduced into the interlayer space of Sap and interact
374 with the anionic layers of Sap. The confinement of organometallic complexes in the interlayer space of
375 Sap can regulate the molecular structure and the relevant arrangements, and increase the stability of the
376 complexes (Pimchan et al., 2014). Much importantly, the intercalation of organometallic complexes
377 into the interlayer space of Sap brings additional functions caused by the organometallic complexes. In
378 other words, the organometallic complex-Sap hybrids can act as catalysts (Pimchan et al., 2014;
379 Kurokawa et al., 2014; Goto and Ogawa, 2016), catalyst support (Goto and Ogawa, 2015) or optical
380 materials (Sato et al., 2014a; Hosokawa and Mochida, 2015; Tamura et al., 2015; Eguchi et al., 2017).

381 Up to now, many organometallic complexes, including bis(8-hydroxyquinoline)zinc(II) complex
382 (Znq_2) (Pimchan et al., 2014), iridium(III) complexes (Sato et al., 2014a; Tamura et al., 2015), nickel(II)

383 complexes with diketonato and diamine ligands (Hosokawa and Mochida, 2015), tris(2,20-bipyridine)
 384 ruthenium(II) complex ($[\text{Ru}(\text{bpy})_3]^{2+}$) (Goto and Ogawa, 2016), and iron(II)-based
 385 metallo-supramolecular complex polymer (polyFe) (Eguchi et al., 2017) have been used to modify Sap
 386 to produce organometallic complex-Sap hybrids. Typically, the intercalation of an organometallic
 387 complex in the interlayer space of Sap is achieved by exchanging the inorganic cations in the interlayer
 388 space of Sap with cationic organometallic complexes. Recently, a new process to produce
 389 organometallic complexes -Sap hybrids have been developed by Kurokawa et al. (2014) (Fig. 5). In
 390 this process, transition-metal complex/Sap hybrids have been in situ synthesized successfully, instead
 391 the complexes should be pre-synthesized usually. The Fe^{3+} - and Ni^{2+} -exchanged Sap acted as an acid
 392 catalyst and promoted ligand formation from an aniline derivative and a ketone derivative. The formed
 393 ligand then simultaneously coordinated to the metal ions located in the interlayer space of Sap to form
 394 bis(imino)pyridineiron(III), α -diiminonickel(II), and iminopyridinenickel(II) complexes, respectively.
 395 Such methodology tactically combines catalysis, ligand synthesis, complex synthesis and
 396 immobilization together in a one-pot process and can be regarded as a more efficient and cleaner
 397 approach to producing organometallic complex -Sap hybrids.

398



400

Fig. 5 One-pot preparation of transition-metal complex/saponite hybrid (Adapted and reprinted from Kurokawa et

401

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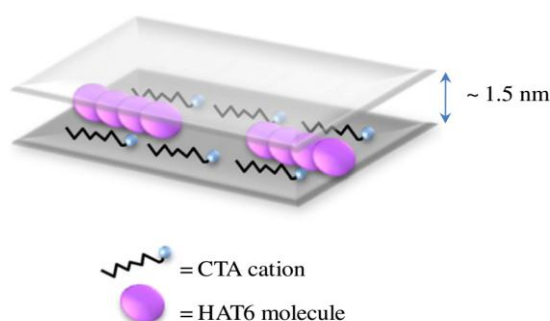
402

403 3.4 Grafting organic moiety and silylation

404 Beside cations, neutral organic molecules can also be intercalated into the interlayer space of Sap.
405 Generally, cation exchange method cannot be used to introduce neutral organic molecules into Sap.
406 Instead, in the case of neutral organic molecules, the possible chemical interactions including covalent
407 bonds, hydrogen bonding, co-ordination, ion-dipole interaction, charge transfer, acid-base reactions,
408 and van der Waals forces can be used (Marcal et al., 2015; Tao et al., 2016). In particular, in grafting of
409 organic moiety onto Sap, covalent bonds between surface -OH groups of Sap and reactive organic
410 groups form. As such, the reactive hydrophobic organic groups durably immobilized on Sap,
411 preventing the organic moiety from leaching (He et al., 2005; Marcal et al., 2015; Tao et al., 2016). By
412 contrast, when organic cation-intercalated Sap is dispersed in solution, the long alkyl chain of organic
413 cations can leach into the medium. In addition to grafting, neutral organic compounds can also form
414 complexes with the interlayer cations of Sap (Kurokawa et al., 2014).

415 In the context of grafting organic moiety onto Sap, silylation, has captured particular attention.
416 The hydroxyl groups (Si-OH-) on the external surface and/or edges of Sap can react with the silyl
417 groups (R₃Si) of silanes to form covalent bonds (Marcal et al., 2015). In particular, the broken edge
418 of Sap possesses active Si-OH, Mg-OH and Al-OH groups (Wu et al, 2015; Honda et al, 2016; Tao et al.
419 2016). Namely, the active groups of Sap readily react with Si-O groups of silane and then produce
420 silylated Sap hybrids (Herrera et al., 2004, 2005; He et al., 2014). After the edge of Sap is silylated with
421 properly-chosen silane, then it is possible for the Sap particles to be linked by silane (Zhou and Keeling
422 2013).

423



425

425 Fig. 6 Schematic drawing of the structure of CTA-HAT6-Saponite hybrid (Reprinted Nanan et al., 2015, Copyright 2015,
426 with permission from Elsevier). CTA: Cetyltrimethylammonium cation, and HAT6: Hexakis(hexyloxy) triphenylene (a

triphenylene-based liquid crystal molecule,)

427

428

429 Alternatively, Sap can be firstly intercalated by organic cations, then the OSap enables neutral
430 organic molecules to be attracted into the interlayer space by hydrophobic interaction. For example,
431 Ishida et al. (2013) successfully prepared a supramolecular host-guest hybrid composed of a cationic
432 organic cavitand (octaamine, OAm, host), two neutral aromatic molecules (pyrene and thracene,
433 guests), and Sap. Due to strong Coulombic attraction between the ammonium groups of OAm and the
434 anionic layer of Sap, the OAm was anchored to the layer of Sap. OAm can then form capsular
435 assembly with organic neutral guest molecules. Namely, the cationic organic cavitand OAm enabled
436 neutral organic molecules to be intercalated into the layer space of Sap. More recently, Nanan et al.
437 (2015) successfully prepared a functional hybrid of a triphenylene-based liquid crystal molecule,
438 hexakis(hexyloxy) triphenylene, and Sap, by the reaction between colloidal Sap in the presence of a
439 cationic surfactant, cetyltrimethylammonium (CTA⁺) cation, and hexakis(hexyloxy) triphenylene
440 (HAT6) (Fig. 6). Such findings mean that one-pot facile process for introducing cationic and neutral
441 organic species into the interlayer space of Sap is a lot feasible.

442 4 Saponite/polymer nanocomposites

443 The idea of Sap/polymer nanocomposites might be borrowed from the Mt /polymer
444 nanocomposites (Lambert and Bergaya, 2013). Similarly, the preparation of Sap/polymer
445 nanocomposites is also achieved by solution intercalation (Jairam et al., 2013; Shin et al., 2013; Yang et
446 al., 2013; Chang et al., 2014; Wu et al., 2014; Wang et al., 2015; Xi et al., 2015; Ju and Chang, 2016;
447 Eguchi et al., 2017; Sas et al., 2017), melt mixing or melt intercalation (Zhen et al., 2012; Kitajima et
448 al., 2013; Zhen and Wang, 2016) or *in situ* polymerization (Jairam et al., 2013; Nakamura and Ogawa,
449 2013; Tong and Deng, 2013; Bandla et al., 2017) (Table 3).

