Research paper

Modification of kaolinite by Grafting of siderophilic ligands to the external octahedral surface

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ABSTRACT

The modification of the external octahedral surface of kaolinite (Kaol) was investigated using two siderophilic ligands (SL): 3,4-dihydroxybenzophenone (DBP) and quercetin (Qu). These SL have a 1,2-dihydroxyphenyl group that forms chelate-complexes with aluminum cations. Adsorption isotherms were obtained colorimetrically. PXRD patterns proved that the adsorption was attributed only to the external surfaces. Furthermore, adsorption of fluoride ions was applied to quantify the non-μ-hydroxy groups of the edges and derive the surface area of edges.
Comparing maximum adsorption capacities with surface area of edges, it can be safely concluded that SL are indeed capable to coordinate to the aluminol basal surface of Kaol. This conclusion is corroborated by significant bathochromic shifts upon adsorption of the ligands that indicate the formation of a surface complex with exposed Al^{3+}. Thus even small amounts of adsorbed SL changed the surface tension of Kaol significantly. Consequently, forced sedimentation experiments showed that the modified Kaol is rendered hydrophobic enough to form stable dispersions in organic solvents fostering preparation of clay polymer nanocomposites (CPN).

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1. Introduction

Kaol [$Al_2Si_2O_5(OH_4)$] is the main component of the wide spread rock kaolin and thus is an abundant, ubiquitous, and inexpensive (200 €/tonne) clay mineral. Although the structure of the dioctahedral 1:1 layered clay mineral is polar, usually no twinning has been observed (Kogure et al., 2010). Kaol is found as strongly anisometric platelets with large aspect ratios that are typically in the range of 10–40. Consequently, polar basal planes dominate the external surface area which exhibit two chemically different types of external basal surfaces i) a siloxane surface formed by basal oxygen atoms of the tetrahedral sheets of SiO_4 (tetrahedral surface, TS) and ii) a gibbsite surface formed by μ-hydroxy groups of octahedral sheets of $Al_2(OH)_4$ (octahedral surface, OS). The interlayer space of Kaol is tightly bridged by strong hydrogen bonds between opposing tetrahedral and octahedral sheets (Brigatti et al., 2006). Consequently, direct intercalation is restricted to guest capable of forming strong hydrogen bonds (Elbokl and Detellier, 2008). Natural Kaol, though formally neutral in charge, possesses a small cation exchange capacity (CEC) due to some isomorphous substitution in the tetrahedral sheets, which can only be counterbalanced at the outer TS by hydrated cations (Weiss and Russow, 1963). The TS, because of the permanent negative charge, may be modified through simple ion exchange using cationic modificators such as metal cation

complexes or polyelectrolytes, during which the non-charged OS maintains unmodified.

Selective modification of the OS by covalent grafting (Hirsemann et al., 2011a; Letaief and Detellier, 2007; Murakami et al., 2004; Tunney and Detellier, 1994; Yah et al., 2011) is more challenging as compared to TS modification. It is nevertheless required to fine-tune the intrinsic so-called "Janus-character" of the Kaol particles (Hirsemann et al., 2011b; Weiss et al., 2013). Janus particles in general have been shown to have a wide range of promising industrial application e.g. as a catalyst (Perro et al., 2005; Walther and Müller, 2008).

Moreover, the organic modification introduces organophilization of the initially hydrophilic nature of the OS, and hence, improves the dispersion quality in organic solvents or even in hydrophobic polymer matrices which helps manufacturing CPN (Gardolinski et al., 2000).

