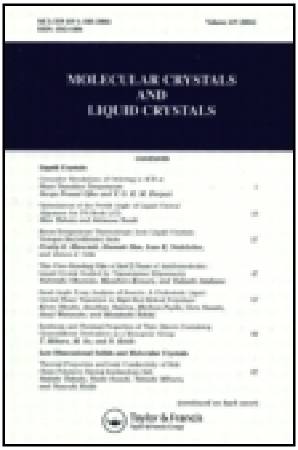

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Synthesis and Characterisation of Transition Metal Fullerdes

Harald Werner [a], Michael Wohlers [a], Thilo Belz [a] & Robert Schlögl [a]

[a] Institut für Anorganische Chemie, Universität Frankfurt, Niederurseler Hang, W-6000, Frankfurt 50, Germany

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SYNTHESIS AND CHARACTERISATION OF TRANSITION METAL FULLERIDES

HARALD WERNER, MICHAEL WOHLERS, THILO BELZ, ROBERT SCHLÖGL
Institut für Anorganische Chemie, Universität Frankfurt, Niederurseler Hang,
W-6000 Frankfurt 50, Germany

Abstract Complexes of group VIII metals in low oxidation numbers react in solution with fullerene to yield structurally ill-defined compounds with reproducible compositions and properties. A variety of characterisation methods (analysis, XRD, FT-IR, TPD) indicate that the transition metals are located in the interstices of the fullerene lattice being distorted by the volume of the olgonuclear complexes with partly coordinated residual ligands. The fullerene molecules complete the coordination shells of these catalytically active materials.

INTRODUCTION

C_{60}, a molecular modification of graphitic carbon has been shown to intercalate alkali and alkaline earth metals. The resulting fullerene intercalation compounds (FIC) exhibit strongly modified properties compared to the 3-dimensional van-der-Waals host lattice giving rise to intense research efforts[1].
Intercalation of transition metals into graphite[2] is more difficult and in elemental form not possible[3]. It is of interest to compare the behaviour of the fullerene host lattice against possible transition metal intercalation with the now established[3] reactivity of graphite. For this purpose we chose a series of complexes of Fe, Pd, Ru with low formal oxidation states of the metal and easy to strip-off ligands (CO or di-benzylidene-acetone, DBA) and used the valuable property of fullerene to be soluble in order to possibly create intercalation compounds in homogeneous phase. The characterisation emphasizes their structure and the possible residual ligand content. In addition, we report first data on catalytic properties.

EXPERIMENTAL

The compounds were prepared in toluene solution using stoichiometric mixtures of C_{60} and $Fe(CO)_5$, $Ru_3(CO)_{12}$ and Pd $(DBA)_2$[4]. Thermal or photochemical energy gave rise to a loss of ligands yielding precipitates of homogeneous composition (SEM / EDX analysis). The samples described here had the compositions of $C_{60}Fe(CO)_4$, $C_{60}Ru_3(CO)_x$ and $C_{60}Pd_3$.

The characterisation experiments were conducted under strict exclusion of air as all samples decompose visibly under ambient conditions. XRD was done with samples in Lindemann or quartz capillaries on a focussing Bragg-Brentano diffractometer equipped with a computer-controlled hot stage and a parallel detection system. Cu or Co radiation (for the Fe samples) were used. TPD was done using a transfer cell from the glove box into a UHV system equipped with a quadrupole mass spectrometer and a furnace with linear heating controller. FT-IR spectra were collected with a BRUKER ISF 66 instrument with samples in transmission geometry as KBr disks produced in the glove box and analysed in protective gas. Catalytic conversion tests were done in the ammonia synthesis reaction and with a liquid phase hydrogenation of cyclohexene. From the latter reaction the results presented were obtained with 1% catalyst (active in two consecutive runs) and a cyclohexene/THF substrate solution in hydrogen at atmospheric pressure. Hydrogen consumption and conversion were monitored separately.