450

451 Table 3. Preparation and properties of typical saponite/polymer nanocomposites.

Saponite (Sap)	Polymer	Method	Conditions	Properties	Ref.
raw Sap	PVA	melt mixing	plasticizer: water and formamide; melt temperature: 115, 135, 125, and 110°C.	coexistence of intercalated and partially exfoliated layers of	Zhen et al. (2012)

			Sap.		
QFA-Sap	PLA	melt mixing	plasticizer: ATBC; melt temperature: 170,180°C.	flocculated structure and partially intercalated morphology of the composite.	Zhen and Wang (2016)
synthetic Sap	QAL	solution intercalation	Lignin content: 30 wt%; solvent: water; stirred overnight; dried in vacuum at room temperature.	30.35±0.15 wt% of lignin was absorbed with Sap.	Jairam et al. (2013)
Sap	PVA	solution intercalation	PVA content: 0-10 wt%; solvent: water; vigorous stirring for 2 h at 80°C; dried at 80°C for 24 h.	thickness of resulting films: 54-63µm.	Shin et al. (2013)
synthetic Sap	PVA	solution intercalation	Sap content: 0-10 wt%; solvent: water; vigorous stirring for 3h; dried at 80°C for 24 h.	thickness of PVA hybrid films: 20-31µm.	Chang et al. (2014)
synthetic Sap	cellulose	solution intercalation	cellulose content: 4 wt%; solvent: LiOH/urea water solution; stirred at 1200 rpm for 10 min; air-dried at ambient temperature.	the longitudinal directions of cellulose and Sap oriented parallel to the film surface.	Yang et al. (2013)
synthetic Sap	TOCN	solution intercalation	Sap content: 0-50 wt%; solvent: water; stirring for 1 h; dried at 40°C for 3 d.	thickness of resulting films: 5.0-11.7µm.	Wu et al. (2014)
HTCC-Sap	PLA	solution intercalation	content of HTCC-Sap: 0.3-5 wt%; solvent: trichloromethane; vigorous stirring in a water bath at 60°C.	thickness of resulting films: about 0.5 mm.	Xi et al. (2015)
QFA-Sap	PLA	solution intercalation	content of QFA-Sap: 0.3-5 wt%; solvent: trichloromethane; vigorous stirring at 60°C for 4 h;	thickness of resulting films: about 0.5 mm.	Wang et al. (2015)
Sap	PAA	solution intercalation	Sap content: 0 to 40 wt%; solvent: DMAc; vigorous stirring at 30°C for 1 h; ultrasonication 6 times for 5 min each; heating at 80°C for 1 h; at 100,130, and 160°C for 30 min.	thickness of resulting films: 68-71µm.	Ju and Chang (2016)
synthetic Sap	RhPEG	solution intercalation	polymer content: 0.05-0.25 wt%; solvent: water; films were prepared using vacuum filtration technique.	-	Sas et al. (2017)
synthetic Sap	Poly-(NIPAm)	in situ polymerization	Sap content: 11, 23 and 46 wt%; monomer: NIPAm; cross-linking agent: 14.8 mmol L ⁻¹ KPS solution; react for 4 h at 70°C under nitrogen atmosphere;	Well-defined spherical particles of poly(NIPAm) hydrogel with the particle size of 800-1300 nm.	Nakamura and Ogawa (2013)
QAL-Sap	PSBA	in situ polymerization	co-stabilizer: hexadecane, AIBN; monomers: styrene, butyl acrylate; at temperature of 80±2°C for 6 h under continuous magnetic stirring; drying at 60°C for 12 h.	mini-emulsions were only stable in lignin-Sap nanohybrid concentrations from 1.6 to 5.2 wt %.	Jairam et al. (2013)

VBTAC-Sap	PS	in situ polymerization	Sap content: 4–30 wt%; co-stabilizer: hexadecane and AIBN; monomer: styrene; degassing with N ₂ at RT for 30 min, and increasing temperature to 80±2°C keeping >6h under continuous mechanical stirring (600 rpm).	asymmetric polystyrene nanoparticles (hemispherical or truncated particles) with a size about 100–500 nm were synthesized.	Tong et al. (2013)
raw Sap	PAAm	in situ polymerization	Sap content: 1–3 wt%; monomer: AAm; solvent: water; initiator: potassium persulfate, accelerator: TEMEDA	The 3 wt% Sap hydrogel showed the highest swelling capacity than other hydrogels.	Bandla et al., (2017)

452 AAm: acrylamide; AIBN: 2, 2 azoisobutyronitrile; ATBC: acetyl tributyl citrate; DMAc: N, N-Dimethylacetamide; HTCC:
453 N-(2-hydroxyl) propyl-3-trimethyl ammonium chitosan chloride; KPS: potassium persulfate; NIPAm: N-Isopropylacrylamide;
454 PAA: poly(amic acid); PAAm: poly acrylamide; PLA: Poly(lactic acid); poly(NIPAm): poly(N-isopropylacrylamide); PSBA:
455 polystyrene co-butyl acrylate; PS: polystyrene; PVA: Poly(vinyl alcohol); QAL: quaternary ammonium lignin; QFA:
456 quaternary fulvic acid; TEMEDA: N,N,N',N'-tetramethyl ethylenediamine; TOCN: 2,2,6,6-tetramethylpiperidinyl-1-oxyl
457 (TEMPO)-oxidized cellulose nanofibrils; RhPEG: rhodamine B (RhB) modified polyethylene glycol (PEG); VBTAC:
458 (ar-Vinylbenzyl) trimethylammonium chloride.

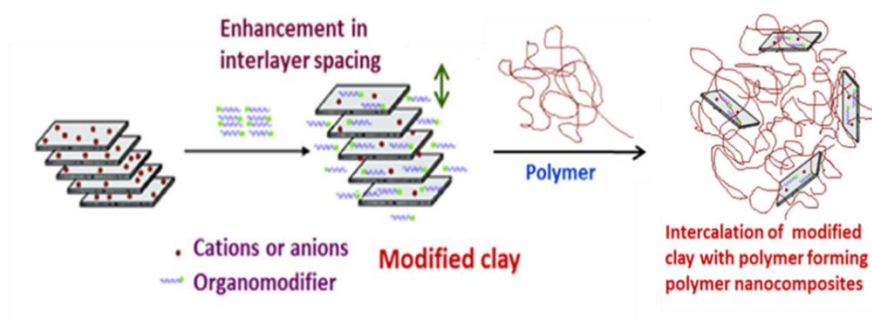
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460 Melt mixing is the simplest method since it is easily operated, economic and environmental
461 friendly (Shen et al., 2002; Pandey et al., 2005; Zou et al., 2008). During melt mixing, Sap is firstly
462 mixed with thermoplastic polymers such as poly(vinyl alcohol) (PVA) and poly(lactic acid) (PLA)
463 (Zhen et al., 2012; Zhen and Wang, 2016). The mixture is then heated to the softening point of the
464 polymer in the presence of a plasticizer. With the mechanic force under heating, the Sap can be
465 exfoliated and dispersed in the polymer matrix to yield a CPN. Comparatively, solution intercalation is
466 a liquid-state process that brings about a good molecular level of mixture of Sap nanolayers and the
467 polymer molecules (Zou et al., 2008). During this process, the soluble polymers (e.g. PVA, PLA,
468 poly(amic acid) (PAA), polyethylene glycol (PEG)) or the dispersion of macromolecules (e.g. lignin
469 and cellulose) in the solution are expected to be introduced into the interlayer space of Sap. Ideally, the
470 polymers are soluble in a certain solvent such as water, aqueous alkali/urea solutions, trichloromethane,
471 N, N-Dimethylacetamide (DMAc), etc. (Jairam et al., 2013; Shin et al., 2013; Yang et al., 2013; Chang
472 et al., 2014; Wu et al., 2014; Wang et al., 2015; Xi et al., 2015; Ju and Chang, 2016; Eguchi et al., 2017;
473 Sas et al., 2017). However, the solution intercalation on an industry scale could be problematic because
474 of the use of cost-intensive solvent and its recovery (Zou et al., 2008). In *in situ* polymerization process,
475 Sap is firstly dispersed into a monomer(s) solution followed by direct polymerization. In this way, the
476 CPN are formed *in situ* (Jairam et al., 2013; Nakamura and Ogawa, 2013; Tong and Deng, 2013;
477 Bandla et al., 2017).

478 Whatever the process is used, an inherent issue is that ever, Sap is hydrophilic whereas polymers
 479 are mostly hydrophobic. This limits the compatibility between Sap layers and polymer chains (Jairam
 480 et al., 2013; Tong et al., 2013). Micro-phase separation often occurs in the CPN owing to the absence
 481 of interfacial interaction between Sap layers and polymer chains. As a result, the intercalation and
 482 uniform dispersion of Sap in the polymer matrix appear difficult (Wang et al., 2015; Zhen et al., 2016).
 483 Therefore, to solve these issues, it is necessary to modify the surface of Sap with organic species to
 484 increase the hydrophobicity of the surface of Sap nanolayers (Wu et al., 2014; Wang et al., 2015). In
 485 addition, the bulky organic species can expand the interlayer space of Sap, allowing easier intercalation
 486 of the polymer chains into the interlayer space of Sap (Kotal and Bhowmick; 2015) (**Fig. 7**).

