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Intercalation of cyclic imides in kaolinite

Tamer A. Elbokl, Christian Detellier *

Center for Catalysis Research and Innovation and Department of Chemistry, University of Ottawa, Ottawa, ON K1N 6N5, Canada

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ABSTRACT

The intercalation of two cyclic imides, succinimide and glutarimide, in the interlayer spaces of kaolinite was obtained from a "soft guest-displacement method" by displacing previously intercalated guest molecules. The dimethyl sulfoxide (DMSO)–kaolinite preintercalate was particularly efficient for that purpose. The intercalation exchange was done from a concentrated aqueous solution of the cyclic imides, at ambient temperature, in a relatively short time. Complete displacement of DMSO by the cyclic imides was confirmed by the results of several independent characterizations, including XRD, TG/DTA, FTIR, and ^{13}C MAS NMR analyses including dipolar dephasing experiments. The imide intercalates are two dimensionally constrained in the kaolinite interlayer spaces, and are structurally organized in a flattened configuration with their cycle roughly parallel to the *ab* plane of the kaolinite layers. Elemental analysis gives the following compositions: $Al_2Si_2O_5(OH)_4{\cdot}(C_4H_5NO_2)_{0.65}$ and $Al_2Si_2O_5(OH)_4{\cdot}(C_5H_7NO_2)_{0.49}$, respectively for succinimide and glutarimide. The results of the TG/DTA analyses showed enhanced thermal stabilities of the imide intercalates compared with the starting materials. The intercalation process from the aqueous solution is reversible: in prolonged contact with water, the imide molecules are released, resulting in the rebuilding of the kaolinite structure. These results demonstrate the potential use of kaolinite as a slow-releasing agent for molecules structurally related to the cyclic imides of this study.

1. Introduction

Kaolinite (Kao) is the most abundant mineral of the kaolin group, which also includes dickite, nacrite, and halloysite, their hydrated analogue. These are 1:1 phyllosilicates, characterized by a 1:1 dioctahedral structure, with the chemical composition $Al_2Si_2O_5(OH)_4$. Because the interlayer space of kaolinite is made up of two different surfaces, $(SiO)_6$ macro-rings on one side and aluminol groups on the other side, this clay mineral is remarkable by its noncentrosymmetric structure that creates large superposed dipoles in the lamellar structure, resulting in a large cohesive energy [1]. The intercalation chemistry of kaolinite to produce organic–inorganic nanohybrid materials is less developed than that of the swelling smectites [2], but the intercalation of salts, ionic liquids, and dipolar organic molecules is well documented [3–8]. In addition, the functionalization of the aluminol surface of kaolinite has been achieved through the covalent grafting of organic molecules, such as methanol, ethylene glycol, diols, polyols, and, more recently, oxirane, aminoalcohols and 3-aminopropyltriethoxysilane [4,6a–6c,6e,7b,7d,8e–8h]. Not only does the hydroxylated aluminate surface of kaolinite provide an abundance of reactive hydroxyl groups for guest species to be covalently linked to, but the dipolar interlayer environment induced by the second surface may also cause the spontaneous alignment of polar guest species.

Another type of clay-based nanohybrid materials, known as polymer nanocomposites, has also become an effective alternative to conventional polymer composites. Kaolinite has the potential to be an ideal precursor for the preparation of new nanocomposite materials. A few examples of polymer–kaolinite intercalated nanocomposites have been reported [9].

Succinimide is a diketopyrrolidine that is prepared by heating succinic anhydride with aqueous ammonia, followed by rapid distillation of ammonium succinate [10a,10b]. Derivatives of succinimide and glutarimide, its piperidine analog, are of important biological and pharmacological interest. Succinimide and other cyclic carboximides are used as starting materials in organic synthesis. Their nitranions are also important intermediates in many chemical reactions [10a–10d]. In addition, succinimide itself is a hypooxaluric agent. On the other hand, glutarimide derivatives possess anticancer activity, and they are also components of some modern antibiotics with antiviral and fungicidal activities. The biological activity of glutarimide drugs is determined by the hydrogen bonding of the CO–NH–CO imide groups and the other molecules in the biological system. It is believed that the ability of glutarimide drugs to intercalate between nucleic base pairs in the DNA helix is significantly due to the flattening of the glutarimide ring [10e].

In this paper, intercalation compounds of kaolinite with these two cyclic imides, namely 2,5-pyrrolidinedione (succinimide, SIM)

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* Corresponding author.
E-mail address: dete@uottawa.ca (C. Detellier).