RESULTS AND DISCUSSION

The comparison between metal elemental analysis and weight uptake showed that all samples contained excess organic material. The iron samples are stoichiometric in this additional content, the Ru samples contain both solvent and some CO in

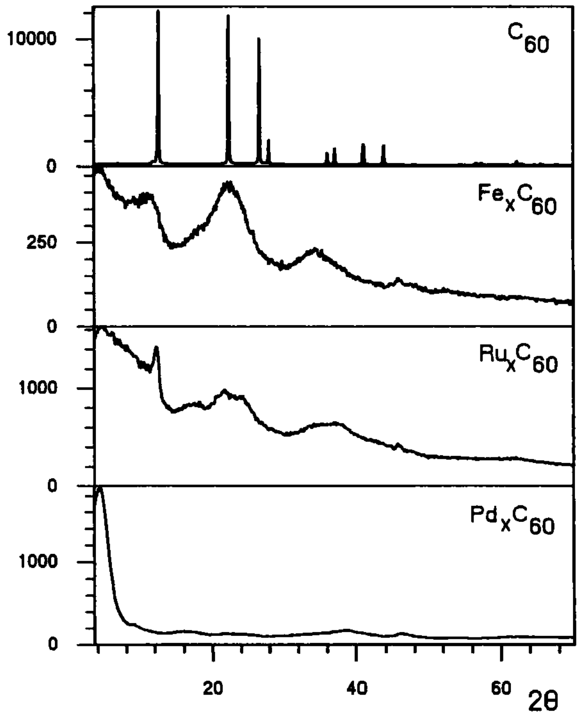

Figure 1 : Powder X-ray diffractograms of pristine and intercalated C_{60}. All samples were measured measured with Co radiation. The ordinates are expanded to show the very weak Bragg diffraction.

variable amounts and abundancies less than the metal, the Pd sample was found by IR to be contaminated with traces of residual ligand and solvent both not coordinated to the metal (IR frequencies).

The powder diffraction data from Figure 1 clearly show that all products are poorly crystalline. The broad peaks are at the positions of the crystalline host lattice indicating that the structural motif of a close-packed lattice may be a crude model for the FIC structure, much in contrast to e.g. the iodine-C_{60} structure which is not related to the host lattice. The additional intensity at low angles is characteristic of the samples indicating a maximum in the pair correlation function at about 2.5 nm, far larger than the molecular diameter of C_{60} (1.4nm). The small peak at about $2\Theta=45^0$ is due to the presence of a few particles of the free element ((111) reflections) which were, however, not found in SEM/EDX studies indicating that such particles must be rare.

In order to test possible improvements of the sample crystallinity upon thermal annealing and to find the limit of thermal degradation, all materials were also investigated in closed capillaries at high temperatures. Figure 2 shows results for the Pd sample.

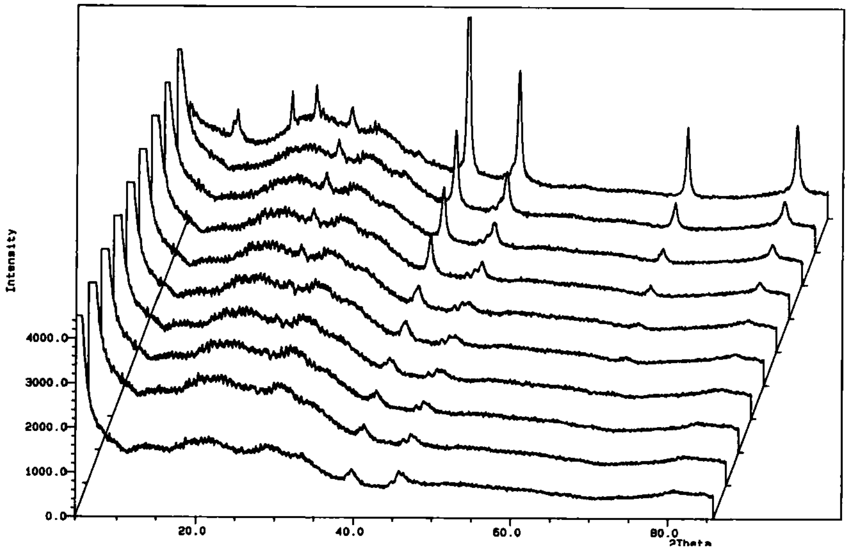

Figure 2: High temperature XRD (Cu radiation) of Pd_3C_{60}. The temperature ranges from 300 K (front end) up to 550 K (30 K intervals). The asymmetric line at $2\Theta=26^0$ is due to the graphite heater element deforming during heating.

