

Organo-layered Silicates. Interlamellar Intercalation and Grafting of Ethylene Glycol in Magadiite

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New organo-mineral nanocomposites are prepared by reacting ethylene glycol and other diols with the interlamellar silanol groups of the layered silicic acid, H-magadiite, to afford organically pillared layered silicates.

Magadiite is a naturally occurring, albeit rare, layered silicate of approximate formula $\text{Na}_2\text{Si}_{14}\text{O}_{29}\cdot x\text{H}_2\text{O}^1$ or $\text{Na}_2\text{H}_2\text{Si}_{14}\text{O}_{30}\cdot x\text{H}_2\text{O}^2$. It was discovered by Eugster in 1967 from sediments of Lake Magadi, Kenya, a lake characterized by a very high alkalinity.³ Upon acidification, this mineral becomes the layered silicic acid H-magadiite ($\text{H}_2\text{Si}_{14}\text{O}_{29}\cdot x\text{H}_2\text{O}^4$ or $\text{H}_4\text{Si}_{14}\text{O}_{30}^{2,5}$). This species was found to be a very useful precursor in the design of pillared structures because of the presence of reactive hydroxy groups on its interlayer surface⁵ and its ability to swell in polar organic solvents (NMF, DMF, DMSO).⁴

Pillaring of H-magadiite has previously been achieved primarily through silanol condensation on the hydroxy sites.^{2,6,7} There has been, however, no report of covalent pillaring of this mineral using purely organic pillaring agents. The grafting of alcohols and diols to the hydroxy groups of silica *via* high temperature condensation is well known and has much applicability, especially in chromatography.^{8,9} Grafting of ethylene glycol in the interlayer space of kaolinite has also recently been reported.¹⁰ Here the preparation of a novel organo-magadiite composite material, involving the condensation of ethylene glycol and other alcohol/diol species to the interlayer hydroxys of H-magadiite, is reported.

Sodium magadiite was prepared from silica gel following a slightly modified published procedure.^{1,7} The acid titration method of Lagaly *et al.*⁴ was performed to obtain a crystalline batch of H-magadiite (H-MAG). Subsequently, *N*-methylformamide (NMF) was intercalated in H-MAG,⁴ and the NMF/H-MAG⁺ intercalated species was used in further reactions. The general procedure involved refluxing NMF/H-MAG in ethylene glycol (EG) for 24 h. The product (EG-MAG) was then centrifuged, thoroughly washed with acetone and air dried. As a blank, ethylene glycol was stirred with H-magadiite at room temperature for 5 d to produce the

intercalated compound (EG/H-MAG). The products (sodium magadiite, H-MAG, NMF/H-MAG) were characterized by powder XRD, FTIR, TGA, ²⁹Si CP-MAS, ²⁹Si NMR with high power ¹H decoupling, elemental analysis and particle size analysis. They were in very good agreement with the published data.

Fig. 1 shows the TGA curves for H-MAG, NMF/H-MAG, EG-MAG, and EG/H-MAG. The EG-MAG sample shows two well-defined weight losses, the first between 100 and 180 °C, the second between 450 and 590 °C. In strong contrast, the intercalated species, EG/H-MAG, shows only the loss at 100–180 °C. This is in strong support of the hypothesis that Si–O–C bonds were formed upon reaction of EG with the interlamellar silanol groups in the case of EG-MAG. This material, obtained after the reaction described above, shows the coexistence of intercalated and grafted species. After Soxhlet extraction (24 h over chloroform), the loss of weight at 180 °C could no longer be observed, indicating the extraction of the intercalated EG molecules, and the formation of a purely grafted organo-mineral material. Fig. 2 shows the ²⁹Si CP-MAS NMR spectra of H-MAG and EG-MAG. The cross-polarization of the peak at $\delta -100$ has recently been clearly identified, for the case of dried sodium magadiite, to be due to Q₃ silanol groups ((SiO)₃SiOH), the strong intensity increase being due to -O¹H cross polarization, and not to residual water molecule.¹¹ It is reasonable to assume that this is also the case for the dried H-MAG used in this study. The

