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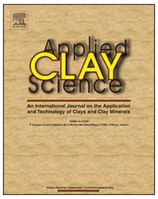

Research paper

Molecular control of the functional and spatial interlayer environment of kaolinite by the grafting of selected pyridinium ionic liquids

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ABSTRACT

The synthesis and characterization of new kaolinite nanohybrid materials derived from pyridinium based ionic liquids with different functionalities located at the para position are described in this paper. Four ionic liquids (1-(2-hydroxyethyl)-4-methylpyridinium chloride (Mepyr), 1-(2-hydroxyethyl)-4-ethylpyridinium chloride (Ethpyr), 1-(2-hydroxyethyl)-4-(tert-butyl)pyridinium chloride (Tbutpyr) and 1-(2-hydroxyethyl)-4-benzylpyridinium chloride (Benzpyr)) were grafted on the aluminol interlayer surfaces of kaolinite by a melt intercalation method. The molecular structure of the grafted compounds was kept, as demonstrated by ^{13}C CP-MAS NMR and FTIR spectroscopies. The grafted moieties have similar orientations in the interlayer space, as evidenced by a linear relationship between the observed d-value and the size of the ionic liquids ($R^2 > 0.99$). This study highlights how it is possible to control, tune and functionalize the interlayer spaces of modified kaolinite. Pyridinium ionic liquids are particularly suitable for that purpose. Their substituents in the para position are the main agents of control of the rigidly fixed interlayer distance. Their choice permits also to tune the functionality of the interlayer space. Preliminary applications (adsorption of 2,4-dichlorophenoxyacetic acid(2,4-D) and electrochemical detection of thiocyanates ions) confirm the anion exchanger nature of these modified kaolinite. They confirm also that the spatial and functional controls of the interlayer environment drive the sequestration of the anions.

1. Introduction

Clay minerals are abundant and low-cost natural materials with interesting applications in various fields, due to their particular structural and physicochemical properties. Kaolinite is one of the most abundant clay minerals. Its use is mainly restricted to ceramics, bricks, paper coating, paint additive and polymer filler in its native form with no or minor physical treatments (Bundy and Ishley, 1991; Detellier and Schoonheydt, 2014; Murray, 2000; Murray et al., 1993; Murray and Kogel, 2005; Rissa et al., 2006). Reasons for this limited use are found in the structure of kaolinite and the resulting physicochemical properties. In a kaolinite 1:1 layer, a silicon oxide tetrahedral sheet is linked to an octahedral sheet (with aluminum as cation) by Si—O—Al bonds. In the interlayer space defined by two consecutive layers, oxygen plane (siloxane surface) faces a plane of hydroxyl (aluminol surface), creating a permanent dipole and multiple hydrogen bonds between the layers. Kaolinite layers are thus strongly held together, which explains its relative non-swelling behavior and the tendency of the mineral to form book-like structures (Brigatti et al., 2013). Kaolinite is a mineral with small amounts of structural charges, due to few isomorphic substitutions in the tetrahedral and octahedral sites. Kaolinite is thus considered as a relatively non-reactive clay mineral. However, it was shown that despite the exceptional strength of the network of interlayer bonds, some compounds such as dimethylsulfoxide (DMSO), urea, *N*-methyl formamide (NMF), among a few selected others, could be intercalated directly between the kaolinite layers (Lagaly et al., 2013; Letaief and Detellier, 2009a; Olejnik et al., 1970; Tonle et al., 2009; Wada, 1961; Weiss, 1961). The resulting intercalated materials can then be used as intermediates for the intercalation of other compounds having less affinity with the interlayer of kaolinite, and can even lead to the exfoliation of the mineral (Dedzo and Detellier, 2016; Komori et al., 1999; Koteja and Matusik, 2015; Kuroda et al., 2011; Lagaly et al., 2013; Letaief and Detellier, 2009b; Sato, 1999; Yang et al., 2002; Zhang et al., 2015b; Zulfiqar et al., 2015). These pre-intercalates also provide the availability of reactive and abundant interlayer OH groups, which can be used advantageously for the formation of chemical bonds with

