Synthetic organic chemistry using solid catalysts with nanosized pores

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Abstract

We have designed and prepared our own solid catalyst, V-MPS4 (Fig. 1), in which oxovanadium is covalently immobilized on the inner surface of pores (inner diameter: 4 nm) of mesoporous silica, a porous inorganic material. Several highly selective catalytic chemical transformations, such as dynamic kinetic resolution, direct coupling of aromatic compounds, and direct nucleophilic substitution of alcohols, were realized using V-MPS4 (Fig. 2).

Background & Results

Solid catalysts that are insoluble in organic solvents are often inferior in terms of catalytic activity and selectivity to homogeneous catalysts that are soluble in organic solvents. On the other hand, V-MPS4 catalyzes reactions and exhibits high catalytic activity and functional group selectivity that surpasses those of the corresponding homogeneous oxovanadium catalysts due to its unique nano-sized pore environment. In addition, the advantages of the solid catalyst have enabled its easy recovery and reuse and also the application to flow synthesis in which catalysts are packed in a reaction tube (Fig. 3).

A range of organic compounds, which serve as important synthetic intermediates for pharmaceuticals, agrochemicals, and highly functional chemicals, have been synthesized by using V-MPS4. This method has several advantages, such as production of little wastes, high conversion rate, high atom efficiency, and excellent chemoselectivity and enantioselectivity. In addition, this method is safe, simple to operate, and easy to scale up, and is expected to be easily applied to industrialization.

Significance of the research and Future perspective

Chemical products are used in every aspect of our lives today, including clothing and pharmaceuticals. Catalysts are essential for the efficient production of these products. Catalysts can be classified as either “homogeneous catalysts”, which dissolve in solution, or “heterogeneous catalysts”, which are solid and do not mix with the solvent. Homogeneous catalysts are widely used in the production of fine chemicals such as pharmaceuticals and agrochemicals, which require precise reaction control. On the other hand, homogeneous catalysts require complicated operations to separate the product from the catalyst after the reaction, and their reuse is not always easy. Our own solid catalyst, V-MPS4 has achieved several highly selective catalytic chemical transformations to solve some of these problems.

Some synthetic applications of V-MPS4 include a) the dynamic kinetic resolution (Fig. 2a), in which racemic alcohols are completely converted into optically pure compounds when used in combination with immobilized hydrolytic enzymes., viz., lipases; b) the direct coupling of aromatic compounds (Fig. 2b); c) the direct nucleophilic substitution of alcohols (Fig. 2c); and continuous flow synthesis (Fig. 2d).

We speculate that the nanosized pore space of V-MPS4 is the key to promoting these reactions, and we are currently investigating the mechanism of reaction promotion and further applications of our method.

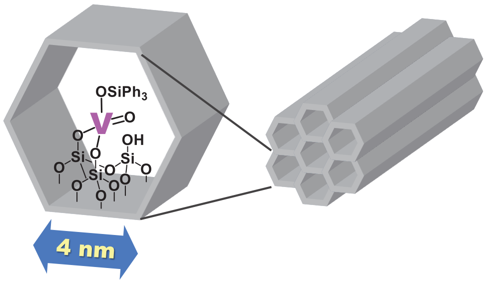

Fig. 1 Mesoporous silica-supported vanadium catalyst, V-MPS4.

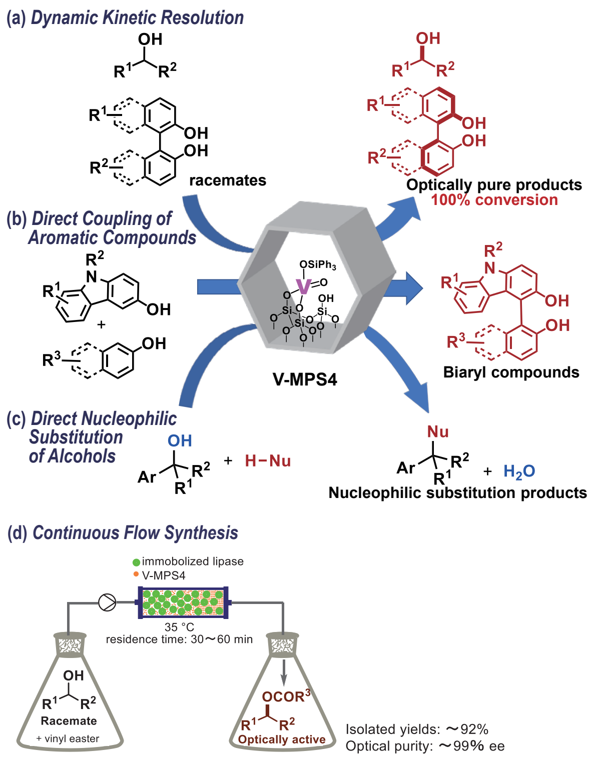

Fig. 2 Examples of chemical transformation using V-MPS4.

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