Photoreduction of Methylviologen in the Interlayer of $K_4Nb_6O_{17}$

Teruyuki Nakato, Kazuyuki Kuroda, and Chuzo Kato*

Department of Applied Chemistry, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo 169, Japan

Methylviologen was directly intercalated into the interlayer space of $K_4Nb_6O_{17}$; the u.v. irradiated intercalation compound showed a stable blue colour even under an air atmosphere.

Among a large number of inorganic layered materials, layered transition metal oxides are interesting in intercalation chemistry because they provide a broad range of compositions and exhibit various physicochemical properties. In particular, potassium niobate, $K_4Nb_6O_{17}$, has a unique layered structure,[1] with two alternating interlayer spaces; interlayer I having hydrated K^+ ions and interlayer II containing unhydrated K^+ ions. Thus, potassium niobate may have a high intercalating ability and has a potential application as a useful host of intercalation compounds.[2,3] Recently, Domen *et al.* reported complete water splitting by using $K_4Nb_6O_{17}$ as a photocatalyst.[4,5] In this case, the layered structure of $K_4Nb_6O_{17}$ largely contributed to the specific photocatalysis. It is interesting to investigate the intercalation compounds in which $K_4Nb_6O_{17}$ is used as the host.

Viologens are suitable for the study of the host–guest interaction in intercalation chemistry of layered transition metal oxides because of their reversible reduction with a sharp colour change. We have already synthesized methylviologen–tetratitanate and –titanoniobate intercalation compounds, and shown that electron transfer from the hosts to the guest occurred.[6,7] However, the photochemical reactions occurred only under oxygen-free conditions. Our present results on the methylviologen–$K_4Nb_6O_{17}$ intercalation compound show a remarkable photochemical reaction even in air.

$K_4Nb_6O_{17}\cdot 3H_2O$ was prepared by the method reported by Nassau *et al.*[8] [confirmed by *X*-ray powder diffraction (x.r.d.) and i.c.p. (inductively coupled plasma emission spectroscopy)]. Intercalation was carried out by the reaction of $K_4Nb_6O_{17}\cdot 3H_2O$ with aqueous methylviologen (MV^{2+}) solution at 60 °C for 3 weeks. The product was washed with methanol and dried at room temperature. The sample was irradiated using a 100 W super high pressure mercury lamp. Visible spectra were measured by diffuse reflection.

The formation of the intercalation compounds was confirmed by x.r.d. and i.r. The d_{020} value corresponding to the sum of the two interlayer spacings increased to 20.5 Å in the product dried under reduced pressure at 60 °C from 16.4 Å in unhydrated $K_4Nb_6O_{17}$. These values suggest that methylviologen (MV^{2+}) lies only in the interlayer I, possibly flat because of its molecular thickness.

The i.r. spectrum of the product exhibited many absorption bands due to methylviologen, in spite of thorough washing. Treatment of the sample with KCl reformed $K_4Nb_6O_{17}\cdot 3H_2O$, which retained the layered structure. These results confirmed that a methylviologen–$K_4Nb_6O_{17}$ intercalation compound was formed by the direct reaction of $K_4Nb_6O_{17}$ with methylviologen. Displacement of the guest cations, using alkylammonium–tetratitanate and –titanoniobate intercalation compounds, was necessary,[6,7] which showed the higher intercalating ability of $K_4Nb_6O_{17}$ compared with the other layered transition metal oxides.

The composition of the product was $MV^{2+}:K:Nb = 0.3:2.7:6.0$. This result means that about 2/3 of potassium ions in the interlayer I were exchanged with methylviologen and protons (or oxonium ions).

The colour of the methylviologen–$K_4Nb_6O_{17}$ intercalation compound changed to blue on irradiation under nitrogen, *in vacuo*, or even in air. The visible spectra of the coloured samples showed the characteristic absorption of viologen radical cations (Figure 1). Therefore, it is apparent that methylviologen dications in the interlayer of $K_4Nb_6O_{17}$ were photoreduced. This phenomenon is similar to observations for methylviologen–tetratitanate and –titanoniobate intercalation compounds,[6,7] and indicates electron transfer from the transition metal oxide host to the guest. The viologen radical cations which formed under an oxygen-free atmosphere did not decay unless air was introduced.

The photoreduction occurred even in air, in contrast to the viologen–tetratitanate or –titanoniobate intercalation compound. We suppose that the difference is due to the particular layered structure of $K_4Nb_6O_{17}$. It is known that the structure of $K_4Nb_6O_{17}$ is different from that of $K_2Ti_4O_9$ or $KTiNbO_5$. In a study on water splitting, Domen *et al.* described that the charge separations on $K_4Nb_6O_{17}$ were carried out with high efficiency by the use of the two kinds of interlayers.[9] Actually, the efficiency of water splitting with $K_4Nb_6O_{17}$ was higher than that with $K_2Ti_4O_9$ or $KTiNbO_5$.[10,11] In the present study, we consider that the effective charge separations are carried out at the initial steps of the reaction, and that the electrons formed by irradiation can reduce the viologen in air without deactivation.

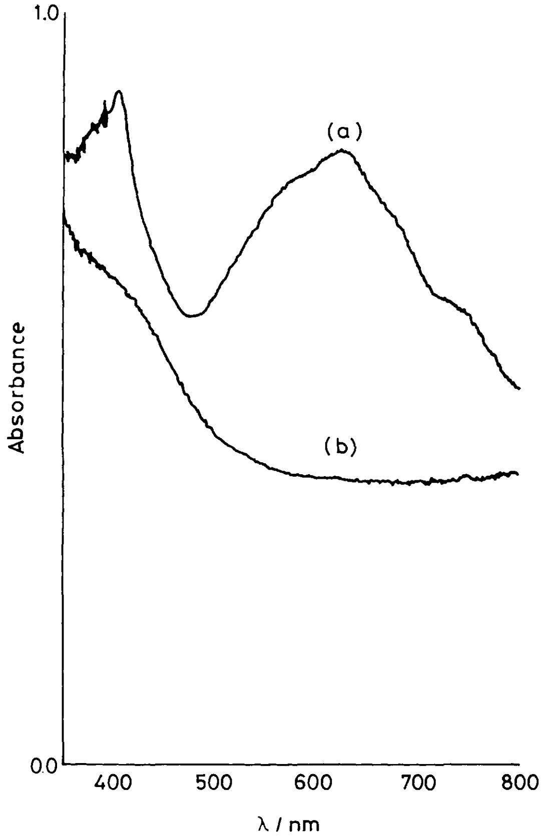

Figure 1. Visible spectra of methylviologen–$K_4Nb_6O_{17}$ intercalation compound (a) after irradiation in air and (b) before irradiation.

The viologen radical cations decayed very slowly in air. It took a few days for the coloured sample to fade completely. This fact indicates that the peculiarity of the structure of $K_4Nb_6O_{17}$ contributes not only to the formation of viologen radical cations but also to their stability. However, potassium ions are still present with viologens in the interlayer, in contrast to the tetratitanate and titanoniobate systems. When an intercalation compound containing a smaller amount of potassium ions (less than 10% in interlayer I) was used,[12] the decay was faster than that of the other samples, although the reduction processes did not show any large differences. Thus, the remaining potassium ions can contribute to the stability of the radical cations by hindering the contact of the viologens with oxygen.

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