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carefully chosen chemical compounds (Dedzo and Detellier, 2016). The obtained grafted materials are more stable (little or no release) than intercalates and offer a wide range of potential applications. For example, they may find applications in biological medium with minor adverse effects to the host organism (Dedzo and Detellier, 2014). Several studies report the use of these pre-intercalates to functionalize the internal aluminol surfaceof kaolinite, generally with compounds having at least one alcohol function (Avila et al., 2010; de Faria et al., 2009; Dedzo and Detellier, 2016; Dedzo et al., 2012; Gardolinski and Lagaly, 2005; Itagaki and Kuroda, 2003; Janek et al., 2007; Matusik, 2014; Tunney and Detellier, 1993). Several robust materials were synthesized in the recent years by grafting the cationic part of ionic liquids (mainly based on alkylammonium and imidazolium groups) on the kaolinite aluminol internal surfaces (Dedzo et al., 2012; Letaief and Detellier, 2009a; Letaief et al., 2008; Tonle et al., 2009).

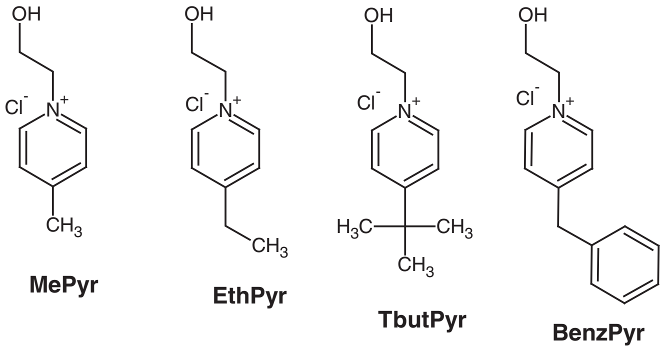
The resulting materials possessed substantial anion exchange capacity with promising applications for accumulation and detection of anions (Dedzo and Detellier, 2013; Dedzo et al., 2012; Letaief et al., 2008; Tonle et al., 2009). More recently, a pyridinium ionic liquid was grafted in kaolinite and found new applications in the sequestration of phenolic acids and in their controlled release (Dedzo and Detellier, 2014).

To date, only one ionic liquid derived from pyridinium was successfully grafted in kaolinite. In this work, the grafting of a series of pyridinium ionic liquids whose chemical structure differs by the nature of the substituent in para position (Scheme 1), is reported for the first time. In addition to provide controlled interactions with the interlayer environment, these substitutions can also control the expansion of the interlayer space following the size of the substituent (Dedzo et al., 2012). This study highlights how it is now possible to control, tune and functionalize the interlayer spaces of modified kaolinite. Pyridinium ionic liquids are particularly suitable for that purpose. Their substituents in the para position are good candidates to act as efficient agents of control of the interlayer distance due to the increase of the length of the pyridinium cations with minor effect on their rigidity. These substituents can also modify the chemical environment of the internal surfaces. These investigations were carried out using XRD, TGA, FTIR, MAS-NMR and porosimetry. The potential applications of these nanohybrid materials were evaluated on the basis of their anion exchange properties in water, through the sequestration of 2,4-dichlorophenoxyacetic acid (2,4-D), a widely used herbicide, and through the electrochemical detection of thiocyanate anions.

2. Experimental section

2.1. Chemicals

2-chloroethanol 99%, 4-methylpyridine 99%, 4-ethylpyridine 98%, 4-(tert-butyl) pyridine 96%, 4-benzylpyridine 98% and 2,4-dichlorophenoxyacetic acid ≥98% were purchased from Sigma-Aldrich. All other chemicals (sodium thiocyanate, sodium nitrate, dimethylsulfoxide (DMSO), anhydrous diethylether and methylene dichloride) were of analytical grade.



