Chem. Mater. 1993, 5, 747-748

Interlamellar Covalent Grafting of Organic Units on Kaolinite[†]

James J. Tunney and Christian Detellier[*]

Ottawa-Carleton Chemistry Institute
University of Ottawa Campus
Ottawa, Ontario, Canada K1N 6N5

Received January 20, 1993
Revised Manuscript Received March 29, 1993

In recent years, many materials, resulting from the covalent grafting of organic units on inorganic surfaces, have been developed, mainly for chromatographic applications.[1] However, reports in the literature of such covalent grafting on natural minerals, aluminosilicates particularly, are rather scarce. We report here the first interlamellar grafting of organic moieties on kaolinite.

Choudary *et al.*[2] have reported the anchoring of palladium(II) catalysts[2a-c] and of onium salts[2d] in the interlamellar spaces of montmorillonite. Organochlorosilane reagents have been used to graft organic units on silanol groups of various minerals.[3] An unsuccessful attempt on kaolinite was reported.[3b] Recently, silanization of the external surfaces of kaolin clays was achieved.[3e]

Reactions on the aluminum hydroxyl groups of minerals have been very rarely reported. Inoue *et al.* have reacted ethylene glycol,[4a] other glycols, and amino alcohols[4b] on gibbsite to obtain organoboehmite derivatives. Johnson and Pinnavaia[4c,d] have silylated the external AlOH surfaces of a tubular aluminosilicate, imogolite.

Kaolinite is a 1:1 layered aluminosilicate whose aluminum side is made of a gibbsite-type layer, hydrogen bonded to the silicate side of an adjacent layer.[5] This provides kaolinite with a large cohesive energy, which prohibits expansion like which is found in the smectite family. However, the Al–OH layer would be a candidate for grafting organic moieties, if access could be provided to the reagent. Intercalation of polar organic molecules, such as dimethyl sulfoxide (DMSO) or *N*-methylformamide (NMF) in the interlamellar spaces of kaolinite has been extensively studied.[6] In this work, intercalates of DMSO or NMF in kaolinite were treated with ethylene glycol and a series of alcohols to provide organokaolinite derivatives.

Well-crystallized Georgia kaolinite from the Source Clays Repository of the Clay Mineral Society, University of Missouri (KGa-1), was purified by sedimentation, and the <2-μm esd fraction (>98% of the sample) was used in the subsequent experiments. The DMSO intercalate was prepared following a slightly modified version of the procedure reported by Costanzo *et al.*[6g] and isolated in powder form after washings with dioxane to remove excess DMSO (kao-DMSO; d_{001} = 11.2 Å). The NMF intercalate was prepared by mixing kaolinite with excess NMF for 1 week. The resulting powder was then filtered and washed with dioxane, followed by air drying (kao-NMF; d_{001} = 10.8 Å). Kao-DMSO (typically 2 g) was then refluxed in 100 mL of alcohols (ethylene glycol (EG; 197 °C), ethylene glycol monomethyl ether (EGMM; 124 °C), diethylene glycol monobutyl ether (DEGMB; 231 °C), 1,2-propanediol (1,2-PD; 187 °C), 1,3-propanediol (1,3-PD; 214 °C), for periods of time ranging from 12 to 18 h. After filtration, the powder obtained was washed thoroughly with methanol, ethanol, or water and dried overnight under vacuum at 120 °C over P_2O_5. In the case of EG, the same procedure was followed using kao-NMF as the starting material, instead of kao-DMSO. Identical kao-EG materials were obtained in both cases.

