



## Research paper

## Functional nanohybrid materials derived from kaolinite

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## ARTICLE INFO

## Article history:

Received 27 September 2015

Received in revised form 7 December 2015

Accepted 12 January 2016

Available online 23 January 2016

## Keywords:

Kaolinite

Intercalation

Grafting

Kaolinite polymer nanocomposite

Delamination

Exfoliation

Nanorolls

## ABSTRACT

The first studies reporting the intercalation of organic compounds in kaolinite appeared in the 1960's. From that time, many advances have been achieved in this field. They are mainly concerned with the mastering and control of the intercalation processes, with the elucidation of various structural interactions between the intercalated compounds and the functionalities of the interlayer spaces, and with the covalent grafting of a variety of compounds on the internal surfaces. A new type of nanohybrid materials was developed, which displayed several potential interesting applications in various research area as clay polymer nanocomposites, adsorbents, electrochemical sensors or catalysts, among others.

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## 1. Introduction

The continuous need for new technologies drives the important development of materials chemistry. The production of fully synthetic materials such as polymers, mesoporous silica and MOF, requests high amount of chemicals. Consequently, this generates problems related to pollution and the management of natural resources. Nature has produced cheap and abundant minerals that can be used as starting materials or as substrates to minimize production costs and associated environmental impacts (Decarreau, 1990; Murray et al., 1993; Mousty, 2004; Murray, 2007; Bergaya and Lagaly, 2013). Clay minerals are very well suited for this purpose, because they have regular structures and chemical compositions generally well known, joined with accessible chemically reactive sites. They are robust materials whose reactivity is increasingly mastered for modification by organic compounds in order to extend their areas of application. While clay minerals of the smectite family are largely used in the nanocomposite field, kaolinite, which is very abundant and is used in large quantities in classical applications (paper coating, paint, ceramics, ...) (Murray, 2007), is still under-exploited in functional chemistry mainly because of its structure which results in difficult modifications.

Kaolinite (chemical formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) is a 1:1 dioctahedral clay mineral abundant in the earth's crust. (Murray et al., 1993) Layers are composed of a sheet of silicic tetrahedra linked to a sheet of

aluminum octahedra by Si–O–Al bonds. It is mainly this elemental composition that explains the particularities of kaolinite. The layers are stacked along the c-axis and define the interlayer space in which a siloxane surface faces aluminol surfaces. This disposition creates a dense network of hydrogen bonds between two adjacent surfaces in addition to extended permanent dipoles in the individual layers. Both effects work synergistically to ensure the strong cohesion of kaolinite stacking with a d-value of 7.1 Å. Unlike smectites, these cohesive forces are very important. They account for the difficult intercalation of compounds between the layers. For this reason, kaolinite is generally considered as a non-swelling clay mineral. Moreover, kaolinite has a very low cation exchange capacity because of the low isomorphous substitution in both the tetrahedral and octahedral sheets (Ma and Eggleton, 1999). Because of its characteristic book-like structure, its specific surface area is very small (between 8 and 12 m<sup>2</sup> g<sup>-1</sup>). For all these reasons, kaolinite was and is still regarded as a non-reactive mineral, not easily suitable for applications in fine chemistry. However, the aluminol functions confined in the interlayer spaces are reactive and, if made accessible, could be reacted with organic moieties to produce functional organo-inorgano nanohybrid materials, such as polymer based nanocomposites. One could expect these new materials to be gifted with significant improvements in mechanical properties.

In addition, the intrinsically asymmetric molecular nature of kaolinite makes the fine, submicrometric, particles of kaolinite also asymmetric, with a duality of interactions with organic substrates, depending if they interact with the tetrahedral siloxane or the octahedral aluminol surfaces (Fafard et al., 2013; Huang et al., 2014).

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From these perspectives, one could reasonably assume that, if the chemistry of kaolinite was well mastered, this clay mineral would be more promising in terms of areas of application and effectiveness compared to smectites. Prior to any other chemical modification in the kaolinite interlayer space, the intercalation of organic compounds between the layers is a requirement, in order to enable the accessibility of reactive aluminol functions present in this confined space.

