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Research paper

Functional nanohybrid materials derived from kaolinite

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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.

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 $Al_2Si_2O_5(OH)_4$) 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 $m^2 g^{-1}$). 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 cm^{-1} to 3600 cm^{-1}) pointing in the interlayer space. The one of the Al–OH group inside the octahedral sheet, at 3620 cm^{-1}, is not affected. The Al–OH bending vibrations of groups present in the interlayer space (900–950 cm^{-1}) are also affected. The intensity of the band at 940 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

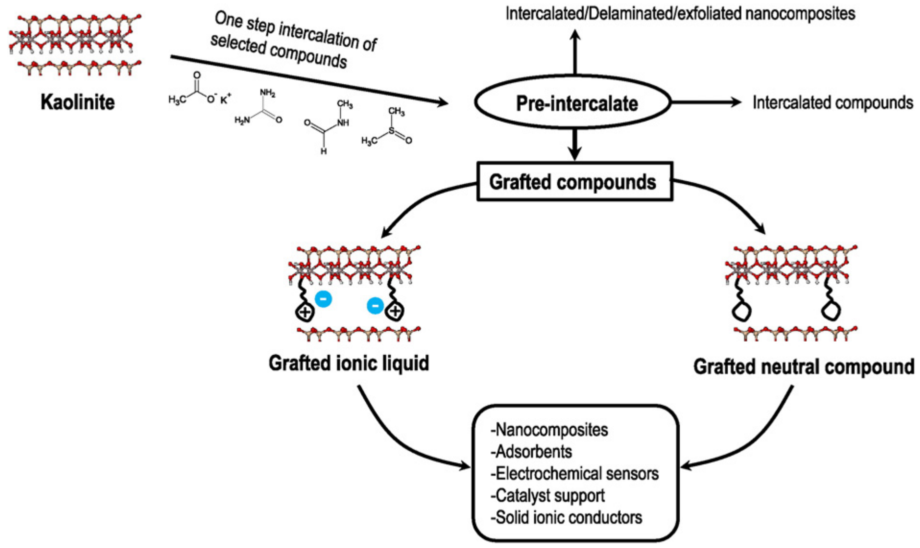

Fig. 1. Modification of kaolinite and applications.