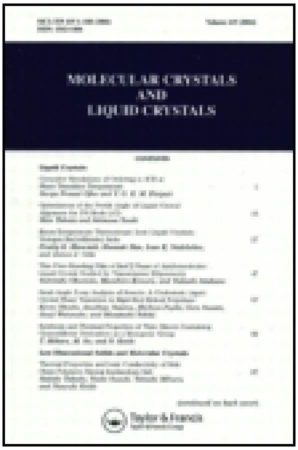

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Structure of Transition Metal Graphite Compounds: Iron- and Ruthenium-Graphite

D. Herein [a] , T. Braun [a] & R. Schlögl [a]
[a] Institut fur Anorganische Chemie der J. W. Goethe Universität, Marie Curie Str. 11, 60439, Frankfurt am Main, Germany

Version of record first published: 23 Oct 2006.

To cite this article: D. Herein , T. Braun & R. Schlögl (1994): The Structure of Transition Metal Graphite Compounds: Iron- and Ruthenium-Graphite, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 189-194

To link to this article: http://dx.doi.org/10.1080/10587259408051687

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 189–194
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

THE STRUCTURE OF TRANSITION METAL GRAPHITE COMPOUNDS: IRON- AND RUTHENIUM-GRAPHITE

D. HEREIN, T. BRAUN AND R. SCHLÖGL
Institut für Anorganische Chemie der J. W. Goethe Universität, Marie Curie Str. 11, 60439 Frankfurt am Main, Germany

Abstract: The so called iron- and ruthenium-graphite compounds prepared by the reduction of stage-1 $FeCl_3$-GIC and stage-2 $RuCl_3$-GIC with hydrogen and K-naphthalenide/THF solutions were investigated by XRD, SEM with EDX and TEM. The structural properties of these compounds are discussed with regard to possibly exisisting two-dimensional iron- and ruthenium-graphite.

INTRODUCTION

The recent development of various methods for the reduction of transition metal chloride-GIC to the corresponding transition metal compounds has produced a range of materials. The resulting compounds were obtained by reduction with hydrogen[1], alkali metals[2], Li-diphenylide, $LiAlH_4$, $NaBH_4$[3] and n-BuLi[4]. Their structures were speculated to be two-dimensional transition metal-GIC[1-4] or transition metal graphite-π-complexes[3] with various amounts of three-dimensional transition metal particles between the graphite sheets. In some cases the formation of small three-dimensional transition metal particles in either metallic or oxidized states at the surface of the graphite flakes[1] and between the graphite[3,4] sheets was reported. Nevertheless, there remain some open questions, such as the structure of these so called transition metal-graphite compounds.

In search for the chemical and physical properties of possibly existing iron- and ruthenium-GIC we reduced stage-1 $FeCl_3$-GIC and stage-2 $RuCl_3$-GIC with hydrogen and K-naphthalenide/THF solutions under various conditions. The reduced materials were investigated by XRD, SEM with EDX and TEM with micro diffraction. The air sensitivity of the materials obtained and the influence of moisture and oxygen during the reduction procedure were investigated as the possibly existing transition metal-GIC are expected to be air sensitive as known from other donor- and acceptor-GIC.

EXPERIMENTAL

For the preparation of the starting GIC we used natural graphite (AFS, flake size 1-10 μm) from the Kropfmühl AG, Passau, Germany with impurities less than 1 %. All work was carried out carefully applying the Schlenk technique. The THF was dried under argon with potassium and was freshly distilled before use. The gases were of high purity (argon 4.8 and hydrogen 5.0). Handling of the samples after reaction was carried out in a glove box with a high purity argon atmosphere (moisture and oxygen < 0.1 ppm). The XRD pattern of the samples were recorded under argon in sealed Lindemann capillaries using Co $K_{\alpha 1}$ radiation and after sample exposure to air with Cu K_α radiation.

Preparation of the $FeCl_3$- and $RuCl_3$-GIC

Stage-1 $C_{10}FeCl_{3.3}$: was prepared from freshly sublimed $FeCl_3$ and AFS graphite under a chlorine pressure of 1 bar at 573 K using the conventional two-zone method.

Stage-1 $C_{13}FeCl_{3.2}$: was obtained from $C_{10}FeCl_{3.3}$ by washing with THF and drying in vacuum at room temperature for 24 h.

Stage-2 $C_{17}RuCl_3$: was prepared from commercially available $RuCl_3$ (Heraeus, Germany) and AFS graphite at 1132 K using the zwo-zone method.

Preparation of the Fe- and Ru-graphite compounds

The reduction of $C_{10}FeCl_{3.3}$ and $C_{17}RuCl_3$ with hydrogen was done in a glass tube which was protected against moisture at both ends by bubble meters filled with concentrated H_2SO_4 at 423-773 K with a heating rate of ~1 Kh^{-1}.

$C_{13}FeCl_{3.2}$ and $C_{17}RuCl_3$ were reduced with 2.5 to 6 eq of 0.05 M and 0.2 M K-naphthalenide/THF at 200 K and room temperature. After stirring for 24 h the samples were filtered, washed with THF under argon and dried for 12 h at 300 K in vacuum (10^{-3} mbar).

No.	Conditions	T [K]	t	Starting GIC
1	2.8 eq, 0.05 M K-naphthalenide/THF	300	18 h	$C_{13}FeCl_{3.2}$
2	6 eq, 0.2 M K-naphthalenide/THF	200	24 h	$C_{13}FeCl_{3.2}$
3	Hydrogen	423-773	14 d	$C_{10}FeCl_{3.3}$
4	2.5 eq, 0.05 M K-naphthalenide/THF	300	18 h	$C_{17}RuCl_3$
5	5 eq, 0.2 M K-naphthalenide/THF	200	24 h	$C_{17}RuCl_3$
6	Hydrogen	773	2 d	$C_{17}RuCl_3$

Table 1: Preparation conditions of the reduction of $FeCl_3$-GIC and $RuCl_3$-GIC

The general results will be discussed using three iron-graphite compounds and three ruthenium-graphite compounds. More details of the preparation conditions of these samples are summarized in table 1.

RESULTS AND DISCUSSION

Fe-graphite compounds

Reduction of $FeCl_3$-GIC with hydrogen leads to graphite, α-iron and residual $FeCl_2$-GIC. XRD revealed the presence of strong and sharp reflections of α-iron. This is an indication of well ordered particles of 100 nm size. The presence of a residual $FeCl_2$-GIC was clearly identified by the increase of the background at 2Θ = 9°, 17°, 34°, 40° and near the (002) reflection of graphite in the XRD pattern of sample 3 recorded under argon (figure 1). The formation of a two-dimensional Fe-GIC[1] was not observed. After sample exposure to air the same pattern was obtained. No reflections of iron oxides or hydration products of $FeCl_2$ were observed.

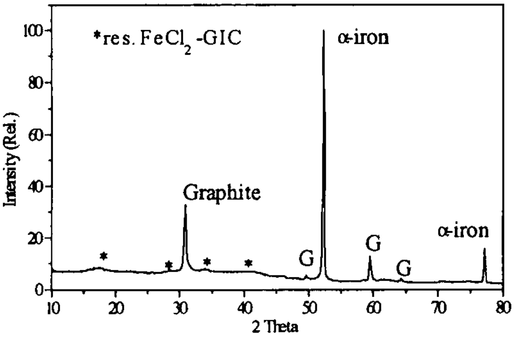

FIGURE 1 XRD pattern of sample 3 under argon

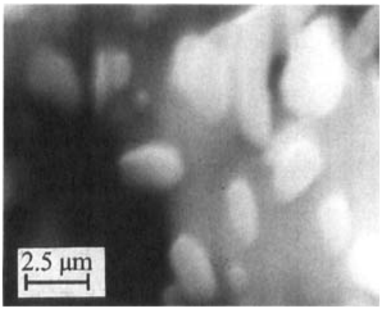

FIGURE 2 SEM image of sample 3

SEM revealed a distribution of iron particles all over the surface of the graphite flakes with an accumulation at the prismatic faces (figure 2). The nearly hexagonal platelets were identified by EDX as iron (ratio Fe:Cl = 1:0.2). The average ratio Fe:Cl = 1:0.8 revealed the presence of some residual $FeCl_2$-GIC within the bulk of the flakes.

The reduction of $FeCl_3$-GIC with K-naphthalenide/THF leads to KCl, disordered graphite with various amounts of residual $FeCl_2$-GIC and small α-iron particles. The reflections of α-iron were weak and broad indicating small and disordered particles of 10 nm size. The presence of a residual $FeCl_2$-GIC was identified by the increase of the background near the (002) graphite reflection. In the case of using a large excess of K-naphthalenide (sample 2) the formation of a stage-2 $K(THF)_1$-GIC with an I_c-value of 1065 pm was observed in the XRD pattern recorded under argon (figure 3a, b). All reflections were due to three-dimensional phases or were caused by residual conventional GIC. Reflections of a two-dimensional Fe-GIC were not observed.[2-4]