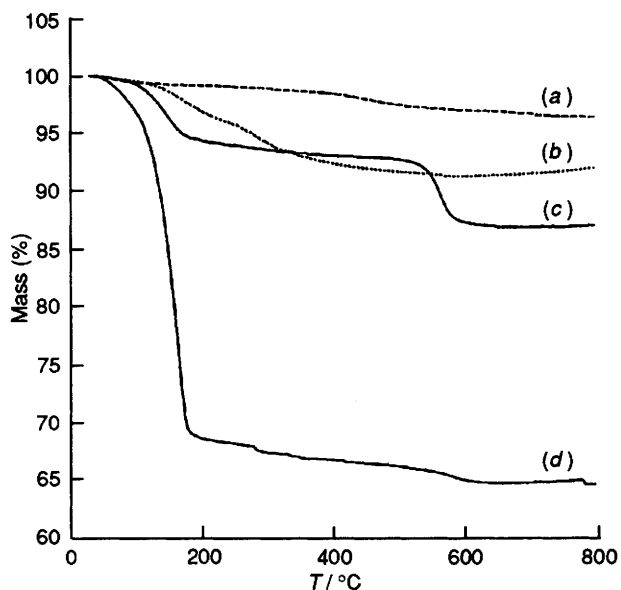


Fig. 1 TGA curves for (a) H-magadiite; (b) NMF-H-magadiite; (c) EG-magadiite; (d) EG/magadiite

