Investigations of exfoliating graphite intercalation compounds using time-resolved DEXAFS

T. Ressler, U. Hatje, S. Twumasi, K. Lochte, W. Metz

► To cite this version:

T. Ressler, U. Hatje, S. Twumasi, K. Lochte, W. Metz. Investigations of exfoliating graphite intercalation compounds using time-resolved DEXAFS. Journal de Physique IV Proceedings, 1994, 04 (C9), pp.C9-167-C9-170. 10.1051/jp4:1994927 . jpa-00253488

HAL Id: jpa-00253488

<https://hal.science/jpa-00253488>

Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Investigations of exfoliating graphite intercalation compounds using time-resolved DEXAFS

T. Ressler, U. Hatje, S. Twumasi, K. Lochte and W. Metz

Institute of Physical Chemistry, University of Hamburg, Bundesstr. 45, 20146 Hamburg, Germany

Abstract

The exfoliation processes (rapid thermal decomposition) of CuCl_2 graphite intercalation compounds (GICs) cointercalated with FeCl_3 or AlCl_3 were investigated using time resolved X-ray absorption spectroscopy in an energy dispersive mode. The experiments were carried out at the DEXAFS beam line at HASYLAB (Hamburg). The evolution of the absorption spectra of the Cu K-edge was compared with the reaction of pure CuCl_2 under the same conditions. From the exfoliation of the $\text{CuCl}_2/\text{AlCl}_3$ -GIC a CuO graphite compound can be obtained. The formation resembles the reaction of pure CuCl_2 , whereas the exfoliation of the $\text{CuCl}_2/\text{FeCl}_3$ -GIC results in a mixture of Cu_2O , CuO and Cu clusters. The reduction of the Cu(II) at a reaction temperature of 500°C is correlated with an oxidation of Fe(II) to Fe(III).

1. Introduction

Graphite compounds with catalytic activity in heterogeneous catalysis could be obtained by exfoliation (rapid thermal decomposition) of graphite intercalation compounds (GICs) [1,2]. During this process, in which the GICs are heated up very fast, the structure of the GICs is partially destroyed and the inner surface increases. Starting with GICs of the acceptor type with transition metal chlorides the exfoliation in air can result in metal oxides of various oxidation states or highly dispersed metal clusters. GICs with intercalate layers consisting of more than one transition metal are supposed to show a different behaviour in the exfoliation process leading to graphite compounds with different properties. We report time resolved X-ray absorption spectroscopic (XAS) investigations of the evolution of different compounds during the exfoliation of cointercalated copper(II) chloride GICs compared to the reaction of CuCl_2 in air.

2. Experimental

Two different CuCl_2 GICs, cointercalated with FeCl_3 or AlCl_3 , were investigated, a stage 2 $\text{CuCl}_2/\text{AlCl}_3$ -GIC and a stage 6 $\text{CuCl}_2/\text{FeCl}_3$ -GIC. Due to the preparation process of the GICs a residual content of water can not be excluded. Therefore a $\text{CuCl}_2 \cdot x\text{H}_2\text{O}$ compound instead of pure CuCl_2 was chosen to compare with the intercalation compounds.

The $\text{CuCl}_2/\text{FeCl}_3$ GIC and the $\text{CuCl}_2/\text{AlCl}_3$ GIC were prepared in sealed glass tubes containing a chlorine pressure of 0.5 bar at 350°C and 200°C , respectively. The graphite flakes were ground, mixed with the same amount of NaY zeolite as a stabilising matrix, and pressed to a self supported wafer (thickness 1.3 mm).

XAS experiments were carried out at the DEXAFS station at HASYLAB (Hamburg). The standard set-up for dispersive XAS was used [3] with a bent Si(111) monochromator crystal in reflection geometry and a cooled photo diode array as detector. The sample was installed in a flow-through reactor. The exfoliation was carried out in air in a temperature range of 30°C to 600°C and with a heating rate of $35^\circ/\text{min}$ to avoid the deintercalation of the metal chloride. Absorption spectra were taken every 6 s averaging 40 single spectra with an integration time of 120 ms each. Reference absorption spectra were measured at the EXAFS II and the RÖMO II beam line at HASYLAB.

3. Data analysis

The dark signal of the detector, the I_0 signal without a sample and a metal foil were measured before and after the reaction for each experiment. During the reaction the 1024 photo diodes of the detector were read out continuously without any movement of the system components. To obtain a single absorption spectra the appropriate I_0 was calculated from a linear interpolation between the two measured I_0 signals.

The conversion from photo diodes to the photon energy was performed by applying a second order polynomial on the data. The coefficients of the polynomial were obtained from a computer supported comparison of the metal foil spectrum with a Cu metal reference spectrum.

The spectra were background corrected by an 1-order polynomial and normalised to an edge jump equal one. The E_0 value was chosen as the first inflection point of the absorption edge. The atomic absorption was calculated by fitting a third order polynomial to the k weighted data. After that the extracted $\chi(k) \cdot k^3$ was multiplied by a Kaiser-Bessel window and Fourier transformed (FT) to obtain the radial distribution function.

4. Results

The X-ray diffraction (XRD) diagram of the two GICs are shown in Fig.1 together with the positions and theoretical intensities of the 00L Bragg reflections for a stage 2 and a stage 6 CuCl_2 GIC. Due to the small difference in the scattering factor of Cu and Fe it is impossible to distinguish between them using a common structure refinement procedure. The non-appearance of superstructure peaks between the normal 00L Bragg reflections indicates the existence of a cointercalation. Therefore a mixture of FeCl_3 and CuCl_2 or AlCl_3 and CuCl_2 in the intercalate layer must be assumed, which can result in a chemical interaction between the different metals. In the case of the Cu/Fe-GIC the appearance of Fe(II) can be concluded from a comparison of the XANES region of the Fe K-edge of the GIC, FeCl_2 , and FeCl_3 (Fig. 4). Although the intercalation was carried out under chlorine atmosphere with FeCl_3 , the obtained intercalation compound seems to consist of a mixture of FeCl_2 and FeCl_3 .

