



Research paper

Influence of physical/chemical treatments to delamination of nanohybrid kaolinite-dipicolinate



Adrieli Cristina da Silva, Katia J. Ciuffi, Márcio José dos Reis, Paulo Sergio Calefi, Emerson Henrique de Faria *

Grupo de Pesquisa em Materiais Lamelares Híbridos – (GPMatLam-UNIFRAN), Universidade de Franca, Av. Dr. Armando Salles Oliveira, 201, Parque Universitário, 14404-600 Franca, SP, Brazil

ARTICLE INFO

Article history:

Received 18 September 2015

Received in revised form 8 March 2016

Accepted 12 March 2016

Available online 1 April 2016

Keywords:

Kaolinite

Functionalization

Hybrid material

Delamination pyridine-carboxylic acid

ABSTRACT

This work shows how submitting kaolinite grafted with dipicolinic acid (Kaol-dpa) to treatment with different solvents and physical/chemical treatment (e.g., ultrasound bath, magnetic stirring, or thermal treatment in water) influences Ka-dpa delamination. X-ray powder diffraction, chemical analysis (C, H, and N), thermal analysis, Fourier-transform infrared spectroscopy, and transmission electron microscopy aided examination of all the samples. Delamination of the treated Kaol-dpa samples elicited changes in the intensity of the characteristic Kaol-dpa d_{001} reflections. Treatment with different solvents reduced the intensity of the d_{001} reflections, which almost disappeared for the sample treated with water suggesting the exfoliation. Ultrasound bath, thermal treatment, and magnetic stirring in water also decreased the typical Kaol-dpa d_{001} reflection and increased the reflection at $2\theta = 12.2^\circ$, the reflection due to the basal spacing of purified kaolinite. Long treatment times eliminated the dipicolinic acid that was only adsorbed onto Kaol-dpa nanohybrid. In conclusion, different types of physical treatment in water were able to delaminate Kaol-dpa, thereby exposing the reactive pyridine-carboxylic groups present in the hybrid matrix.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The possibility of using inorganic materials or organomodified inorganic materials as (i) additives for polymers and rubbers (Pavlidou and Papispyrides, 2008), (ii) heterogeneous catalysts and photocatalysts (Araújo, et al., 2014; Barbosa et al., 2015; de Faria et al., 2012), (iii) adsorbents (Marçal et al., 2015; Matusik and Badja, 2013), and (iv) electrochemical sensors (Dedzo and Detellier, 2012) has aroused extensive scientific and technological interest. In this context, various materials like sepiolite, bentonite, and kaolinite have been developed. For example, Khalaf and Hegazy (2012) used organobentonites as fillers and additives in styrene-butadiene rubber, to demonstrate that the organobentonite-polymer compounds reinforced the rubber and improved its vulcanization rate and torque value. According to these authors, additive dispersion in a polymer depended on the polymer physical structure, and the functionalizing agent played an important role in the dispersion process.

Kaolinite is a layered material that can be intercalated (via weak interactions) or functionalized (via grafting/covalent bonds) with organic molecules by chemical/physical modification of kaolinite by means of different strategies (Letaief et al., 2006). Valášková et al. (2007) investigated the structural modification of kaolinite and verified how ball milling affected the kaolinite particles. The kaolinite precursor

employed by these authors had been previously intercalated with urea and exfoliated/delaminated at low temperature.

From a structural standpoint, kaolinite corresponds to a clay mineral of the 1:1 or TO type with theoretical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$; it consists of layers combining SiO_4 tetrahedral sheets with $\text{Al}(\text{OH})_6$ octahedral sheets. Kaolinite delamination is the formation of particles with a few layers, while exfoliation results in the formation of single layers and generally results on the curling of kaolinite layers to tubular phases like halloysite (Gardolinski and Lagaly, 2005).

Exfoliation/delamination of kaolinite is an important industrial process: it influences the clay rheological properties and dispersion, which is valuable in the ceramic industry, and it impacts the clay coating properties, which is useful in the paper industry. Exfoliation of kaolinite can modify the clay surface (by exposing functional groups of the functionalized clay molecules), reduce particle size, and increase the specific surface area, thereby paving the way for new applications (Corrêa et al., 2008; Valášková et al., 2007).