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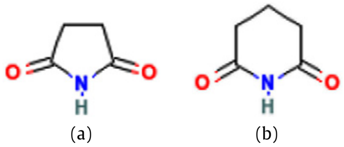

Chart 1. Structures of (a) succinimide and (b) glutarimide.

and 2,6-piperidinedione (glutarimide, GIM) (see Chart 1), are reported for the first time by displacing other intercalated guest molecules (intermediates). The intercalation exchange was done from a concentrated aqueous solution of the cyclic imides. Interestingly also, the new cyclic-imide intercalates of kaolinite were prepared by what can be called a “soft guest-displacement method”, as the displacement reactions were performed at ambient temperature, similar to the temperatures at which the guest molecules were intercalated, yet at a relatively short time (hours) compared with the intercalation of the intermediate dipolar molecules to prepare the starting materials (1–2 months).

The investigation of the first kaolinite–cyclic imides intercalated materials is expected to contribute to the continued series of studies on the interlayer chemistry of kaolinite and to the potential development of kaolinite as a slow drug-delivery system. The results of the XRD, FTIR, and TG analyses confirmed the intercalation of the cyclic imide molecules in the interlayer spaces of kaolinite. ^{13}C CP and DD/MAS NMR spectra indicated the complete displacement of the guest molecules of the starting materials by the imides in the interlayer space. ^{29}Si and ^{27}Al MAS NMR spectra of the starting materials and the products are also discussed.

2. Experimental

2.1. Chemicals and reagents

All chemicals used were of reagent-grade quality and were not further purified. 2,5-Pyrrolidinedione (succinimide, SIM) and 2,6-piperidinedione (glutarimide, GIM) were obtained respectively from Alfa Aesar (99%) and from Aldrich (98%). Well-crystallized kaolinite from Georgia (labeled KGa-1b) was obtained from the Source Clays Repository of the Clay Minerals Society (Purdue University, West Lafayette, IN). This was purified according to the previously reported sedimentation techniques [11], and the <2 μm size fraction was used.

2.2. Analysis and characterization

XRD powder patterns were performed on a Philips PW 3710 diffractometer using a generator voltage of 45 kV and a generator current of 40 mA. Typically, a step size of 0.04° (2θ) was used with a dwell time of 0.5 s/step in a continuous scan mode. The sample was spun during the acquisition, and a 12 mm automatic divergence slit was used together with a 0.2 mm fixed receiving slit, 1° secondary antiscatter slit, and a 10 mm fixed incident-beam mask. The ratio of intercalation (RI) was calculated as an approximation from the relative intensities of the (001) reflections of the organo-kaolinite phase and of the residual kaolinite phase [3c].

Infrared spectra were acquired on a Thermo–Nicolet Nexus 670 FTIR spectrometer under dry air using 32–256 scans with a resolution of 2–4 cm^{-1}. The samples were prepared as KBr pellets from 50 mg of a mixture of 0.25–0.5 wt% sample in KBr. Peak positions were either picked manually or automatically, using the instrument installed software.

^{13}C CP/MAS NMR spectra were obtained on a Bruker ASX-200 instrument operating at 50.31 MHz at a spinning rate of 4.0–5.0 kHz and a contact time of 2 ms in most cases. ^{13}C DD/MAS spectra were obtained on the same instrument, using a dipolar dephasing time of $\tau = 10$–50 μs with the same number of scans used for the cross-polarization experiment. The spectra were referenced to adamantane at $\delta = 38.4$ ppm. Some spectra were obtained on a Bruker AVANCE-500 instrument operating at 125.77 MHz at a spinning rate of 12.0–14.5 kHz.

^{29}Si CP/MAS NMR spectra were obtained on a Bruker AVANCE-500 instrument operating at 99.35 MHz at a spinning rate of 6.0 kHz and a contact time of 8–10 ms. The spectra were referenced to tetramethylsilane (TMS) at 0.0 ppm.

^{27}Al MAS NMR spectra were obtained on a Bruker AVANCE-500 instrument operating at 130.32 MHz at a spinning rate of 12.0–14.0 kHz. All ^{27}Al spectra were referenced to a 0.1 mol/L solution of $Al(NO_3)_3 \cdot 9H_2O$.

All thermal analyses (TG and DTA) were carried out on an SDT 2960 Simultaneous DSC–TG instrument (TA Instruments) under air flow (100 mL/min) at a heating rate of 10–20 °C/min. Approximately, 10- to 20-mg samples were used for each run. In all cases, the given TG mass-loss data were determined approximately.