Fig.1 XRD of a stage 2 $\text{CuCl}_2/\text{AlCl}_3$ -GIC (left) and a stage 6 $\text{CuCl}_2/\text{FeCl}_3$ -GIC (right), 00L reflections. The lines show the calculated intensities and peak positions for an ideal stage 2 (left) and stage 6 (right) CuCl_2 GIC.

The XAS measurements were performed at the Cu K-edge and the Fe K-edge for the Cu/Fe-GIC. Fig.2 and 3 show the evolution of the absorption spectra of the CuCl_2 -GICs during the exfoliation and during the reaction of CuCl_2 in air, respectively. The similar behaviour of the Cu/Al-GIC and pure CuCl_2 can easily be seen (Fig.2), whereas the exfoliation of the Cu/Fe-GIC proceeds in two steps (Fig.3), leading to a different graphite compound. Fig.5 and 6 show the shift of the Cu K-edge in relation to the edge position of a Cu metal foil during the exfoliation. Whereas the edge shift of the Cu/Al-GIC and the pure CuCl_2 differs only slightly, a large shift of the edge position for the Cu/Fe-GIC in a temperature range of 500 °C - 520 °C can be observed. This edge shift indicates the reduction of Cu(II) to Cu(I) and is correlated to the oxidation of Fe(II) to Fe(III) in the same temperature range (Fig.6, right). Compared to the CuCl_2 and the Cu/Al-GIC the copper in the Cu/Fe-GIC seems to be partially reduced, leading to a smaller edge shift relative to the Cu metal foil and a different XANES (Fig.3). The XANES of the Cu/Fe-GIC at room temperature resembles the XANES of the Cu/Al-GIC at 250 °C.

Fig.2 Evolution of the Cu K near edge structure during the reaction of CuCl_2 (left) and the exfoliation of $\text{CuCl}_2/\text{AlCl}_3\text{-GIC}$ (right).

Fig.3 Evolution of the Cu K near edge structure during the exfoliation of the $\text{CuCl}_2/\text{FeCl}_3\text{-GIC}$.

Fig.4 Normalised Fe K near edge structure of the $\text{CuCl}_2/\text{FeCl}_3\text{-GIC}$ compared to absorption spectra of FeCl_3 and FeCl_2 .

Fig.5 Change of the Cu K-edge position (circle) relative to the edge position of a Cu metal foil for CuCl_2 (left) and $\text{CuCl}_2/\text{AlCl}_3\text{-GIC}$ (right) during the exfoliation.

Fig.6 Change of the Cu K-edge position (circle) relative to the edge position of a Cu metal foil (left) and the Fe K-edge position relative to the edge position of a Fe metal foil (right) for the $\text{CuCl}_2/\text{FeCl}_3\text{-GIC}$ during the exfoliation.

The reduction of Cu(II) to Cu(I) in the Cu/Fe compound turned out to be reversible. After three days at room temperature in air the Cu(I) was reoxidised to Cu(II) and the reaction could be carried out again including the reduction of Cu(II) to Cu(I) at 500 °C correlated to an oxidation of Fe(II) to Fe(III).

Fig. 7 and 8 show the evolution of the $FT(\chi(k) \cdot k^3)$ at different reaction temperatures. A shift of the first shell around the copper atom to a smaller distance, due to the reaction of CuCl_2 to copper oxide, can be observed in all three cases. For the reaction of CuCl_2 and the exfoliation of the Cu/Al-GIC the FTs indicate the loss of residual water in a temperature range between 120 °C and 180 °C. For the exfoliation of the Cu/Fe-GIC the first shell is slightly shifted to a higher distance, compared to the first shell of the product of the reaction of CuCl_2 . Additionally, a decreased coordination number of the first shell can be seen from Fig. 8. Together with the large shift in the edge position to lower photon energy (Fig. 6) this points out to a mixture of CuO , Cu_2O , and Cu clusters.

Fig. 7 Fourier transformed $\chi(k) \cdot k^3$ of the Cu K-edge of CuCl_2 (left) and the $\text{CuCl}_2/\text{AlCl}_3$ -GIC (right) at different reaction temperatures.

Fig. 8 Fourier transformed $\chi(k) \cdot k^3$ of the Cu K-edge of the $\text{CuCl}_2/\text{FeCl}_3$ -GIC at different reaction temperatures.

5. Conclusion

The exfoliation of two cointercalated GICs ($\text{CuCl}_2/\text{AlCl}_3$ -GIC and $\text{CuCl}_2/\text{FeCl}_3$ -GIC) were compared with the reaction of pure CuCl_2 in air. At a temperature of 350 °C the copper(II) chloride in the Cu/Al-GIC reacts to copper(II) oxide, whereas the reaction of the pure CuCl_2 starts at a temperature of 430 °C. The exfoliation of the Cu/Fe-GIC results in a mixture of copper(II) oxide, copper(I) oxide and copper clusters. The reduction of the copper(II) is correlated with an oxidation of the Fe(II) and turned out to be reversible at room temperature.

Financial support by the *Bundesministerium für Forschung und Technologie* (project no.: 05 5GUFAB 8) is gratefully acknowledged.

References :

- [1] G. Sirokman et al., *Carbon*, **26**, 35 (1990)
- [2] H.-P. Eickhoff, Dissertation, Hamburg 1993
- [3] M. Hagelstein, S. Cunis, R. Frahm, W. Niemann, P. Rabe, *Physica B*, **158**, 324 (1990)