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Intercalation of Organic Compounds in the Layered Inorganic Host V_2O_5

Tsuneo Kuwahara
Technical Center, TDK Corporation, Higashi-Ohwada, Ichikawa, Chiba 272-8558, Japan
Fax: 81-47-378-9493, e-mail: tnkuwa@mb1.tdk.co.jp

Organic molecules positively chargeable were intercalated into interlayers of V_2O_5 through thermal methods in liquid phase. In the case of aliphatic amines as guest, the interlayer spacing of aliphatic amine / V_2O_5 intercalation compounds was increased linearly with the carbon number of the guest, indicating the guests were stacked in the interlayers. The average gradient of the interlayer spacing: 0.21 nm/carbon atom suggests bilayer structures of the guests in V_2O_5 and tilting angle of the guests is about 60 deg. On the other hand, it is suggested that pyridines intercalated form monolayer structures in the interlayers of V_2O_5 and the guests are perpendicular to the inorganic planes of V_2O_5 from the interlayer spacing of the intercalation compounds.
Keywords: Aliphatic amines, Intercalation, Pyridines, Vanadium pentoxide

1. INTRODUCTION

In recent years, the preparation of novel organic / inorganic nanocomposites has received considerable attention. Layered hosts, inorganic compounds with layered structure, can hold organic / inorganic ions or molecules in their interlayers and it is expected to produce novel composites and to provide novel functions from the preparation based on them.

Vanadium pentoxide, V_2O_5, is of highly two-dimensional structure, applied to the catalysis of hydrocarbon conversion [1], and also to the cathode materials in lithium batteries [2]. Fig.1 shows the layered structure of V_2O_5. The interlayer distance as measured by the distance between the apical oxygen atoms in one layer and the vanadium atoms in an adjacent layer is 0.28 nm, and V-O distance to the apical oxygen is 0.16 nm [3], so the basal spacing of V_2O_5 is 0.44 nm.

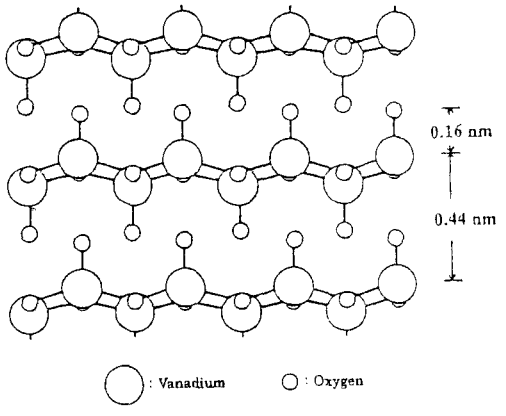

Fig.1 Layered structure of V_2O_5.

Intercalation compounds of polyaniline-V_2O_5 [4] and polyoxyethylene-V_2O_5 [5-6] are already reported, however, their preparations were started with V_2O_5 xerogels. In this study, preparations of intercalation compounds from V_2O_5 powder sample were attempted. Slightly the interlayers of V_2O_5 are negatively chargeable by electron donating compounds, and cations could be intercalated in the interlayers. Aliphatic amines were known to be intercalated in layered compounds and the structures were minutely investigated [7], the orientation of pyridines intercalated in clay interlayers was affected with the water molecules incorporated with organic guests [8]. Organic compounds such as alkylpyridines, methyl viologen and azo compounds were intercalated into MoO_3 layers by ion exchange method [9].

V_2O_5 is a class of optical semiconductors and applications using novel optical and electronic characteristics in the V_2O_5 intercalation compounds are expected.

In this study, organic molecule / V_2O_5 intercalation compounds were prepared and their structures were investigated.

2. EXPERIMENTAL

2.1 Preparation of aliphatic amine / V_2O_5 intercalation compounds

Aliphatic amines, whose carbon-number is 3 to 9, from Tokyo Kasei and V_2O_5 powder from Aldrich were used as received. 5 ml of each aliphatic amine was added to 0.2 g of V_2O_5 powder, the mixture was stirred at room temperature for a few hours. Then the mixture was dispersed to 30 ml of ethanol, the suspension was refluxed at boiling point of ethanol for 72 h. The intercalation compound obtained was separated and dried.

2.2 Preparation of pyridine / V_2O_5 intercalation compounds

Pyridine and methylpyridines from Wako and aminopyridines from Tokyo Kasei were used as received. In the case of pyridine or methylpyridines, 5 ml of guest compound was added to 0.2 g of V_2O_5 powder, the mixture was refluxed at boiling point of the guest compound for 72 h. The intercalation compound

obtained was separated and dried under reduced pressure. In the case of aminopyridines, 3 g of each aminopyridine and 3ml of ethanol were added to 0.2 g of V_2O_5 powder, the mixture was refluxed at 80 ℃ for 120 h. The intercalation compound obtained was separated and dried under reduced pressure.

