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智能微凝胶催化体系的构建与性能研究

Synthesis and Performance of Responsive Catalytic Microgels

吴清实

指导教师姓名：吴伟泰 教授

专 业 名 称 ：高分子化学与物理

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By

Qingshi Wu

Supervised By

Prof. Weitai Wu

Department of Chemistry

Xiamen University

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摘要

均相金属催化剂由于其催化活性高、选择性好，被广泛应用于有机合成和能源转化等领域，一直以来在学术界和工业界都备受关注。然而，反应后繁琐的分离纯化步骤，使其难以回收利用，限制了其在工业上的大规模应用。随着“绿色与可持续化学”概念的普及，发展高效且可重复利用的催化剂已成为当今催化研究急需突破的瓶颈之一。

高分子凝胶，一类具有三维交联网络结构、在溶剂中溶胀而不溶解的高分子材料，兼有固体和液体的性质，适合作为物质输运介质或载体，进而在催化、生物医药等方面得到广泛应用。尤其受重视的是能够对周围环境变化而自身发生体积相转变的凝胶，即刺激响应性高分子凝胶。将刺激响应性凝胶与金属催化剂结合，不仅可保持催化剂良好的催化性能，实现“准均相催化，多相分离”，还可以利用外界刺激来调控催化剂的催化性能。目前，相关研究已经取得了一些进展，但如何构建智能、高效且可重复利用的催化剂仍存在许多挑战性难题亟待解决。

本论文通过合理设计，合成新型葡萄糖响应性高分子微凝胶、温度响应性高分子微凝胶等，并研究微凝胶的刺激响应性体积相转变行为，进而从微观水平理解从识别到体积相转变、光学变化等响应的内在机制；在此基础上，本论文采用葡萄糖、温度等响应性高分子微凝胶来负载贵金属纳米颗粒、过渡金属离子等，发展了一系列新型智能微凝胶催化体系，并研究刺激响应性高分子微凝胶体积相转变调控催化性能等，探索识别、响应与催化的协同性等规律。具体研究内容包括以下四方面：

（1）针对“聚苯硼酸微凝胶对葡萄糖的选择性较差”等挑战性问题，借鉴去辅基葡萄糖氧化酶等天然糖结合蛋白与葡萄糖结合的机制，提出利用苯硼酸基团和苊酰亚胺基团形成特定链结构，人工模拟合成出具有高选择性识别葡萄糖等特征的聚苯硼酸微凝胶。

（2）采用聚苯硼酸微凝胶负载贵金属纳米颗粒，构建具有葡萄糖响应性的微凝胶催化体系。通过改变葡萄糖浓度来改变凝胶的亲疏水性和网孔，调控反应底物分子在凝胶中的扩散性质等，进而实现对反应速率的调控。利用不同反应底物分子的

亲-疏水性等，呈现不同的调控效果（促进反应，或抑制反应），进而提高反应的选择性，为仿酶催化提供新思路。

（3）对壳聚糖进行羧基化等修饰，并通过京尼平交联得到具有氨基和羧基等官能团的高分子微凝胶，以实现温度响应性，进而利用微凝胶对金属离子的强吸附作用，直接从硫酸铜溶液中吸附 Cu^{2+}离子，制备获得了含铜微凝胶。所得含铜微凝胶可较高效催化 Huisgen[3+2]环加成反应；利用温度响应性凝胶体积相转变还可实现对催化剂催化性能的非线性调控。

（4）通过将膦配体乙烯基功能化来合成具有可聚合双键的膦配体单体，再与温度响应性高分子相应单体（寡聚乙二醇甲醚甲基丙烯酸酯等）共聚，制备获得含配体微凝胶，进而用于直接从醋酸钯溶液中吸附 Pd^{2+}离子，获得含钯-配体微凝胶。所得含钯-配体微凝胶作为催化剂用于催化水相 Suzuki 反应时，表现出较优异的稳定性和催化活性；利用温度响应性凝胶体积相转变还可实现对催化剂催化性能的非线性调控。

关键词：微凝胶，刺激响应性，金属催化剂，智能催化体系，催化，调控

Abstract

Homogeneous metallic catalysts are attracting increasing attention for application in catalysis and energy conversion, due to their high activities and reaction selections. However, the difficulty in purity and recycling restricts their more extensive applications. Enhanced environmental consciousness has promoted efficiency of the chemical reactions under benign conditions with recycling and reuse of the catalysts, a trait that has become an integral part of chemical research today.

Polymer microgels, colloids of three-dimensional crosslinked polymer networks that combine the properties of solids and fluids, are suitable for molecular transition, and thus have various applications for catalysis and biomedicions. Especially, stimuli-responsive microgels, which can respond to external stimuli and switch their properties, have attracted much attention in recent years. The introduction of the stimuli-responsive microgels into the metallic catalyst systems is a fascinating approach to intelligent catalytic system, which can display the merits of both homogeneous (high efficient catalytic activity) and heterogeneous (recyclability) catalysis in organic synthesis. Moreover, the catalytic performance of catalyst can be tuned via stimuli-responsive volume phase transition of the microgels. Despite the exciting progress, the challenge of facilitating the catalytic microgels with high catalytic acticity, long-term stability, easy to separate and good regulated performance still remains.

Herein, we developed a series of glucose-responsive microgels and temperature-responsive microgels under reasonable design, studied the stimuli-responsive conformational/volume phase transition behavior, and thus understood the internal mechanism of the recognition and stimuli-responsive properties of microgels. From that, a series of responsive catalytic microgels were fabricated through the combination of stimuli-responsive microgels and catalytic metal nanoparticles/ions. The catalytic performance of catalyst tuned via stimuli-responsive volume phase transition of the

microgels was studied and thus the synergistic effect of recognition, response and catalysis was explored. The works can be summarized as follows:

(1) To address the issue of poor glucose selectivity of poly(phenylboronic acid) (pPBA) gels, we developed a class of pPBA microgels with high glucose selectivity at a physiological pH, as inspired by the binding of saccharides to proteins in nature for carbohydrate recognition. The strategy behind is to introduce suitable aromatic moieties (perylene bisimides) into pPBA microgels to create specialized chain structures that have perylene bisimides adjacent to the PBA groups.

(2) We developed a class of glucose responsive catalytic microgels composed of Au nanoparticles embedded in PBA-containing polymer microgels. In view of the fact that the mesh size and the hydrophobicity of the polymer gel networks and thus mass transfer process can be tuned in a well-defined manner by the concentration of glucose, glucose was used as an additive to mediate the catalytic chemical reactions with the microgels as catalysts. Upon adding glucose into the reaction media, the model Au-catalytic reduction of hydrophilic 4-nitrophenol was accelerated, while the reduction of relatively more hydrophobic nitrobenzene slowed down. This work may provide a new insight into mimic enzyme catalysis.

(3) By simply stirring the microgel dispersion with copper sulfate, copper was immobilized on a temperature-responsive polymer microgel made of *O*-carboxymethylated chitosan, crosslinked with genipin. The ensuing catalyst was highly active for a model azide-alkyne [3+2]-cycloaddition reaction; the catalytic activity can be tuned in a non-monotonous way via swelling–deswelling transitions of the polymer gels upon change of temperature.

(4) A class of ligand-based temperature-responsive microgels was prepared by copolymerizaton of oligo(ethylene glycol)methyl ether methacrylate with vinyl modified phosphine ligand. Then palladium was immobilized on the microgel by simply stirring the microgel dispersion with palladium acetate. The ensuing catalyst showed enhanced activity and excellent recyclability in a model Suzuki coupling reaction; the catalytic