Organic elemental analyses (CHNOS; combustion analysis) were performed on selected samples by Chemisar Laboratories Inc. (Guelph, ON, Canada).

2.3. Preparation and characterization of Kao–DMSO intercalate

Kao–DMSO intercalate was typically prepared by mixing 20 g of KGa-1b with 100 mL of DMSO in a sealed container for a sufficient time (2 months) with occasional stirring to achieve maximum intercalation. The product was vacuum-filtered and washed with 1,4-dioxane to remove excess DMSO and then air-dried to yield an off-white powder. Characterization of a representative sample gave the following results. XRD: $d_{001} = 11.16$ Å (100.0), d_{001}(Kao) $= 7.15$ Å (9.7), $d_{002} = 5.6$ Å (4.2), $d_{003} = 3.72$ Å (45.7), d_{002}(Kao) $= 3.57$ Å (14.6), $d_{004} = 2.8$ Å (1.8), $d_{060} = 1.49$ Å (7.6), RI $= 0.91$–0.98 (various samples). FTIR (KBr, cm^{-1}): ν(OH) 3696 (m), ν(OH) 3665 (s), ν(OH) 3621 (s), ν(OH) 3540 (m), ν(OH) 3505 (m), ν(C–H) 3022 (w), ν(C–H) 2937 (w), δ(C–H) 1429 (w), δ(C–H) 1407 (w), δ(C–H) 1394 (w), δ(C–H) 1318 (w); (Si–O) vibrations: 1123 (s), 1101 (s), 1039 (s), 1016 (s); δ(Al–OH): 958 (m), 940 (w), 905 (s); other bands: (Si–O–Si) 790 (w), (Si–O–Si) 744 (w), (Si–O–Si) 688 (m), 606 (w), (Al–O–Si) 552 (s), (Si–O) 465 (s), (Si–O) 435 (s). ^{13}C CP/MAS NMR (50.31 MHz, ppm) δ: 43.98 and 42.89 (CH_3). ^{29}Si CP/MAS (ppm): -90.9, -91.5, and -92.7. ^{27}Al MAS (ppm): 1.78. TG/DTA (air): RT–245 °C (17.5% mass loss, $T_{\mathrm{endo}} = 98$ °C and 195 °C); 245–725 °C (11.4% mass loss, $T_{\mathrm{endo}} = 513$ °C); $T_{\mathrm{exo}} = 1000$ °C; total TG mass loss = 28.7%.

2.4. Preparation of Kao–NMF intercalate

Approximately 20 g of KGa-1b was mixed with 100 ml of *N*-methylformamide in a sealed container for a sufficient time ($\sim$1 month) with occasional stirring to achieve maximum intercalation. After that, the product was filtered and washed with 1,4-dioxane to remove excess NMF and then air-dried. A representative sample gave the following results. XRD: $d_{001} = 10.71$ Å (100.0), d_{001}(Kao) $= 7.15$ Å (18.9), $d_{002} = 5.28$ Å (0.6), $d_{003} = 3.58$ Å (71.7), RI = 0.87. FTIR (KBr, cm^{-1}): ν(OH) 3695 (m), ν(OH) 3652 (vw), ν(OH) 3620 (s), ν(OH) 3600 (w), ν(OH) 3550 (m, br), ν(N–H) 3420 (s), ν(C–H) 2924 (w), ν(C–H) 2910 (w), ν(C=O) 1682 (s), (amide II) 1529 (m), δ(C–H) 1419 (w), δ(C–H) 1384 (m), δ(C–H) 1318 (w), δ(C–H) 1232 (vw); (Si–O) vibrations: 1104 (s), 1034 (s), 1009 (s); δ(Al–OH): 958 (m), 949 (vw), 911 (s); other bands: (Si–O–Si) 791 (w), (Si–O–Si) 746 (w), (Si–O–Si) 688 (m), 637 (w), (Al–O–Si) 545 (s), (Si–O) 470 (s), (Si–O) 434 (s). ^{13}C CP/MAS (ppm) δ: 26.81 ($N–CH_3$) and 163.98 (C=O). TG: RT–300 °C (10.9% mass loss, $T_{\mathrm{endo}} = 55$ °C and 190 °C); 300–704 °C (12.5% mass loss, $T_{\mathrm{endo}} = 519$ °C); $T_{\mathrm{exo}} = 1002$ °C; total TG mass loss = 23.8%.