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論文題目	Preparation and Application of Hierarchically Porous Monolithic Materials with Embedded Nanoscale Interfaces		
(論文内容の要旨) 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. In chapter 1 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. In chapter 2 an in-situ transformation method was applied for the synthesis of hierarchically porous titanium phosphate (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 ($\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, π-TiP and α-TiP) with high mechanical properties were for the first time achieved. In chapter 3 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. In chapter 4 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). 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 temper			

ature of the solvothermal treatment. Such phenomenon is for the first time observed in TiP systems.

In chapter 5 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 zirconium phosphate (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 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.

In chapter 6 application of hierarchically porous ZrP monolith as acidic catalyst for the dehydation 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.

In chapter 7 Sol-gel method was again proven as a versatile methodology for the synthesis of metal zirconium phosphate 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. Polycrystalline metal zirconium phosphate macroporous monoliths were obtained after calcination at 1000°C . 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.

(続紙 2)

(論文審査の結果の要旨)

朱陽氏は液相法を基本とする無機材料合成手法を駆使して、ナノスケール界面を導入した階層的多孔構造をもつ塊状材料を作製し、その細孔表面の物理化学的特徴を生かした機能化の可能性を開拓した。シリカ多孔体の銀ナノ粒子による表面修飾では、液体クロマトグラフィー分離媒体として、不飽和結合を有する有機化合物の分離を実現した。リン酸と酸化チタン微結晶の液相反応によって、様々な形態を有するリン酸チタン結晶を制御して形成させ、塊状の形態を保った階層的多孔材料の作製を実現した。リン酸ジルコニウム系多孔材料に関しては、相分離を伴うゾルーゲル法によって、精密に細孔構造を制御した塊状ゲルを作製する方法を、2種類の水溶性高分子を共存させ、結晶析出を抑制する溶媒を用いる独自の方法により開拓した。この手法を基礎として、リン酸ジルコニウムに様々な金属イオンを含む、NASICON型結晶相から成る多孔材料を作製することが出来た。多孔性金属リン酸ジルコニウム多孔体は、焼結によって超低熱膨張セラミックスの特徴を示し、イオン交換能、酸性触媒能にも優れることを、流通型反応デバイスを考案して実証した。

よって、本論文は博士(理学)の学位論文として価値あるものと認める。また、平成28年1月12日、論文内容とそれに関連した事項について試問を行った結果、合格と認めた。

要旨公表可能日： 2016 年 3 月 23 日以降