Preparation and Magnetic Properties of Saponite Clays Intercalated with Stable Organic Radicals

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The organic radical cations, 2-(3- and 4-*N*-methylpyridinium)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide, are intercalated into saponite clay $\{Na_{0.46}[Si_{3.54}Al_{0.46}Mg_3O_{10}(OH)_2]\cdot nH_2O\}$ by means of cation exchange, and display Curie paramagnetic behaviour in the interlayers.

Physical and chemical properties of nanocomposites of organic guests and inorganic hosts have attracted much recent interest.[1,2] A layered material, saponite $\{Na_x[Si_{4-x}Al_xMg_3O_{10}(OH)_2]\cdot nH_2O\}$ has a lamellar structure consisting of a two-dimensional array of a mineral lattice. The sodium ions are located in the interlayer, compensating for the negative charges in the layer, together with the water molecules. The interlayer is bound by a weak van der Waals interaction, in contrast to the strong covalent bonds connecting the intralayer species, so that various guest molecules and ions are easily inserted into the gap.[3] Here we report the intercalation of 2-(3- and 4-*N*-methylpyridinium)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide (or *m*- and *p*-*N*-methylpyridinium nitronyl nitroxide, abbreviated as *m*- and *p*-MPYNN$^+$, respectively) into the saponite interlayer by means of cation exchange. The organic radical family nitronyl nitroxide is being studied extensively in the field of molecular ferromagnetism.[4] It is known that the isomers show different magnetic couplings in the bulk crystals of their iodide salts: *p*-MPYNN$^+$ has a strong antiferromagnetic intermolecular interaction of $2J/k_B = -149$ K, while *m*-MPYNN$^+$ has a weak ferromagnetic interaction of $2J/k_B = 20$ K.[5,6]

Saponite clay $\{Na_{0.46}[Si_{3.54}Al_{0.46}Mg_3O_{10}(OH)_2]\cdot nH_2O\}$ (Kunimine Chemical Co. Ltd) with a cation exchange capacity (CEC) of 100.43 mequiv. per 100 g of the clay was used. Compounds *m*- and *p*-MPYNN$^+\cdot I^-$ were prepared according to the reported methods.[7,8] The intercalation was carried out by stirring the aqueous solution of the clay and *m*- or *p*-MPYNN$^+\cdot I^-$ for 3 h. The precipitate was filtered with a membrane filter (Toyo Roshi Ltd, 5 mm), and dried under vacuum at room temperature. The amount of inserted guest was estimated from the difference in the UV absorption intensity between the original solution and the filtrate. Fig. 1 shows the intercalation curves for *m*- and *p*-MPYNN$^+$, where the horizontal axis is defined as the ratio of the radical in the original solution to the CEC of the saponite. The curves depend little on the isomers: intercalation increases exponentially with increasing the radical concentration and, after passing through an inflection point, it reaches the saturation value of *ca.* 70% of the CEC.

The interlayer distances of the parent sodium saponite and the saturated intercalates were determined by powder X-ray diffraction. The results are shown in Table 1, where the calculated molecular heights of *m*- and *p*-MPYNN$^+$ and the diameter of a sodium ion are also listed. The interlayer distance of the sodium saponite is more than double the sodium diameter, presumably because the sodium ions are hydrated in the interlayer. On the other hand, the interlayer distances of the intercalates almost correspond to the molecular heights. Since the effect of hydration on the size of the organic radicals is smaller than that on the sodium ion, the guest molecules are thought to be aligned nearly perpendicularly to the layer.

The temperature dependences of the magnetic susceptibilities of the parent saponite and the saturated intercalates were measured with a Faraday balance in the temperature range 3–280 K. Paramagnetic susceptibilities, χ_p, were obtained by compensating the diamagnetic susceptibilities, which were evaluated from the experimental data by assuming that the paramagnetic part follows the Curie law above 200 K. Fig. 2 shows the plots of χ_pT *vs.* T. The parent sodium saponite, which is intrinsically diamagnetic, is found to include a small Curie paramagnetic component. The Curie constant, $C = 6.75 \times 10^{-7}$ emu K g^{-1}, is so small that it could be because of transition metal ion impurities. The anomaly around 65 K can be assigned to the effect of the oxygen adsorbed on the sample surface and/or in the interlayers. The temperature dependences of χ_p of the two intercalates also follow the Curie law, and also show anomalies around 65 K. The Curie constants are $C = 2.12 \times 10^{-4}$ emu K g^{-1} for the *m*-MPYNN$^+$–saponite, and $C = 2.17$

Table 1 Interlayer distances of the parent and intercalated saponite clays

Interlayer cation	Interlayer distance/Å	Molecular height[a] or ion diameter/Å
Na$^+$	5.8	2.0
m-MPYNN$^+$	9.7	9.4
p-MPYNN$^+$	9.0	10.2

[a] Molecular heights of the radicals were estimated from PM3 molecular orbital calculations.

