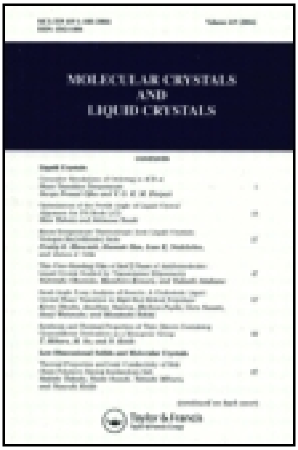

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Adsorption and Electronic Properties in Tetramethylbenzidine-Intercalated Tetrasilicicfluormica

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Adsorption and electronic properties in tetramethylbenzidine-intercalated tetrasilicicfluormica were investigated by powder X-ray diffraction, ESR, TG, and DC-electric conductivity measurements.

Keywords: tetrasilicicfluormica; tetramethylbenzidine; XRD; ESR; TG; conductivity

INTRODUCTION

Colour reactions of clay minerals with aromatic amines are known as amine oxidation in the interlayer space of clays[1]. 3,3',5,5'-Tetramethyl-benzidine (TMB) exhibiting this reaction shows the molecular arrangement dependence on the adsorption level in the interlayer space of hectorite[2]: A low adsorption level gives yellow free radicals whose molecular plane is parallel to the clay surface, while green π-π charge-transfer complexes with the molecular axis vertical on the surface are formed at high adsorption levels.

In mica, which is a higher charged clay than hectorite, the density of charge transfer complexes in the interlayer space increases, the overlapping of their π orbitals is expected to spread over many amine molecules. At the same time, this system can be expected to be a development of new pillared clays[3-4] with characteristic adsorption and interlayer environment. In this study, we examined the adsorption and electronic properties of TMB-intercalated tetrasilicicfluormica (TSFM) by thermo-gravimetry (TG), and measurements of electron spin resonance (ESR) and DC electric conductivity.

Experimental

Synthetic tetrasilicicfluormica ($Na_{0.75}Si_4Mg_{2.7}F_{0.85}OH_{1.2}O_{10}$) was kindly gifted by CO-OP Chemical Co. Ltd. Dihydrochloride (TMB•2HCl) of TMB was recrystallized from an HCl solution of TMB (Tokyo Kasei Co. Ltd.). Intercalation compounds were obtained by following procedure: An aqueous solution of TMB•2HCl was poured to Na-TSFM suspensions in distilled water and stirred for 30 min. and another solution for 12 hours, where the final suspensions was shown to contain TMB^{2+} ions 0.45 times Na^+ ions in original TSFM. The suspensions were centrifuged and washed by distilled water. The apparent colour of dried precipitations is yellow in the specimen after the stirring of 30 min. and dark yellow after 12 hours stirring. The specimen stirred for 30 min. was stable for more than several weeks, while the colour in the latter was immediately changed to deep green in moist air. They are abbreviated to TMB-TSFM(y) and TMB-TSFM(g) in the same order in the following discussion.

TG curves were recorded on a Seiko EXSTAR6000 TG/DTA, ESR spectra on a Bruker EMX-T spectrometer, and DC conductivity was measured by using an ADVANTEST R6144 programmable DC voltage generator and an Iwatsu model 7411 digital multimeter. The crystal (001) spacing in intercalated compounds was measured with a Philips X'pert PW3040 diffractometer. All measurements were carried out on powdered samples.

RESULTS AND DISCUSSION

Elemental Analysis, X-Ray Powder Diffraction and TG

The results of elemental analysis are shown in Table 1. Calculated values were obtained on the assumption that all TMB^{2+} ions in the suspensions exchanged Na^{+} ions in TSFM. From Table 1, it was found that both C and N contents are almost 90 % of calculated values in both TMB-TSFM(y) and TMB-TSFM(g) (the rest seems to be Na^{+} ions), *i.e.*, the adsorption process was mostly completed within 30 min. An increase of H contents in TMB-TSFM(g) implies the existence of adsorbed or coordinated water.

TABLE1 Results of elemental analysis

specimens	C(%)	H(%)	N(%)
TMB-TSFM(y)	12.2	1.72	1.83
TMB-TSFM(g)	12.6	2.10	1.87
calc.	14.0	2.23	2.04

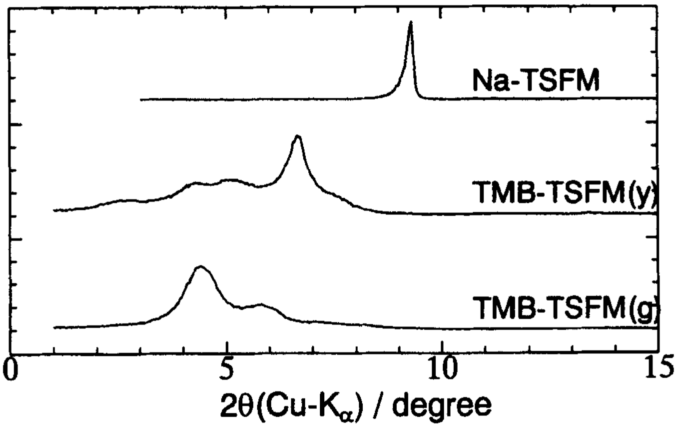

FIGURE 1 X-Ray reflections from (001) in powdered Na-TSFM, TMB-TSFM(y) and TMB-TSFM(g).