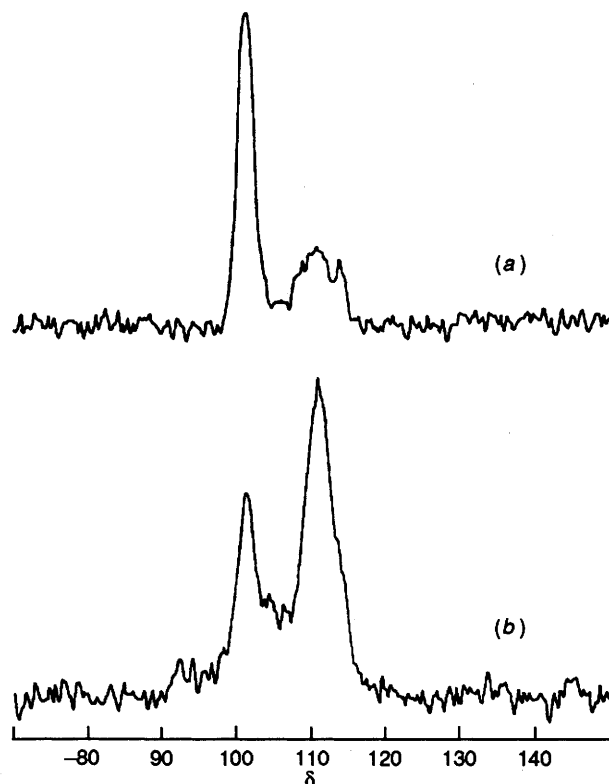


Fig. 2 ²⁹Si CP-MAS NMR spectra of (a) H-magadiite; (b) EG-magadiite

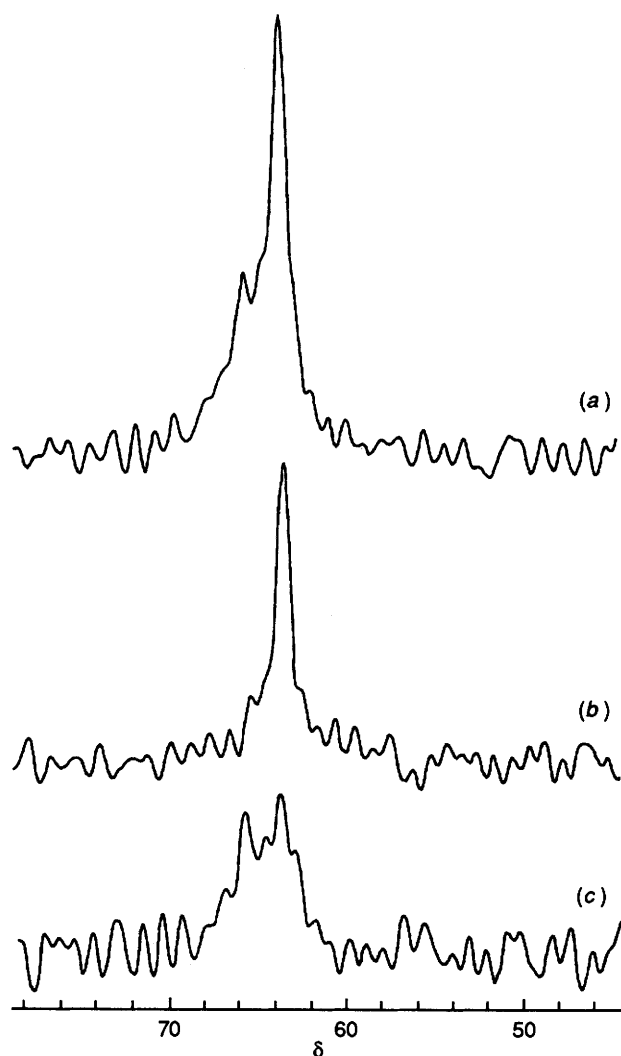


Fig. 3 ^{13}C NMR spectra for EG-magadiite: (a) CPMAS; (b) dipolar dephasing; (c) subtraction of (b) from (a)

decoupled spectrum (not shown) is quite similar to that reported by other authors,^{7,12,13} featuring a Q_3/Q_4 peak intensity ratio of about 1/3 (Q_4 : $(\text{SiO})_4\text{Si}$). The ^{29}Si CP-MAS spectrum of EG-magadiite showed a dramatic reduction of the Q_3/Q_4 peak intensity ratio when compared with that of H-magadiite, indicating that most of the interlayer surface hydrogens of the parent H-MAG (*i.e.* the Q_3 sites) were removed as a result of the reaction with ethylene glycol. This is strong evidence supporting the existence of grafting and pillaring in the interlamellar region of H-magadiite. Also, the ^1H decoupled, ^{29}Si MAS and ^{29}Si CP-MAS spectra of EG-MAG are virtually identical, indicating also that a very large fraction of the silanol hydrogens have been removed and replaced by ethyleneoxy groups. This is further confirmed by ^{13}C CP-MAS NMR. Fig. 3(a) shows the ^{13}C CP-MAS NMR spectrum of the EG-MAG sample resulting from the reaction described above, and whose TGA curve is shown on Fig. 1. In

Figs. 3(b) and 3(c) are respectively shown the dipolar dephased spectrum¹⁴ (dephasing delay of 40 μs) of the same material, and the difference spectrum between 3(a) and 3(b). The resonance for the mobile EG chain is present in the dipolar dephased spectrum in 3(b) due to the reduced ^{13}C - ^1H dipolar interactions. On the other hand, the resonance for the rigidly fixed ethyleneoxy units could not be observed as the CP signal decays almost completely during the 40 μs dephasing time. The difference spectrum in Fig. 3(c) shows primarily the grafted ethyleneoxy segments. Thus, this ^{13}C NMR experiment confirms the TGA data, and shows the simultaneous presence of two types of ethyleneoxy units: intercalated, mobile EG and grafted, rigid $(\text{SiO})_3\text{SiO}$ -EG units.

This work shows the potential for controlling the formation of a large variety of organo-magadiite nanocomposites, intimately mixing, covalently and/or non covalently, silicate layers with organic functionalities.

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Footnote

† The following convention is used to distinguish between intercalated (host-guest complex) and grafted (the host and guest have chemically reacted, and are covalently bound) species: they are respectively described by 'guest/MAG' and 'guest-MAG'.

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