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杨志远 著

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序

中国不仅是世界上煤炭生产的第一大国,也是煤炭消费的第一大国。煤炭大量直接燃烧利用,不仅造成了严重的环境破坏和污染,也直接导致了煤炭这一不可再生碳烃原料资源的极大浪费。这与坚持科学发展观、树立循环经济理念及建立节约型 and 与环境协调发展社会的要求极不协调。从宏观及微观显微煤岩组成上讲,煤是一种有机岩石,其显著特点是,结构以芳烃结构单元为主,同时含有多种常量及微量金属元素。因此,充分认识煤的特殊结构和性质,挖掘其结构和性质特点,探索煤的新的利用途径和理论,不仅具有重要理论和科学意义,而且具有重要的环境、经济和社会意义。未来煤炭利用的发展方向是强化其在非能源领域(如精细化学品、功能材料)应用的新理论与新技术的开发研究,使煤的结构特点和潜在优势(如富含缩合芳环、杂环,以及诸如萜类和蒽类生物活性化合物等)得到充分有效利用。

随着人类对环境的日益重视和“白色污染”的加剧,对可降解材料的研究成为世界瞩目的热点问题之一。我国是一个农业大国,到目前为止,我国地膜覆盖面积已超过 1333 万 hm^2 ,但我国可覆盖的地膜面积高达 3667 万 hm^2 。传统的白色农地膜已给农业生态环境造成了严峻的“白色污染”,并使土壤退化及农作物减产。因此,近年来可降解多功能材料研究工作发展的重点是研究光、生可降解材料。目前,新型可降解材料的开发主要有聚合型和添加型,前者是通过与光、生可降解性单体进行共聚合以制备可降解共聚产品,后者主要添加光、生可降解材料,如淀粉等进行复合制备。淀粉可降解膜存在与人及牲畜争夺有限的粮食及加工和降解不完全性等缺点。

人类利用煤炭以来一直为其低温自燃所困惑,研究如何防治煤自燃,极少考虑利用煤自燃原理,为人类服务。我们课题组将这一原理成功地用于光、生物双降解材料的制备,并取得了成功,利用煤的光氧化降解原理以超细煤粉体作为降解活性组分制备全降解复合材料,呈现出煤炭资源多目的串联式高效利用的特点。

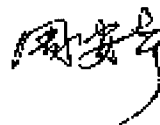
课题组前期表明:用以优质神府煤为原料的功能性复合材料制得的降解黑色增肥农膜制品,性能完全达到白色地膜的质量要求,而且具有光、生降解性,降解产物是一种高效有机质复合肥,有很好的环境效益。此外,该功能复合材料还可用于其他可降解塑料制品。但要使所制备的材料达到降解特性和物理力学性能精确可控,必须搞清楚煤的光氧化机理及煤基降解复合材料降解控制规律。另一方面,煤中的芳香缩合环、含氧官能团、过渡金属离子均是重要光分解剂和促进剂。但如何从煤质煤岩组成及煤的结构特征上认识煤光氧化降解机理,如何通过调节煤中光敏性促进剂的相对比例、各组分的降解协同作用规律,以及控制降解的控制理论和方法研究,这些科学问题都有待深入研究。

杨志远博士的“超细煤粉的光氧化——机理·动力学·应用”从超细煤粉制备和性质研究入手,首次将分形理论与球磨工艺联系起来,而后,将煤结构与光化学理论相结合,采用分形分析及现代测试方法逐步深入研究典型煤种的光氧化反应性;首次提出以煤的不同密度级组分代替煤岩组分,深入阐明了煤结构与反应性关系;进一步探明了不同金属离子、纳米二氧化钛及其稀土金属盐与煤大分子的光催化氧化的协同作用,首次发现通过改变外加催化剂可以控制煤光氧化产物的组成,提出了煤光催化氧化控制参数

体系。基于煤特殊的组成和结构提出了煤自光敏化光催化氧化降解机理,初步建立了煤光催化氧化的动力学模型。首次利用人工神经网络理论建立了煤光敏化薄膜降解控制因素预测模型和降解性能高精度预测模型。该书较为系统地建立了用煤光氧化方法制备煤基精细化学品及煤基降解材料的理论基础,开拓了煤温和转化的新思路。

该书的研究内容是作者近年来从事煤炭温和绿色转化的主要研究成果,也是我们负责完成的国家自然科学基金(20676056,20676110)的重要组成部分。研究工作涉及煤化学、光化学、化学动力学、分形理论和计算机模拟,研究内容翔实,数据准确可靠,可供从事煤转化、煤化工、煤炭自燃防治等方面的研究人员参考和借鉴。