487 Alternatively, the modification of polymers, instead of modification of Sap, can make the polymer
 488 chains partly hydrophilic, thereby getting compatible with Sap so that polymer chains can well
 489 penetrate into the interlayer space of Sap to produce CPN (Wu et al., 2014; Xi et al., 2015; Sas et al.,
 490 2017). For example, recently, Sas and co-workers (2017) produced a water-soluble and
 491 positively-charged polymer (RhPEG) polyethylene glycol (PEG) with a reactive rhodamine B (RhB)
 492 fluorophore and then RhPEG was successfully intercalated into the interlayer space of Sap by solution
 493 intercalation with a vacuum filtration technique. In addition, certain polymer molecules or their
 494 derivatives can be used to modify Sap first to produce OSap and such OSap is then used with other
 495 polymers to produce CPN (Jairam et al., 2013; Xi et al., 2015)

496



497

498 **Fig. 7. Schematic drawing of modification of saponite followed by intercalation of polymer to form clay/polymer**
 499 **nanocomposites (CPN) (Reprinted Kotal and Bhowmick, 2015, Copyright 2015, with permission from Elsevier).**

500

501 Recently, bionanocomposites have attracted much attention (Shchipunov et al., 2012a,b; Migal, et
 502 al., 2016). The conventional methods to produce CPN cannot be directly used to produce

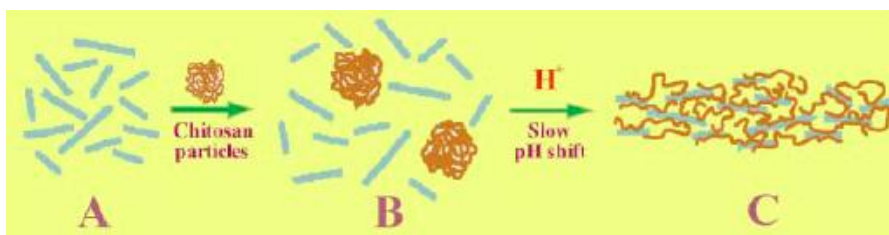
503 Sap/biopolymer nanocomposites. Firstly, melt intercalation does not work since the majority of
504 biopolymers suffers from degradation upon heating. Secondly, the *in situ* polymerization, which starts
505 polymerization from monomers in dispersion of Sap, can also not be used, because under such a
506 circumstance the synthesis of biomacromolecules such as polysaccharides and proteins seems
507 impossible (Shchipunov et al., 2012a,b). In addition, Sap/biopolymer nanocomposites cannot be made
508 by a conventional solution intercalation because the flocculation or the precipitation caused by
509 cooperative electrostatic interactions between biomacromolecules and Sap nanoparticles, for example
510 the oppositely charged polysaccharide and Sap nanoparticles, usually occur (Shchipunov et al., 2009).

511 Chitosan, natural cationic polysaccharide containing free amino groups, have been intercalated
512 into Sap (Shchipunov and Postnova, 2010; Shchipunov et al., 2012a,b; Budnyak et al., 2016; Migal et
513 al., 2016). Shchipunov et al. (2009) demonstrated an effective way to achieve monolithic chitosan /Sap
514 hydrogel by shifting the pH of the reaction solution). The procedure to form Sap/chitosan hydrogel
515 nanocomposites includes several steps (**Fig. 8A**): (1) dispersing of chitosan in an aqueous dispersion of
516 Sap nanoparticles at a pH value corresponding to the neutral state of chitosan, (2) gradually acidifying
517 the dispersion medium to make chitosan macromolecules positively charged, and (3) forming network
518 structure via electrostatic attraction between Sap nanoparticles and chitosan macromolecules. These
519 physical cross-linked, a three-dimensional network exhibited a gradual increase in the viscosity and
520 finally got hydrogellation in later studies have also suggested that in such a hydrogel, part of the
521 protonated amino groups of chitosan were electrostatically cross-linked to the oppositely charged
522 surface of delaminated Sap nanoparticles in an aqueous solution (Shchipunov et al., 2012b; Budnyak et
523 al., 2014). Recently, Budnyak et al. (2016) revealed that the interaction between chitosan with Sap
524 involves both the electrostatic attraction and hydrogen bonding (**Fig. 8B**). It is noteworthy that this
525 method and the chitosan/Sap system can also be used to fabricate CPN films, similar to the structure of
526 mollusk shells (Shchipunov et al., 2012a).

527

528 (A)

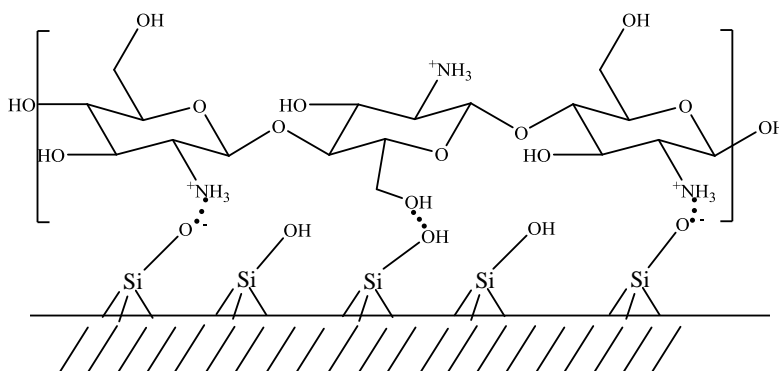
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531

532 (B)



533

534 Fig. 8 (A) Schematic drawing of main stages of formation of monolithic hydrogel by chitosan and saponite (Reprinted

535 from Shchipunov et al., 2009, with permission from The Royal Society of Chemistry). (B) Schematic diagram showing that the

536 interactions between chitosan and saponite involves the electrostatic interaction as well as hydrogen bonding (Reprinted

537 from Budnyak et al., 2016, Copyright 2016, with permission from Springer under the terms of the Creative Commons

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539

540 5 Organic - inorganic hybridization

541 Organic-inorganic modified Sap can be prepared through the reaction between organic species and

542 inorganic-modified Sap, or by combining inorganic species with organic-modified Sap. The

543 organic-inorganic modification of Sap can be achieved by the *in situ* polymerization of polymers in

544 pillared Sap (Zhen et al., 2014) or pillared organic Sap (Albeniz et al., 2014; Zhen and Sun, 2014; Zhen

545 and Zheng, 2016) and the formation of metal nanoparticles in organically modified Sap

546 (Venkatachalam et al., 2013; Khumchoo et al., 2015; Bandla et al., 2016).

547 The pillaring treatment of Sap can improve cation exchange and enlarge the interlayer space of

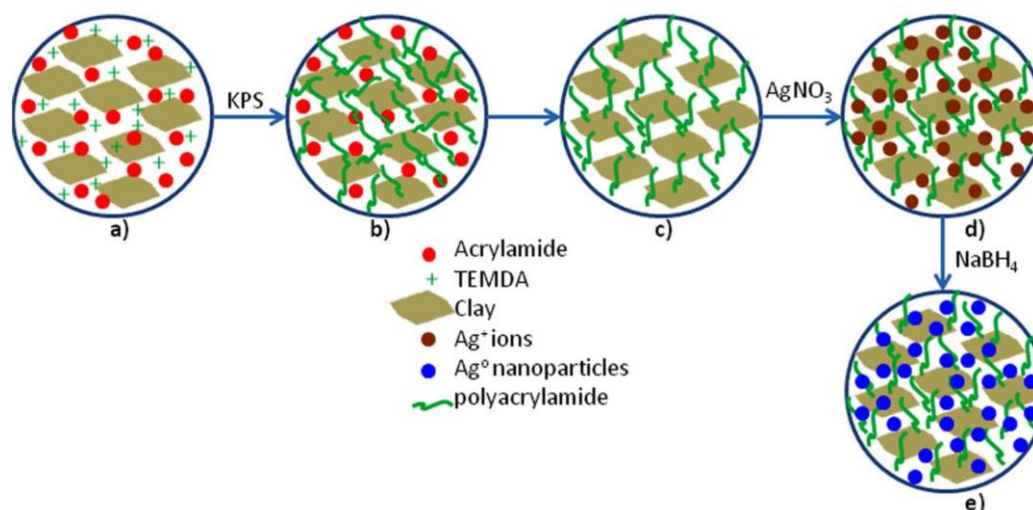
548 Sap, hence allowing the smooth insertion of polymer chains into the interlayer space of Sap during the

549 preparation of CPN by *in situ* polymerization (Zhen et al., 2014). However, the interfacial compatibility

550 between pillared Sap and the polymer is very low and the organic modification of pillared Sap can be
551 used to solve this problem efficiently (Zhen and Sun, 2014; Zhen and Zheng, 2016). The pillared and
552 organic pillared Sap help in eliminating the toxic effects in the *in situ* polymerization process of
553 polymers and facilitate the green polymerization of polymers. Moreover, pillared and organic pillared
554 Sap can accelerate the crystallization process of polymer matrixes, hence improving their thermal
555 stability.