2.3 Characterization

Powder X-ray diffraction (XRD) spectra were recorded on a Rigaku powder diffractometer unit using Cu-K α (filtered) radiation at 40 kV and 20 mA. Elemental analyses were carried out using Perkin Elmer 2400 II organic elemental analyzer. Thermal analyses (TG/DTA) were performed on a Seiko SSC5000 thermal analysis system using a heating rate of 10 ℃ min^{-1}. X-ray photoelectron(XP) spectra were collected on a Shimadzu ESCA using a monochromatic Mg-K α X-ray source.

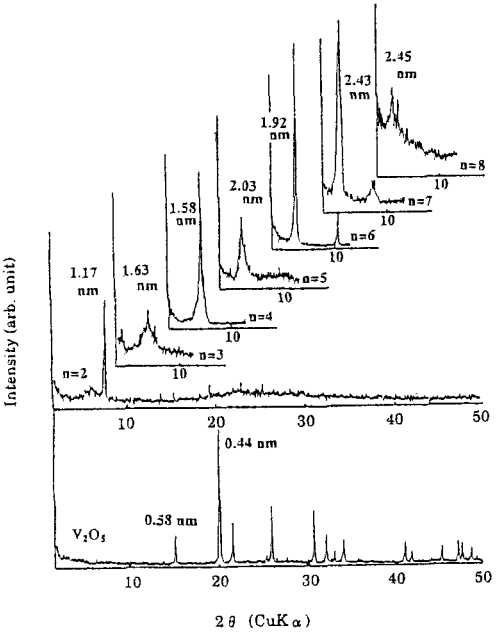

Fig.2 XRD patterns of V_2O_5 powder and aliphatic amine / V_2O_5 intercalation compounds.

3. RESULTS AND DISCUSSION

3.1 Aliphatic amine / V_2O_5 intercalation compounds

The XRD patterns of V_2O_5 powder and aliphatic amine / V_2O_5 intercalation compounds are shown in Fig.2. In the XRD pattern of V_2O_5 powder, the maximum peak at 0.44 nm can be ascribed to the plane (010). In the XRD patterns of intercalation compounds, the maximum peaks at 1.17 to 2.45 nm indicate the expansions of basal spacing of the V_2O_5 layered structure by the intercalation of the organic guests. The interlayer spacing, the layer expansion and composition calculated by elemental analyses for intercalation compounds were summarized in Table I . The ratios of organic guest / V_2O_5 host in the intercalation compounds were calculated to 1.26 to 2.36. The relationship between the carbon number of aliphatic amines and the value of interlayer spacing of the intercalation compounds is shown in Fig.3. The interlayer spacing increased linearly with the carbon number and the average gradient was 0.21 nm/carbon atom. The guest / host ratios and the interlayer spacing indicated the formation of tilting bilayer structure of aliphatic amines in the layers.

Table I Intercalation of aliphatic amines into the layers of V_2O_5

guest(n) $CH_3(CH_2)_nNH_2$	interlayer spacing (nm)	layer expansion (nm)	Elemental analyses C (%)	H (%)	N (%)	x in host-(guest)x
propylamine(2)	1.17	0.73	18.71	5.02	7.08	1.36
butylamine (3)	1.63	1.19	22.06	5.10	5.98	1.26
pentylamine(4)	1.58	1.14	30.66	6.91	6.38	1.67
hexylamine (5)	2.03	1.59	35.38	7.37	6.43	1.78
heptylamine(6)	1.92	1.48	39.51	8.29	6.40	1.86
octylamine (7)	2.43	1.99	46.59	9.22	6.79	2.36
nonylamine(8)	2.45	2.01	42.75	8.31	5.54	1.66

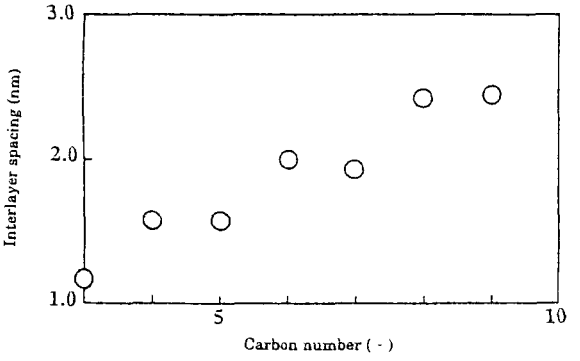

Fig.3 Relationship between the carbon number of aliphatic amines and interlayer spacing of the intercalation compounds.