The main information is that the sample decomposed into its constituents, pristine C_{60} (characteristic lines between $2\Theta=12^0$ and $2\Theta=28^0$) and elemental Pd (sharp lines of the 111, 200, 220 and 311 reflections at high angles). The resulting fullerene contained many stacking defects (pre-peak of the 111 reflection at ca. $2\Theta=12^0$), the Pd crystallized with some disorder indicated by the (200) profile. Most of the host material which was structurally destroyed during synthesis remained disordered also at temperatures up to 800 K. All these findings are also characteristic of de-intercalation reactions of GIC classifying the thermal treatment of FIC as de-intercalation reaction.

The peak at $2\Theta=6^{o}$ in Figure 2 disappeared with the crystallisation of C_{60} allowing to conclude that the buckyball molecules contribute to the long-distance maximum in the pair correlation function of the intercalated state.

The Fe and Ru materials undergo similar de-intercalation into the constituents without forming any carbide phase up to 700 K. The Fe sample decomposed sharply at 450 K. The host lattice restructured with the loss of the guest phase in the same way as shown with the Pd sample. The Fe was oxidised by autocatalytic decomposition of CO ligands, the very pronounced stacking faults in the C_{60} remained unrelaxed up to 700 K.

Evidence for the molecular nature of the guest species and the coordination of residual ligands together with the host material came from FT-IR data as shown in Figure 3

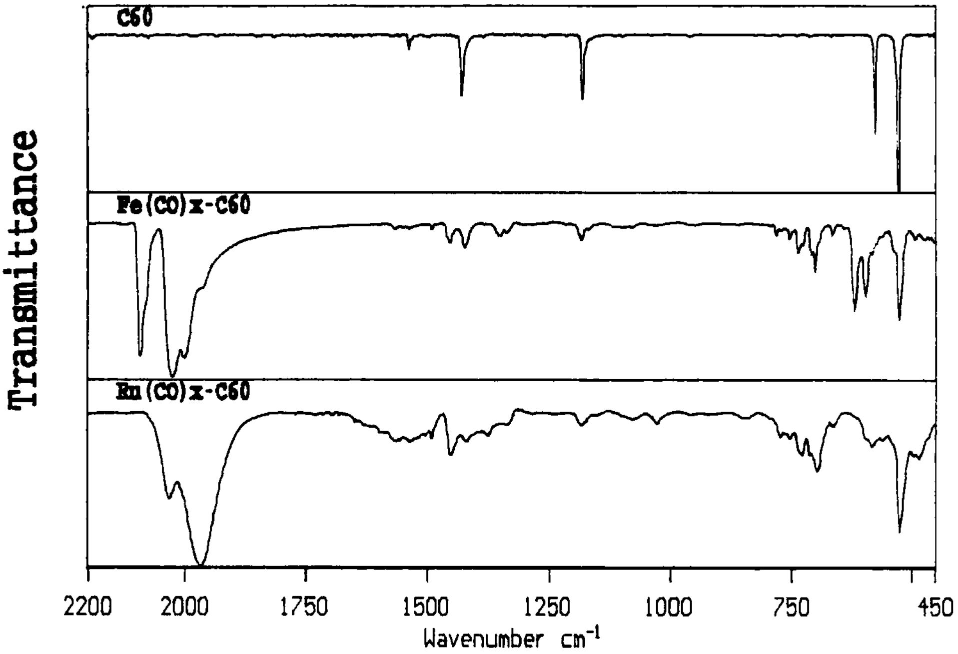

Figure 3: FT-IR data of pristine and intercalated C_{60}. The band at 1526 cm^{-1} in the top spectrum is an IR forbidden vibration of the C_{60} molecule, becoming IR active in the Ru complex.

The spectra show the presence of CO molecules coordinated to one metal atom. Reference spectra indicate the absence of all bridging CO ligands in the sample although the splitting of the CO bands indicate the presence of oligonuclear complexes. This means that the C_{60} molecules participate in the ligand sphere of the complex replacing bridgeing CO ligands. Consequently drastic changes[5] in the spectrum of the host material occur. The fullerene fingerprints are distinctly different and split into several less-degenerate groups of absorptions than in the fee host material. Only a minor contribution in the aromatic ring fingerprint region arised from traces of toluene, as only weak C–H vibrations were detected. The two different intercalated metal complexes result in clearly distinguishable spectra pointing to different local geometries in the two compounds.

