CHEMISTRY LETTERS, pp. 423-426, 1993.

Intercalation/Polymerization of the Anilinium Cation in the $VOPO_4$ Interlayer Space

Hiroshi NAKAJIMA and Gen-etsu MATSUBAYASHI*
Institute of Chemistry, College of General Education,
Osaka University, Toyonaka, Osaka 560

Powdered $VOPO_4 \cdot 2H_2O$ suspended in excess neat aniline gives intercalation compounds $VOPO_4 \cdot (H_2O)_x \cdot (PhNH_3^+)_y$ ($0.6 < x < 1.1$; $0.5 < y < 1.0$) with the reduction of the V(V) to V(IV) state. The compounds with $y > 0.7$ lead to the polymerization of the cation by addition of the Cu(II) ion to afford polyaniline. Suspended $VOPO_4 \cdot 2H_2O$ powders react with $PhNH_3^+Cl^-$ dissolved in ethanol to give the compound intercalated with both the anilinium cation and polyaniline.

Although organic molecules such as aniline and pyrrole are well known to be polymerized to afford electrically conducting materials,$^{1)}$ there remains still much difficulty for elucidation of real microstructures because of their amorphous nature. Anisotropic studies of oriented polymer chains with low-dimensional structures are important. From this standpoint, some studies have been made on intercalation of polyaniline and polypyrrole into the constrained van der Waals gaps of layered inorganic solids, such as $V_2O_5 \cdot nH_2O$,$^{2)}$ FeOCl,$^{3,4)}$ and $VOPO_4$,$^{5)}$ and into isolated spaces of zeolite channels.$^{6)}$ However, factors necessary for the polymerization within the inorganic layered spaces remain equivocal. In this communication we report the intercalation of the anilinium cation into the $VOPO_4$ interlayer space and its oxidative polymerization to polyaniline within the constrained space.

Finely powdered $VOPO_4 \cdot 2H_2O$$^{7)}$ was suspended in excess neat aniline and the solution was stirred at 0-35 °C for 1-5 d in darkness to afford intercalation compounds $VOPO_4 \cdot (H_2O)_x \cdot (PhNH_3^+)_y$ ($0.6 < x < 1.1$; $0.5 < y < 1.0$) depending on the reaction conditions.$^{8)}$ Contents (y) of the guest molecule were increased with longer reaction time and at higher temperature. Aniline molecules were inserted into the $VOPO_4$ interlayer space to cause the reduction of the V(V) ion, followed by their location as the $PhNH_3^+$ cation. The compounds gave X-ray powder diffraction (XRD) spectra corresponding to the single interlayer spacings. An intense ESR signal due to the V(IV) ion was observed at g=1.97 at room temperature and IR absorption bands appeared at 2900 and 740 cm^{-1} which are characteristic of the $PhNH_3^+$ cation.[9] Figure 1 shows plots of the $VOPO_4$ interlayer distances *vs*. the content (y) of the cation for $VOPO_4\cdot(H_2O)_x\cdot(PhNH_3^+)_y$. The interlayer distance is enlarged with the increase of y. The maximum content (y=1.0) corresponds to the reduction of all of the V(V) ions in $VOPO_4$.

The $PhNH_3^+$ cation can be polymerized through oxidizing agents.[10] Solids of the intercalation compound, $VOPO_4\cdot(H_2O)_{0.6}\cdot(PhNH_3^+)_{0.7}$, were suspended in an ethanol solution containing an excess amount of Cu(II)-Cl_2 and the solution was stirred for 48 h at 35 °C in darkness. The resulting solid exhibited IR absorption bands of the proton-doped polyaniline[11] as well as those of the $VOPO_4$ moiety, as shown in Fig. 2. This indicates the oxidative polymerization of the $PhNH_3^+$ cation in the $VOPO_4$ interlayer space through the Cu(II) ion, which was also confirmed by the XPS bands due to both Cu(II) and Cu(I) $2p_{3/2}$ electrons (935.6 and 934.0 eV, respectively) observed for the solid. Although the solid gave the IR bands at 680 and near 1050 cm^{-1} ascribed to the vibrations of the layered $VOPO_4$ skeleton,[12] no appreciable XRD peaks appeared. These findings indicate that the layered $VOPO_4$ structure is greatly modified by rearrangement of the guest molecules

