Synthesis and catalytic performance of hierarchical porous titania-phosphonate hybrid nanocomposite materials

Tian-Yi Ma, Xue-Jun Zhang, and Zhong-Yong Yuan*
Institute of New Catalytic Materials Science, College of Chemistry, Nankai University, Tianjin 300071 (* e-mail: zyyuan@nankai.edu.cn)

Porous materials with hierarchical structure have been attracting tremendous research interest because they have made a great impact in many applications, including catalysis, sorption and separation. Hierarchical meso-/macroporous materials have enhanced properties compared with single-sized pore materials due to increased mass transport through the material and maintenance of a specific surface area on the level of fine pore systems. However, it has been always a challenge to design the architecture and tailor the porous hierarchy of the synthesized materials. Our efforts were invested in the designed synthesis of micro/nanocomposite structured titania-diphosphonate hybrid materials with a porous hierarchy, of which the mesoporosity was caused by the self-assembling of titania and titanium phosphonate clusters and the microstructure of macropores was generated from the further aggregation of the mesostructured titania-phosphonate nanorods. The hybrid titania-diphosphonate (Ti-HEDP) was prepared via a simple hydrothermal method with the use of precursor tetrabutyl titanate and 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP). Mesoporous titanium phosphate and pure titania materials were also prepared by the same method for comparison. The prepared hybrid Ti-HEDP presented semicrystalline anatase phase, exhibiting a hierarchical macroporous structure composed of mesostructured Ti-HEDP nanorods with length of 80-150 nm and thickness of 18-38 nm. The BET surface area is 257 m²/g and the pore size calculated by BJH method is about 2.0 nm, which corresponds to the irregular mesostructure observed in titania-phosphonate hybrid nanorods. The hydroxyethylidene-bridged organophosphonate groups were homogeneously incorporated in the network of the hybrid solid, as revealed by the FT-IR, MAS NMR, XPS, and TGA measurements. The synthesized hybrid was used for photodegradation of Rhodamine B under UV and visible-light irradiation, compared with titanium phosphate and pure titania materials. The efficient photocatalytic ability of the hierarchical nanostructured titania-phosphonate material should be due to the homogeneous incorporation of phosphonate groups into the titania framework and the high surface area over the the mesoporous titania phosphate material. Thus, these materials can be potentially useful for environmental purification applications. Also, the fabrication of other titanium/titania phosphonates with different organic bridging groups and hierarchical nanostructures can also be expected.