The samples were characterized by X-ray diffraction, elemental analysis, TGA/DSC, and FTIR, ^{27}Al, ^{29}Si, and ^{13}C solid-state MAS NMR spectroscopies. In all the cases, the basal spacings were increased compared to kaolinite (kao) (9.5 Å (kao-EG), 10.6 Å (kao-EGMM), 11.2 Å (kao-DEGMB), 10.9 Å (kao-1,2-PD), 9.8 Å (kao-1,3-PD) compared to 7.2 Å (kao)). In strong contrast, the intercalates kao-DMSO and kao-NMF, when submitted to the same washing and drying treatments, gave the characteristic kaolinite d_{001} distances of 7.2 Å, and not their respective characteristic 11.2- or 10.8-Å distance anymore. Elemental analysis gave ratios C/Al for kao-EG of 0.8. The kaolinite and kao-DMSO intercalate FTIR spectra were identical to those reported in the literature.[7] However, they showed strong modifications of the OH stretching region after reaction with all the alcohols mentioned above. In all the cases, the band at 3620 cm^{-1}, characteristic of the internal OH groups,[7] was unperturbed, in strong contrast with the bands of the surface OH groups. In addition, C–H stretching bands were apparent in the region 2800–3000 cm^{-1}, replacing the DMSO C–H stretching bands. After water washing and drying (see above), the kao-DMSO intercalate FTIR spectrum became identical to the kaolinite one, while the alcohol-reacted materials spectra remain unchanged.

The ^{29}Si MAS NMR spectrum (at 35.76 MHz) of kaolinite, of its DMSO intercalate, and of kao-EG all show a single resonance[8] centered at −92.0, −92.9, and −92.6 ppm,

---

[†] Dedicated to the memory of Professor Jean-Louis Roustan.

(1) Pesek, J. J. In *Chemically Modified Oxide Surfaces*; Leyden, D. E., Collins, W. T., Eds.; Gordon & Breach: New York, 1990; Vol. 3, pp 93–108.

(2) (a) Choudary, B. M.; Kumar, K. R.; Jamil, Z.; Thyagarajan, G. *J. Chem. Soc., Chem. Commun.* **1985**, 931–932. (b) Kumar, K. R.; Choudary, B. M.; Jamil, Z.; Thyagarajan, G. *J. Chem. Soc., Chem. Commun.* **1986**, 130–131. (c) Choudary, B. M.; Bharati, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1505–1506. (d) Choudary, B. M.; Rao, Y. V. S.; Prasad, B. P. *Clays Clay Miner.* **1991**, *39*, 329–333.

(3) (a) Ruiz-Hitzky, E. *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* **1988**, *161*, 433–452. (b) Ruiz-Hitzky, E.; Fripiat, J. J. *Clays Clay Miner.* **1976**, *24*, 25–30. (c) Ruiz-Hitzky, E.; Van Meerbeek, A. *Colloid Polym. Sci.* **1978**, *256*, 135–139. (d) Van Meerbeek, A.; Ruiz-Hitzky, E. *Colloid Polym. Sci.* **1979**, *257*, 178–181. (e) Porro, T. J.; Pattacini, S. C. *Appl. Spectrosc.* **1990**, *44*, 1170–1175. (f) Ruiz-Hitzky, E.; Rojo, J. M. *Nature* **1980**, *287*, 28–30. (g) Yanagisawa, T.; Kazwywki, K.; Kato, C. *React. Solid* **1988**, *5*, 167–175. (h) Sprung, R.; Davis, M. E. Kauffman, J. S. Dybowski, C. *Ind. Eng. Chem. Res.* **1990**, *29*, 213–220.

(4) (a) Inoue, M.; Kondo, Y.; Inui, T. *Inorg. Chem.* **1988**, *27*, 215–221. (b) Inoue, M.; Tanino, H.; Kondo, Y.; Inui, T. *Clays Clay Miner.* **1991**, *39*, 151–157. (c) Johnson, L. M.; Pinnavaia, T. J. *Langmuir* **1991**, *7*, 2636–2641. (d) Johnson, L. M.; Pinnavaia, T. J. *Langmuir* **1990**, *6*, 307–311.

(5) (a) Giese, R. F. Kaolin Minerals: Structure and Stabilities. In *Reviews in Mineralogy: Hydrous Phyllosilicates*; Bailey, S. W., Ed.; Mineralogical Society of America: Washington, DC, 1988; Vol. 19. (b) Hess, A. C.; Saunders, V. R. *J. Phys. Chem.* **1992**, *96*, 4367–4374.