## 2. The modification strategies of kaolinite

Only simple and superficial modifications of kaolinite are needed for the classical industrial applications such as its use as an additive in paints, as filler in the paper industry or synthetic rubbers or as major component of bricks and ceramics. These modifications include impurities removal, brightness improvement, particle size reduction or platelet disaggregation for better compatibility and dispersion. (Murray, 2007) For the development of new advanced materials based on kaolinite, intercalation is certainly the *sine qua non* modification method which is now relatively well controlled. Grafting on the internal aluminol surfaces of kaolinite is then the subsequent modification that appeared in the mid-nineties. These two modification methods and their applications are summarized in Fig. 1. They will be described and discussed in this paper.

### 2.1. Intercalation

From the first report on the intercalation of a chemical compound (potassium acetate) in kaolinite by Wada (1961), followed the same year by the report by Weiss of the intercalation of urea (Weiss, 1961), only a selected number of compounds with well-defined structures, such as dimethylsulfoxide (DMSO), hydrazine or N-methylformamide (NMF) have been intercalated in a single step in kaolinite (Lagaly et al., 2013). These compounds present some similar chemical properties among which high polarity and/or excellent ability to form hydrogen bonds. The intercalation in kaolinite can be described as occurring in two major steps. First, the compounds to be intercalated interact strongly with functions near the edges of the clay mineral particles, promoting the opening of the interlayer space. Secondly, the compounds become intercalated progressively from this starting point until all the space is occupied (Deng et al., 2002; Lagaly et al., 2013; Detellier and Schoonheydt, 2014). A summary of the characteristics of the most

frequent intercalates was reported in the general review by Lagaly et al. (2013).

To confirm the intercalation is relatively easy. XRD pattern of the resulting material is sufficient: it is related to the displacement of the 001 reflection from 7.1 Å to higher values. The location of the 060 reflection at 1.4 Å is a good indication that, during the intercalation, the a,b structure of the clay layer was preserved. XRD is also used to estimate the intercalation ratio by determining the ratio of the intensity of the 001 reflection of the intercalate and the sum of the one of the unreacted kaolinite and the intercalate. This method however gives only an estimate of the intercalation ratio since the intensity of a peak is also related to the crystallinity of the material.

FTIR can also be used to confirm the intercalation. The presence of guest compounds in the interlayer space strongly modifies the stretching vibrations of the OH groups ( $3700\text{ cm}^{-1}$  to  $3600\text{ cm}^{-1}$ ) pointing in the interlayer space. The one of the Al–OH group inside the octahedral sheet, at  $3620\text{ cm}^{-1}$ , is not affected. The Al–OH bending vibrations of groups present in the interlayer space ( $900\text{--}950\text{ cm}^{-1}$ ) are also affected. The intensity of the band at  $940\text{ cm}^{-1}$  is reduced considerably as a result of the presence of intercalated compounds in the interlayer space.

### 2.2. Grafting

Compounds to be grafted on the reactive aluminol internal surfaces, must initially be intercalated before reacting to form covalent bonds. (Fig. 1) One has still to find a compound fulfilling these two major conditions: being able to intercalate in one step (such as DMSO or urea do) and being reactive enough to be linked permanently to the aluminol surface through covalent bond. To the best of our knowledge, no report in the literature has stated such a one-step grafting on the internal surfaces of kaolinite. The strategy is to use a pre-intercalate as starting material. Tunney and Detellier (1993, 1994) were the first to report the grafting of organic compounds in the kaolinite interlayer by displacement of pre-intercalated DMSO or NMF. These grafted compounds were diols and a series of compounds derived from ethylene glycol. Subsequently, several compounds (alcohols, amino alcohol, ionic liquids, alkoxysilanes, ...) were grafted, using similar strategies (Tunney and Detellier, 1996a; Komori et al., 1998; Brandt et al., 2003; Gardolinski and Lagaly, 2005a, 2005b; Letaief and Detellier, 2007; Tonle et al., 2007; Letaief et al., 2008b; Letaief and Detellier, 2009a; Hirsemann