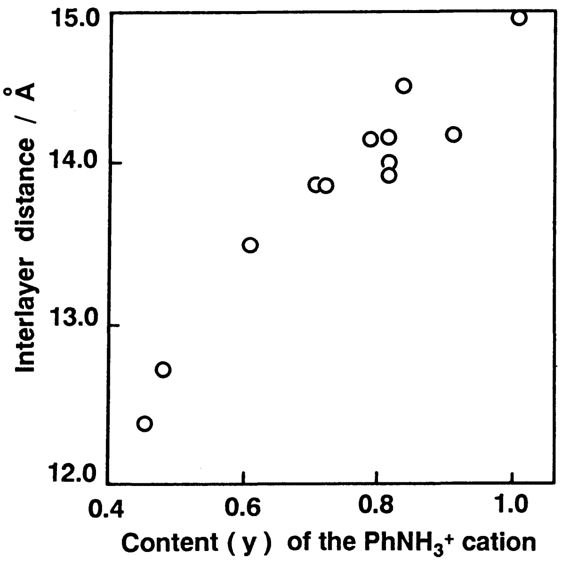

Fig. 1. Plots of the interlayer distance vs. the content (y) of the $PhNH_3^+$ moiety for intercalation compounds $VOPO_4\cdot(H_2O)_x\cdot(PhNH_3^+)_y$.

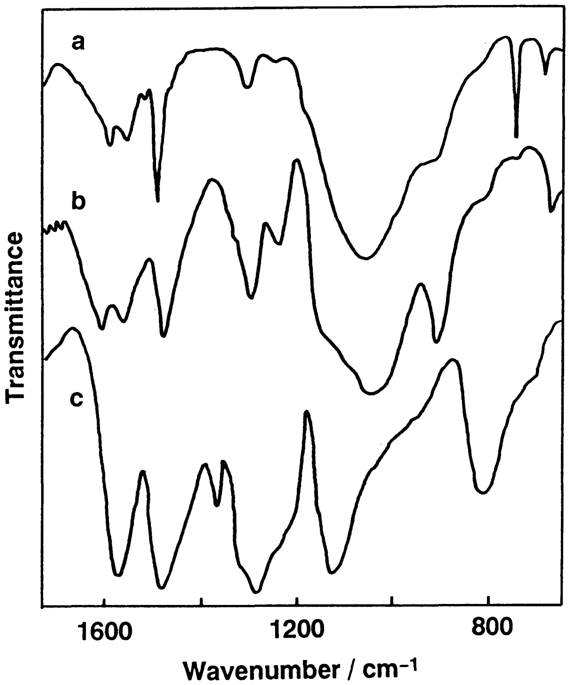

Fig. 2. IR spectra measured in KBr disks: (a) $VOPO_4\cdot(H_2O)_{0.6}\cdot(PhNH_3^+)_{0.7}$, (b) the solids (a) treated with the Cu(II) ion, and (c) polyaniline prepared by the literature method.[11]

accompanied with the polymerization within the interlayer space. The reaction of the Cu(II) ion in ethanol with solids of the $VOPO_4$-$PhNH_3^+$ intercalation compounds with $y<0.7$ resulted in an exchange of the $PhNH_3^+$ cation with the Cu(II) ion instead of the polymerization of the cation moieties. They gave the final interlayer distance of 6.8 Å, which is consistent with distances of 6.64-6.84 Å reported for $VOPO_4$ compounds intercalated with Fe(III), Co(II) and Ni(II) ions.[12] Thus, the $PhNH_3^+$ cations crowdedly arranged in the V(IV)OPO_4 interlayer space can be oxidatively polymerized to lead to polyaniline.

The V(V) ion of the $VOPO_4$ layer is expected to cause the oxidative polymerization of the $PhNH_3^+$ cation moieties forming polyaniline in the interlayer space. Powdered $VOPO_4 \cdot 2H_2O$ was suspended in an ethanol solution containing excess amounts of $PhNH_3^+Cl^-$, which immediately turned dark green on the surface of the powders. The powder reflectance visible spectrum of the resulting solid indicated the formation of polyaniline on the surface of the solid through the oxidation by the V(V) ion; the band ascribed to the quinone-diimine group was observed at 780 nm.[11,13] The suspended solution of powdered $VOPO_4 \cdot 2H_2O$ was further stirred for 72 h. The resulting solid exhibited IR bands due to both the $PhNH_3^+$ cation and the proton-doped polyaniline. The XRD spectrum showed diffraction peaks corresponding to the interlayer distances of 15.0 Å and 9.0 Å (*), as shown in Fig. 3-a. The XPS showed the V $3d_{3/2}$ electron peaks due to both the V(IV) and V(V) states (517.1 and 518.0 eV, respectively). These findings indicate the formation of polyaniline through the oxidative polymerization of the $PhNH_3^+$ cation by the V(V) ion. The Cl $2p_{3/2}$ electron peak was observed at 197.6 eV, indicating the presence of the chloride ion in the interlayer space. The suspended ethanol solution of the solid was further stirred for 72 h at room temperature. The resulting solid analyzed as $VOPO_4 \cdot (H_2O)_{0.6} \cdot (EtOH)_{0.4} \cdot (C_6H_4NH)_{0.55}$[8] showed only the IR bands due to polyaniline without those of the $PhNH_3^+$ cation. No XPS bands due to the chlorine

