ANALYSIS OF METALLOCARBOHEDRENE CONTAINING SOOT

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Introduction

Since the initial discovery of metallocarbohedrenes (Met-Cars) by our group [1], as both neutrals and ions, there has been growing interest in these molecular clusters, particularly in their proposed structure [select references: 1-5]. In order to experimentally determine their structure, Met-Cars must be analyzed in the solid state. Recently, it has been shown that Met-Cars can be formed via arc-discharge [6] and direct laser vaporization of metal carbides [7]. In this study soot is produced from laser vaporization of various metal carbides (TiC, ZrC, VC, and NbC) in an argon atmosphere inside a modified Erlenmeyer flask (Inert Gas Erlenmeyer, IGE). These soots can be extracted in a Sohxlet extractor using various solvents. Analysis is performed on both the soot and extracted solutions.

A new instrument (Figure 1) has been designed where we can perform laser vaporization (LV), in one chamber, on these metal carbides, at various conditions and collect the vaporized material on different substrates. The substrate can then be translated into the next chamber where the deposited material is analyzed via laser desorption time-of-flight mass spectrometry (LD TOF-MS). This new instrument also allows us to analyze materials not produced in the first chamber by laser desorption (LD) or thermal desorption (TD) and analyze products from laser vaporization (LV) events.

Experimental

Soot produced in the IGE has been analyzed via LD and is shown to contain Met-Car species. In these experiments, a metal carbide (TiC, ZrC, NbC, or VC) is placed in a sample holder and is ablated in an inert gas atmosphere (Ar 6-8 psi). The ablation laser is the second harmonic of a Nd:YAG laser (532 nm) focused to a line by a cylindrical lens. This lens is rotated at 1 rpm in order to continually ablate new material and to avoid drilling through the sample and into the quartz holder at one location. A typical experiment will run from 6-8 hours and the soot produced will form an opaque coating on the walls of the vessel. Analysis of the Met-Car containing soot (other than the aforementioned LD) include: STM and NMR. The results of these analysis are in the preliminary stages. The STM images were taken with material deposited onto a gold substrate. Two depositions (ZrC starting material), one at 10 minutes and another at 30 minutes were imaged at 1V, 50pA and 1V, 10pA respectively. Solid state ^{13}C NMR (400 MHz, Chemagnetics instrument) was also performed on the solid material (VC starting material). These experiments had to be performed as static one-pulse experiments as opposed to magic angle spinning due to the fact that the Met-Car containing soot could not be spun in the magnetic field of the NMR. Analysis were also performed on Sohxlet extracted soot (in various solvents) using UV-Vis spectroscopy and metal ($^{45,47}Ti$, ^{91}Zr, ^{93}Nb, or ^{51}V) NMR. UV-Vis experiments are performed first and are used as a litmus test for determining whether or not NMR experiments should be performed on liquid samples.

Figure 1 shows a schematic of the new LV/LD/TD TOF-MS. This new instrument will allow us to have better control over the experimental conditions in which the Met-Car containing soot is generated. The pressure in the vaporization chamber may be varied from 4×10^{-6} to a few thousand torr, also the ambient atmosphere in which the vaporization and deposition take place may be altered. In addition the substrate that the soot is deposited on may be constructed from a variety of coated or non-coated materials. The largest advantage over the previous production method (IGE) is the ability to immediately analyze any products produced from the vaporization event and deposited on the substrate via LD.

The LD/TD TOF-MS portion of the spectrometer may also be operated independently of the DLV chamber. A sample crucible may be placed just below the TOF lenses where the laser can be: loosely focused to perform LD analysis on a material in the crucible or focused tighter, with increased power to perform direct laser vaporization (DLV) of materials. With one laser performing the LD or DLV we can examine the ions produced, using pulsed TOF lenses. With the addition of a second laser we can also examine any neutrals produced in either a LD or DLV experiment via multi-photon ionization (MPI). The sample crucible may also be restively heated in a tungsten basket just below the TOF lenses and analysis of either neutrals or ions desorbed from the material in the crucible may be analyzed in the same manner as the LD species

described above. The overall greater flexibility gained by the implementation of this new LV/LD/TD TOF-MS will allow us to greatly expand our current efforts at producing and isolating the various Met-Car species.

Results and Discussion

Comparison between the mass spectra of DLV of ZrC and LD analysis of Zr_8C_{12} containing soot show remarkably different patterns leading up to the Met-Car species. The DLV pattern matches the build-up pattern shown when Met-Cars are made from a LAVA source. For a further discussion of DLV vs. LD see [3].

An STM images of the 10 minute deposition shows structure similar to that of the bare gold with one major differences. An image (940 X 940 A) shows three terraces (adjusted to show the features of the middle terrace) and chemisorbed particles on the lower portion of the middle terrace. The 30 minute STM scans indicate that the sample is highly covered with particles, indicating full or multiple monolayers of the Met-Car soot. At smaller scales, features of 4-6 A in diameter are viewed. Another image (200 X 200 A) shows these smaller as well as some larger features, which may be conglomerates of the smaller spheres.

^{13}C NMR of Met-Car containing soot (VC starting material) produce a peak shifted to -7300 ppm. This peak does not appear in ^{13}C NMR of the VC and is seen to decrease, to no signal, over a period of two weeks, when the sample is kept in air. We are currently engaged in further studies of this species.

UV-Vis analysis of V based Met-Car soot extracted in methanol showed some features not seen in the UV-Vis spectra of the VC extracted in methanol. The different absorbances prompted us to perform ^{51}V NMR experiments on both solutions. The NMR spectra shows us different peaks for each solution. The VC/methanol solution shows a peak shifted to -544.406 ppm, where as the VC-soot/methanol solution yields a peak shifted to -548.367 ppm. Although the difference in the chemical shifts between these two species is small the differences in peak shape is further evidence that these peak are due to two different species.

Conclusions

These preliminary results show promise that these new materials can be produced, isolated, and characterized. Further investigation needs to be undertaken to fully interpret both the solid and liquid state NMR. The STM imaging of metal-carbon deposits on gold, needs to be refined in order to perform more informative studies. Performing extractions with varied solvents will allow us to identify a solvent that is able to solublize greater amounts of Met-Cars which would facilitate characterization. In addition, a higher concentration of Met-Cars in the soot would greatly enhance any attempts to isolate and characterize these species. It has also been shown that Met-Cars may be analyzed via laser desorption. The new LV/LD/TD TOF-MS combines greater experimental control during the DLV event, so that Met-Car concentration may be maximized in the soot. With this new instrument we also gain the ability to perform LD analysis on the DLV products, and TD analysis on various samples. The uniting of these techniques should give us the ability to eventually fully characterize these unique molecular species.

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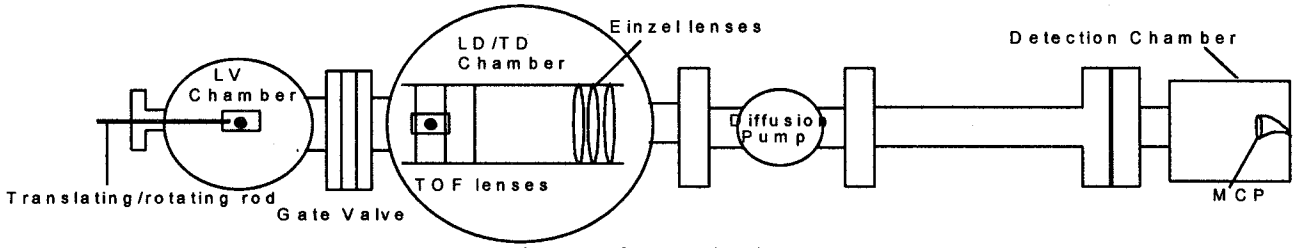

Figure 1. Diagram of our LV/LD/TD TOF-MS