556 In addition, the organically modified Sap can be used to stabilize and tune the size and
557 morphology of metal nanoparticles in the interlayer space. The interaction of the organic species and
558 Sap layers can affect the properties of the metal nanoparticles (Venkatachalam et al., 2013; Khumchoo
559 et al., 2015; Bandla et al., 2016). For example, Khumchoo et al. (2015) found that the
560 photoluminescence intensities and energy of zinc oxide in CTA-Sap were controlled by the host–guest
561 interactions of Sap and CTA. Bandla et al. (2016) presented a new process of developing silver
562 nanoparticles via the reduction of silver ions with NaBH₄ in aqueous solutions, using Sap/poly
563 acrylamide (PAAm) nanocomposite hydrogels (**Fig. 9**). The AgO nanoparticle-containing hydrogel
564 exhibited a strong antibacterial activity against two bacteria. These agents can easily find applications
565 in wound and burn dressings. The incorporated organic compound not only entered the interlayer space
566 of Sap, but also coated on the structural unit layer of the outer surface of Sap. In such
567 inorganic–organic hybrids, the nanospace of Sap can be tuned by spatially controlling the number and
568 size (molecular structure) of the organic moieties, which affects their spatial distribution (Okada et al.,
569 2014; Marcal et al., 2015).

570



571

572 Fig. 9 Schematic representation of formation of AgO nanoparticle hydrogel (Reprinted from Bandla et al., 2017,
573 Copyright 2017, with permission from John Wiley & Sons). KPS: potassium persulfate; TMEDA: N,N,N',N'-tetramethyl
574 ethylenediamine.

575 **6. Applications**

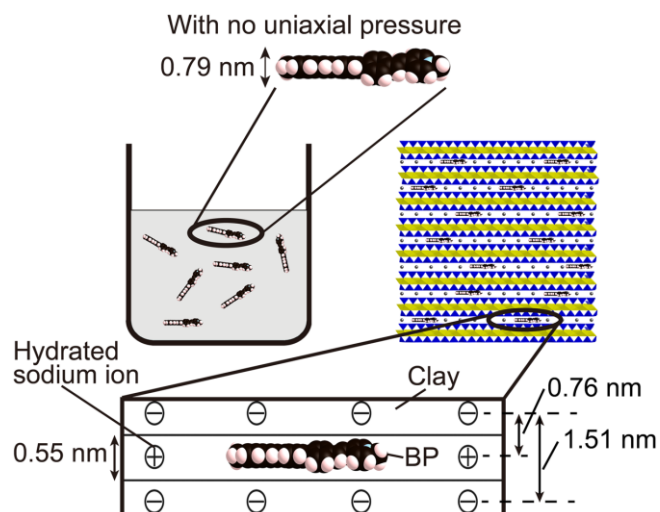
576 Earlier, Sap and its modified hybrids are often considered to be used as adsorbents (Marcal et al.,
577 2015; Seki et al., 2015; Sato et al., 2016), catalysts and catalyst supports (Carniato et al., 2014; Fatimah
578 et al., 2016). Over the last decades, increasing studies aim at using Sap as functional additives in CPN
579 (Wu et al., 2014; Wang et al., 2015). It involves improving mechanical properties, gas permeability,
580 degradation, thermal stability and flame retardancy of the CPN. More recently, Sap has also been used
581 as a support for the immobilization of luminescent entities to prevent fluorescence from quenching by
582 suppressing dye molecular aggregation and promoting luminescent energy transfer between donor and
583 acceptor dye pairs inside the interlayer space of Sap. In addition, dye molecules may exhibit unique
584 optical imaging (Tsukamoto et al., 2016b) and optoelectronic properties (Nanan et al., 2015).

585 **6.1 Optical materials**

586 Among clay minerals, Sap could be the most ideal host materials for the immobilization of
587 luminescent entities. Firstly, Sap easily delaminates to single nanolayers in water. Secondly, such an
588 aqueous dispersion of Sap is transparent in the range of UV–visible light. Thirdly, Sap itself is not
589 photo or redox active (Tsukamoto et al., 2016b). Fourthly, many luminescent organic dye molecules or
590 cations can be facilely introduced into the interlayer space of Sap to produce clay-based
591 nanocomposites. In this way, the aggregation of luminescent entities can be controlled so their
592 luminescent intensity can be stabilized or enhanced. In addition, the luminescent energy transfer
593 between donor and acceptor dye pairs in the interlayer space of Sap can be promoted. Thus the
594 resultant clay-based nanocomposites exhibit unique optical properties.

595 During fabricating luminescent materials, the aggregation of luminescent dye molecules often
596 occurs. The formation of irregular aggregates, such as H-aggregates, which are sandwich-type
597 structured molecular assemblies (Donauerová et al., 2015), significantly decreases the excited-state
598 lifetime of luminescent dye molecules. Moreover, irregular aggregates could lead to fluorescence

599 quenching or lower photoactivity (Takagi et al., 2013; Bujdák et al., 2016). Hence, suppressing the
 600 aggregation of luminescent dye molecules is a critical issue. Saponite has a rigid structure and can
 601 provide a confined microenvironment to luminescent molecules on a nanoscale. Hence, in the
 602 interlayer space of Sap, J-aggregates with a more open geometry in which the luminescent dye
 603 molecules better contact with the surface of Sap become favorable (Epelde-Elezcano et al., 2016). A
 604 good dye distribution in the interlayer space of Sap can be achieved reducing molecular aggregation.
 605 The net negative charge at the external tetrahedral sheet in the films of Sap permits strong electrostatic
 606 Sap-dye interactions in a dye molecule/Sap hybrid. These interactions are conducive to suppressing dye
 607 molecule aggregation. They can also increase luminous intensity of the dye molecules and extend the
 608 fluorescence lifetime (Wu et al., 2015; Epelde-Elezcano et al., 2016; Boháč et al., 2016; Bujdák et al.,
 609 2016). In addition, in a confined microenvironment of the interlayer space of Sap, the dye molecules
 610 have to occur in a parallel orientation with respect to the surface of the Sap nanoparticles (Tominaga et
 611 al., 2017) (**Fig. 10**). Moreover, dye molecules in the interlayer space of Sap may undergo a
 612 conformational change when the thickness of the intercalated molecule is larger than the interlayer
 613 spacing of the Sap. Such intercalation renders a pseudo uniaxial pressure to an organic molecule
 614 under ordinary temperature and pressure. In a high hydrostatic pressure field, the organic molecule
 615 favors a planar conformation. Intercalating the fluorescence dye into the interlayer space of Sap
 616 represents a promising progress in developing inorganic-organic luminescent hybrid films of high
 617 performance.



620

621 **Fig. 10 Schematic representation of molecular confinement of biphenyl derivative (BP) in solution and in a hybrid film**
622 **fabricated at 27% CEC. Sodium ions and anion sites in the smectite are indicated by circles that contain plus and minus**
623 **signs, respectively (Reprinted from Tominaga et al., 2017, Copyright 2017, with permission from Springer Nature under**
624 **the terms of Creative Commons CC By License).**

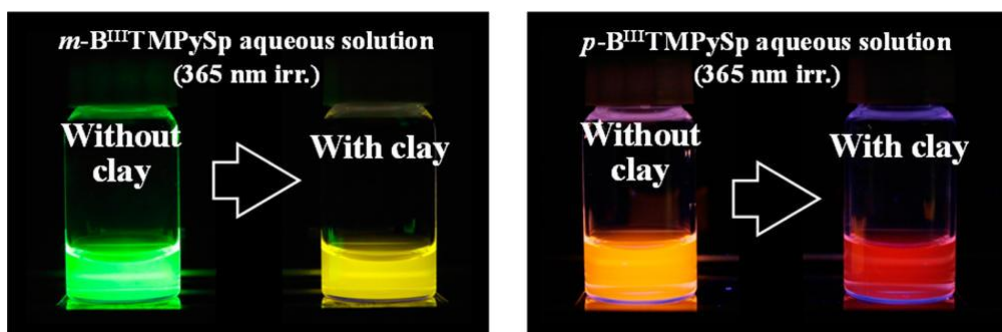
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626 Aggregation of luminescent dye molecule can be further tuned by the co-adsorption of
627 alkylammonium cations because they compete with dye cations for adsorption sites, thereby isolating
628 each dye molecule and suppressing the aggregation (Belušáková et al., 2015; Donauerová et al., 2015;
629 Epelde-Elezcano et al., 2016). In other words, co-intercalation of alkylammonium cations in the
630 interlayer space of Sap allows potential fluorescent J-aggregates rather than undesirable H-aggregates
631 (Epelde-Elezcano et al., 2016). It is noteworthy that the layer charge of Sap and the solvents also
632 remarkably affect the aggregation of luminescent dye molecule in the interlayer space, hence
633 influencing the properties of the Sap/dye hybrids (Wu et al., 2015; Czímerová et al., 2017).

