

学位論文の要約

題目 Preparation and Application of Hierarchically Porous Monolithic Materials with Embedded Nanoscale Interfaces

(ナノスケール界面を導入した階層的多孔構造をもつものリス材料の合成と応用研究)

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序論

In spite of the immense researches and applications of nanomaterials in almost all modern scientific fields, the stabilization of nanomaterials while maintaining their interesting and useful properties still remains as a big problem. One of the effective solutions is to support nanomaterials onto a substrate or to assemble them in a controlled manner where they are self-supported. The generation of a heterogeneous nanoscale interface between the nanomaterial and the substrate possibly results in dramatic change of the chemical properties of the material. Another issue however arises despite of the great potentials. In order to maximize the efficiency of the reaction or interaction at the supported nanoscale interface, full accessibility of the guest molecules to the reactive or interactive sites become necessary. Here hierarchically porous monolithic materials serve as good substrates for the embedment of nanoscale interfaces. The 3 dimensionally interconnected macropores ($d_{\text{pore}} > 50 \text{ nm}$) ensures efficient mass transport over the whole substrate, especially when a pressure driven flow is applied. Meanwhile a network of mesopores ($2 \text{ nm} < d_{\text{pore}} < 50 \text{ nm}$) and micropores ($d_{\text{pore}} < 2 \text{ nm}$) veined in the continuous skeletons provides high surface area as well as enormous short diffusion passes to the reactive nanoscale interfaces. In this thesis, various methods to introduce nanoscale interfaces into hierarchically porous monoliths are demonstrated. The obtained monolithic materials are found applicable to separation, ion adsorption and catalysis.

Chapter 1 High Performance Liquid Chromatography Separation of Unsaturated Organic Compounds by Ag Nanoparticles Embedded Monolithic Silica Column

An in-situ nanoscale interface generation method was tried for the introduction of Ag NPs into a hierarchically porous silica monolith. Homogeneous distribution of Ag NPs over the whole monolith was achieved via the reduction of Ag^+ by ethanol at room temperature, which offered a

mild and controlled reduction kinetics. In order to enhance the separation performance of Ag NPs embedded silica column, a hierarchically porous silica monolith with optimized porous structure was used and the obtained monolithic material is applied for HPLC separation of various unsaturated organic compounds. Baseline separation of PAHs (benzene, naphthalene, anthracene and pyrene) with the theoretical plate number for naphthalene to be 36000 m^{-1} and retention factor for anthracene to be 0.74 was achieved. Outstanding separation of *cis/trans* stilbene isomers with theoretical plate number to be 76000 m^{-1} and 38000 m^{-1} , respectively, and separation factor as 7 was obtained. However the retention of *trans* stilbene was longer than the *cis* isomer which was contradictory to the long established retention rules of Ag^+ HPLC. Such separation behavior was attributed to the more planar molecular geometry of *trans* stilbene, which provides more insights into the detailed separation mechanism of unsaturated compounds by Ag NPs embedded silica column.

Chapter 2 A Series of Hierarchically Porous Crystalline Titanium Phosphate Monoliths: Synthesis and Mechanical Properties

An in-situ transformation method was applied for the synthesis of hierarchically porous TiP monolith from a hierarchically porous titania monolith as the substrate. Simply by reacting a hierarchically porous titania monolith with phosphoric acid of different concentrations at different reaction conditions, a series of hierarchically porous crystalline TiP monoliths ($Ti_2O_3(H_2PO_4)_2 \cdot 2H_2O$, π -TiP and α -TiP) with high mechanical properties were for the first time achieved. Even after calcination at 800 °C and the condensation of α -TiP phase into TiP_2O_7 phase, the original macroporous morphology of the α -TiP monolith was maintained. Further increase the calcination temperature to 1000 °C led to the drastic growth of TiP_2O_7 crystal size and the formation of a bimodal macroporous structure due possibly to the big macropore size derived from the alignment of α -TiP nanosheets into a card-of-house morphology and the much more milder crystal growth process of TiP_2O_7 at ≥ 800 °C than those of $Ti_2O_3(H_2PO_4)_2 \cdot 2H_2O$ and π -TiP cases. The flexural modulus values obtained from 3 point bending test showing high mechanical properties of the obtained hierarchically porous TiP monoliths.

Chapter 3 Nanostructured Titanium Phosphates Crystals Prepared by Hydrothermal Reaction

Successes in the transformation of titania monolith into TiP monolith preserving the original macroporous structure led to the attempt for the synthesis of TiP particles from titania particles. Systematic study was carried out leading to the availability to various TiP particles with novel

nature-mimicking morphologies simply by changing the reaction parameters. The concentration of phosphoric acid and the reaction temperature are two important factors for the determination of pH value in the reaction mixture. The change of pH value at different conditions then led to the change of the stable type of Ti cationic species and phosphate anionic species, which gave rise to different types of TiP crystals. In the meantime, the adsorption of phosphate groups on the surface of TiP crystals is deduced to be responsible for the formation of a variety of morphologies.