The tilting angle of carbon chain of guest molecules incorporated in inorganic layers could be estimated by the following relationship [10]. In the case of two layers of organic molecules are stacked in the interlayers, the angle (α) between the molecule axis and inorganic plane is

$$\sin\alpha = \Delta d / (2 \times 0.127)$$

where Δd (nm) is the increase of interlayer spacing per one carbon atom. Then α is assumed about 60 deg in this study.

The peaks of V(3d) in the XP spectra for the aliphatic amines / V_2O_5 intercalation compounds shifted by more than 2 eV from that for the V_2O_5 powder. It indicates the effects of the guest molecules to the electronic state of Vanadium in the host layer.

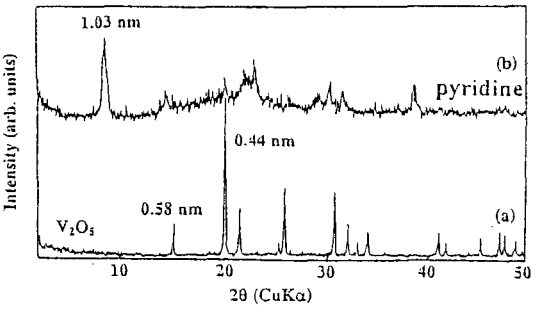

Fig.4 XRD patterns of (a) V_2O_5 powder and (b) pyridine / V_2O_5 intercalation compounds.

3.2 Pyridine / V_2O_5 intercalation compounds

The XRD patterns of V_2O_5 powder and pyridine / V_2O_5 intercalation compounds are shown in Fig.4. The interlayer spacing increased by intercalation of the pyridine, from 0.44 to 1.03 nm. The XRD patterns of aminopyridine / V_2O_5 and methylpyridine / V_2O_5 intercalation compounds are shown in Fig.5 and Fig.6, respectively. The interlayer spacing, the layer expansion and composition calculated by elemental analyses for intercalation compounds were summarized in Table II. The ratios of organic guest / V_2O_5 host in the intercalation compounds were calculated to 0.05 to 1.05.

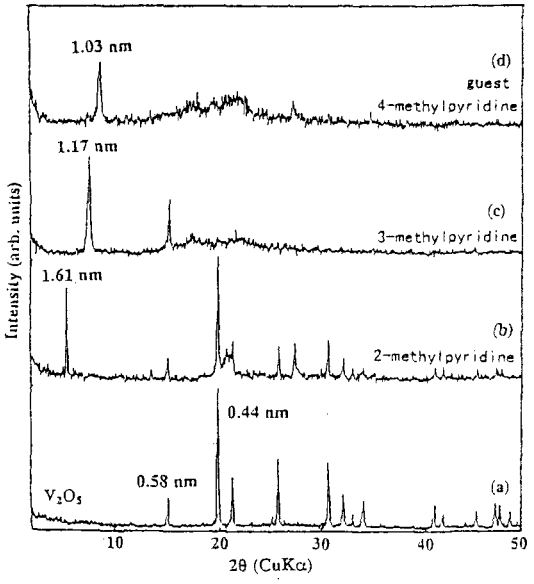

Fig.5 XRD patterns of (a) V_2O_5 powder and (b) 2-methylpyridine / V_2O_5 (c) 3-methylpyridine / V_2O_5 (d) 4-methylpyridine / V_2O_5 intercalation compounds.

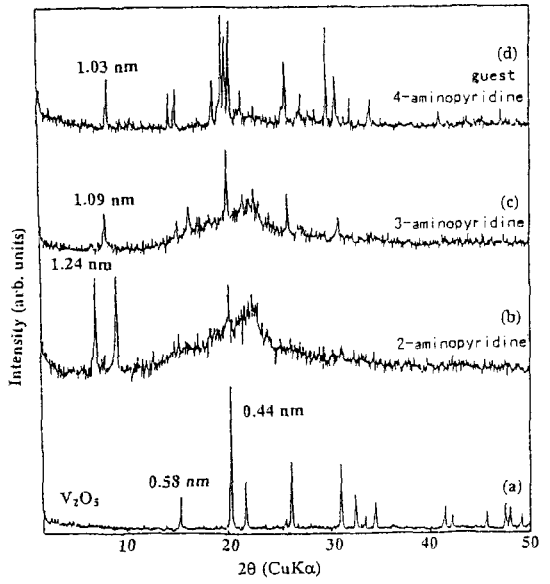

Fig.6 XRD patterns of (a) V_2O_5 powder and (b) 2-aminopyridine / V_2O_5 (c) 3-aminopyridine / V_2O_5 (d) 4-aminopyridine / V_2O_5 intercalation compounds.

