Local Structure of Ru in Ru-C60 and Ru-Fullerene Black Compounds

To cite this version:

HAL Id: jpa-00255368
https://hal.archives-ouvertes.fr/jpa-00255368
Submitted on 1 Jan 1997

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.
Local Structure of Ru in Ru–C₆₀ and Ru-Fullerene Black Compounds


* Fachbereich Physik, Universität-GH Paderborn, 33095 Paderborn, Germany
** Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany

Abstract: We studied the x-ray absorption fine structure (EXAFS) of Ru-C₆₀ and Ru in fullerene black employing the K-edge of ruthenium. The EXAFS analysis of the local structure in both systems allows the observation of small metallic particles and their modification caused by the effect of temperature and/or the usage of the samples as catalyst.

1. INTRODUCTION

We studied Ru-C₆₀ and several Ru-fulleren black compounds (Ru-FB) using x-ray absorption spectroscopy (EXAFS). The aims of these studies were to increase the basic understanding of the catalytic activity of these systems. The most relevant point in this context is the local structure of the Ru particles on the base material (C₆₀, FB). The size and properties of these particles are depending on the sample preparation and on the different properties of the base materials.

2. EXPERIMENTAL DETAILS

The EXAFS measurements at the Ru K-edge (22117 eV) were performed at the RÖMO-II beamline of HASYLAB using a Si(311) double crystal monochromator. For measuring at low temperatures a He-flow cryostat was used. Energy calibration was performed by measuring Ru metal in powder form as reference absorber. The higher harmonics were suppressed by detuning the monochromator to 40% of the maximum x-ray flux. The experimental phases and amplitudes of Ru powder measured at room temperature were used for the EXAFS analysis.

The samples were prepared using Ru₂(OH)₁₂ and C₆₀ or FB in solutions with toluene at a temperature of 120°C. Parts of these samples were used for annealing at 300°C, 600°C or as catalyst for CO hydrogenation during a programmed temperature scan up to 350°C. Two different FB hosts were used, normal FB and extracted FB (FBex), where the C₆₀ molecules and higher fullerenes were removed. A more detailed information of the sample preparation is given in [1,2].

3. RESULTS AND DISCUSSION

Fig. 1 shows the Fourier transforms of the normalized x-ray absorption spectra of Ru-C₆₀, annealed at 600°C, and Ru powder. The EXAFS analysis in the harmonic approximation yields the nearest neighbour distances R, coordination numbers N and the second cumulants σ². The nearest Ru-Ru neighbor distances in Ru-C₆₀ are identical within the error bars with those in Ru powder at all temperatures. The coordination numbers are, however, drastically different. They changed from N=12 for Ru powder to N_{eff} = 4.0(4) for Ru-C₆₀ annealed at 600°C. This behavior is accompanied by a considerable increase of σ², as shown in Fig. 2. In addition, the intensity of the higher Ru neighbor shells observed for Ru-C₆₀ is decreasing more rapidly as function of distance than for the Ru reference. All these observations are pointing to the presence of Ru clusters in the Ru-C₆₀ sample, because clusters exhibit, due to the increased number of surface atoms, smaller coordination numbers and larger σ² values than bulk material. In addition, there is evidence for some Ru-C bonds.

Fig. 3 shows the Fourier transforms of Ru-C₆₀, Ru-FB and Ru-FBex samples. The spectra were taken before and after using these samples as catalysts. Strong changes in the local structure of the samples were observed, similar to those produced by annealing the samples after heating to 300°C or 600°C (as shown for Ru-C₆₀ (600°C), see Fig. 1). This finding agrees with TEM images taken of the same samples [2]. It is interesting for the catalytic properties that the sample prepared using FBex did show the smallest effect of particle agglomeration during the usage as catalyst. This indicates that FBex is, caused by it’s microstructure, a suitable base for carrying small clusters avoiding agglomeration. It is well known that an increase of particle size during the catalytic process is contraproductive to the catalytic properties.
Fig. 2.: Temperature dependences $\sigma^2 - \sigma_0^2$ of Ru-C$_{60}$ and Ru powder. $\sigma_0^2$ is the value of the Ru powder sample at room temperature.

Fig. 3.: Fourier transforms of the Ru K-edge x-ray absorption spectra of Ru-FBex, Ru-FB and Ru-C$_{60}$ after sample preparation at 120°C in toluene and after using these samples as catalysts.

Acknowledgements:

This work was supported by the BMBF, project numbers 05 5PPACB and 13N6660/3.

References: