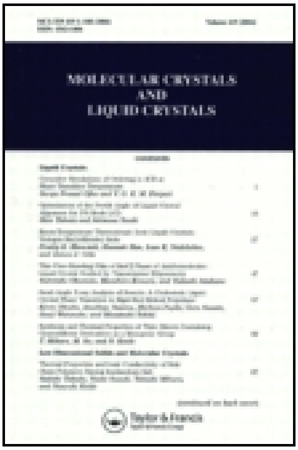

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FTIR and Thermal Studies of $FeCl_3$-CrO_3-Graphite Bi-Intercalation Compound

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$FeCl_3$-CrO_3-graphite bi-intercalation compound ($FeCl_3$-CrO_3-GBC) encompassing the double $FeCl_3$-CrO_3 co-intercalation layers was examined by FTIR spectroscopy and thermal analysis. The results obtained for $FeCl_3$-CrO_3-GBC were compared to those for the binary graphite intercalation compounds: $FeCl_3$-GIC and CrO_3-GIC. In FTIR spectrum for $FeCl_3$-CrO_3-GBC the bands observed in both $FeCl_3$-GIC and CrO_3-GIC were preserved with a slight shifting and new band around 1100–1200 cm^{-1} appeared. The reason for this feature is suggested to arise from the donor-acceptor interaction within $FeCl_3$-CrO_3-graphite system. Such an explanation is consistent with TG, DSC and XRD measurements.

Keywords: $FeCl_3$- CrO_3-graphite bi-intercalation compound; FTIR; DSC; TG XRD

INTRODUCTION

Graphite bi-intercalation compounds (GBCs) involve the graphite systems in which alternating layers of two or more different intercalates occupy separate interlayer spacings of graphite, and the intercalate layers are separated by one or more graphene layers. Due to the ingress of the secondary intercalate to the interlayer spacing filled with the primary intercalate the co-intercalation domains are created. Novel physicochemical properties of GBCs, especially those containing co-intercalation domains, are determined by both chemical character of intercalates and electron interaction between different intercalates accommodated in the graphite gallery as well as between intercalates being separated by graphene layers[1]. The knowledge of this interaction is a way to predict the practical application of GICs. Among acceptor GBCs described in the literature the compounds composed of metal chlorides and metal oxides are not numerous. Recently $FeCl_3$-CrO_3-GBC[2] and $ZnCl_2$-CrO_3-GBC[3] have been reported. In the present paper $FeCl_3$-CrO_3-GBC was characterized by FTIR, DSC and TG methods and the results obtained were compared to those for $FeCl_3$-GIC and CrO_3-GIC.

EXPERIMENTAL

The preparation conditions for stage-2 $FeCl_3$-GIC (I_c = 1.281 nm) and $FeCl_3$-CrO_3-GBC (for lattice parameters see Fig. 1) were described earlier in detail[2]. $FeCl_3$-GIC was prepared from a vapour phase at 300°C using Sri Lanca graphite (flakes 30-100 µm in diameter). This compound was then subjected to the subsequent intercalation of CrO_3 to give $FeCl_3$-CrO_3-GBC. Stage-3 CrO_3-GIC (I_c = 1.462 nm) was prepared from a liquid phase (CrO_3/CH_3COOH) using the preparation conditions identical to those reported in[4]. XRD analysis was performed with a Philips diffractometer using CuKα radiation. The obtained binary compounds, $FeCl_3$-GIC and CrO_3-GIC, were admixed with the phase of unreacted graphite. FTIR measurements were made by diffuse reflection techniques with Harrick equipment coupled with Jasco-430 spectrometer. DSC and TG curves were recorded in argon with a scan rate of 20 °C/min using Netzsch STA-409 apparatus. The changes in the structure of $FeCl_3$-GIC and $FeCl_3$-CrO_3-GBC effected by their heat treatment (in argon at 320 °C for 0.5 h) were examined based on the XRD data.

RESULTS AND DISCUSSION

The structural model of $FeCl_3$-CrO_3-GBC derived from X-ray diffraction is illustrated in Fig. 1. The peripheral collar of $FeCl_3$-GBC (about 15 μm in thickness[2]) contains the double co-intercalation layers whereas stage-2 $FeCl_3$-GIC constitutes the flake core.