634 Luminescent energy transfer is the dynamic process and occurs via the excited state of a donor dye
635 molecule (Calzaferri, 2012; Verma and Ghosh, 2012; McLaurin et al., 2013). The process plays a
636 critical role in natural and artificial photochemical processes such as photosynthesis, photo-sensitized
637 molecular transformation and solar cells (Gust et al., 2009; Hasobe, 2013). Intercalating luminescent
638 cationic dye species in the confined interlayer space of Sap can promote Förster resonance energy
639 transfer (FRET) between donor and acceptor dye pairs (Ishida et al., 2013; Olivero et al., 2014; Sato et
640 al., 2014b; Belušáková et al., 2015; Goto et al., 2015; Fujimura et al., 2016; Tsukamoto et al., 2016a;
641 Belušáková et al., 2017). In addition, FRET is sensitive to surface concentration, which could be easily
642 controlled by an appropriate selection of the dye/Sap ratio (Belušáková et al., 2017). Promoting FRET
643 between donor and acceptor dye pairs in the interlayer space of Sap provide a new way for developing
644 new artificial light harvesting systems.

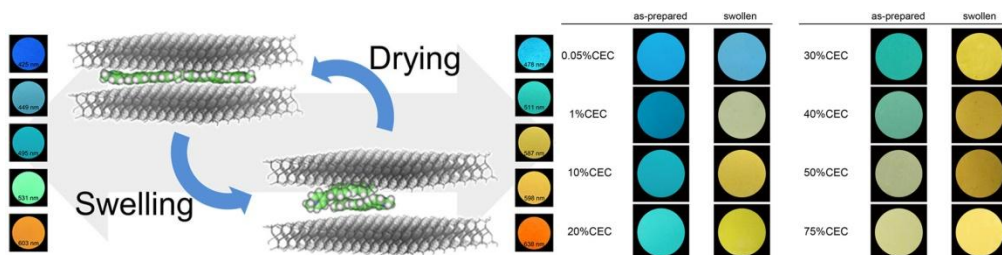
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648 (B)



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Fig. 11. (A) Changes in fluorescence color of $m\text{-B}^{\text{III}}\text{TMPySp}$ and $p\text{-B}^{\text{III}}\text{TMPySp}$ without and with the saponite excited at 365 nm in water. [subporphyrin] = 2.7×10^{-6} M (0.4% versus CEC of the saponite) (Reprinted with permission from Tsukamoto et al., 2016b. Copyright (2016) American Chemical Society). (B) Fluorescence colors of saponite-DPDP hybrid films with various %CEC loading. Left and right columns correspond to the as-prepared and swollen states, respectively. DPDP:4,4'-[4,1-phenylenedi-2,1-ethenediyl]bis[1-methylpyridinium] diiodide (Adapted and reprinted with permission from Tominaga et al., 2016. Copyright (2016) American Chemical Society)).

Luminescent dye-Sap complexes can act as highly sensitive sensors and can be used in artificial photosynthesis systems (Tominaga et al., 2016; Tsukamoto et al., 2016b; Ogawa et al., 2017). For example, Tsukamoto et al. (2016b) intercalated two types of meso-substituted +3-charged subporphyrin derivatives having m-methylpyridinium and p-methylpyridinium ($m\text{-B}^{\text{III}}\text{TMPySp}$ and $p\text{-B}^{\text{III}}\text{TMPySp}$) into the interlayer space of Sap. The photo- or optical properties, with and without the anionic layers of Sap of the two subporphyrin derivatives proved to be different. The absorption and fluorescence spectra of subporphyrin-Sap complexes shifted to longer wavelengths because of luminescent molecules lying flat on the surface of Sap. Changes in fluorescence color of $m\text{-B}^{\text{III}}\text{TMPySp}$ and $p\text{-B}^{\text{III}}\text{TMPySp}$ without and with the Sap excited at 365 nm in water can be observed (Fig. 11A). Tominaga et al. (2016) prepared chromic hybrid films consisting of fluorescent organic molecules with planar π -conjugated systems and synthetic Sap. The swelling and drying of Sap can reversibly switching fluorescence color (Fig. 11B). In the hybrid films, the organic molecules formed an excimer in the swollen interlayer space of Sap, whereas they were a monomer in the dried interlayer space. The emission wavelengths of the excimer and monomer were different, leading to the switching

671 fluorescence color of the hybrid films. Formation and deconstruction of the excimer can be controlled
672 under a mild external stimulus. Moreover, the color switching can be repeated for many cycles. The
673 findings imply that both the confined microenvironment by the interlayer space of the Sap and the
674 reversible swellability can be used for switching optical properties of the resultant hybrids and such
675 intelligent methodology and mentality can be extended to make many other smart materials with
676 switchable properties.

677 **6.2 Adsorbents**

678 Saponite can be used as cation exchangers and adsorbents to remove radioactive ions in nuclear
679 wastes (Srinivasan, 2011; Sato et al., 2016; Adraa et al., 2017; Sato and Hunger, 2017). It can also be
680 applied to separation of heavy metals from wastewater and fixation of the hazardous cations in soil
681 (Budnyak et al., 2016; Franco et al., 2016a; Petra et al., 2017). After organic modification of Sap, the
682 affinity of OSap for organic species is increased and thus can be used to remove dyes and pigments
683 from wastewater (Nakamura and Ogawa, 2013; Makarchuk et al., 2016; Tangaraj et al., 2017). It can
684 also be used to remove carcinogens from foods and food additives (Seki and Ogawa, 2010; Carraro et
685 al., 2014; Marcal et al., 2015; Okada et al., 2015; Seki et al., 2015).

686 **6.2.1 Adsorption of metallic cations**

687 Heavy metal pollution is a severe problem and threatens ecological systems and human health.
688 Typically, nowadays with the increasing relevant mining and uses of the heavy metal resources. Some
689 waters, groundwater and soil have been polluted by Cd^{2+} , Cu^{2+} , Hg^{2+} , and Pb^{2+} (Cruz-Guzmán et al.,
690 2012; Yang et al., 2016; Zhu et al., 2016). Numerous methods for handling the pollution of the heavy
691 metals have been reported in the literature, but little is satisfactory, in view of the high expenses and
692 low efficiency (Padilla-Ortega et al., 2016).

693 Over last few years, the use of inorganically pillared, organically modified, chemical and
694 mechanochemical activated Sap has been studied to adsorb and fix heavy metal cations. Franco et al.
695 (2016a) evaluated the effectiveness of adsorption of heavy metal cations (As^{3+} , Cd^{2+} , Cr^{3+} , Cu^{2+} , Hg^{2+} ,
696 Ni^{2+} , Pb^{2+} and Zn^{2+}) at very low concentrations (10–100 ppb) by natural Sap and Fe-pillared and
697 Al-pillared Sap, aiming at purifying the drinking water. Natural Sap and pillared Saps showed notably

698 higher adsorption capacities of those cations except Hg^{2+} than carbon used as a reference. In particular,
699 both natural and pillared Sap appeared to be highly efficient to adsorb Cr^{3+} . The adsorption capacity is
700 in the order: Fe- pillared Sap > natural Sap > Al-pillared Sap. Recently studies have shown that
701 Sap/chitosan nanocomposites can act as efficient adsorbents for the removal of heavy metals from
702 polluted water. The adsorption behavior is influenced by the pH value of the medium, contact time, and
703 initial metal ion concentration (Budnyak et al., 2016). For such nanocomposite, in addition to the
704 interlayer space of Sap to adsorb the cations, the adsorption can occur through complexation of aqua,
705 acetic, or bi-ligand complexes of the cations with amino groups of chitosan and such formation of
706 complexes heavily depends on the pH value of the medium, namely, acidic basic and neutral one.

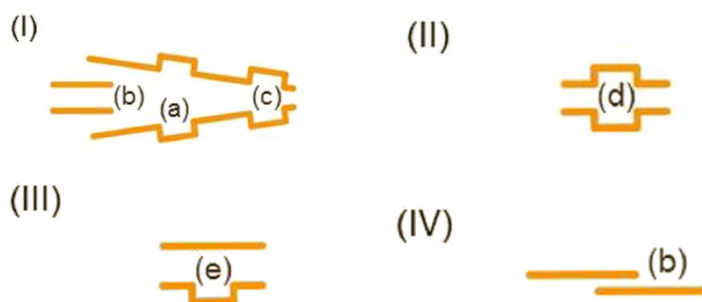
707 Besides chemical modification, mechanochemical activation by high-energy ball milling or
708 grinding have recently been demonstrated to activate Sap for effective fixation of heavy metal cations.
709 Comparatively speaking, mechanochemical activation is a relatively low-cost, effective, and green
710 method to practical application. Such activated Sap can be produced effectively in a planetary ball mill,
711 where the impact energy arising from the ball to ball and ball to wall collisions is transferred to the Sap
712 powder. Such mechanochemical activation can substantially produce fresh and active surfaces for Sap
713 particles. As a result, the surfaces are active for adsorbing heavy metal cations (Vdović et al., 2010).
714 Owing to the existence of many $-\text{OH}$ groups on the surface of Sap, the adsorbed metal cations can
715 form insoluble hydroxides on the surface of Sap. Hence the cations are well fixed. More recently, Petra
716 et al. (2017) disclosed that the adsorption for Cu^{2+} by activated Sap was more efficient than for Ni^{2+} .
717 Nevertheless, for producing effective Sap adsorbents for fixation of heavy metals, tedious screening for
718 the types of metal cations, condition and the modification of Sap remain necessary and challenging.