Exfoliated/delaminated kaolinite can be obtained by submitting kaolinite intercalated with organic molecules, such as urea, ammonium acetate, and hydrazine, to mechanical treatment like milling, ultrasound, and magnetic stirring, in combination or alone (Frost et al., 2001; Valášková et al., 2007). Delamination means the splitting of kaolinite crystals into particles consisting of several layers, while exfoliation refers to the splitting to single layers which could promote in some cases the curling process, as described in the literature (Gardolinski and Lagaly, 2005; Matusik et al., 2009; Valášková et al., 2007), producing nanorolls similar to halloysite.

* Corresponding author.

E-mail address: emerson.faria@unifran.edu.br (E.H. de Faria).

Exfoliation and/or delamination of kaolinite intercalates with organic molecules including dimethyl sulfoxide, potassium acetate, urea, alcohols, and amines has been investigated (Matusik et al., 2009; Niu and Guo, 2006; Zhenbang et al., 2007). The intercalated molecule usually weakens the bond between the kaolinite layers, to facilitate delamination (Linlin et al., 2008). According to Matusik et al. (2009), kaolinite rolling to form nanotubes largely depends on the type of intercalated molecule and on the intercalation efficiency.

Various hybrids of kaolinite and other clays such as laponite and saponite with higher intercalation and functionalization ratios had been obtained. Literature data presents some results on kaolinite functionalization with pyridine-2-carboxylic and pyridine-2,6-dicarboxylic acids (de Faria et al., 2009), tris(hydroxymethyl)aminomethane (de Faria et al., 2012), 3-aminopropyltriethoxysilane (Ávila et al., 2010), and alginic acid (Bandeira et al., 2012). Compounds based on pyridine carboxylic acids can form complexes with transition metals (Araújo et al., 2014; de Faria et al., 2012) and lanthanides (de Faria et al., 2011), enabling their application as catalysts and luminescent devices, respectively (Bushuev et al., 2011; de Faria et al., 2012). The presence of immobilized pyridine carboxylic acids in delaminated hybrid materials allows application of these materials as adsorbents, additives in organic polymers, and supports for immobilization of macromolecules, just to mention a few examples.

In this sense, this work has evaluated delamination of kaolinite functionalized with pyridine-2,6-dicarboxylic acid (or dipicolinic acid, dpa) with different solvents and physical/chemical treatment such as ultrasound bath, magnetic stirring, or thermal treatment in water. The delaminated materials were characterized by X-ray powder diffraction, chemical analysis (C, H, and N), thermal analysis, Fourier-transform infrared spectroscopy, and transmission electronic microscopy.

2. Experimental

2.1. Materials

Except for kaolinite, all solvents and reagents were of high purity commercial grade (Merck and Sigma-Aldrich), most of them used as received.

2.2. Kaolinite purification

Raw kaolinite was obtained by Darcy R.O. Silva & Cia. in the municipality of São Simão, State of São Paulo, Brazil. Purification involved suspending raw kaolinite in distilled water (Pérez-Santano et al., 2005; de Faria et al., 2009), which provided pure kaolinite (designated Kaol herein) with particle size of 2 μm or less. The chemical composition of the purified kaolinite was previously established by us (de Faria et al., 2009) following this deduced chemical formula: $\text{Si}_{2.0}\text{Al}_{1.96}\text{Fe}_{0.03}\text{Mg}_{0.01}\text{K}_{0.02}\text{Ti}_{0.03}\text{O}_{7.06}$ that is very close to theoretical one of kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$.

2.3. Intercalation of pure kaolinite with dimethyl sulfoxide

Dimethyl sulfoxide (DMSO) intercalation into Kaol was conducted by adding 40 g of Kaol to 270 mL of DMSO and 30 mL of water (Tunney and Detellier, 1993; Brandt et al., 2003), which was followed by stirring at 60 °C for 10 days. The resulting material, kaolinite intercalated with dimethyl sulfoxide was denominated as Kaol-DMSO, was separated by centrifugation, washed with ethanol, and dried at 60 °C.