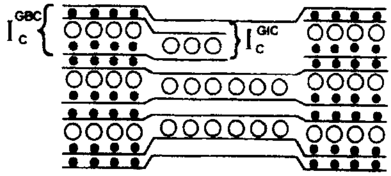
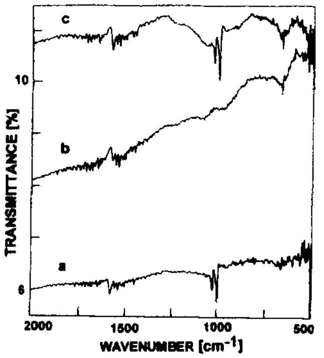


FIGURE 1 Schematic structure of $FeCl_3$-CrO_3-GBC. ● = CrO_3, O = $FeCl_3$. I_c^{GIC} = 1.281 nm, I_c^{GBC} = 2.231 nm.

In Fig. 2 the FTIR spectra for CrO_3-GIC and $FeCl_3$-GIC are compared to that of $FeCl_3$-CrO_3-GBC. In Fig. 2a representing CrO_3-GIC, new bands at 1026 and 1001 cm^{-1} are observed apart from those at 1581 and at about 680 cm^{-1}, belonging to stretching vibration of aromatic C=C bonds, which were found for the pristine graphite (spectrum not presented here)[5]. For $FeCl_3$-GIC the bands arising from graphite persist and new bands are recorded at 1079 and 668 cm^{-1} (Fig. 2b). These bands characteristic of aromatic C-Cl stretching and ring deformation[5] can be assigned to the effects of intercalation. On the FTIR spectrum obtained for $FeCl_3$-CrO_3-GBC (Fig. 2c) the 1079 cm^{-1} band still exists suggesting the $FeCl_3$-C interaction to occur. This feature may be related to stage-2 $FeCl_3$-GIC located in the flake centre of $FeCl_3$-CrO_3-GBC. The bands characteristic of CrO_3-GIC which are present on the FTIR spectrum for $FeCl_3$-CrO_3-GBC can be related to the C-CrO_3 interaction in the peripheral regions of GBC. It is worth noting that on the FTIR curve recorded for $FeCl_3$-CrO_3-GBC the bands associated with CrO_3-GIC and $FeCl_3$-GIC broadened and increased in intensity and a new broad band at around 1100-1200 cm^{-1} appeared. The presence of this band and a slight shifting the CrO_3-GIC and $FeCl_3$-GIC bands are assumed to arise from the modified donor-acceptor interaction within $FeCl_3$-CrO_3-graphite system[6] due to the changes in chemical composition and staging structure effected by intercalation of CrO_3 into $FeCl_3$-GIC.



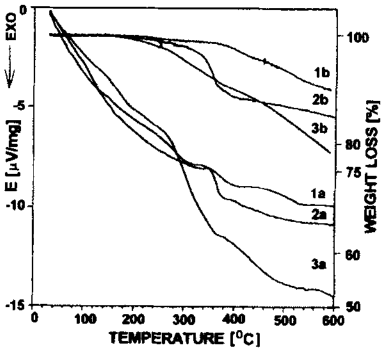


FIGURE 2 FTIR spectra for CrO_3-GIC (a), $FeCl_3$-GIC (b) and $FeCl_3$-CrO_3-GBC (c).

FIGURE 3 DSC (a) and TG (b) curves for CrO_3-GIC (1), $FeCl_3$-GIC (2) and $FeCl_3$-CrO_3-GBC (3).