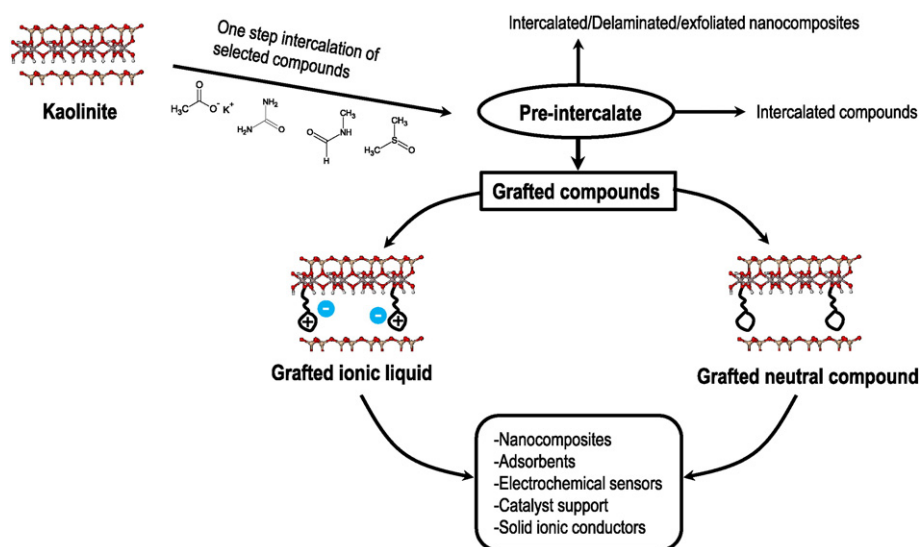


Fig. 1. Modification of kaolinite and applications.

et al., 2011; Letaief et al., 2011b; Letaief and Detellier, 2011; Hou et al., 2014).

From the description of the grafting processes reported so far in the literature, the major conditions required for successful grafting on the kaolinite internal surfaces can be summarized as follows:

- The compound to be grafted should have good affinity with the interlayer space functionalities, in order to easily displace the pre-intercalated compound. For this reason, it should be a polar compound and/or a good donor or acceptor of hydrogen bonds.
- The compound to be grafted should have a function that can react with the aluminol function to form a covalent bond. The hydroxyl group is the most used for the condensation reaction to form an Al–O–C bond with production of a water molecule (Tunney and Detellier, 1993, 1994, 1996a; Matusik and Scholtzová, 2012; Mako et al., 2015). Grafting has also been achieved by formation of Al–O–Si bond using an alkoxysilane (Tonle et al., 2007, 2011; Avila et al., 2010).
- When the grafting is performed at high temperature, the compound to be grafted should be more thermally stable than the pre-intercalated compound. The grafting temperature is generally close to the boiling point of the pre-intercalated compound, which facilitates the displacement reaction. At high temperature, the condensation reaction and the elimination of water molecules (in the case of reaction with alcohol) or alcohol (in the case of reaction with alkoxysilane) produced in the form of vapor, are accelerated.

One should mention grafting processes reported in the literature that do not follow the above described conditions: (i) The grafting of diols in kaolinite by a transesterification process, using methoxy-kaolinite as a precursor (Itagaki and Kuroda, 2003): during the grafting,

the Al–O–CH<sub>3</sub> bonds of methoxy-kaolinite were replaced by Al–O–C bonds with the grafted diol; (ii) The covalent grafting of a carboxylic acid with the formation of Al–O–CO bond (de Faria et al., 2009).

Reports on the grafting of new compounds in kaolinite remain quite scarce because the fulfillment of the requirements presented above is not without challenges. Table 1 reports several grafted compounds from the literature.

To confirm grafting on the interlayer surfaces of kaolinite is not as easy as in the case of intercalation. For XRD, there is not, to the best of our knowledge, significant differences between the patterns of a grafted or an intercalated kaolinite. This is explained by the fact that the formation of the Al–O–C bond is not supposed to induce crystallographic change in the a, b plan. Expansion along the c-axis is expected as in the case of intercalated compounds. Similar behavior is observed for FTIR spectra; it is not possible to distinguish a grafted and an intercalated material. During the grafting the organic moiety occupies no more than 1/4 of OH (in the literature, this ratio is generally less than 1/8 OH). The remaining OH groups will behave similarly to those in the intercalation compounds. TGA is more efficient to discriminate the two types of materials. Letaief and Detellier (2011) have showed that for ethanolamine, di and triethanolamine series, the kaolinite dehydroxylation in the grafted materials occurs at lower temperatures (less than 500 °C). This particular behavior was obtained for several other grafted materials (Dedzo et al., 2012; Dedzo and Detellier, 2014). Hirsemann et al. (2011) have used solid state NMR techniques, such as MQMAS and REAPDOR, to demonstrate convincingly the grafting of ethylene glycol on the interlayer surfaces of kaolinite. A method to highlight the grafting involves a hydrolysis test by suspending the prepared kaolinite material in water (at least 24 h) (Letaief and Detellier, 2007). If after this test XRD confirms an expansion of the clay layers, one