2.4. Kaolinite grafting with pyridine dicarboxylic acid (or dipicolinic acid)

Functionalized kaolinite was prepared by keeping Ka-DMSO and dipicolinic acid (dpa) under reflux at 180 °C for 48 h, at a Kaol-DMSO/dpa molar ratio of 1:5 (de Faria et al., 2009). The resulting material,

denominated Kaol-dpa, was washed with ethanol and dried at 60 °C. Fig. 1 brings a schematic representation of Kaol-dpa synthesis.

2.5. Delamination procedures

I) Solvent effect

The solvent effect was evaluated by suspending 0.1 g of Kaol-dpa in 5 mL of toluene, ethanol, ethanol/water (1:1 v/v), or pure water for 2 h, under magnetic stirring. The treated material was separated by centrifugation and dried at 60 °C.

II) Physical/chemical treatment

Kaol-dpa (0.2 g) was suspended in 5 mL of distilled water and submitted to ultrasound bath at room temperature for 30 min or 1 h, magnetic stirring at room temperature for 2 or 4 h, or hydrothermal treatment at 95 °C for 30 min or 1 h. At the end of the treatment, the solid material was separated by centrifugation and dried at 60 °C.

2.6. Characterization techniques

X-ray powder diffraction (XRD) patterns (random preparation) of the Kaol-dpa submitted to different types of treatment (solvent or physical/chemical treatment) were obtained on a Rigaku, Miniflex II Desktop X-ray Diffractometer operating at 40 kV and 30 mA, with Cu Kα radiation (0.15406 nm). The samples were measured by varying the angle from 2 to 65°. All the analyses were processed at a scan speed of 2° per minute, with steps of 0.05 and a counting time of 5 s.

Fourier-transform infrared spectra (FTIR) were recorded over the range 400–4000 cm^{-1} on a Perkin-Elmer 1730 spectrometer. A total of 32 scans were collected; the resolution was 4 cm^{-1} . The dispersed sample was pressed in KBr pellets (2% w/w).

C, H, and N elemental analyses were accomplished on a Perkin-Elmer 2400 analyzer in the Analytical Center of the Chemistry Institute of the University of São Paulo.

Thermogravimetric analyses (TGA) and thermal analyses (TG/DTA) were carried out on a TA Instruments SDT Q600 Simultaneous DTA-TGA thermal analyzer operating between 25 and 1000 °C. The heating rate and the airflow were 20 °C/min and 100 mL/min, respectively.

Transmission electron microscopy (TEM) was performed on a Jeol-Jem CX-II equipment-1200 at an accelerating voltage of 100 kV. The sample was prepared by immersing a copper grid (300 mesh copper grids) directly into a suspension of the material in water, followed by drying.

Nitrogen adsorption-desorption was carried out at −196 °C using a static volumetric apparatus (Micromeritics ASAP 2020 adsorption analyzer). Prior to the adsorption measurements, the sample (ca. 0.2 g) was outgassed at 120 °C for 24 h under a vacuum better than 0.1 Pa.

The cationic exchange capacity (CEC) of kaolinite and nanohybrids was calculated by adsorption of methylene blue (MB), which also allowed the calculation of the specific surface area accessible to this molecule (SSA). The methylene blue solution was prepared by dissolving 1 g of dry MB powder in 200 cm^3 of distilled water. 50 mg of oven-dried samples was suspended in 10 cm^3 of distilled water, and then the MB solution was added to this sample suspension in 0.5 cm^3 aliquots. After the addition of each 0.5 cm^3 aliquot, the suspension was mixed by magnetic stirring for 1 min; then, a small drop was removed from the solution and placed onto Fisher brand filter paper. If the un-adsorbed MB forms a permanent blue halo around the suspension aggregate spot onto the filter paper, it means that MB has replaced cations in the double layer and coated the entire surface. The cation exchange capacity was determined from the MB amount required for reaching the end-point from the following equation:

$$\text{CEC} = \frac{[\text{MB}] \cdot V}{W} \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/1694064>

Download Persian Version:

<https://daneshyari.com/article/1694064>

[Daneshyari.com](https://daneshyari.com)