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富勒烯及多环芳烃的燃烧法合成
和分离研究

Studies on the Synthesis and Separation of
Fullerenes and PAHs from Flame

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A Dissertation Submitted to the Graduate School in Partial Fulfillment of
the Requirements for the Degree of Doctor Philosophy

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厦门大学博硕士学位论文摘要库

摘要

自从1985年C₆₀发现以来，人们一直致力于富勒烯新物种的发现和表征，及它们的物理和化学性质以及它们在各个领域的应用。对于具有独立五元环的富勒烯如C₆₀，C₇₀等已经能够大量合成出来，而对于具有相邻五元环的非经典富勒烯及其衍生物，由于它们非常不稳定，它们的合成分离和表征具有很大的挑战性。目前主要是通过石墨电弧等离子体法通过内嵌或外接的方法，将它们稳定下来并得到。可以说，由于合成的量太少制约着这类数目繁多的富勒烯物种被深入认识和应用。C₆₀等经典富勒烯是从石墨电弧法实现了宏量合成，火焰燃烧的方法则实现了规模化生产。对于非经典富勒烯，如果能够通过燃烧的方法形成，那么就有可能实现大量生产。本工作对苯氧低压下火焰中富勒烯的形成进行了探索，希望能够得到具有相邻五元环的非经典富勒烯。本文从玻璃燃烧装置的试制开始，在苯氧扩散火焰中碳灰的合成，以及分离方面开展工作。

在自己试制的玻璃扩散燃烧装置上，进行苯氧低压扩散燃烧。多次的合成实验的考验表明，本装置密封性好，燃烧过程稳定，能够小规模合成富勒烯，对燃烧状况能够方便的观测和调整，在15-20 Torr，苯蒸气流速为1.5L/min，O₂流速为1.5-2L/min的条件下(C/O=1.5-3)，富勒烯能够生成。

富勒烯的分离，本文主要是通过Buckyprep-M柱和C18柱进行分离的，对燃烧产物具有不错的分离效果。

燃烧的产物主要是多环芳烃和富勒烯，这些多环芳烃具有16-34个碳原子，获得了部分物质的质谱和光谱信息，它们主要是平面的结构，它们的质量数基本遵循24/26规则，其中C₃₂H₁₄的结构得到了单晶表征，是由10个苯环组成的多环芳烃，晶体的堆积类似于石墨。通过氯化方法能够将多环芳烃的分子组成准确的确定下来，而且氯化多环芳烃具有很好的检测灵敏度。

燃烧产物中的富勒烯除了C₆₀，C₇₀外还包括C₆₀的氢化物，衍生物等以及其它的富勒烯。C₆₄H₄经过质谱，色谱保留时间以及光谱表征，可以确定与电弧法得到的C₆₄H₄是同一物种，整个分子呈C_{3v}对称，具有三重相邻的五元环。C₆₀的氢化物中的C₆₀H₈和C₆₀H₁₂很有可能是I_h C₆₀经过Stone-Wales重排的异构体的氢化物，具体的表征还需要深入进行。在燃烧产物中还有一类质量数在600-720之间的物质，它们可能是一类重要的物种，对富勒烯的形成可能具有重要意义。一些

特殊的物种，它们的质量数分别为824，878，932，只能得到它们的质谱信号，可能是几种特殊的富勒烯，在以后的分离过程中需要引起关注。

本文中的非经典富勒烯是首次在火焰中发现，如果能够通过改善实验条件提高它们在产物中的含量，就有希望实现大量合成。此外其它结构的非经典富勒烯也完全有可能通过火焰法合成。这对非经典富勒烯的合成方法和规模化生产都具有一定的指导意义。

对于富勒烯的形成过程，本文的实验证据支持热力学机理，即认为富勒烯的形成在低温下是按照双分子的增加方式生长，在高温下主要是带状芳香聚合物按照单分子的重组成笼以及笼状结构的去氢从而形成，一些氢化物是富勒烯形成的中间体，在火焰的温度降低时碳灰粒子开始形成，碳灰和富勒烯具有相同的中间体。