**Table 1**

Materials obtained by covalent grafting of compounds in the kaolinite interlayer space, type of covalent bonds and d-values.

Grafted compound	Starting material	Type of bond	d-Value (Å)	Reference
Ethylene glycol	Kao-DMSO and Kao-NMF	Al–O–C	9.5	Tunney and Detellier (1993)
Ethylene glycol monomethyl ether	Kao-DMSO	Al–O–C	10.6	Tunney and Detellier (1993)
Diethylene glycol monobutyl ether	Kao-DMSO	Al–O–C	11.2	Tunney and Detellier (1993)
1,2-Propanediol	Kao-DMSO	Al–O–C	10.9	Tunney and Detellier (1993)
1,3-Propanediol	Kao-DMSO	Al–O–C	9.8	Tunney and Detellier (1993)
Methanol	Kao-DMSO	Al–O–C	8.2	Tunney and Detellier (1996a)
D-Sorbitol	Kao-DMSO	Al–O–C	11.9	Komori et al. (2000)
Adonitol	Kao-DMSO	Al–O–C	10.3	Brandt et al. (2003)
1,2-Propanediols	Kao-Methoxy	Al–O–C	10.8	Itagaki and Kuroda (2003)
1,3-Propanediols	Kao-Methoxy	Al–O–C	11.0–11.1	Itagaki and Kuroda (2003)
1,2-Butanediols	Kao-Methoxy	Al–O–C	11.8	Murakami et al. (2004)
1,3-Butanediols	Kao-Methoxy	Al–O–C	11.6	Murakami et al. (2004)
Diethanolamine	Kao-DMSO	Al–O–C	10.2	Letaief and Detellier (2007)
Triethanolamine	Kao-DMSO	Al–O–C	10.7	Letaief and Detellier (2007)
Glycerol	Kao-KAc	Al–O–C	11.0	Janek et al. (2007)
Glycidol	Kao-DMSO	Al–O–C	11.4	Letaief and Detellier (2008)
Tris(hydroxymethyl)aminomethane	Kao-DMSO	Al–O–C	12.7	de Faria et al. (2010)
3-Aminopropyltriethoxysilane	Kao-DMSO	Al–O–Si	15.9–16.4	Tonle et al. (2007)
	Kao-DMSO	Al–O–Si	10.0	Yang et al. (2002)
3-Mercaptopropyltrimethoxysilane	Kao-DMSO	Al–O–Si	8.7	Avila et al. (2010)
Alkylammonium ionic liquids	Kao-DMSO	Al–O–C	11.6–11.2 (11.5, 11.6, 11.3, 11.3, 11.2)	Letaief et al. (2008b); Letaief and Detellier (2009a)
1-(2-Hydroxyethyl)-3-methylimidazolium chloride	Kao-DMSO	Al–O–C	10.3	Tonle et al. (2009)
1-Benzyl-3-(2-hydroxyethyl) imidazolium chloride	Kao-DMSO	Al–O–C	13.1	Dedzo et al. (2012)
	Kao-DMSO	Al–O–C	15.8	Dedzo et al. (2012)
1-(2-Hydroxyethyl)-pyridinium chloride	Kao-DMSO	Al–O–C	12.8	Dedzo and Detellier (2014)
Pyridine-2-carboxylic acid	Kao-DMSO	Al–O–CO	13.5	de Faria et al. (2009)
Pyridine-2,6-dicarboxylic acid	Kao-DMSO	Al–O–CO	11.9	de Faria et al. (2009)
2-Amino-2-methyl-1,3-propanediol	Kao-DMSO	Al–O–CO	10.8	Letaief et al. (2011b)

can conclude with good confidence that the grafting process was successful.