719 Earlier studies have revealed that radioactive Cs firmly stays on Sap in soil or water (Kim and
720 Kirkpatrick, 1997; McBride, 1997; Sato et al., 2016; Dzene et al. 2017). 2D nanolayered Sap can
721 form several types of structures and provide several types of sites for adsorption (**Fig. 12**) (Sato and
722 Hunger, 2017). The adsorption can occur at the external surfaces (oxygen plane), the broken-bond
723 edges, the wedge-shaped parts, the surfaces in the oncoming hexagonal cavities, and the surfaces in the
724 hexagonal cavities. Consequently, at different sites, the amount and the strength of adsorption appear
725 different due to the different geometrical confinement, physisorption, and chemical bonds. The edges
726 can significantly contribute to the Cs adsorption, along the oxygen planes. Both the oxygen planes
727 and the edges of Sap should be used as the active sites for adsorbing and decontaminating radioactive

728 Cs. Such subtle analysis and findings have much deepened into the insights into the adsorption of Sap
729 for radioactive elements. Finally, it should be pointed out that few studies are reported on the
730 adsorption of radioactive U, Th and Pu ions from nuclear wastes. These elements are more practically
731 used for nuclear energy, so such studies could be more needed (Bian, et al., 2015).

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736 **Fig.12 Schematic drawings of local molecular structures formed by 2D nanolayers in the dehydrated state: (I)**

737 **two-nanolayer insertion type, (II) oncoming hexagonal cavities, (III) hexagonal cavities, and (IV) steps. Cs adsorption**

738 **occurs at (a) surfaces, (b) edges, (c) wedge-shaped parts, (d) surfaces in the oncoming hexagonal cavities, and (e) surfaces**

739 **in the hexagonal cavities (Adapted and reprinted from Sato and Hunger, 2017, with permission from the PCCP Owner**

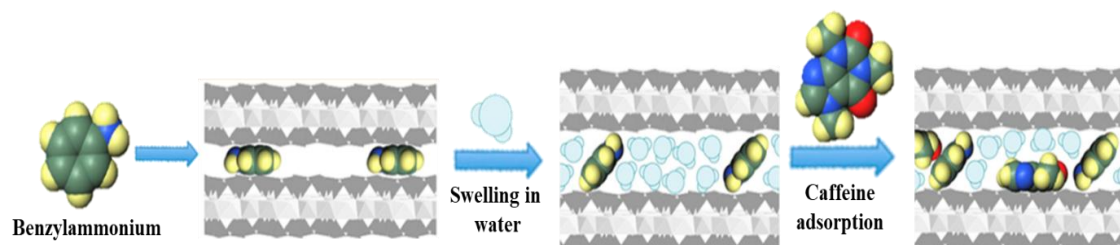
740 **Societies).**

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742 6.2.2 Removal of carcinogens and caffeine

743 In addition to cation species, the adsorption of nonionic species is also possible through ion-dipole
744 interactions and hydrogen bonding (Theng, 1974). When the cations in the interlayer space of Sap are
745 replaced with organic cations, the surface of the resultant Sap become active for the adsorption of
746 various ionic and nonionic organic species (Ogawa, and Kuroda, 1997). The applications of Sap based
747 on the adsorption is now expanded to the selective adsorption and removal of carcinogens and additives
748 from foods and plants. 2-phenylphenol (also known as 2-hydroxybiphenyl, 2PP) is an antifungal agent
749 used for oranges. On-site removal of 2PP by organically-modified Sap can improve the safety of fresh
750 orange juice (Seki and Ogawa, 2010). Even in the presence of sucrose in the starting aqueous solution,
751 2PP can also be selectively adsorbed on organically-modified Sap. Interestingly, Seki et al. (2015)
752 found that the removal of 2PP by CONH-modified Sap (CONH-Sap) from aqueous sucrose solution

753 was even more efficient than that from the solution without sucrose. Monolayer 2PP adsorption to
754 CONH-Sap reached 0.067 g/g in the presence of sucrose and 0.062 g/g in the absence of sucrose. The
755 basic reason is ascribed to the difference in the 2PP solubility in water and in aqueous sucrose solution.
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759 **Fig. 13 Schematic drawing of the process of preparation of benzylammonium (BA)-saponite and the adsorption of**
760 **caffeine over water dispersed BA-saponite** (Reprinted and adapted with permission from **Okada et al., 2015**, Copyright (2015)
761 American Chemical Society).

762
763 The large consumption of coffee worldwide has made caffeine a chemical marker or indicator of
764 water pollution. Microorganisms in wastewater usually cannot metabolize the compound effectively.
765 Recently, OSap can act as an efficient adsorbent of caffeine. Adsorption capacity depends primarily on
766 the intercalated organic cations. For example, Okada et al. (2014) have clearly demonstrated the
767 enhanced adsorption of caffeine in water on benzylammonium (BA)-modified Sap (BA-Sap,
768 respectively) (**Fig. 13**). By contrast, CONH-Sap adsorbed less caffeine than raw Sap and BA-Sap. It
769 was suggested that BA enlarges the siloxane surface area of Sap and make it more available for the
770 adsorption of caffeine. The interlayer space of BA-Sap is further expanded significantly in water by
771 the intercalation of water molecules into it, making the nanospaces suitable for accommodating
772 caffeine molecules. By interacting with BA, the siloxane in the layers of the Sap plays an important
773 role in caffeine adsorption. Marcal et al. (2015) found that CTAB- and APTS-modified synthetic Sap
774 are also efficient adsorbents for the adsorption of caffeine from aqueous solutions. The kinetic studies
775 the adsorption fitted into the pseudo-second-order equation, implying that chemical adsorption
776 controlled the process. Comparatively, APTS-Sap exhibited a high affinity for caffeine and possessed a
777 maximum adsorption capacity of 80.54 mg/g after 4 h. The above studies indicated that Sap-based

778 materials are promising candidates for the selective adsorption and removal caffeine from aqueous
779 solution.

780 **6.2.3 Removal of dyes and pigments from wastewater**

781 Dyes and pigments are widely used in the textiles, paper, plastics, leather, and cosmetic industries
782 for coloring products. Most dyes and pigments are toxic and not biodegradable, so they need to be
783 removed from wastewater in industry (Hashemian et al., 2015). A wide range of physicochemical and
784 biological methods for removing dyes and pigments from wastewaters have been studied. The
785 adsorption process proves more effective (Bhatnagar and Sillanpää, 2010). In recent years, there has
786 been increasing interest in using OSap to adsorb organic molecules of dyes and pigments (Rafatullah et
787 al., 2010; Nityashree et al., 2014).

788 As always, the organic modification of Sap increases its affinity for dyes. The OSap can also be
789 made into hydrogel for adsorption. For example, Nakamura and Ogawa (2013) examined the
790 adsorption of a cationic dye (rhodamine 6G) on the spherical particle of a Sap-containing
791 poly(N-isopropylacrylamide) hydrogel. The cation adsorption capacity of the hybrid hydrogel particles
792 was mainly determined by the cation exchange capacity of Sap. Tangaraj et al. (2017) investigated the
793 adsorption capacities of CTA-Sap with three fluorescent dyes, namely Rhodamine 640 perchlorate
794 rhodamine (Rho), sulforhodamine B (SR), and Kiton red 620 (KR). The edges and faces of Sap
795 particles was found responsible for the adsorption of dyes. The adsorption isotherms fitted well into the
796 non-linear Langmuir isotherm model. Most of the dye molecules can be released in aqueous solution.
797 Another issue is that after adsorption, the separation of Sap particles from the aqueous solution are
798 considerable difficulty due to their easy delaminate and high dispersion. To overcome this, a suggested
799 method is to endow saponite particles with magnetic properties (Chen et al., 2016). As a result,
800 magnetized Sap can be separated by the simple procedure of magnetic separation and removed from
801 the water (Xu et al., 2012; Giakisikli and Anthemidis, 2013). Moreover, magnetite/Sap nanocomposites
802 can possess a microporous and mesoporous structure and thus have enhanced adsorption performance
803 in comparison to Sap alone and magnetite alone (Makarchuk et al., 2016).