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2007 年 8 月

前 言

在西部大开发中,如何对煤炭资源进行高效、洁净、高附加值转化利用,是目前迫切需要解决的战略问题。与此同时,废旧塑料引起的“白色污染”也是亟待解决的严重环保问题。煤基可降解材料的生产是实现煤炭非燃料高附加值利用和解决“白色污染”的有效途径。

西安科技大学周安宁教授领导的“煤非能源转化”课题组长期从事煤基材料方面的教学和科研工作,在制备煤基降解材料期间先后完成了国家科技部项目:“COPO 树脂制备技术与工业中间实验研究(编号 99D110)”,陕西省科技攻关项目“煤基 COPO 树脂制备与应用开发研究”以及“煤基互穿网络合金材料制备研究”等多项国家级、省部级重点煤基材料科研项目,开发的全降解煤基黑色地膜产品获国家专利。目前处于产业化阶段,而需要解决的问题是煤基地膜的精确控制降解。

煤基薄膜降解的实质是煤自发氧化反应原理,煤粉作为光降解薄膜的引发剂和促进剂。因而,阐明煤粉自身光催化氧化反应性及降解动力学是解决煤基地膜精确时控降解的关键。笔者参与完成的国家自然科学基金项目“超细煤粉体光氧化降解机理及其动力学研究”(20276056)、主持完成的陕西省自然科学基金“超细煤粉光化学反应中分形特征及数值模拟研究”(2003E₂₅)和陕西省教育厅专项科研基金“可降解薄膜精确时控降解分析与预测模型研究”(03JK190),对这方面进行了系统深入的研究。同时,笔者正在参与进行的国家自然科学基金“煤的光氧化和生物转化耦合作用机理及应用研究”(20276110)”,国家重点基础研究规划(973 计划)(2003CB214602)一部分的工作“煤的光氧化预处理”的研究成果也包含在本书中。近年来,公开发表相关论文 20 余篇,国际会议论文 2 篇,国内会议论文 1 篇,其中 SCI 收录 2 篇,EI 收录 10 篇。在煤的光催化控制定向氧化制取煤基功能性化学品、复合光敏剂方面取得了一些创新性成果。近期,相关成果将申请国家发明专利,同时进一步整理成高水平论文,向国际期刊投稿。通过分析总结发现,煤的光催化氧化将有望发展成为煤温和定向转化的有效方法之一。通过煤的光催化定向转化,不仅可获得高附加值的精细化学品,还有望与煤的生物转化耦合,进一步将煤定向转高附加值的化学品和新材料。因此,本书的撰写旨在解决煤基降解材料推广应用中深层次的科学问题,同时为煤定向转化开创了新途径,并且在促进煤化工学科发展和自主创新方面有一定实际意义。

本书涉及的实验是在西安科技大学曲建林工程师、李天良高级工程师、邵水源高级工程师、阎兰英高级工程师等人协助下完成的。西安科技大学侯永刚硕士、王健硕士、姜玉凤硕士、沙保峰硕士、刘彦平硕士参与了书中大量的实验工作。杨伏生博士在热分析、汪广恒博士在红外光谱测试、安群力博士在扫描电镜分析、李莉博士在气相色谱分析方面给予了热情的帮助。西安近代化学研究所李晓宇高级工程师和潘清工程师分别在 XPS 和红外光谱图谱解译方面进行了协助,陕西省煤田地质局综合实验室耿志军工程师完成了部分煤质分析工作。沈思馆员、刘朋硕士、郭俊刚硕士在图书资料查阅、联系出版和文字校对方面提供了有益的帮助。在此,向他们表示诚挚的谢意!

本书写作过程中,周安宁教授协助制定了编写大纲,对全文进行了审定。葛岭梅教

授、李侃社教授、李建伟副教授、杜美利教授、杨建业教授、刘向荣副教授、刘转年博士、于占江博士与作者进行了有益讨论,提供了重要的建议和修改意见。在此,一并致谢。

最后感谢国家自然科学基金(20676110)和国家重点基础研究发展规划(973 计划)项目基金(2003CB214602)在本书出版时提供的经费支持。

作者

2007 年 5 月于大雁塔

Mechanism, Kinetics and Application of Ultra-fine Coal Powder in Photo-Oxidation

Abstract

How to utilize coal resource with high efficiency, cleanliness and high-attached value is a strategic problem in the Grand Development of the West China. Due to "white pollution" becoming more and more serious and human focusing more and more on environment protection, the R & D of degradable materials are becoming a hotspot. The preparation of coal-based degradable materials is one effective way of coal in non-fuel utilization and high-attached value processing transformation. The technique key problem of accurate control in the degraded periods of the coal-based degradable materials is to clarify the reactivity and kinetics in coal photo-catalytic oxidation.