(6) (a) Ledoux, R. L.; White, J. L. *J. Colloid Interface Sci.* **1966**, *21*, 127–152. (b) Olejnik, S.; Posner, A. M.; Quirk, J. P. *Clay Miner.* **1970**, *8*, 421–434. (c) Theng, B. K. G. *The Chemistry of Clay-Organic Reactions*; Adam Hilger: London, 1974; Chapter 6. (d) Sugahara, Y.; Satokawa, S.; Kuroda, K.; Kato, C. *Clays Clay Miner.* **1990**, *38*, 137–143. (e) Duer, M. J.; Rocha, J.; Klinowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 6867–6874. (f) Costanzo, P. M.; Giese, R. F., Jr.; Lipsicas, M.; Straley, C. *Nature* **1982**, *296*, 549–551. (g) Costanzo, P. M.; Giese, R. F., Jr.; Lipsicas, M. *Clays Clay Miner.* **1984**, *32*, 419–428. (h) Costanzo, P. M.; Giese, R. F., Jr.; Clemency, C. V. *Clays Clay Miner.* **1984**, *32*, 29–35.

(7) Johnston, C. T.; Sposito, G.; Bocian, D. F.; Birge, R. R. *J. Phys. Chem.* **1984**, *88*, 5959–5964.

0897-4756/93/2805-0747$04.00/0

respectively. These data, characteristic of the $Q^3(OAl)$ structure,[9a] are in agreement with previously reported values for kaolinite and its DMSO intercalate.[10] The slight shift observed for kao-EG is in agreement with a perturbation of the H-bond network in the interlamellar region, with no major perturbation of the tetrahedral silica sheet structure. In strong contrast with ^{29}Si were the ^{27}Al MAS NMR spectra. The ^{27}Al resonance of kaolinite (at 78.1 MHz) is at −3 ppm,[11] characteristic of the Al octahedral coordination. The spectrum of kao-EG, centered at −8 ppm, was strongly broadened. This broadening was not observed on lower field spectra (46.86 MHz), which rules out an interpretation of the 78.1-MHz spectrum broadening based on an increase of the second-order quadrupolar interactions. Rather, the spectrum can be interpreted as the result of an increase of the chemical shift dispersion, showing the superposition of a higher field resonance on the signal of residual AlOH units. This is in agreement with the grafting of EG units on the aluminum hydroxide sheet, to form Al-O-C bond. This is also in agreement with the X-ray fluorescence and chemical analysis data which give a ratio C/Al lower than 1, as well as with the IR spectra showing residual AlOH groups.

The ^{13}C CP/MAS and DD/MAS NMR spectra of kao-EG were also recorded at 75.37 and at 45.27 MHz. A ^{13}C NMR signal was observed at 64 ppm. The dipolar dephasing experiment[12] (dephasing period = 40 μs) results in an almost complete disappearance of the ^{13}C signal, diagnostic of a very rigid organic unit.

On Figure 1 are shown the TGA of the kao-DMSO intercalate (1a) and of kao-EG (1b). In both cases the dehydroxylation converting kaolinite to metakaolinite is observed around 490 °C.[13] However, while the loss of the organic component was observed around 120 °C in the case of the kao-DMSO intercalate,[14] for kao-EG, it did not occur until approximately 350–400 °C.

All the observations reported are in agreement with the covalent grafting of alcohols on the interlamellar aluminum hydroxide sheet of kaolinite to form an aluminum alkoxide sheet. In the case of ethylene glycol, which was more particularly studied in this preliminary communication, it is probable that one end of EG is grafted to form an Al–O–C bond, while the remaining OH group is keyed into the $(-Si-O-)_6$ macro-ring of the silicate side by hydrogen bonding.[15] However, at this stage, we can not exclude the possible reaction of the diol with two adjacent AlOH groups to form a rigid bridged species. We are currently extending this study to other organic moieties and other minerals. Also, we are characterizing further these organomineral materials, particularly by ^{2}H NMR, to probe the mobility of the organic units.