804 6.3 Catalysts

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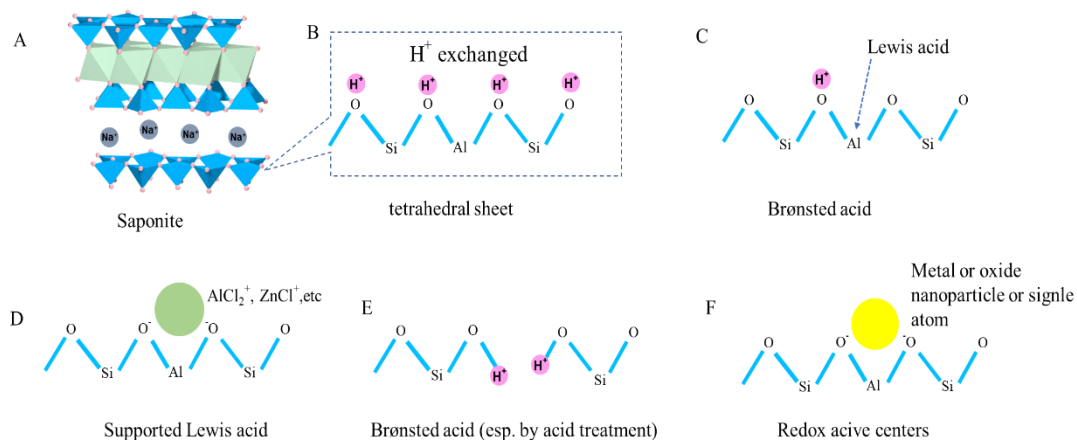
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814 **Fig. 14 Schematic drawing of Brønsted acid, Lewis acid and redox sites on saponite catalyst or saponite-supported**
 815 **catalyst.**

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Over the past few decades, many strategies have been developed to produce clay minerals-based catalysts (Zhou, 2011). In the layer of Sap, isomorphous substitution of some Si(IV) by Al(III) in the tetrahedral sheet not only make the layer to be negatively charged but also creates Lewis acidity. The exchangeable cations in the interlayer space of Sap, typically Na^+ , K^+ , and Ca^{2+} , which compensate the layer charge, can be exchanged with H^+ , thereby creating Brønsted acidity (**Fig. 14B**). Besides, more Brønsted acid sites can be created through H^+ coordination or silanol group $-\text{Si}-\text{O}-\text{H}^+$ (**Fig. 14C**). Such acidity can be enhanced by proper acid treatment of Sap to partly remove Al and create more edges or broken bonds (**Fig. 14E**). Many studies have proved that Al in the tetrahedral sheet exhibits Lewis acidity. In addition, two-dimensional nanolayer possesses the large surface and the surface can be used to support Lewis acid reagents like AlCl_3 , ZnCl_2 and FeCl_3 (**Fig. 14D**). Such Sap prove to be an efficient catalyst for acid-catalyzed organic reactions, for example the synthesis of β -amino ketones via Mannich-type reactions under mild conditions (Gómez-Sanz et al., 2017). In addition, the synthesis of Sap can be easily adapted to introduce some metal or metal oxide centers in the octahedral or tetrahedral sheet of Sap so that the M-Sap are able to catalyze redox reactions (**Fig. 14F**). Moreover, due to its easily and controllably expandable interlayer space with large surface area, Sap can also be used as catalyst supports. (**Table 4**)

834 **Table 4. Catalytic activity of saponite (Sap) and Sap supported catalysts.**

Catalyst	Reaction	S _{BET} (m ² /g)	T (K)	t (h)	Conversion (%)	Yield (%)	Ref.
Cs (1.25 wt%)/Al ₁₃ -pillared Sap	Synthesis of N-alkyl pyrazoles	47	353	1	100	100	Velasco et al. (2011)
Ni (20 wt%)/Sap	Hydrogenation of styrene oxide	RT	344	1	100	100	Vicente et al. (2011)
MgFe-Sap NiMgAl-Sap	Epoxidation of (Z)-cyclooctene by hydrogen peroxide	467 334	RT	48	7.5 8.8	7.5 8.8	Trujillano et al. (2011)
Acid activated V(0.05mmol/g) / Sap ¹	Oxidative dehydrogenation of propene into coke	-	773	0.5	21	-	Ostinelli et al. (2012)
Zirconia-cluster (1mmol/g)/ Sap	Isomerization of 1-butene	410	573	2.5	82	-	Kameshima et al. (2013)
Nb ^V /Sap	Oxidative abatement of CEES	-	298	8	98	71.5*	Carniato et al. (2014)
TiO ₂ (0.42 g/L) / [Ru(bpy) ₃] ²⁺ -Sap	Oxidation of benzene to phenol	-	VIS	5	72	69	Goto and Ogawa (2016)
ZnO/Sap	Photocatalytic decomposition of Methylene Blue	168	UV	3	93	-	Khumchoo et al. (2016)
Sulphated zirconium pillared Sap	Conversion of citronellal	190*	MW	10 min	100	-	Fatimah et al. (2016)
Cu (5 wt%)/Na-Sap	Diesel soot combustion	-	673	-	100	99	Gebretsadik et al. (2016)
Ni (40 wt%)/H-Sap	Glycidol hydrogenolysis to 1,3-propanediol	229	453	1	100	29	Gebretsadik et al. (2017b)

Re (7 wt%) modified Ni (40 wt%)/ acid Sap	Glycidol hydrogenolysis to 1,3-propanediol	331	393	4	98	46.1	Gebretsadik et al. (2017a)
Raw Sap	Synthesis of β -amino ketones by Mannich reaction	131	318	5	80	-	Gómez-Sanz et al. (2017)

835 * For clarity, consistency, and easy comparison, some original data have been rounded off.

836 T: Temperature; t: Time; VIS: Visible light irradiation; UV: UV irradiation; MW: Microwave irradiation; RT: Room temperature;
837 CEES: (2-chloroethyl)ethyl sulfide.

838

839 The incorporation of transition elements, such as Ni (Trujillano et al., 2011), Fe (Trujillano et al.,
840 2011), V (Ostinelli et al., 2012), and Nb (Carniato et al., 2014), into the framework of Sap, including
841 acid activated Sap, allows the combination of high surface area and porosity of the Sap with the solid
842 acidic and redox catalytic active centers. Theoretically, the transition metal atoms can be incorporated
843 in the octahedral or tetrahedral sheets of Sap. When transition elements are introduced into the
844 tetrahedral sheet of Sap, the co-existence of active transition metal cations, for example V (Ostinelli et
845 al., 2012) and Nb cations (Carniato et al., 2014), and the tetrahedral silicon cations, a synergetic effect
846 of the redox properties of the transition metals and the Brønsted acid sites makes the transition
847 metal-containing Sap an effective catalyst (Ostinelli et al., 2012; Carniato et al., 2014). Recent studies
848 demonstrated that the transition metal-containing Sap can be used to catalyze the epoxidation of
849 (Z)-cyclooctene by hydrogen peroxide (Trujillano et al., 2011), the conversion of propene into coke
850 (Ostinelli et al., 2012) and the oxidative abatement of chemical warfare agents (Carniato et al., 2014).
851 Moreover, the active cations in the framework of Sap could be more stable and leaching of the active
852 metallic cations during catalytic reaction in a liquid phase can be mitigated to some extent (Trujillano
853 et al., 2011). Pillaring treatments of Sap can increase the SSA, the pore volume and the surface acidity
854 and re-dox catalysis of Sap. In particular, pillars in the pillared Sap can be designed and made with
855 additional specific catalytic performances (De Stefanis et al., 2013; Zhen et al., 2014; Zhen and Zheng,
856 2016). In pillared Sap, the major sources for Brønsted and Lewis sites are associated with the lattice
857 hydroxyls of Sap and the pillars in the interlayer space of Sap. For example, Kameshima et al. (2013)
858 successfully prepared zirconia-cluster pillared Sap and revealed that both the amounts of Brønsted and
859 Lewis acids remarkably increased after pillaring Sap with zirconia-cluster. The zirconia-cluster was a
860 main source for generating Lewis acidity besides the tetra-coordinated Al in the tetrahedral sheet of Sap

861 while Brønsted acidity was provided by H^+ coordination and silanol group generated by removal of
862 some Al from the tetrahedral sheet of Sap (**Fig. 14E**). Recently, regarding sulphated zirconia-pillared
863 Sap, Fatimah et al. (2016) discovered that the sulphate anions on the surface can increase the number
864 and strength of the Brønsted acid sites of zirconia-pillared Sap.