Scheme 1. Chemical structures of the pyridinium ionic liquids used in this study. 1-(2-hydroxyethyl)-4-methylpyridinium chloride (Mepyr), 1-(2-hydroxyethyl)-4-ethylpyridinium chloride (Ethpyr), 1-(2-hydroxyethyl)-4-(tert-butyl) pyridinium chloride (Tbutpyr), 1-(2-hydroxyethyl)-4-benzylpyridinium chloride (Benzpyr).

2.2. Synthesis of ionic liquids

1-(2-hydroxyethyl)-4-methylpyridinium chloride (Mepyr), 1-(2-hydroxyethyl)-4-ethylpyridinium chloride (Ethpyr), 1-(2-hydroxyethyl)-4-(tert-butyl) pyridinium chloride (Tbutpyr) and 1-(2-hydroxyethyl)-4-benzylpyridinium chloride (Benzpyr) was prepared by reacting 4-methylpyridine, 4-ethylpyridine, 4-(tert-butyl)pyridine and 4-benzylpyridine respectively with 2-chloroethanol in dichloromethane as solvent. Details of the synthesis are available as Supplemental material.

2.3. Preparation of kaolinite and nanohybrid materials

Well crystallized kaolinite (KGa-1b, Georgia) was obtained from the Source Clays Repository of the Clay Minerals Society (Purdue University, West Lafayette, Indiana, USA). The K-DMSO pre-intercalate was prepared by previously described procedures (Letaief and Detellier, 2009a; Tonle et al., 2009). The preparation of kaolinite nanohybrids derived from MePyr, EthPyr and TbutPyr (named respectively K-MePyr, K-EthPyr and K-TbutPyr) was performed as follow: 0.6 g of K-DMSO was dispersed in 2 g of ionic liquid; the mixture was then stirred under nitrogen flow for 5 h, the temperature being gradually increased up to 180 °C. The resulting mixture was submitted to three series of washed centrifugation with isopropanol to remove the excess of ionic liquids and dried in oven at 80 °C for 2 h. Each material was then stirred for 72 h in 100 mL of distilled water to remove the intercalated ungrafted ionic liquid and dried in oven at 80 °C for 5 h. In the particular case of modified kaolinite derived from BenzPyr (K-BenzPyr), after the washing step using isopropanol, the dried solid was submitted to a thermal treatment at 180 °C for 5 h. The solid was then stirred for 72 h in 100 mL of distilled water and dried in oven at 80 °C for 5 h.

2.4. Adsorption of 2,4-D

5 mg of pristine kaolinite and of kaolinite nanohybrids was introduced. in a series of glass vials containing 5 mL of a 0.2 mmol L^{-1} 2,4-D solution. NaOH at equivalent concentration (0.2 mmol L^{-1}), was also added in the solution to ensure the total conversion of the pesticide in anionic form. A control experiment was performed with a vial containing 5 mL of 2,4-D solution without kaolinite. Sealed vials were then stirred vigorously for 24 h at ambient temperature. The supernatant was collected by centrifugation and the UV–vis spectra collected on a GENESYS 10S Thermo Scientific spectrophotometer. The adsorbed percentage was determined using the 283 nm wavelength by comparing the absorbance of 2,4-D solution before and after desorption.

2.5. Preparation of the modified electrodes and electrochemical analyses

Clay dispersions were prepared by mixing 4 mg of raw or modified kaolinite in 1 mL of deionized water, followed by mixing for one hour on a magnetic stirrer. Prior to its modification, the bare glassy carbon electrode (GCE) was first polished on a 1 µm followed by a 0.3 µm alumina slurries. The electrode was then rinsed with deionized water and submitted to sonication to remove all residual alumina particles. 5 µL of the suspension were then deposited on its surface by “drop coating”, followed by drying in air for about 45 min. The resulting thin film electrode was used as working electrode, a platinum wire as counter electrode and a saturated calomel electrode as reference electrode. All the potential values in this work are referred to this reference electrode. Cyclic voltammetry was used for the electrochemical experimentations using a µ-Autolab potentiostat controlled by the