There are various studies that investigated adsorption and surface complexation of different organic ligands on a wide range of clays and metal oxides surfaces (Blesa et al., 2000; Guez et al., 1996; Talbot et al., 2003). Most of these studies focused on the uptake of humic acid, catechols, and phenols, from waste water using clays and metal oxides. Fewer studies investigated neutral organic ligands as potential surface modificators for gibbsite-like surfaces (Diar-Bakerly et al., 2012; Sedo et al., 2013). Kummert and Stumm (1980) found that the adsorption of catechol on γ-Al_2O_3 surfaces is related to the pK_a value of the ligand and its affinity towards the Al-cations, which is in turn comparable with complex building constants in solution. Haderlein and Schwarzenbach (1993) proved that the adsorption of catechol on Kaol is not related to the adsorption of nitrophenols, which adsorb on

the tetrahedral surface of Kaol. In the literature, it was proven (Hirsemann et al., 2011b; Weiss et al., 2013) that catechols are selective towards the OS of Kaol. This was achieved by adsorption of ^{31}P-labeled catechol on Kaol followed by solid-state ^{31}P NMR. Moreover, selective modification could be proven by secondary ion mass spectrometry analysis of oriented platelets. It was also unequivocally proven (Hirsemann et al., 2011a) that intercalated ethylene glycol was covalently grafted to the μ-hydroxy groups by probing the chemical environment of aluminum nuclei using solid-state NMR techniques. However, the external specific surface area (SSA) is very small (typically < 9 m²/g) compared to the huge total internal area of the basal surfaces (typically about 850 m²/g, Michot and Villieras, 2013) that is available for intercalates. Consequently, most sensitive analytics are required to follow adsorption purely restricted to the OS.

Proving modification of OS by 1,2-dihydroxyphenyl functions is further complicated by the fact that terminal aluminol groups at the edges are expected to be more reactive as compared to the μ-hydroxy groups at the OS and will be complexed first (Weiss et al., 1956).

Herein, the modification of the OS of Kaol using SL, such as substituted catechols and flavones, containing a 1,2-dihydroxyphenyl group, was investigated. The 1,2-dihydroxyphenyl group is considered as an extremely reactive functional group (compared to the related alcohol or phenols) and forms stable chelate-complexes with Al-cation. The main focus was on optimization of reaction conditions to maximize adsorption capacities and hence grafting density of the surface modificators. Brazilian Kaol was used and modified using two different SL i) DBP and ii) Qu. As the adsorption capacities of external surfaces are very small, UV–Visible spectrometry, sedimentation kinetics test, X-ray diffraction and reflectance spectroscopy were applied to characterize and confirm the modification. Optimization and quantification of the absorption then allows that to unequivocally prove that these modificators are not only adsorbed at the edges but also clearly on the aluminol basal surfaces.

2. Experimental

2.1. Materials and instruments

Kaol (Amazone 88/90) from Brazil was provided by Vale International S.A. (Saint-Prex, Switzerland). The clay mineral was size fractioned by a hydrocyclone but no dispersing agent and no sedimentation agent were added. Kaol was further purified through three steps i) removal of magnesium and calcium carbonate using ethylenediaminetetraacetic acid (EDTA), ii) deferration using dithionite–citrate–bicarbonate method (Mehra and Jackson, 1958) and iii) removal of organic impurities by ozonization. This fine-grained Kaol showed typical dimensions of the ideally hexagonal platelets around 1 μm in diameter and up to 100 nm in height (see SEM in Fig. 5). The SSA was calculated using the Brunauer, Emmett, and Teller (BET) method (Quantachrome Nova 2000e analyzer, N₂-adsorption).

SL used for the surface modification, 3,4-dihydroxybenzo-phenone (DBP) and quercetin (Qu); 2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-chromen-4-one, were purchased from Alfa Aesar. The organic solvents, tetrahydro-furan (THF) and ethanol (EtOH) were purchased from Sigma Aldrich. Sodium fluoride (NaF) was purchased from Merck. Ethylenediaminetetraacetic acid disodium salt, glacial acetic acid, sodium citrate, sodium dithionite, sodium hydroxide and sodium chloride were purchased from Grüssing GmbH.