865 Saponite, acid activated Sap, pillared Sap, and other related hybrids can also be used as a catalyst
866 support. The support offers expandable interlayer space, high SSA, surface acidity, and good thermal
867 stability (Garciano et al., 2014; Gebretsadik et al., 2016; Khumchoo et al., 2016). In particular, in view
868 of synthesis, swellability, surface acidity, and thermal stability, Sap has an advantage over Mt. Such
869 Sap-supported catalysts can catalyze a wide range of reactions. Recent examples are Cs/Al-pillared Sap
870 catalysts for the synthesis of N-alkyl pyrazoles (Velasco et al., 2011), Ni/Sap catalysts for the
871 hydrogenation of styrene oxide (Vicente et al., 2011), Co–Mo/Sap catalysts for upgrading squalene
872 ($C_{30}H_{50}$) (Garciano et al., 2014), TiO_2 /Al-pillared Sap catalysts for photocatalytic phenol
873 photo-oxidation (Fatimah and Wijaya, 2015), Ni/Zr-pillared Sap catalysts for hydrogenation of
874 isopulegol (Fatimah et al., 2015), TiO_2 / $[Ru(bpy)_3]^{2+}$ -Sap catalysts for photocatalytic oxidation of
875 benzene to phenol (Goto and Ogawa, 2015, 2016), ZnO/Sap catalysts for photodegradation of
876 Methylene Blue (Khumchoo et al., 2016), Cu/Sap catalysts for soot combustion (Gebretsadik et al.,
877 2016), and Ni (Gebretsadik et al., 2017b) and MO_x -modified nickel-copper catalysts (Gebretsadik et al.,
878 2017a) supported on H-Sap for glycidol hydrogenolysis (**Table 4**). Saponite-supported catalysts are
879 much stable even under irradiation and acid conditions (Khumchoo et al., 2016). In addition, a more
880 recent study from Gebretsadik et al. (2017b) indicated that the acidity of H-Sap is conducive to the
881 dispersion and reduction of NiO catalyst on the surface of H-Sap. The NiO and Ni particles could play
882 a role in changing the amount and strength of surface acid sites of the Ni /Sap (Gebretsadik et al.,
883 2017a). As proved by many reactions, there are indeed interactions between Sap support and metal
884 atoms or metal oxides and the two can have a synergistic catalytic effect. However, the details remain
885 unclear.

886 **6.4 Polymer additives**

887 Recently, Sap and organo-Sap has been used as reinforcing fillers in CPN (**Table 3**). Basically, it
888 has been considered to possess the same functions as Mt nanolayers. By contrast, Sap could be more

889 easily dispersed in the polymer matrix. Compared with pure polymers, CPN exhibit remarkable
890 improvement in mechanical strength, Young's modulus, gas barrier properties, thermal stability, and
891 water resistance (Zhen et al., 2012; Jairam et al., 2013; Yang et al., 2013; Zhen and Wang, 2016). The
892 enhancement of those properties of the CPN is commonly ascribed to the existence of well-dispersed
893 Sap nanolayers with a high aspect ratio in the CPN (Chang et al., 2014; Zhen and Wang, 2016).

894 In addition, Sap can act as a heterogeneous nucleating agent and accelerate the crystallization rate
895 of polymers (Xi et al., 2015; Zhen and Wang, 2016). When the crystallization is improved, it also helps
896 improve the thermal stability of the CPN (Zhen et al., 2014; Zhen and Zheng, 2016). Furthermore,
897 during the *in situ* polymerization process, Sap can act as a green catalyst which catalyzes the
898 polymerization reactions. Besides, Sap as adsorbents can contribute to adsorbing and eliminating the
899 toxic chemicals during the polymerization process (Zhen et al., 2014; Zhen and Zheng, 2016). More
900 recently, the CPN have been endowed with antibacterial properties. (Xi et al., 2015; Bandla et al.,
901 2017). This broadens the functions of Sap and the application of the CPN.

902 It is noteworthy that the amount of Sap in the polymer matrix has a significant effect on the
903 properties of the resultant Sap/polymer nanocomposite. In many cases, the addition of a small amount
904 of Sap is sufficient to improve the thermal and mechanical properties and gas barrier. For example,
905 Chang et al. (2014) found that for even 3–10 wt.% Sap in the PVA matrix, the CPN exhibited much
906 higher transition temperature than pure PVA. Ju and Chang (2016) found that upon the addition of Sap
907 into PI matrix up to a critical loading amount of Sap (20 wt.%), the glass transition temperatures (T_g)
908 and the initial thermal degradation temperature (T_i^d) of the Sap/PI hybrid films were remarkably
909 improved. Nevertheless, the coefficient of thermal expansion (CTE) decreased. If Sap was added more
910 than the critical content, the thermal properties worsened. Wu et al. (2014) found that the Sap/TOCN
911 nanocomposite with 10 wt.% Sap exhibited the Young's modulus of 14.5 GPa, tensile strength of 425
912 MPa, and strain-to-failure of 10.2%. Due to the addition of rigid Sap, the resistance to fracture of the
913 Sap/TOCN nanocomposite increased more than sevenfold when the loading amount of Sap is increased
914 from 0 to 10 wt.%. Finally, it is worth mentioning that Sap is not always just an additive for polymers.
915 In some cases, both the polymer and Sap are main components of the CPN, in particular as it is in the
916 hybrid films (Zhou et al., 2011). In addition, Sap can be the main component and the polymers could be
917 used with a lower amount to improve some functions (Shin et al., 2013).

918 **7. Concluding remarks and future work**

919 Last decade has witnessed great ad advances in modification and hybridization spanning from
920 simple interaction and surface engineering to fabrication of nanocomposite and hierarchical assembly.
921 The researchers have smartly developed many strategies for introducing functional inorganic, organic
922 and organic-inorganic guests into the interlayer space of Sap. In addition to acid activation, inorganic
923 cation exchange, pillaring and catalyst supporting, the nanoscale interlayer space of Sap is increasingly
924 being considered as a nanoreactor to produce a functional metal or metal oxide nanoparticle/Sap hybrid
925 with magnetic, selective adsorptive and catalytic properties. Besides OSap and CPN, organically
926 modified Sap and polymers can be made into functional films and such materials show promising
927 applications in optics, biological and medical materials.

928 Undoubtedly, the great strides in the approaches to the modification and hybridization of Sap,
929 along with the upsurge of inorganic nanotechnology and the discovery of functional organic molecules,
930 provide many opportunities to use Sap for producing advanced materials. Meanwhile, previous studies
931 have highlighted some challenges and problems which need ladder, as prudently and briefly
932 remarked as follows:

933 (1) To the best of our knowledge, Sap is a scarce natural resource and is not as abundant as Mt; At
934 present, the synthesis, modification and applications of Sap or the related studies is still limited on a
935 laboratory scale. In order to scale up the modification and application of Sap, some critical issues need
936 to be resolved. For example, a cleaner, efficient and profitable process of synthetic Sap should be first
937 developed. For the modification of Sap, the wastewater and the toxic solvents need handling properly.
938 In most cases, successful modification of Sap is usually a multiple-step process, which is
939 time-consuming and cost-intensive. A good alternative way could be to integrate the synthesis with the
940 modification of Sap. The one-pot reaction significantly shortens the process and simplifies the
941 procedure, thereby lowering the cost. A few studies have shed new light on this technology. However, it
942 is unknown if many other organic species can be introduced into the Sap in this way. Alternatively, a
943 supercritical continuous flow process could worth be applied to synthesize and modify Sap. Such
944 intensified process can improve mixing of reactants, mass and heat transfer and accordingly shorten the
945 reaction and improve productivity.

946 (2) Although the methods of modifying Sap have been greatly expanded, few studies provide the
947 mechanisms, thermodynamics, and kinetics. Theoretically, molecular dynamics simulations and
948 experimental cryo-electron microscopy (cryo-EM) and other scientific tools are helping throw new
949 light on the mechanisms. In order to get a better understanding of the modification and scale up the
950 relevant process, detailed investigations and data for engineering are of basic necessity.

951 (3) There is a need to put Sap and Sap-based materials onto the practice in industry. A critical issue is
952 to modify Sap with functional species with the practical applications. As Sap is a good player in the
953 hydrogel system, a combination of magnetic nanoparticles with Sap to produce magnetic
954 nanoparticles/Sap hydrogel can bring exceptional properties in magnetism, rheology, adsorption,
955 catalysis, and biocompatibility. Thus, the clay-based nanocomposites have potential to be applied in
956 electromagnetic devices, magnetorheological fluids/ferrofluids, magnetic adsorbents, catalysts,
957 biomaterials, biomedicines or highly simulated robots. In addition, there are various choices of
958 functional guest species that exhibit exceptional biological, electrical, and optical properties and could
959 to be introduced into Sap to produce new functional materials.

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961

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974 **References**

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