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Abstract (Doctor)

Title of Thesis	Development of Sulfonic Acid-Functionalized Polymer Microspheres via Precipitation Polymerization
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Approx. 800 words

Sulfonic acid-functionalized polymer microspheres have attracted considerable attention as polymeric acid catalysts because they combine the strong Brønsted acidity of sulfonic acid groups with the advantages of heterogeneous catalysis, including facile catalyst separation, reusability, and high chemical stability. In addition to catalytic applications, these materials have been widely studied for use in ion-exchange resins, adsorbents, proton-conducting membranes, sensors, and energy-related devices. The catalytic performance of sulfonic acid-functionalized polymer microspheres is strongly influenced not only by the density of acidic functionalities but also by particle architecture, active-site accessibility, and mass-transport characteristics. However, conventional polymer microspheres are generally prepared using highly crosslinked polymer networks to maintain monodispersity and structural integrity. Such highly crosslinked structures often exhibit limited swelling and severe diffusion restrictions, resulting in poor accessibility of catalytic sites, particularly for bulky substrates. Although low-crosslinked, core-shell, and hollow polymer microspheres have been individually developed to address these issues, the precise synthesis of monodisperse sulfonic acid-functionalized polymer microspheres with well-controlled architectures remains challenging.

To overcome these limitations, this thesis presents a molecular design strategy for the synthesis of monodisperse sulfonic acid-functionalized polymer microspheres with controlled architectures via precipitation polymerization. A novel styrene dimer bearing two phenylsulfonate groups (**M**) was designed and synthesized as a multifunctional crosslinking monomer that also serves as a protected precursor of sulfonic acid groups. Through precipitation polymerization using **M**, monodisperse crosslinked polymer microspheres containing phenylsulfonate functionalities were successfully prepared. Subsequent deprotection of the phenylsulfonate moieties regenerates sulfonic acid functionalities while simultaneously modifying the polymer network through selective cleavage of the incorporated dimer units. This unique molecular design enables the preparation of low-crosslinked, core-shell, and hollow polymer microspheres through a common synthetic platform.

Chapter I provides an introduction and background of this thesis.

In **Chapter II**, the proposed molecular strategy was applied to the synthesis of low-crosslinked sulfonic acid-functionalized polymer microspheres. Monodisperse phenylsulfonate-containing

crosslinked polymer microspheres were synthesized by precipitation polymerization of divinylbenzene (DVB), styrene (St), and **M** in acetonitrile. Incorporation of **M** enabled the formation of monodisperse microspheres even at total crosslinker contents below the conventional synthetic limit of 20 mol%. The effects of comonomer composition, monomer ratio, monomer concentration, initiator type and concentration, and solvent composition on particle formation were systematically investigated. Subsequent deprotection and acid treatment regenerated sulfonic acid functionalities while simultaneously reducing the effective crosslinking density of the polymer network, thereby affording low-crosslinked sulfonic acid-functionalized polymer microspheres with uniformly distributed acid sites.

Chapter III describes a novel strategy based on precipitation polymerization for the synthesis of sulfonic acid-functionalized core-shell polymer microspheres. First, DVB and St were polymerized to form monodisperse core particles, followed by seed precipitation polymerization using **M** to form a shell layer containing phenylsulfonate group. Subsequent deprotection and acid treatment afforded monodisperse sulfonic acid-functionalized core-shell polymer microspheres. This strategy enabled precise control of shell thickness, particle size, and active-site distribution while maintaining excellent particle monodispersity. The resulting core-shell microspheres were applied as solid acid catalysts for the esterification of acetic acid with 2-phenylethanol. The catalysts exhibited excellent catalytic activity, affording ester yields of 80-84% within 12 h, and could be easily recovered and reused several times without significant loss of catalytic activity.

In **Chapter IV**, hollow sulfonic acid-functionalized polymer microspheres were synthesized through a chemically cleavable core-removal strategy from core-shell polymer microspheres. Core microspheres were first prepared from **M** and St, followed by shell formation through copolymerization with *N,N'*-1,3-phenylenedimaleimide (**PMI**). Subsequent deprotection selectively cleaved the **M**-containing core network, converting it into soluble polymer species that were removed by solvent washing while preserving the shell structure, thereby affording hollow polymer microspheres bearing potassium sulfonate groups. Subsequent acid treatment regenerated sulfonic acid functionalities. The resulting hollow microspheres possessed internal cavities and thin functional shells, which enhanced mass transport and improved accessibility. Consequently, they exhibited the highest catalytic activity among the architectures investigated and showed excellent reusability over multiple catalytic cycles.

Chapter V summarizes the major findings of this thesis and discusses their scientific significance and future perspectives. Through the systematic development of low-crosslinked to core-shell and hollow architectures, this thesis elucidates the relationships among polymer architecture, active-site distribution, diffusion behavior, and catalytic performance. The results demonstrate that precise control of particle architecture is an effective strategy for improving active-site accessibility and mass transport, thereby enhancing the performance of polymeric acid catalysts. Furthermore, this work establishes a versatile molecular design concept based on a multifunctional cleavable crosslinking monomer, enabling the preparation of monodisperse sulfonic acid-functionalized polymer microspheres with diverse architectures.

The findings demonstrate that functionalized crosslinking monomers can be effectively utilized in precipitation polymerization for the rational molecular design of polymer microspheres. The results presented in this thesis provide fundamental insights and rational design principles for the development of highly efficient, recyclable, and environmentally benign polymer-supported solid acid catalysts and may contribute to the broader design of functional polymer materials for catalytic and energy-related applications.