Table II Intercalation of pyridine, amino- and methylpyridines into the layers of V_2O_5

guest	interlayer spacing (nm)	layer expansion (nm)	Elemental analyses C (%)	H (%)	N (%)	x in host-(guest)x
pyridine	1.03	0.59	23.39	2.17	5.48	1.02
2-aminopyridine	1.24	0.80	16.57	2.06	7.16	0.68
3-aminopyridine	1.09	0.65	12.59	1.26	5.29	0.47
4-aminopyridine	1.03	0.59	22.43	2.47	10.41	1.05
2-methylpyridine	1.61	1.17	1.99	0.37	0.87	0.05
3-methylpyridine	1.17	0.73	21.15	2.13	4.18	0.73
4-methylpyridine	1.03	0.59	13.45	1.25	2.57	0.41

The layer expansions more than 0.59 nm were observed for each intercalation compounds and the large calculated guest / host ratios suggest that the intercalated guests form monolayer in the interlayers of host. The interlayer spacing for 2-methylpyridine / V_2O_5 is 1.61 nm and the value is the maximum value among the samples. The content of guest in the intercalation compounds is not so high indicating that the intercalation of 2-methylpyridine into V_2O_5 occurred heterogeneously. From the layer expansions more than 0.59 nm, it's assumed that the hetero-rings of pyridines are perpendicular to the inorganic planes in the interlayers. The layer expansions of the 4-methyl- and 4-aminopyridine / V_2O_5 intercalation compounds are the same as that of the pyridine / V_2O_5 intercalation compound, and larger expansions are observed for the 2- and 3-substituted pyridines. These results indicate that the nitrogen atoms in the hetero-rings of pyridines are not near to the vanadium atoms of inorganic layers, they are at almost center of the interlayers. The same model was already reported in other systems [8].

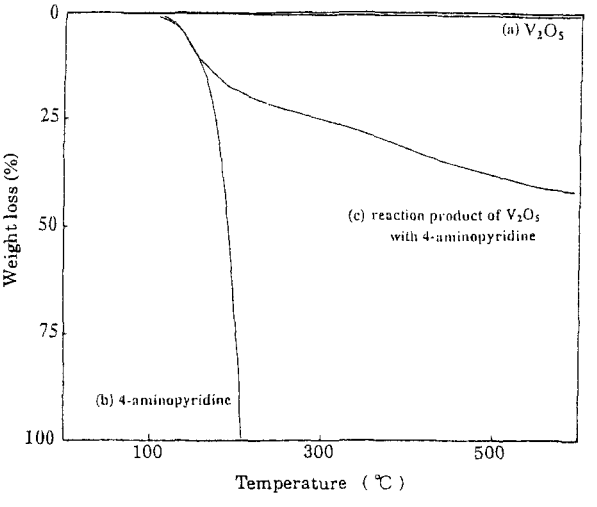

Fig.7 TG analyses for (a) V_2O_5 powder, (b) 4-aminopyridine and (c) the reaction products of V_2O_5 with 4-aminopyridine.

TG spectra for (a) V_2O_5 powder, (b) 4-aminopyridine and (c) the reaction products of V_2O_5 with 4-aminopyridine are shown in Fig.7. The weight loss of

the reaction products continued to 600 ℃, indicating 4-aminopyridine molecules were retained in the interlayers of V_2O_5 at 200 ℃ to 600 ℃. The weight loss up to 250 ℃ indicates a release of the 4-aminopyridine molecules from interactions with the surface of V_2O_5, at more than 300 ℃ it's supposed that the 4-aminopyridine molecules diffused in the space of the reaction products or moved in the interlayers of them.

The amount of the guest molecules in the host lattice is able to estimate from the TG curve of the reaction products (Fig.7(c)). From the weight loss of the reaction products; 39 % at 600 ℃, the molecular formula of the reaction products is represented as follows.

$$V_2O_5\ (4\text{-aminopyridine})_{1.18}$$

The result corresponds to the guest / host ratio determined by the elemental analysis in Table II.

The peak shifts of V(3d) in the XP spectra for the pyridines / V_2O_5 intercalation compounds from that for the V_2O_5 powder were less than 1 eV. It is indicating that the electric interaction between the guests and the hosts in the pyridines / V_2O_5 intercalation compounds is relatively weak refer to that of the aliphatic amines / V_2O_5 intercalation compounds. These results support the positioning of pyridine rings in the V_2O_5 host mentioned above.

4. CONCLUSIONS

Organic molecule / V_2O_5 intercalation compounds were prepared and their structures were investigated. The expansions of basal spacing of the V_2O_5 layered structure and the ratios of aliphatic amines / V_2O_5 in the intercalation compounds suggest the bilayer structure of aliphatic amines in the interlayers. On the other hand, the layer expansions more than 0.59 nm were observed for pyridine / V_2O_5 compounds and the guest / host ratios suggest monolayer structure of pyridines in the interlayers of host. The applications of this preparation method to the other functional organic molecules are expected.

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