Preparation and Characterization of New Intercalates formed between Graphite and Iron Carbonyl Compounds

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Summary Intercalates of graphite with $Fe(CO)_5$, with $Na_2Fe(CO)_4$, and with $Fe_3(CO)_{12}$ have been prepared and characterized by *X*-ray diffraction, thermogravimetric analysis, Mössbauer spectroscopy, and electron microscopy.

MANY of the lamellar compounds of graphite with transition-metal salts exhibit remarkable properties[1] and there is considerable interest in their role as precursors for metal–graphite intercalates and also as catalysts for a number of key industrial processes.[2] As part of a programme of studies which involves both the development of new methods of catalyst characterization[3] and the design of new intercalate catalysts,[4] we have identified novel extended-sandwich compounds which are stable under dry nitrogen at room temperature.

The compounds were prepared from their separate components using, essentially, the photochemical method of Schlögl and Böhm.[3,5] By using mechanically ground crystals of natural graphite [Kropfmuhl (Bavaria) with particle size *ca.* 1 μm] and tetrahydrofuran as the solvent, evidence for intercalation was deduced from the symptomatic[6] disappearance of the 101, 102, and 006 *X*-ray reflections characteristic of rhombohedral graphite, which reverts to hexagonal graphite on intercalation. Proof of the formation of both second- and third-stage compounds came from the *X*-ray powder diffractogram and the thermogravimetric analyses profile. Chemical analysis gave the following compositions: $Fe(CO)_5$; Fe, 3·8%; $Na_2Fe(CO)_4$; Fe, 4·2% $Fe_3(CO)_{12}$: Fe, 6·2%. The ^{57}Fe Mössbauer spectra obtained at room temperature and under dry nitrogen were different from those of the parent carbonyl compounds, in contrast with the spectra obtained when iron carbonyl compounds are merely physisorbed onto the surface of graphite.[7] The Mössbauer spectra also suggest that some disproportionation may have accompanied the intercalation of $Fe_3(CO)_{12}$. Preliminary results using a special cryogenic (10—78 K) electron-microscope technique[8] revealed signs of superlattice ordering of the $Fe(CO)_5$ intercalate at 15 K.

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