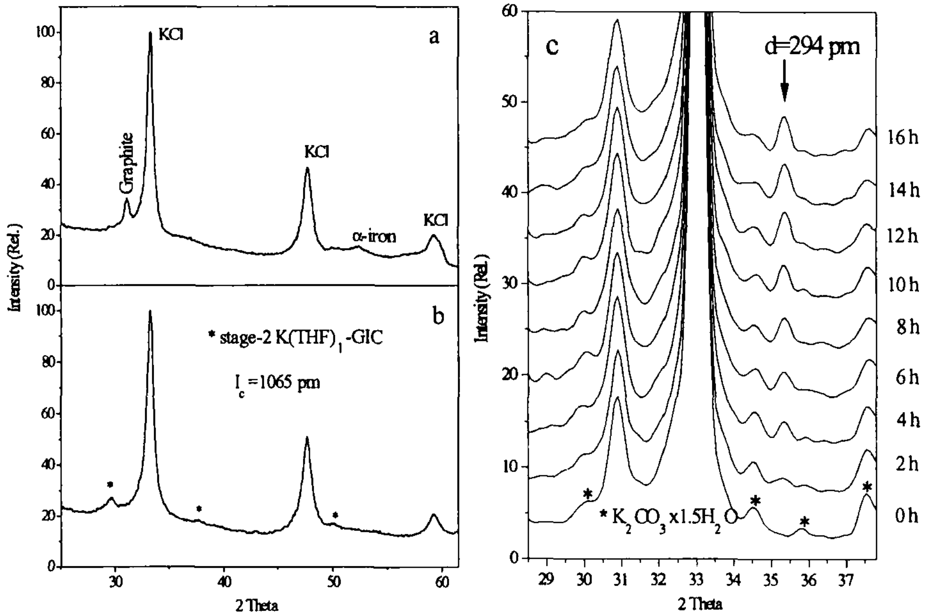

FIGURE 3 XRD pattern of sample 1 (a) and 2 (b) under argon and after exposure to air of sample 2 (c)

Exposure to air caused sample 2 to become hot due to the oxidation of the included K(THF)$_1$-GIC and K-carbonates were formed. XRD revealed the presence of $KHCO_3$ and $K_2CO_3 \cdot 1.5\ H_2O$. In some cases a reflection at a d-value of 294 pm was observed in the pattern after exposure to air. This reflection is not due to a lamellar Fe-GIC with an I_c-value of 590 pm reported elsewhere[3] as its detection required exposure to air. Figure 3c shows a time dependend XRD experiment with sample 2 exposed to air. Subsequent pattern were taken at intervals of 1 h and show the gradual formation of the single reflection with a d-value of 294 pm. This reflection is due to the oxidation of encapsulated deep-lying potassium. The same pattern with a single line at 294 pm was observed after oxidation of a stage-1 K-GIC for several hours in air. This reference experiment is the proof for a residual K-GIC causing the reflection often mistaken as (002) line from Fe-GIC. After exposure of sample 1 to air the XRD pattern shows reflections of α-Fe_2O_3, Fe_3O_4 and β-FeOOH.

By SEM no iron or KCl particles were found at the surface of any samples prepared by reduction in solution. EDX revealed the presence of iron, potassium and chlorine in all samples in various ratios depending on the excess of K-naphthalenide used in the reductions.

Additionally, TEM images show that the iron and thin KCl particles are encapsulated by carbon (figure 4). The samples consist of regions with co-existing iron and KCl and other regions with only one of the two phases being present. A nanocrystalline form of iron, however, was found at the edges of thin KCl particles encapsulated by carbon (figure 5). The lattice fringes in figure 5 are due to the (220) lattice of KCl with a d-value of 222 pm.

