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Inclusion of Substituted Ferrocenes and Aromatic Compounds into MoS_2 Layers as New Intercalation Compounds

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Non electron donors were intercalated into MoS_2 layers by a method of exfoliation followed by its restacking. Interlayer spacings of substituted ferrocene intercalates indicate the formation of a bilayer of guest molecules, whereas, aromatic compounds are included with an orientation of the ring plane perpendicular to the host layers.

It has been well established that the layered structure of transition-metal dichalcogenide (MX_2) permits a variety of atoms or molecules to be intercalated into the van der Waals gap.1) It is believed that, for the host lattices with electronic conductivity, entering of electrons into the conduction band of the host matrix is a first step of the inclusion reaction.1) Therefore, the guests should be electron donors. For example, in the process of metallocene inclusion, the ionization potential of metallocene plays a critical role and metallocenes only having first ionization potentials less than 6.2 eV could be intercalated.2)

Recently, non electron donors such as ferrocene having a high ionization potential, 6.88 eV, were shown to be intercalated into MoS_2 by restacking of exfoliating MoS_2.3) On the other hand, Green et al. reported that 2-aminoethylferrocene was intercalated into TaS_2 because of the donor ability of the functional group.4,5) They suggested the formation of a bilayer of guest molecules within these host lattices.5) Furthermore, an aromatic hydrocarbon, perylene was reported to be intercalated into FeOCl having high oxidizing ability than MX_2 orienting perpendicular to the host layers.6)

We are interested in inclusion of non electron donors into MX_2 to get new intercalation compounds having widely ranging characteristics.

Table 1. Variation of basal spacings of the MoS_2-oraganic intercalation compounds

Guest	Host basal spacing (Å)	Host interlayer expansion (Å)
None	6.2	-
Ferrocene	11.8	5.6
Acetylferrocene	16.3	10.1
1,1'-Diacetylferrocene	20.5	14.3
Phenylferrocene	14.9	8.7
Toluene	14.9	8.7
1,2,4,5-Tetramethylbenzene	15.1	8.9
Tetrahydronaphthalene	14.9	8.7
Decahydronaphthalene	14.7	8.5
Hexamethylbenzene	7.7	1.5
Dibenzyl	7.0	0.8

Here, substituted ferrocenes having higher oxidation potentials than that of ferrocene and non electron donors like aromatic compounds were included into MoS_2 by the method of Divigalpitiya et al.[3)]

Lithium intercalated MoS_2 was prepared from n-BuLi and MoS_2 under dry nitrogen atmosphere by using the Schlenk technique.[8)] It was easily hydrated in the presence of moisture in the air. The lithium intercalate was reacted with water to give a dispersed MoS_2 layer (exfoliating MoS_2).[9)] Such exfoliating MoS_2 reacts with saturated non electron donors in benzene or carbon tetrachloride solution by vigorous mixing, and gives inclusion compounds as shown in Table 1.

The oxidation potential of ferrocene is 0.42 V (vs. SCE) and more positive than conduction band potential of 0.2 V. Those of acetylferrocene and 1,1'-diacetylferrocene are 0.66 and 0.87 V, respectively.[7)] Therefore, such substituted ferrocenes are more difficult to be oxidized than ferrocene. However, XRD shows that substituted ferrocenes are included into MoS_2. Basal spacings expand from 6.2 to 16.3 and 20.5 Å, respectively, although unreacted MoS_2 was also observed. The values of the spacings are larger than 11.8 Å for ferrocene intercalates (5.6 Å of layer expansion). 10.1 Å of layer expansion in the case of acetylferrocene indicates the formation of a bilayer. The value is smaller than twice 5.6 Å. Therefore, structure b) as shown in Fig. 1 is considered. The structure of phenylferrocene