关键词：富勒烯；燃烧合成；形成机理；非经典富勒烯

Abstract

Since the discovery of C_{60} in 1985, the effort of scientists have been devoted to the discovery and characterization of new species of fullerenes, as well as the physical and chemical properties and their applications in a wide range of fields. The fullerenes obeying the isolated pentagon rule, such as C_{60} and C_{70} etc., can be produced in bulk already. For the non-classical fullerenes with abutting pentagons, the synthesis, separation and characterization are of great challenge because of their instabilities. The present methods for synthesizing them are mainly based on endo- or exo-hedral derivatization so as to stabilize them in traditional Krätschmer–Huffman plasma. However, synthesis in macroscopic quantities is required for further understand and application of these fullerenes. The classical fullerenes such as C_{60} can be synthesized macroscopically from the arc method, while the flame method can realize the continuous production in industrial scale. If non-classical fullerenes can also be formed from flame, the largely synthesize the non-classical fullerenes is possible. The present works explore the formation of fullerenes in benzene/oxygen flame at reduced pressure, aiming to obtain some non-classical fullerenes with fused pentagons. In this dissertation, the works include the construction of a combustion setup, the exploration of synthesis and separation of fullerenes. Benzene/oxygen combustion at low pressure was performed using the homemade glass setup. Repeated experiments indicate that the vacuum condition is well and the flame condition allows the synthesis of fullerenes in lab scale and the combustion condition can also be observed and adjusted conveniently. Fullerenes containing soot was produced at the vacuum of 15-20 Torr with the benzene vapor flow rate of 1.5L/min and oxygen of 1.5-2L/min ($C/O=1.5-3$).

In this dissertation, the separation of fullerenes are mainly performed on a Buckyprep-M column and a C18 column, the products from the flame are both separated well using the two kinds of stationary phase.

The products in flame consist of PAHs and fullerenes. These PAHs contain 16-34 carbon atoms, some of them were identified by mass spectra and UV spectra. Most of the PAH structures are planar. Their masses basically obey the 24/26 rules. A molecule

of $C_{32}H_{14}$, characterized by single crystal X-ray diffraction, is composed of 10 six-membered-rings having the intermolecular stacking similar to graphite. The molecular composition of PAHs can be confirmed exactly through chlorination method, and the chlorinated PAHs have high sensitivity.

Besides C_{60} and C_{70} , the fullerenes produced from flame include C_{60} derivatives (e.g., C_{60} hydrides) and other fullerenes. Among them, $C_{64}H_4$ has been characterized by UV spectrum and retention time in the chromatogram. It has a C_{3v} symmetric structure with tripled abutting pentagons, as the same compound produced in arc method. It is possible that $C_{60}H_8$ ($C_{60}H_{12}$) is the hydride of an isomer of $I_h C_{60}$, which may be formed from Stone-Wales rearrangement. Further characterization should be performed later. Other important compounds with mass-to-charge (m/z) between 600 and 720 should be important for understanding of formation mechanism of fullerenes. Some species such as the compounds of 824, 878 and 932 m/z , are probable novel fullerenes. For these fullerenes, only mass spectra are observed at the present time, they should be paid attention in future separation processes.

Non-classical fullerenes formed in flame are revealed in this dissertation for the first time. If their content in raw soot of the flame can be improved by optimizing the conditions, the realization of bulk production of them is desirable. Other non-classical fullerenes may probably form in the flame also. All of these will have certain guidance for not only the synthesis method but also the large scale production of non-classic fullerenes.

As for the formation mechanism, the experimental data support the thermodynamics mechanism. Bimolecular addition reactions predominate at relative lower temperature, while unimolecular rearrangement to the form cage and dehydrogenization of cage dominate at high temperature. Hydrogenized fullerenes are the intermediates during fullerenes formation. The soot and fullerenes have the same intermediates, and the soot particles grow when the flame temperature decrease.

Key words: fullerenes; flame synthesis; formation mechanism; non-classical fullerenes.

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