### 3. Nanohybrid materials derived from kaolinite and applications

#### 3.1. Intercalated kaolinite and applications

##### 3.1.1. Nanocomposites

Generally, dispersion of a clay mineral in a polymer matrix improves its mechanical properties while reducing the production cost. The use of unmodified kaolinite is limited by poor dispersion in the organic matrix due to a strong tendency to form aggregates and to the poor affinity with certain organic compounds. Intercalation appears to be a useful strategy since generally it reduces the aggregation of kaolinite. In addition, the compounds adsorbed on the outer surface of the kaolinite particles significantly improve interactions between the organo-kaolinite and the polymer matrix. Several types of kaolinite/polymer nanocomposite were produced, with a pre-intercalate as starting material (Detellier and Letaief, 2013).

**3.1.1.1. Physical mixing of a pre-intercalate and the polymer.** In this case, the pre-intercalated kaolinite is directly dispersed in a molten polymer or a polymer solution. External interactions (intercalation of the polymer is not necessary) between the organo-clay and the polymer improved the dispersion and the compatibility between the organic and the inorganic components. The result is the improvement of the stability of the composite. Turhan et al. have used this strategy to prepare a kaolinite/polyvinylchloride nanocomposite by mixing K-DMSO with PVC in THF. The resulting composite showed an improvement of the thermal stability (Turhan et al., 2010; Mbey et al., 2012; Zulfiqar et al., 2015).

**3.1.1.2. Direct polymer intercalation in the interlayer space.** The polymer is intercalated between the layers of kaolinite by guest displacement of the pre-intercalated compound. To improve the interaction between the two components of the system, a molten polymer is used. This is the approach which is the most often reported, particularly in the case of smectites. Polyethylene glycol (PEG) (Tunney and Detellier, 1996b) and a block co-polymer (Fafard and Detellier, 2015) were intercalated in kaolinite using this strategy.

**3.1.1.3. Intercalation of the monomer and in situ polymerization.** In this case, the monomer is stable enough to be intercalated by guest displacement, followed by polymerization. Using this strategy, acrylonitrile was intercalated in kaolinite by displacement of ammonium acetate followed by the formation of polyacrylonitrile in the interlayer space (Sugahara et al., 1988). This technique also allowed the intercalation of nylon-6, polystyrene, and polymethacrylamide (Matsumura et al., 2001; Elbokl and Detellier, 2006; Elbokl and Detellier, 2009).

**3.1.1.4. Exfoliated kaolinite/polymer nanocomposite.** When interactions between a bulky polymer and the clay layers are strong enough, it is possible to obtain exfoliation, with complete loss of the layers ordering. In this nanocomposite, individual clay mineral layers are uniformly and randomly dispersed in the polymer matrix. Such a system is ideal because homogeneity and strong interactions between the components of the system increase the physico-chemical properties of the polymer. Letaief et al. reported the exfoliation of kaolinite by polyacrylate and by a polyionic liquid. In the case of the ionic liquids, monomers were intercalated by guest displacement of urea followed by in-situ polymerization. The polymer formation promotes a complete separation of elemental layers of kaolinite (Letaief and Detellier, 2009a, 2009b; Letaief et al., 2011a).

##### 3.1.2. Ionic conductors

In the area of fuel cells, there is a need for ionic conductors in the solid state that can operate at high temperatures (>100 °C). Letaief

et al. (2008a) studied the electrical conductivity of a series of ionic liquids-kaolinite intercalates. In some cases an ionic conductivity was observed that increased with temperature in the stability domain of the material with a maximum value of  $4 \times 10^{-4} \text{ S cm}^{-1}$  at 170 °C. In the case of some other intercalated ionic liquids the materials behave like an isolator. The computational simulation of the spatial organization of the ionic liquid molecules in the kaolinite interlayer space permitted to interpret the observed electrical properties. For the conductive materials, the cations were organized so that regular tunnels were formed in the interlayer spaces, creating channels occupied by the anions. These anions could move freely in these channels when an electrical field was applied. For non-conductive material, the complex structure of the cation induced occlusion of the channels, leaving the anions trapped in the cages formed by the spatial organization of the cations in the interlayer space.