X-ray powder diffraction data revealed expansion of *d*-spacing for (001) by intercalation. Broad and dispersed peaks imply inhomogeneity in the intercalation compounds. Observed several broad peaks suggest that the obtained samples contain some mixtures with different *d*-spacings, but they were used without farther purification in this study. The main peak corresponds to 13.3 Å spacing for (001) in TMB-TSFM(y) while 20.1 Å in TMB-TSFM(g). This suggests that TMB^{2+} ions were adsorbed as flat on the clay surface at first then they rearranged to vertically to the surface[2]. The TG measurement on TMB-TSFM(g) showed a weight-loss attributable to the desorption of water in a wide temperature range above room temperature, while TMB-TSFM(y) showed no considerable loss. The amount of water adsorbed on TMB-TSFM(g) was estimated from the weight-loss to be *ca.* 2.4 molecules per TMB^{+} ion. These facts imply that the water molecules adsorbed in micro- or mesopore in TMB-TSFM(g).

ESR spectra

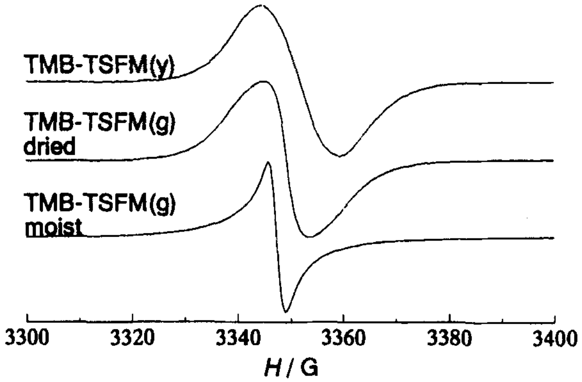

FIGURE 2 ESR spectra of TMB-TSFM complexes observed at room temperature.

ESR spectra were measured at room temperature in a specimen of TMB-TSFM(y) and two of TMB-TSFM(g): one of green specimen was dried *in* *vacuo* and, in the other, water was adsorbed in moist air (Fig. 1). A broad

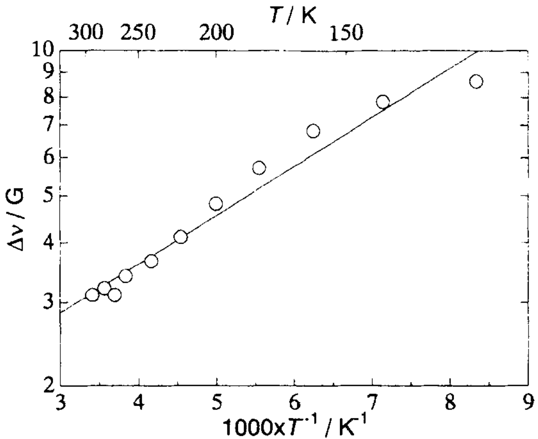

FIGURE 3 Temperature dependence of the ESR line-width (Δv) in moist TMB-TSFM(g). The solid line represents a best-fitted line.

ESR absorption line observed in TMB-TSFM(y) indicates that TMB ions are adsorbed as free radicals[2]. In desiccated TMB-TSFM(g) giving dark yellow colour, the absorption line was broad, whereas narrow in the moist green specimen. This implies that the charge transfer between TMB ions was assisted by adsorbed water molecules.

The ESR line-width of the moist TMB-TSFM(g) was increased with decreasing temperature (Fig. 3) and coincided at 120 K with that of the dried specimen at room temperature. This temperature dependence corresponds to an activation process of electron transfer and the activation energy of this process can be roughly estimated to be *ca.* 9±1 kJ mol^{-1} from the slope.

DC electric conductivity

It is expected in this system that the charge transfer occurs not only in pairs of

TMB ions but over many ions arranged vertically in the interlayer space. DC electric conductivity was measured at room temperature to confirm the delocalization of electrons. Because of the large resistance, conductivities could not be obtained in TMB-TSFM(y) and dried TMB-TSFM(g) where TMB is intercalated as free radical, for their large resistance. On the other hand, moist TMB-TSFM(g) showed a time dependent conductivity of *ca.* 10^{-6} S m^{-1} at immediately after starting the measurement, then it decreased continuously to a constant value of *ca.* 10^{-7} S m^{-1}, within *ca.* 10 min. The time dependent component is assignable to the polarization of ammonium protons in TMB^{2+} ions associated with the intercalated water, and the constant component is attributed to the electron conduction.

Because the electric conduction is limited in the 2-D interlayer space, the observed conductivity was low in our powder experiments. To get a higher conductivity, we need a measurement of oriented films.

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References

[1] D. T. B. Tennakoon, J. M. Thomas, M. J. Tricker, *J. Chem. Soc. Dalton Trans.*, **20,** 2211(1974).
[2] M. B. McBride, *Clays Clay Mineral.*, **33,** 510(1985).
[3] R. M. Barrer and D. M. MacLeod, *Trans. Faraday Soc.*, **51,** 1290(1955).
[4] *Pillared Clays*, edited by R. Burch, *Catal. Today*, **2,** 185(1988).