学校编号: 10384 分类号: 密级:
学 号: 9925007 UDC:

厦门大学理学硕士学位论文

I 碳纳米管的合成及其生长机理的研究
II MCM-41 上氘苯动力学行为的 DQF NMR 研究

蔡 云

指导教师: 廖代伟 教授
申请学位级别: 硕士
专业名称: 物理化学
论文提交日期: 2002. 06
论文答辩日期: 2002. 06
学位授予单位: 厦门大学
答辩委员会主席:

Thesis Submitted to Xiamen University for Master Degree of Science

I Studies on Synthesis and Growth Mechanism of Carbon Nanotubes

II Investigation of the Benzene Molecule Adsorbed on MCM-41 Using Double Quantum Filtered NMR Spectral Analysis

YUN CAI

Supervised by

Prof. Dai-Wei Liao

Department of Chemistry

Xiamen University

June, 2002

目 录

第二部分 以双量子滤波核磁共振法（DQF NMR）研究 MCM-41 上的动力学行为

第一章 绪论

第二章 MCM-41 上苯的自旋-晶格弛豫光谱和双量子滤波核磁共振谱

CONTENTS

CHAPTER 2

CARBON NANOTUBES SYNTHESIS ON DIFFERENT METAL CATALYSTS

CHAPTER 3

STUDIES ON MECHANISM OF CARBON NANOTUBES SYNTHESISED

摘　要

第一部分 碳纳米管的合成及其生长机理的研究

目前碳纳米管的合成有诸多的方法，而 CVD 法是最适合于今后工业化生产的，因此有着广泛的应用前景。本文以 CVD 方法制备碳纳米管并探讨了其可能的生长机理。

以催化剂 Co-2CeO 为例，从碳纳米管产率及所制备的碳纳米管的 TEM, Raman, XRD 的比较表征，考察了温度对碳纳米管制备的影响。随着温度的升高，碳纳米管的产量、石墨化程度也随升高，而石墨层间距缩小，管壁结构趋于致密。因此，高温有利于管壁中缺陷、错位的消除，即提供能量使石墨层六元环网进行重排，以达到更规整稳定的结构。

考察了不同催化剂对碳纳米管制备的影响，发现含 Ce 的催化剂易于形成陀螺型的碳纳米管。而其中 Ni-2CeO 制备的碳纳米管的石墨化程度较 Co-2CeO 和 Fe-2CeO 的差，且石墨层间距较大，易于产生缺陷及位错。但 Ni-2CeO 制备的碳纳米管管径分布较其余二者来得均匀。

通过原位时间可分辨红外和原位拉曼光谱观测了碳纳米管的生长过程，了解了催化剂的还原过程及石墨碳和无定型碳在催化剂上的沉积情况。

本文还通过对碳纳米管的形态，催化剂颗粒在碳纳米管中的位置、形态和大小的分析，以及碳纳米管生长方向的讨论，结合已有的碳纳米管生长机理，对产物中各种形态的碳纳米管的生长提出了自己的看法，认为碳源分解后产生的碳部分形成碳化物，部分沉积在碳化物表面，形成一温度梯度，而使碳熔融出来形成内层管壁。在本机理中，强调了温度的影响，认为温度梯度的产生是产生不同管径大小碳纳米管的关键。对碳纳米管的径向和横向生长有所选择，高温有利于其径向生长，提高其石墨化程度。对于陀螺式盘旋及其它形态的碳纳米管，赞同 Daeschler 等的观点，认为与催化剂的各项异性有关，形成“ 五元

环-七元环对”使其产生弯曲。

第二部分 以双量子滤波核磁共振法（DQF NMR）研究 MCM-41 上的动力学行为

分子筛是催化研究中应用很广泛的一种物质，而了解其吸附行为，研究吸附分子之间、吸附分子与分子筛之间的相互作用情况，无疑将有助于我们更全面地了解分子筛的吸附和催化性质，从而更有效地使用它。近年来，除了其它化学方法检测吸附分子与分子筛之间的相互作用力外，用核磁共振的方法研究分子筛系统中的吸附动力学情况也日益成为热点，而双量子滤波核磁共振(DQF NMR) 技术是近年来开发的一种用于探测微观无序体系的各向异性运动的检测手段，由于其高灵敏度而被用于探测吸附体系中吸附质与被吸附物种间的残存四极作用力，从而了解吸附质在吸附体系中的动力学行为，并获取被吸附物种的吸附位分布情况。