##### 3.1.3. Other applications

Intercalated kaolinite also found applications in the adsorption of pollutants in water. Matusik and Matykowska (2014) reported the successful use of alkylammonium intercalated kaolinites for adsorption of chromate and arsenate. Dielectric properties of kaolinite intercalates were studied. An interesting dielectric relaxation behavior was observed, which was probably related to the dynamics of the intercalated molecules (Qiao et al., 2014).

#### 3.2. Grafted kaolinites and applications

Compared to intercalates, the applications of grafted kaolinite are rare, mainly because of the significant challenges of the grafting process. However, there are some applications reported in the literature in the fields of electrochemical sensors, nanocomposites, sequestration and release of organic compounds and catalysis, among others.

##### 3.2.1. Electrochemical sensors

Metal electrodes usually used in electrochemistry (gold, platinum, glassy carbon, graphite) for amperometric sensors have limitations in terms of performance (poor detection limits, lack of selectivity and poor reproducibility). These problems are frequently solved by coating the surface of the working electrode by a thin film of a material capable of providing the desired properties to the sensor. Particular selectivity for a compound or class of compounds or an improvement in the sensor sensitivity could then be achieved.

The poor physicochemical properties of unmodified kaolinite (low surface area and poor ion exchange capacity) render this clay mineral unsuitable for this type of application. Tonle et al. (2007) reported for the first time, to the best of our knowledge, an electrochemical sensor based on modified kaolinite, by depositing a thin film of kaolinite with the interlayer functionalized by an aminosilane. A noticeable improvement of the hexacyanoruthenate ions ( $[\text{Ru}(\text{CN})_6]^{4-}$ ) signal was observed on this sensor. This particular property was achieved through the protonation of the amine function in acidic medium. The protonated material behaved as an anion exchanger that accumulated ( $[\text{Ru}(\text{CN})_6]^{4-}$ ) in the interlayer space. One year later, this concept was improved by using a kaolinite modified by an ionic liquid (Letaief et al., 2008b). The organic cation was permanently grafted and the counter anion could move independently between the layers. The anion exchange properties remained independent of the pH of the solution. These materials have shown promising applications for the electroanalysis of cyanide and thiocyanate ions (Letaief et al., 2008b; Tonle et al., 2009). Dedzo et al. (2012) have shown that by grafting ionic liquids of variable sizes on the internal surfaces, one could precisely control the  $d$ -value of the grafted materials, resulting in potential applications for the selective electrochemical detection of electroactive anions, according to their sizes. The same authors have subsequently shown that such anionic exchanger materials (1-benzyl-3-(2-hydroxyethyl) imidazolium chloride) could be effectively used for the quantitative detection of iodide

**Table 2**  
Modifiers used for the grafting of the internal surfaces of kaolinite and applications.

Grafted molecule	Application	Reference
Terbium pyridine picolinate	Optical application (luminescence)	de Faria et al. (2011)
1-(2-Hydroxyethyl)-3-methylimidazolium chloride	Electroanalysis of thiocyanate	Tonle et al. (2009)
1-Benzyl-3-(2-hydroxyethyl) imidazolium chloride	Anions electroanalysis with respect to size.	Dedzo et al. (2012)
	Anions electroanalysis with respect to size.	Dedzo et al. (2012)
	Electrochemical determination of iodide	Dedzo and Detellier (2013)
Trihydroxyethylmethylammonium iodide	Electroanalysis of cyanide	Letaief et al. (2008b)
	Anions electroanalysis with respect to size.	Dedzo et al. (2012)
	Adsorption of some anionic pollutants	Matusik and Bajda (2013); Matusik (2014)
	Exfoliated kaolinite-polyacrylate nanocomposite	Letaief and Detellier (2009a)
1-(2-Hydroxyethyl)-pyridinium chloride	Sequestration and release of phenolic organic compounds	Dedzo and Detellier (2014)
3-Aminopropyltriethoxysilane	Electrode modifier for anions	Tonle et al. (2007)
3-Mercaptopropyltrimethoxysilane	Carbon paste electrode modifier for electrochemical detection of Pb(II)	Tonle et al. (2011)
Fe(III)-picolinate and Fe(III)-dipicolinate	Epoxidation of cis-cyclooctene, oxidation of cyclohexane and cyclohexanone	de Faria et al. (2012)
Methanol	Amitrole sequestration and controlled release	Tan et al. (2015)
	Nanorolls	Gardolinski and Lagaly (2005b); Matusik et al. (2009); Kuroda et al. (2011)
	Polymer intercalation and kaolinite polymer nanocomposites	Komori et al. (1999); Fafard and Detellier (2015)
Triethanolamine	Heavy metals adsorption	Koteja and Matusik (2015)
Diethanolamine	Heavy metals adsorption	Koteja and Matusik (2015)
2-Amino-2-methyl-1,3-propanediol	Gold nanoparticle deposition and reduction of carbon monoxide	Letaief et al. (2011b)