The grades of ultra-fine coal powder's uniformity and coal granular surface morphology were characterized by the fractal dimensions. The functional groups of ultra-fine coal powder were studied by Fourier Transform Infrared spectroscopy (FTIR) and curve-fitting analysis. The results showed that oxygen-containing functional groups and content of aliphatic hydrogen (Al-CH) decreased, whereas the degree of ring condensation and content of aromatic hydrogen (Ar-CH) increased with increasing coal rank. Meanwhile, main hydrogen bonds in coal structure were OH-OH, cyclic OH tetramers and OH-ether O. With increasing coal rank, OH-OH and cyclic OH tetramers reduce, but OH-ether increases.

The reactivity and their affecting factors of different rank coals in photo-catalytic oxidation were firstly systemically studied in a self-made photo-catalytic oxidation reactor on the basis of the combination of coal structure and photochemistry in theory, fractal analysis and modern characteristic methods. The experimental results indicated that the temperature, rate of oxygen flow, ultraviolet radiation intensity and coal particle's size were important exterior factors in coal photo-catalytic oxidation, the reaction procedure of coal photo-catalytic oxidation could be divided into three periods. Low-rank coal has higher activity than high-rank coal in the photo-catalytic oxidation. It can be deduced that there is the photolysis reaction of Norrish II of coal macromolecule in photo-catalytic oxidation because the gases released in the reaction are CO_2 , CO, CH_4 and C_2H_4 , etc.

The different density grade components of coal were selected by the method combining the coal ultra-fine pulverization and the float-sinking experiment. It showed that the density grade components of Shenfu coal were three main density groups of D2 (1.350-1.375 g/cm^3), D3 (1.375-1.400 g/cm^3) and D4 ($>1.400 \text{ g/cm}^3$). It's firstly discovered the relationships between coal's structure and its activity in photo-catalytic oxidation by studying the structure of coal different density grade components. The order of coal components' activity in photo-catalytic oxidation is $\text{D2} > \text{D3} > \text{D4}$. The humic yield ratio of coal different component increases

with increasing the time of photo-catalytic oxidation. The order of humic yield ratio also is $D2 > D3 > D4$. There are two kinds of competing reaction, decomposed and cross-linked reaction, and the surface functional groups of coal components change in the coal photo-catalytic oxidation. The activity of coal in photo-catalytic oxidation is higher than in the thermal oxidation. The humic yield ratio of photo-oxidized coal is also higher than thermal-oxidized coal.

The synergic photo-catalytic effects between transition metal ions, nano-TiO₂, rare metal ions compound catalysts and coal macromolecules were discovered. It's also found that the products of coal photo-catalytic oxidation can be controlled by addition of metal ions/nano-TiO₂. The relationships between reactivity of coal in photo-catalytic oxidation and its structural parameters were discussed and the linear formula was proposed. The mechanism of self-photo-sensitized photo-catalytic oxidation degradation of coal was firstly proposed and the dynamics model of photo-catalytic oxidation of coal was presented. The active energy of coal loading metal ions in photo-catalytic oxidation decreases.

The degraded properties and degradation control theory of coal photosensitive degradable films were illustrated. It's discovered the photosensitive activity of coal powder for polymers is correlated to the coal quality and its adding amount, the synergic photosensitivity between coal powder and ferric stearic acid for polymers degradation is existed, the degraded periods of the coal photosensitive degradable films can be holed by adjusting the species and amount of coal/ferric compound photosensitizer.

The method of prediction and control of coal degradable films was established based on artificial neural network (ANN). The ANN model had been carried out by the neural network toolbox of MATLAB 6.5 software and Visual Basic 6.0. This book discussed partition of sample data and model's parameters, and then selected the best configuration of ANN network. The accurate scope of predicting results was analyzed. This model has a high precision in predicting on properties of the coal- photosensitized films degradation.

The book is not only directive significance in theory for the development and application of coal photosensitized degradable films, but also exploits a new route for coal oriented transformation by photo-catalytic oxidation.

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