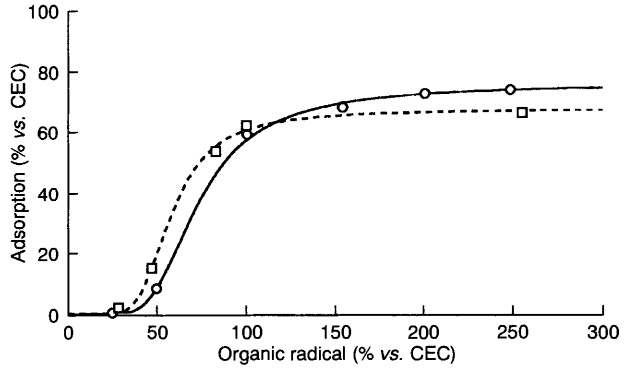

Fig. 1 Intercalation curves of *m*- (○) and *p*-MPYNN$^+$ (□) into the saponite clay (for definitions of the horizontal and vertical axes, see text)

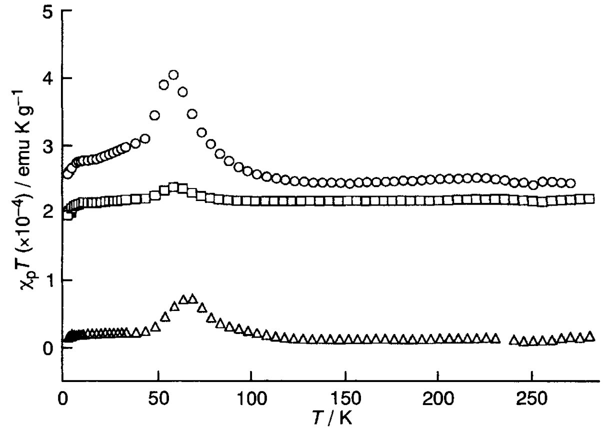

Fig. 2 Temperature dependence of the paramagnetic susceptibilities of the sodium (△), *m*-MPYNN$^+$ (○) and *p*-MPYNN$^+$ (□) saponite clays

$\times$ 10^{-4} emu K g^{-1} for the *p*-MPYNN$^+$–saponite, which are two orders of magnitude larger than that of the parent saponite. The Curie constants agree with the theoretical value of $C = 2.10 \times 10^{-4}$ emu K g^{-1}, assuming a reasonable chemical formula, $Na_{0.14}(MPYNN)_{0.32}[Si_{3.54}Al_{0.46}Mg_3O_{10}(OH)_2]\cdot 10H_2O$. The anomalies† prevent us from calculating the Weiss constants exactly, but the temperature dependence above 100 K suggests that their absolute values are < 5 K. The organic cation radicals remain stable in the interlayers, although the magnetic interactions of the organic radicals observed in the iodide salts disappear.

The average distance between the cation exchange sites (namely negative sites) in the inorganic lattice is *ca.* 11 Å.[9] Assuming that the negative sites withdraw the organic cations from both sides of the layer surfaces and govern the arrangement of the guest molecule more effectively than the intermolecular force between the guests does, the distance between the inserted cations could be *ca.* 5.5 Å. The observed weak magnetic interaction can be understood in terms of the long distance between the organic guest radicals. In other words, the magnetic behaviours suggest the dominance of the host–guest interaction and the homogeneous distribution of the cation exchange sites in the saponite interlayer.

We have carried out intercalation of stable organic radicals into the saponite clay and magnetic measurements. There are precedents for organic radical insertion into inorganic interlayers; DPPH–saponite, DPPH–montmorillonite, and TTF$^+$–MPS_3 (M = Fe, Mn and Cd).[10,11] However, the amount of DPPH is very small in the clays, and there is no quantitative magnetic measurement revealing the magnetic interaction of TTF$^+$ in MPS_3. In this work, *ca.* 70% of the sodium ions in the orginal saponite are replaced by organic radical cations without chemical decomposition. Monitoring the magnetic properties, dominance of the host–guest interaction and homogeneous distribution of the cation exchange sites are concluded.

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Footnote

† Since the *m*-MPYNN$^+$– and *p*-MPYNN$^+$–saponite experienced same evacuation time before the magnetic measurements, the difference in the amount of adsorbed oxygen between the two reflects the intrinsic nature of the guest molecules.

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