ions in trace level (detection limit of 0.15  $\mu\text{M}$ ) (Dedzo and Detellier, 2013). To reduce the effect of interfering anions, iodide was first accumulated in the clay film during an open-circuit pre-concentration step. Detection was then performed in sodium nitrate electrolytic solutions. These sensors showed poor selectivity with respect to other halides.

The affinity of the thiol function for heavy metal cations is frequently used to improve the sensibility of clay based sensors (Tonle et al., 2005; Tchinda et al., 2007). This approach was used by Tonle et al. (2011), where the kaolinite interlayer space was functionalized by a thiol group. 3-chloropropyltriethoxysilane was first grafted by guest displacement of DMSO. The chlorosilane/kaolinite was then reacted with NaSH to yield thiol functionality. The nanohybrid clay material was mixed with graphite powder to prepare a carbon paste electrode and was applied at the pre-concentration analysis of Pb(II). At optimized experimental conditions, a detection limit of  $6 \times 10^{-8}$  M was obtained.

### 3.2.2. Sequestration and release of organic compounds

The unmodified kaolinite has a low specific surface area and only specific compounds can be inserted between adjacent layers. However, grafting a compound in the interlayer space should increase considerably the space that can be exploited to encapsulate compounds for various applications. For example, drug delivery at a specific location in the body and at a specific rate is a major objective in pharmaceutical research. Recent works have shown that it is possible, by judicious modification of kaolinite, to use this clay mineral to encapsulate chemical compounds of pharmaceutical interest, followed by a controlled release. A pyridinium based ionic liquid grafted in the kaolinite interlayer space yielded a robust anion exchanger capable to encapsulate quantitatively gallic and salicylic acid in anionic form (Dedzo and Detellier, 2014). These compounds were subsequently released into phosphate buffer solution by an anion exchange process. Compared to salicylic acid, the release of gallic acid is slower, probably due to stronger interactions with the organic functions of the interlayer space.

More recently, other authors have successfully encapsulated a pesticide (amitrole) in methoxy kaolinite. The composite system appears to slow the release of the pesticide (Tan et al., 2015).

### 3.2.3. Kaolinite polymer nanocomposites

Methoxy-kaolinite is the grafted kaolinite derivative most commonly used for the preparation of intercalated or exfoliated nanocomposites. The grafting of methanol allows a permanent and stable layer expansion of kaolinite in comparison to intercalates. When intercalates are used as starting materials for the preparation of nanocomposites, it is imperative to properly select the operating conditions to prevent deintercalation before the intercalation of the guest polymer, whereby the parent kaolinite would be regenerated. With methoxy-kaolinite, there is more flexibility because it is possible to work with a variety of solvents, including water, without regenerating kaolinite during the preparation of the nanocomposite. In addition, the presence of methanol provides an organophilic character to the interlayer space of kaolinite and allows the intercalation of compounds difficult to encapsulate even through a pre-intercalate as intermediate. For instance, amines of various sizes were easily intercalated in methoxy modified kaolinite (Gardolinski and Lagaly, 2005b). PVP was intercalated in methoxy-kaolinite using methanol as solvent (Komori et al., 1999). By grafting a quaternary amine in the interlayer space of kaolinite, Letaief and Detellier (2009a, 2009b) have introduced a permanent positive charge in kaolinite to yield an anion exchanger material. By exploiting this property, a bulky anionic polymer (polyacrylate) was inserted into the cationic kaolinite with exfoliation of the clay layers.