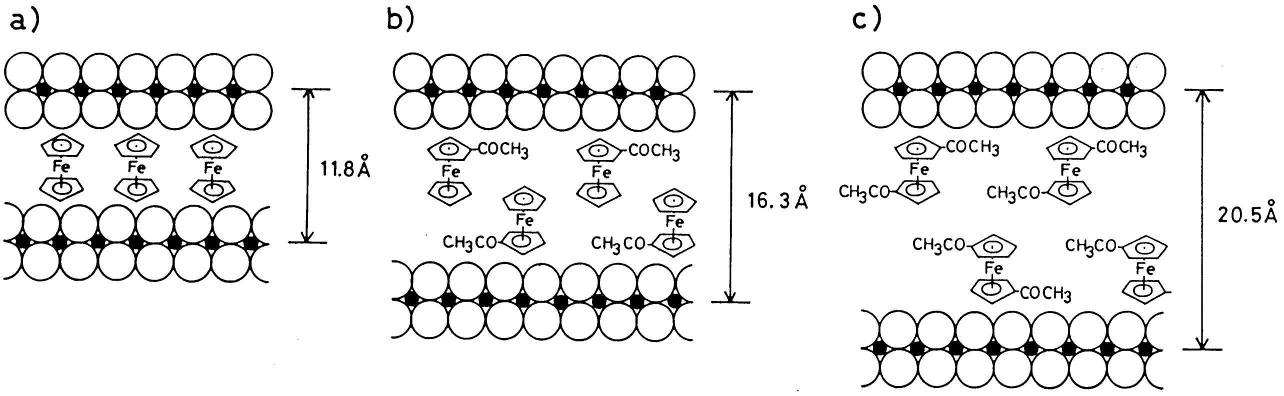

Fig. 1. Schematic representation of substituted ferrocenes - MoS_2 intercalation compounds.

intercalate having 8.7 Å of layer expansion was also suggested as having the same bilayer structure as in Fig. 1b. Green et al. showed a similar structure in the case of 2-aminoethylferrocene intercalate into MoO_3.$^{5)}$ 14.3 Å of layer expansion in the case of 1,1'-diacetylferrocene indicates the formation of a complete bilayer c) as shown in Fig. 1.

Aromatic compounds and decahydronaphthalene were also intercalated. Expansions of the host interlayer from 6.2 to 14.7 - 15.1 Å indicate that decahydronaphthalene, 1,2,4,5-tetramethylbenzene, and tetrahydronaphthalene are included with an orientation of the ring or cyclohexane plane perpendicular to the host layers. A large expansion by toluene intercalation indicates the formation of a bilayer within host lattices. Small expansions from 6.2 to 7 - 7.7 Å suggest that hexamethylbenzene and dibenzyl are included with an orientation of the ring plane parallel to the host layers. In the case of dibenzyl, unreacted MoS_2 was not observed. TG analysis gave a stoichiometry $MoS_2(dibenzyl)_{0.078}$. The maximum stoichiometry calculated for a close-packed dibenzyl molecule for the parallel orientations is $MoS_2(dibenzyl)_{0.063}$ for a single layer and $MoS_2(dibenzyl)_{0.125}$ for continuous layers indicating that the intercalate contains very nearly close-packed dibenzyl molecules.

To get information on whether there is a difference between the traditional intercalation method and this method, an electron donor, decylamine was intercalated by two methods: One is a traditional thermal method with MoS_2 and the other is a restacking method of exfoliating MoS_2 and decylamine solution. Two methods gave the same X-ray results in which MoS_2 layers expanded 22-24 Å. This fact and the results of Table 1 suggest that the conformation of guests in MoS_2 layers don't depend on intercalation methods.

It is known that bis(indenyl)cobalt was not intercalated thermally into 1T TaS_2.10) Electroreduction of the host also was not effective. However, multistep intercalation in which preintercalated TaS_2 by ammonia was reacted with bis(indenyl)cobalt was successful.11) This indicates that the expansion of the host layers is a reaction-limiting step and more important than an electron transfer reaction to the host lattices. Actually, the presence of organic radicals was not confirmed in ESR measurements of aromatic compound intercalates in this study. It is suggested that aromatic compounds were included physically when dispersed host restacked, and host - guest interaction was small.

The intercalation process leads to the synthesis of new classes of materials.12) New intercalation compounds have the potential both for practical applications and for the study of novel physical phenomena.

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