2.2. Modification of the OS of kaolinite

In a tightly closed glass vessel, 0.25 g of Kaol was dispersed in 25 mL of a solution of SL in EtOH (concentration ranging between 0.05 and 0.5×10^{-3} mol/L). The reaction mixture was ultrasonified (2 min) and shaken for equilibration using an overhead shaker for two days at temperatures of 25 or 60 °C.

The dispersions were immediately centrifuged (Heraeus Multifuge 1L) at 9000 rpm for 10 min using closed polypropylene centrifuge tubes. Finally, the supernatants were analyzed using UV–vis spectrometer (Cary 300 UV–vis, Varian, cell path length of 1 cm) to determine the remaining amount of the SL in solution. Kaol-Qu and Kaol-DBP represent the Kaol modified by Qu and DBP, respectively.

2.3. Quantifying the adsorption capacities of the edges

An estimate of the adsorption capacities of the edges was achieved by monitoring the adsorption isotherm of fluoride ions by potentiometric titration. The determination of fluoride ions in dispersion was achieved using a fluoride ion selective electrode (F⁻-ISE Ω Metrohm, 905 Titrando). The titration was carried out in a hydrous total ionic strength adjustment buffer (TISAB) in polypropylene beakers. This buffer was prepared by dissolving 58 g of NaCl (1 mol), 4 g of Na₂EDTA (0.01 mol), 57 mL of glacial acetic acid in 0.5 L bi-distilled water. Anion exchange at the edges works best at the point of zero charge, which was reported to lie between 4.5 and 5.0 (Scroth and Sposito, 1997). The pH value of the mixture was therefore adjusted to 5.5 by adding NaOH (10 mol/L) after cooling the mixture in an ice bath. The total volume was adjusted to 1 L by adding bi-distilled water. The potentials of a series of standard concentrations ($0.05–1.5 \times 10^{-3}$ mol/L) were measured and a potential vs. concentration curve was obtained. After that, a dispersion of 1 g Kaol was prepared in 100 mL of a 1:1 mixture of TISAB and an aqueous solution of NaF (final NaF concentrations ranging between 0.05 and 1.5×10^{-3} mol/L) that was equilibrated for 30 min at room temperature.

2.4. Characterization of surface modified kaolinite

To prove that no intercalation occurred, PXRD patterns were recorded in reflection mode (PANalytical Xpert Pro equipped with a X'Celerator Scientific RTMS detector and using Cu Kα radiation). The samples were measured on flat glass holders to foster texture and boost the intensities of the basal reflections.

To compare the stability of different dispersion in an organic solvent upon surface modification, dispersions of 0.25 mass% of pristine Kaol and the surface modified samples, Kaol-DBP and Kaol-Qu, were prepared in THF. The semi-quantitative measurement was carried out applying a Lumifuge (Lumifuge 114 stability analyzer) with stepwise increasing centrifugal velocities.

The reflection spectra of the adsorbed SL on the Kaol were recorded using UV–vis spectrometer (Cary 5, Varian) equipped with a Praying Mantis unit. The modified samples were repeatedly (5 times) washed with EtOH (approximately 25 mL) prior to measurement to ensure complete removal of non-bonded SL. Moreover, the results were compared to the absorption spectra of the SL in an EtOH solution (Cary 300, Varian).

3. Results and discussion

3.1. Siderophilic ligands

As a result of the small size of the trivalent Al-cation, it is considered as a so-called 'hard Lewis acid'. Therefore, stable complexes are expected to be formed with 'hard Lewis bases' such as carboxylates, catecholates, and phenolates. Furthermore, as stated in the introduction, the complexation behavior of Al-cations located at the surface of a layered inorganic material was found to be similar to a solution (Kummert and Stumm, 1980). The most stable complexes of trivalent metal ions are formed by so-called SL that are hard chelate ligands of the catechol type. The two ortho-hydroxy groups are part of a larger conjugated planar π-system which increases the electron density at the coordinating oxygen atoms (Lewis base; electron donor), and hence, improves the reactivity towards metal cations (Lewis acid;