MCM-41 是 1992 年合成出来的一种具有高规整性六方孔道结构的中孔分子筛，一问世就受到广泛关注，其高热稳定性，规整的结构为合成具有均匀孔道、介孔尺寸的催化剂提供了可能性，是一种具有广泛潜在运用前景的新一代催化介孔材料。我们以全氘代的苯作为分子探针，利用 DQF NMR 技术，结合自旋-晶格驰豫时间 (T_1) 分析，研究了 C_6D_6 在 MCM-41 上的动力学行为。借助两位置交换模型，通过对实验核磁共振谱的模拟获得相应参数，并从参数的分析，推测 C_6D_6 和 MCM-41 之间的相互作用，进而了解了 MCM-41 上吸附位的分布情况及其吸附特性。

关键词 碳纳米管 CVD 生长机理 MCM-41 双量子滤波核磁共振 吸附动力学

Abstract

Part I Studies on Synthesis and Growth Mechanism of Carbon Nanotubes

The fascinating properties of carbon nanotubes have opened a great number of potential applications for these unique materials. However, whether these materials can be really taken into commercial practice definitely depends on synthesis methods. From the time carbon nanotubes were discovery to present, scientists have developed various kind of methods to produce carbon nanotubes and CVD method is the most promising one. In this paper, we synthesized carbon nanotubes by CVD method and then discussed the probable growth mechanism for the as-grown carbon nanotubes.

Take the catalyst Co-2CeO as example, the effects of the preparation temperature on the growth of carbon nanotubes were discussed and found that high temperature will favour to obtain carbon nanotubes in high yield and to remove the defects and dislocations in carbon nanotubes walls and then get the high quality carbon nanotubes.

Different catalysts were compared in the preparation of carbon nanotubes and found that the carbon nanotubes prepared on catalysts containing metal Ce were easy to form the turbinate spiral shape. The TEM、Raman and XRD results showed that carbon nanotubes made on catalyst Ni-2CeO were less graphitization then one made on catalyst Co-2CeO and Fe-2CeO. The former carbon nanotubes had wider inter-layer space and more defects and dislocations were found. But as to the

diameter distribution of carbon nanotubes, the former had more uniform diameters than the latter two.

The various shapes of carbon nanotubes were discussed as well as the sizes、locations and shapes of catalysts particles . The growth process of carbon nanotubes was also observed via the microscope. Combination with the mechanism provided in lectures, a mechanism for the various shapes carbon nanotubes in our products was put forward. The effects of temperature gradient was considered as the key point during the growth of carbon nanotubes and the carbon cracked from the hydrocarbon gases were partly form the carbide with the catalyst and some others deposited around the carbide then generated the temperature gradient. The high temperature reduced the speed of carbon deposition on catalysts but accelerate the lengthening of carbon nanotubes. About the mechanism of the formation of turbinate spiral nanotubes, the interaction of the components in the catalysts was emphasized and the viewpoint of “pentagon - heptagon pairs” provided by Daeschle was addressed. The whole growth process, the reduction of the catalysts and the carbon deposition were also recorded by *in-situ* Raman and IR spectra.

Part II Investigation of the Benzene Molecule Adsorbed on MCM-41 Using Double Quantum Filtered NMR Spectral Analysis

A detailed understanding of the interaction of adsorbate in molecular sieves system is essential in understanding the adsorption and catalytic properties. These years, except other chemistry approaches, there has been increasing interest in the study of the adsorption process on molecular sieves by using NMR relaxation techniques. Double Quantum Filtered (DQF) NMR technique, which was developed

recently as a diagnostic tool for the detection of anisotropy in microscopically disordered systems, has been used as a sensitive method for the determination of the residual quadrupolar interaction resulting from adsorbate dynamics among interaction sites in molecular sieves.

MCM-41, which was discovered by researchers at Mobil in 1992, possesses a regular hexagonal array of uniform pore diameters between 1.5 nm and 10 nm. Its high stability under heat and regular structures has received widespread interests as a potential materials for catalysts. In this paper, the C_6D_6 has been used as a molecular probe to investigate the dynamics of C_6D_6 adsorbed on MCM-41 by using the combination analysis of Double Quantum Filtered (DQF) NMR spectra and Spin-Lattice Relaxation spectra (T_1). A two-sites exchange model has been used to help to explain the dynamics of benzene adsorbed on MCM-41 and the simulation of the spectra was carried out to obtain the relevant parameters, such as order parameter, motional correlation time and exchange rate between sites, etc., then to understand the site distribution and adsorption of MCM-41.

Keyword Carbon Nanotubes, CVD, Growth Mechanism, MCM-41, DQF NMR Adsorption Dynamic

第一部分

碳纳米管的合成及其生长机理的研究