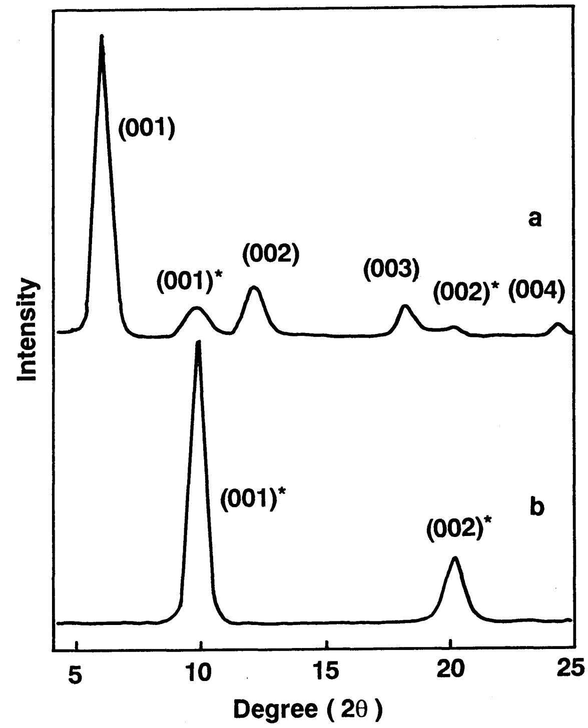

Fig. 3. Powder X-ray diffraction patterns of (a) the $VOPO_4$-$PhNH_3^+Cl^-$/polyaniline and (b) $VOPO_4$-polyaniline intercalation compounds.

electrons were observed. The XRD spectrum exhibited only diffraction peaks corresponding to the single interlayer distance of 9.0 Å, which is 1.6 Å longer than that of $VOPO_4 \cdot 2H_2O$ (in Fig. 3-**b**), indicating the enlargement of the interlayer spacing of 4.9 Å compared with that of anhydrous $VOPO_4$ (4.1 Å).[14] These findings suggest that the polyaniline moieties are present in the $VOPO_4$ interlayer space (the spacing, 9.0 Å) and in the space pillared with the $PhNH_3^+$ cations (the spacing, 15.0 Å), the $PhNH_3^+$ cations being able to be removed in ethanol. Thus, it has been clarified that $PhNH_3^+Cl^-$ can be easily inserted into the interlayer space of the $VOPO_4$ moiety suspended in ethanol and oxidatively polymerized through the V(V) ion.

Studies on arrangements of the $PhNH_3^+$ cation and its related cations in the $VOPO_4$ interlayer space for the polymerization are now in progress.

References

1) "Handbook of Conducting Polymers," ed by T. A. Skotheim, Marcell Dekker, New York (1986), Vols. 1 and 2.
2) M. G. Kanatzidis, C.-G. Wu, H. O. Marcy, and C. R. Kannewurf, *J. Am. Chem. Soc.*, **111**, 4139 (1989).
3) M. G. Kanatzidis, L. M. Tonge, T. J. Marks, H. O. Marcy, and C. R. Kannewurf, *J. Am. Chem. Soc.*, **109**, 3797 (1987).
4) M. G. Kanazidis, M. Hubbard, L. M. Tonge, T. J. Marks, H. O. Marcy, and C. R. Kannewurf, *Synth. Met.*, **28**, C89 (1989).
5) G. Matsubayashi and H. Nakajima, *Chem. Lett.*, **1993**, 31.
6) T. Bein and P. Enzel, *Angew. Chem.*, **101**, 1737 (1989).
7) J. W. Johnson, A. J. Jacobson, J. F. Brody, and S. M. Rich, *Inorg. Chem.*, **21**, 3820 (1982).
8) The compositions of the intercalation compounds were determined by the elemental analyses (C, H, and N).
9) R. D. Kross, V. A. Fassel, and M. Margoshes, *J. Am. Chem. Soc.*, **78**, 1332 (1956).
10) G. Matsubayashi, T. Doi, and T. Tanaka, *Synth. Met.*, **33**, 99 (1989).
11) M. Ohira, T. Sakai, M. Takeuchi, Y. Kobayashi, and M. Tsuji, *Synth. Met.*, **18**, 347 (1987).
12) M. R. Antonio, R. L. Barbour, and P. R. Blum, *Inorg. Chem.*, **26**, 1235 (1987).
13) Y. Furukawa, T. Hara, Y. Hyogo, and I. Harada, *Synth. Met.*, **16**, 189 (1986).
14) E. Bordes, P. Courtine, and G. Pannetier, *Ann. Chim. (Paris)*, **8**, 105 (1973).

(Received November 30, 1992)