### 3.2.4. Other applications

**3.2.4.1. Nanorolls.** Intercalation of long-chain alkylamines in methoxy-kaolinite provides materials with high d-value (up to 5 nm) depending on the length of the amine used (Gardolinski and Lagaly, 2005b). In such materials, the distance between two adjacent layers is such that their separation into individual entities becomes possible. By performing several intercalation-deintercalation cycles of long-chain amines, the formation of nanorolls was observed. Structurally, elementary layers of kaolinite wrap in spiral to form tubular structures similar

to tubular halloysite (Gardolinski and Lagaly, 2005b; Matusik et al., 2009). Recently, this nanorolls preparation technique has been improved by carrying out the synthesis in one step (Kuroda et al., 2011). Instead of alkylamines, these authors used surfactants (quaternary alkylammonium). Nanorolls have the advantage of being at the same time lamellar and mesoporous materials, thus providing several possible applications. For example, they can be used as catalyst support (for metal nanoparticles or enzymes) or as a carrier for the storage and slow release of corrosion inhibitors, pesticides, or of compounds with pharmaceutical interests. Their formation is due to the structural misfit between the tetrahedral and the octahedral sheets (Deng et al., 2002; Detellier and Schoonheydt, 2014) which is not energetically compensated anymore by the strong interactions of the sheets in contact.

**3.2.4.2. Catalysis.** Gold nanoparticles were deposited on kaolinite previously functionalized by 2-amino-2-methyl-1,3-propanediol. The grafting of this compound both at the particles surface and on the internal surfaces of kaolinite ensured better compatibility and a good immobilization of nanoparticles on the clay matrix thanks to the active amine function. The nanoparticles obtained were well dispersed and more than 80% had sizes less than 4 nm. This material was then successfully applied to the reduction of carbon monoxide (Letaief et al., 2011b). Fe(III) pyridine-carboxylate complexes were used for the selective catalytic oxidation of cis-cyclooctene, cyclohexane and cyclohexanone at ambient temperature and pressure (de Faria et al., 2011).

**3.2.4.3. Adsorption.** Most of the specific surface of layered materials is located in their interlayer spaces. To provide access to this surface would thus considerably increase their usable surfaces. Kaolinite is the ideal candidate for this type of challenge since its interlayer space is not easily accessible. Triethanolamine and diethanolamine modified kaolinite materials were used for the adsorption of heavy metals (Cd(II), Zn(II), Pb(II) and Cu(II)). Metal adsorption occurred on the external surfaces and on the modified interlayer space, through the formation of metal complexes with nitrogen ligands (Koteja and Matusik, 2015). Matusik has reported the use of cationic kaolinite (modified by Trihydroxyethylmethylammonium iodide) for the adsorption of several anions (arsenate, orthophosphate, sulfate, nitrate and dichromate) with substantial improvement (more than 10 times) compared to unmodified kaolinite (Matusik and Bajda, 2013; Matusik, 2014).

**3.2.4.4. Application in optic devices.** Recently, picolinic acid was grafted on the internal surfaces of kaolinite, followed by the in situ formation of a stable complex of terbium in the interlayer space. The resulting complex material obtained displayed interesting luminescent properties that could be exploited in optics (de Faria et al., 2011).

Table 2 summarizes the principal applications of kaolinite nanohybrids obtained by permanent grafting in the interlayer space.

#### 4. Conclusion

Despite the limitations imposed by the structure of kaolinite that prevents easy chemical modifications, advances in the chemistry of modified kaolinite were achieved. The applications which have been explored up to date are still scarce, especially in the case of kaolinite whose interlayer space has been modified by grafting. The growing interest in this research area should lead in the near future to significant progress, including:

- The development of simple method for uniform dispersion of individual kaolinite layers in various polymer matrices;
- The grafting on the internal surfaces in a single step;
- The grafting of anionic compounds on the kaolinite internal surfaces to yield a cation exchanger kaolinite;

- The use of the kaolinite interlayer spaces as a nanoreactor for specific reactions;

In this perspective, the spectrum of applications of the abundant kaolinite mineral is undoubtedly expected to grow considerably in the foreseeable future.

#### Acknowledgments

This work was financially supported by a Discovery Grant of the Natural Sciences and Engineering Research Council of Canada (NSERC). The Canada Foundation for Innovation and the Ontario Research Fund are gratefully acknowledged for infrastructure grants to the Center for Catalysis Research and Innovation of the University of Ottawa.

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