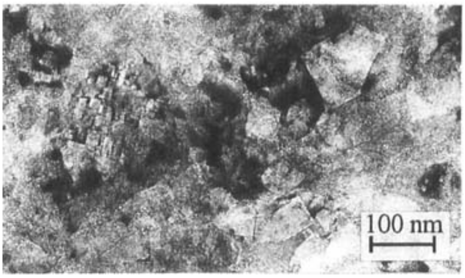

FIGURE 4 TEM image of sample 2

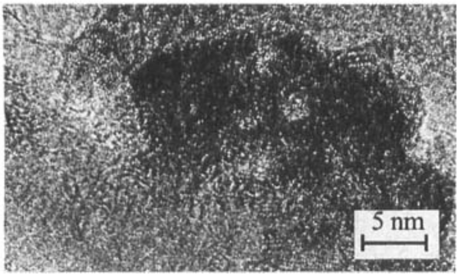

FIGURE 5 TEM image of nanocrystalline iron

Ru-graphite compounds

The reduction of the stage-2 $RuCl_3$-GIC with dry hydrogen at 773 K leads to the formation of zero valent ruthenium with a small amount of residual $RuCl_3$-GIC as shown in figure 6a. The intensity ratios of the ruthenium reflections reveal the presence of strongly textured particles. The linewidth of the (002), (h0l) and (hkl) peaks of the formed ruthenium are much larger than those of the (h00) and (hk0) reflections. This is an indication for a topotactical reduction of the $RuCl_3$ yielding very flat hexagonal platelets with an average diameter of 40 nm and a thickness of 6 nm. It is concluded that these platelets are located inside the graphite flakes. No ruthenium particles could be found at the surface areas of the graphite flakes by SEM. No reflections pointing to the presence of a lamellar Ru-GIC were found.

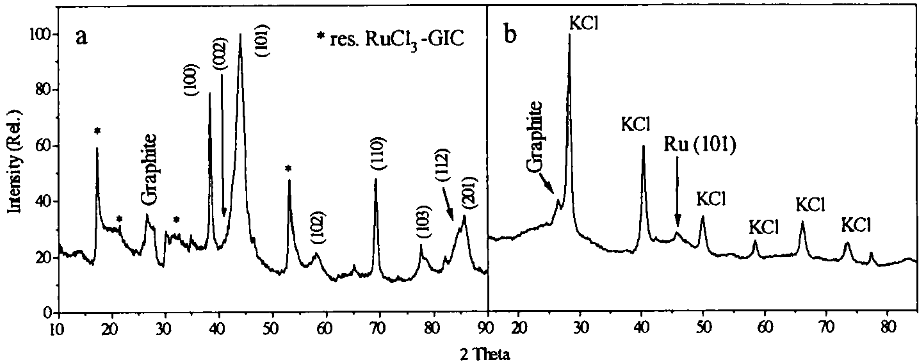

FIGURE 6 XRD pattern of sample 4 (a) and sample 6 (b) under argon

Reduction of $RuCl_3$-GIC with K-napthalenide/THF leads to the formation of disordered graphite, KCl and small ruthenium particles of 10 nm size. The increased background near the (002) graphite reflection points out the presence of some residual $RuCl_3$-GIC (figure 6b). The reduced Ru-samples show the same behaviour after exposure to air as reported for the Fe-samples. In some cases a single line with a d-value of 295 pm was observed in the XRD pattern taken after exposure to air. Again no reflections pointing to the presence of a lamellar Ru-GIC were found.

By SEM no ruthenium or KCl particles were found at the surface of any Ru-samples prepared by reduction in solution. EDX revealed the presence of ruthenium, potassium and chlorine in all samples in various ratios depending on the excess of K-naphthalenide used in the reductions.

CONCLUSIONS

The reduction of $FeCl_3$-GIC and $RuCl_3$-GIC with K-Naphthalenide/THF leads to the formation of small iron or ruthenium particles and thin KCl crystals encapsulated by carbon. Lamellar Fe-GIC reported elsewhere[1-4] or Ru-GIC were not observed. All evidence in the literature can be traced back to other origins than to Fe-graphite in the sense of a lamellar GIC.

The reduction of $RuCl_3$-GIC with hydrogen produced strongly textured ruthenium platelets encapsulated by carbon. The strong texture of these platelets points to a topotactic reduction between the graphite sheets. In the case of the reduction of $FeCl_3$-GIC the nearly hexagonal shape of the iron platelets at the graphite surface is ascribed to a topotactic reduction of the $FeCl_2$ islands, produced in a first reduction step from the $FeCl_3$ islands, immediately after their movement out of the graphite flake.

The formation of a two-dimensional Fe- or Ru-GIC seems to be impossible according to our results using various preparative pathways. The reduction in solution at low temperature produces compounds with very small included three-dimensional transition metal particles. Even in this case, however, the high cohesion energy of iron and ruthenium is the dominating factor and cannot be overcome by the kinetic trick of low temperature production.

REFERENCES

1. K. Kalucki, A. W. Morawski, J. Chem. Biotechnol., 47, 357 (1990)
2. C. Herold, G. Furdin, J. F. Marêché, Mat. Science Forum, 91-93, 51 (1992)
3. M. E. Vol'pin et al, J. Am. Chem. Soc., 97, 3366 (1975)
4. C. Meyer, R. Yazami, G. Chouteau, J. Phys. France, 51, 1239 (1990)