In order to check the possibility of the existence of an iron intercalation compound without coordinated ligands in the temperature regime between formation of the FIC and the decomposition temperature found in XRD, the samples were subjected to CO TPD experiments. A typical result is shown in Figure 4.

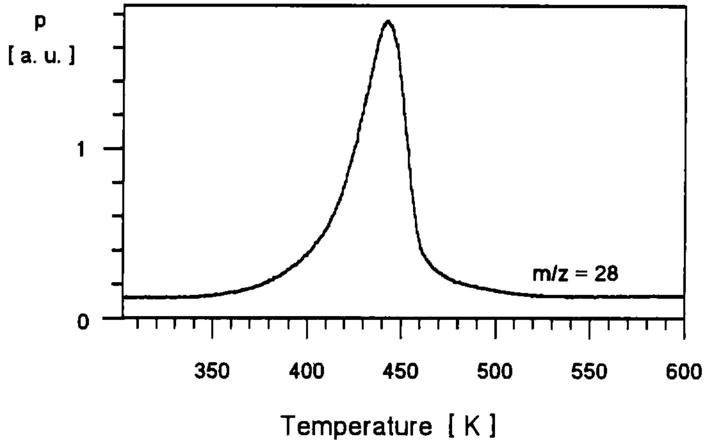

Figure 4: CO TPD of the Fe FIC sample. The heating rate was 1 Ks^{-1}.

The peak shape is characteristic of a single thermally activated process with the sharp fall-off at high temperature indicating little line broadening by diffusion effects. Varying the heating rate had little influence on shape and position of the line. The ligand stripping process coincides exactly with the appearance of the C_{60} lines in the XRD indicating the decomposition of the FIC and pointing against the existence of a FIC with atomic iron intercalated between the buckyballs. The iron formed is nanocrystalline and reacted to an iron oxide (JCPDS 190629) documenting the high initial reactivity of the transition metal.

An example for the catalytic activity[6] of the Pd sample in the standard cyclohexene hydrogenation test is shown in Figure 5. The conversion vs. time curves(determined by GC analysis) were similar for the first and second runs. The hydrogen uptake curves were, however, different. In the initial run the reaction consumed more hydrogen than required for the conversion of all cyclohexene, in the second run the hydrogen consumption was understoichiometric. These data show that the fulleride catalyst can store some hydrogen which is reversibly bound in the solid as it can be utilized in the second run. Attempts to pre-react the catalyst with pure hydrogen were unsuccessful in suppressing the hydrogen anomaly, an observation not uncommon in hydrogenation catalysis.

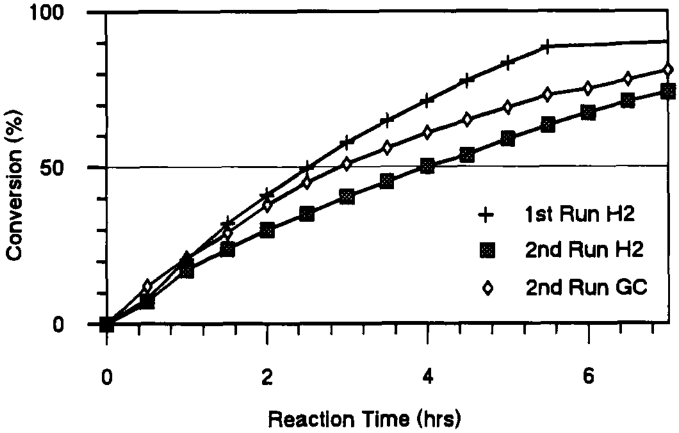

Figure 5: Conversion vs. time plot for cyclohexene hydrogenation at 300 K with the Pd FIC.

The stability of the apparently metallic Pd in the buckyball matrix is in sharp contrast to the frequently observed tendency to sintering of the Pd supported on other carbon materials. It is taken as indication for the topochemical fixation of the Pd within the interstices of the fullerene. Only the few Pd atoms located at the periphery of a C_{60} crystallite would, however, be active in catalysis.

CONCLUSIONS

FICs with transition metal complexes were obtained in homogeneous solution. Stripping-off the ligands caused for the iron FIC de-intercalation. No indication for monoatomic transition metal FIC were found by this preparative approach. De-intercalation lead to separaration of the constituents and to crystallisation of a highly disordered host lattice. Preliminary catalytic hydrogenation tests promise Pd-C catalysts with high stability against sintering.

ACKNOWLEDGEMENTS

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