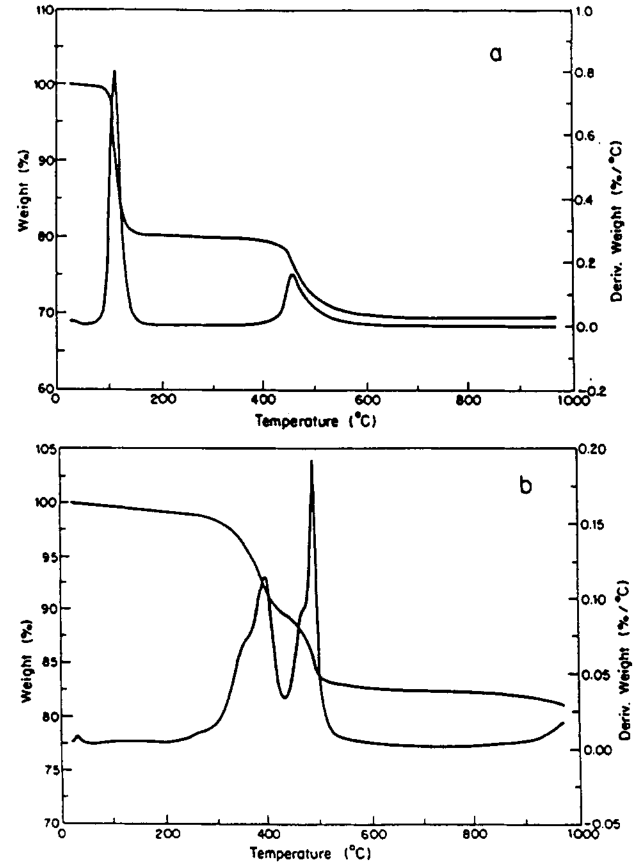

Figure 1. Thermal gravimetric analysis of (a) the kao-DMSO intercalate (the two weight losses were 19.8% and 10.5%); (b) kao-EG (the two weight losses were 9.7% and 7.2%). The TGA were done on a TA instrument 2950, under N_2 atmosphere 100 cm^3/min; 10 °C/min.

Acknowledgment. The University Research Incentive Fund, Government of Ontario (URIF), the Institute for Chemical Science and Technology (ICST), and the Natural Sciences and Engineering Research Council of Canada (NSERCC) are gratefully acknowledged for financial support. We thank Dr. J. Frye (Chemagnetics, Fort Collins, CO) for recording the ^{27}Al and ^{13}C MAS NMR spectra on a Chemagnetics CMX-300 spectrometer. Drs. C. Ratcliffe, G. Facey, and J. Ripmeester (NRC, Ottawa) are thanked for recording ^{27}Al and ^{29}Si MAS NMR spectra on Bruker MSL-300 and CXP-180 instruments. They are also thanked for valuable discussions. We thank Mr. Ron Conlon, X-ray laboratory, department of Earth Sciences, Carleton University, Ottawa, for recording the powder X-ray spectra, Mr. Ron Hartree, department of Geology, University of Ottawa, for recording the X-ray fluorescence spectra, and Mr. Stewart Hunt, Westech Ind. Ltd., Mississauga (Ontario) for recording the TGA data.

---

(8) A splitting of the ^{29}Si NMR resonance of kaolinite in two components has been observed at higher fields (59.61 MHz[9a,b] or 79.5 MHz[9c]). At 35.76 MHz, one could observe only one single, symmetrical peak;

(9) (a) Barron, P. F.; Frost, R. L.; Skjemstad, J. O.; Koppi, A. J. *Nature* **1983**, *302*, 49–50. (b) Thompson, J. G. *Clays Clay Miner.* **1984**, *32*, 233–234. (c) Rocha, J.; Klinowski, J. *J. Magn. Reson.* **1990**, *90*, 567–568.

(10) Thompson, J. G. *Clays Clay Miner.* **1985**, *33*, 173–180.

(11) Lambert, J. F.; Millman, W. S.; Fripiat, J. J. *J. Am. Chem. Soc.* **1989**, *111*, 3517–3522.

(12) Alemany, L. B.; Grant D. M.; Alger, T. D.; Pugmire, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6697–6704.

(13) Lemaitre, J.; Léonard, A. J.; Delmon, B. *Bull. Miner.* **1982**, *105*, 501–507.

(14) Adams, J. M.; Waltl, G. *Clays Clay Miner.* **1980**, *28*, 130–134.

(15) This is based on the presence of a broad OH stretching frequency at 3395 cm^{-1}, not attributable to residual water molecules since the δ_{HOH} is negligible at 1630 cm^{-1}.