Chapter 4 Synthesis of Hierarchically Porous Titanium Phosphate Monoliths and Its Crystallization Behavior in Ethylene Glycol

Sol-gel method for the direct synthesis of hierarchically porous TiP monolith from ionic precursors was demonstrated. The incorporation of both glycerol and DMSO in the gel network via coordination successfully suppresses the otherwise heterogeneous polymerization of titanium phosphate network and leads to the formation of monolithic gel consisting of smaller TiP nanoparticles, the interstitials of which are the origin of relatively large mesopores (21 nm). The polymers PEO and PVP behave as phase separation inducers, which are responsible for the formation of co-continuous macroporous morphology. The as-synthesized TiP monolith is amorphous in nature and pure TiP_2O_7 phase is obtained at 800 °C. An alternative way for the crystallization of the starting amorphous gel network is by solvothermal treatment in EG, which transforms the amorphous globular TiP nanoparticles into platy layered nanocrystals. The control of nanocrystal size can be achieved by changing the temperature of the solvothermal treatment. Such phenomenon is for the first time observed in TiP systems.

Chapter 5 Synthesis of Robust Hierarchically Porous Zirconium Phosphate Monolith for Efficient Ion Adsorption

Sol-gel method accompanied by phase separation as a direct synthetic method for monolithic materials embedded with nanoscale interface was further applied for the preparation of crystalline monolithic materials with ZrP as an example. Hierarchically porous ZrP monoliths with high surface area ($600 \text{ m}^2 \text{ g}^{-1}$) and size-tunable co-continuous macropores have been obtained. The main composition of the as-synthesized ZrP monolith is tunable as well from $\text{Zr}(\text{HPO}_4)_2$ (Zr:P = 1:2) to NaSICON-type ZrP (Zr:P = 1:1.5). Co-continuous macroporous structure is stable against heat treatment, which yields pure ZrP_2O_7 phase at 1000 °C. Mechanical strength of the monolith was measured by uniaxial compression test. The fracture strength and the Young's modulus were found to be 5.6 MPa and 320 MPa, respectively. As a proof of concept, the mechanically robust

as-synthesized ZrP monolith has been applied for ion adsorption. The monolith has been tightly inserted into a syringe and applied to the removal of various metal ions in aqueous solution under a continuous flow condition, which shows promising results as a water purification device.

Chapter 6 Catalytic Dehydration of Xylose into Furfural over Hierarchically Porous Zirconium Phosphate Monolithic

Application of hierarchically porous ZrP monolith as acidic catalyst for the dehydration of xylose was demonstrated. ZrP monolith calcined at 600 °C carries a large fraction of medium strong acidic sites and a small fraction of strong acidic sites. Judging from ^{31}P NMR spectra and the catalytic performances, calcination at 600 °C led to the decrease of Brønsted acid sites and increase of Lewis acid sites as compared with the as-synthesized ZrP monolith. The existence of both acidic sites lowered the overall activation energy for the reaction and high selectivity towards furfural yield was achieved at 170 °C (TON as $8.7 \text{ mmol g}^{-1} \text{ h}^{-1}$) with as-synthesized hierarchically porous ZrP monolith.

Chapter 7

Metal Zirconium Phosphate Macroporous Monoliths: Versatile Synthesis, Thermal Expansion and Mechanical Properties

Sol-gel method was again proven as a versatile methodology for the synthesis of MZP macroporous monolithic ceramics with various compositions. A homogeneous distribution of the metals in the gel has successfully been achieved, because the presence of a small amount of glycerol as a solvent with high boiling point prevents metal salt from recrystallization during the drying process. The post-heat treatment at high temperature ($> 300 \text{ °C}$) removes glycerol from the colloidal ZrP network, which then yields mesopores, while further calcination at higher temperature ($\geq 800 \text{ °C}$) gives rise to crystallization of the gel network to polycrystalline MZP ceramics. The effect of nanoscale interface in MZP monoliths on their thermal expansion properties materials was exhibited with SrZrP as an example. Ultralow thermal expansion (coefficient of thermal expansion (CTE) as $1.4 \times 10^{-6} \text{ K}^{-1}$) over a wide temperature range (38 °C to 1000 °C) together with sufficient mechanical properties has been demonstrated (flexural modulus as 8.0 GPa from 3-point bending and Young's modulus as 1.9 GPa from uniaxial compression). As compared with dense ceramics of the same composition, the lower CTE value is observed and can be attributed to the presence of nanometer-sized small pores in the macropore skeletons, which absorbs the anisotropic thermal expansion of each crystallite at elevated temperatures.