The FTIR considerations were verified by thermal measurements. Figure 3 shows three pairs of DSC and TG curves. Curves 1 are presented for comparison to show thermal changes occurring in CrO_3-GIC. As can be seen from curve 1b, thermal decomposition of CrO_3-GIC, starting at about 220 °C, results in a small weight loss up to 360 °C. On further heating the weight loss is more pronounced. In the temperature range between 300 and 500 °C two exothermic peaks, at about 330 and 420 °C, are observed. These exotherms correspond to the formation of lower chromium oxides, Cr_3O_8 and Cr_2O_5/CrO_2, respectively[8]. On the TG curve for $FeCl_3$-GIC four sections of weight loss can be distinguished. The first (up to 320 °C) and the last section (400- 600 °C) represent a slow weight loss. In the middle temperature region (340-410 °C) two slopes are observed. The abrupt weight loss observed between 340 and 370 °C corresponds to the endothermic peak on the DSC curve and is associated with vaporization of $FeCl_3$. In the range of 370-410°C the decomposition of $FeCl_3$ occurs to produce $FeCl_2$ and Cl_2. This reaction corresponds to a small exothermic peak at 410 °C. The TG and DSC curves are considerably different for $FeCl_3$-CrO_3-GBC. Due to bi-intercalation of CrO_3 into $FeCl_3$ the weight loss in the temperature range 340-410 °C is significantly suppressed, especially an abrupt drop at 350 °C disappears. A simultaneous decay of the corresponding endothermic peaks on the DSC curve can simply be attributed to the presence of bi-intercalated CrO_3 in the $FeCl_3$-CrO_3-GBC lattice. In consistency with the results of the FTIR measurements it can be inferred that a new $FeCl_3$-CrO_3 system, likely the co-intercalation one, is responsible for the decay of the $FeCl_3$ vaporization and decomposition. It is interesting that the weight loss for $FeCl_3$-CrO_3-GBC is higher as compared to that for $FeCl_3$-GIC at temperatures lower than 350 and higher than 450 °C.

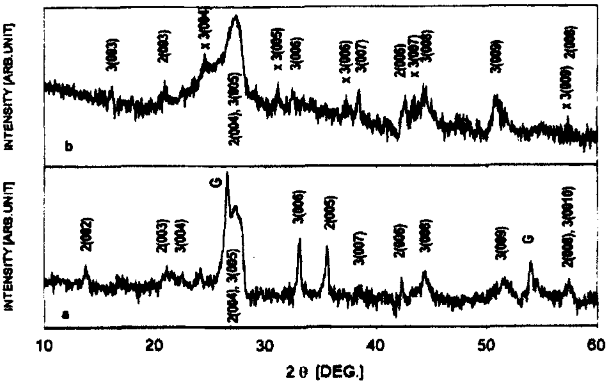


FIGURE 4 XRD patterns for $FeCl_3$-GIC (a) and $FeCl_3$-CrO_3-GBC (b) after heat treatment in argon at 320 °C for 0.5 h. (x): CrO_3-GIC.

The XRD measurements served as a tool to evaluate the thermal stability of $FeCl_3$-GIC and $FeCl_3$-CrO_3-GBC. After 0.5h of heating at 320 °C the weight losses were 15.8% and 10.7% for $FeCl_3$-GIC and $FeCl_3$-CrO_3-GBC, respectively. After heat treatment stage-2 $FeCl_3$-GIC changed to the mixture of stage-(2+3) $FeCl_3$-GIC (d_i = 0.948 nm) and pure graphite (Fig. 4a). Because the original $FeCl_3$-GIC contained only stage-2 structure and graphite, the result obtained shows that a partial deintercalation of $FeCl_3$-GIC occurred on heating. The position of the 2(005) peak well fit the main peak for $FeCl_2$ (lawrencite), hence one cannot exclude that some $FeCl_2$ was deintercalated from the graphite lattice due to a partial decomposition of stage-2 $FeCl_3$-GIC. On the XRD pattern given for heat treated $FeCl_3$-CrO_3-GBC (Fig. 4b) no graphite peaks are observed. The lack of both the graphite phase and the phase of CrO_3-GIC was characteristic feature of the original GBC[2]. For heat treated GBC the peaks arising from stage-2 $FeCl_3$-GIC are preserved and new sets of peaks corresponding to stage-3 $FeCl_3$-GIC and stage-3 CrO_3-GIC appear. Based on this, the conclusion can be drawn that upon heating CrO_3 leaves the co-intercalation layer occupied together with $FeCl_3$ and the structural rearrangement takes place without the compound depletion.

Acknowledgements

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