

Development of Size-Controlled Metal–Organic Frameworks as Heterogeneous Visible Light Photoredox Catalysts

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Metal–organic frameworks (MOF) have attracted much attention as new platform for designing highly functional catalysts owing to their inherent structure designability in addition to high specific surface areas and ordered porous structures [1-3]. In this regard, our group has developed a MOF photocatalyst that behave as a visible-light photoredox catalyst (denoted as Zr-MOF-TCPP) by incorporating a photofunctional organic ligand, tetrakis(4-carboxyphenyl)porphyrin (TCPP), into the MOF framework [4]. However, particle size control is still required to further improve its photocatalytic activity in terms of light utilization efficiency and substance diffusion in the pores. As a continuous research, a size controllable synthesis method for Zr-MOF-TCPP has been developed by using inorganic salts as modulators. The resultant Zr-MOF-TCPPs have been applied to oxidative hydroxylation of arylboronic acids as a heterogeneous photoredox catalyst, and the influence of particle sizes on catalytic activity has been investigated.

A series of size-controlled Zr-MOF-TCPPs were solvothermally synthesized by using $ZrCl_4 \cdot 6H_2O$, TCPP, and various inorganic salts as modulators. The successful formation of 3-dimensional porous framework structure was confirmed by XRD and N_2 adsorption–desorption measurements. The results of FE-SEM observations demonstrated clearly that the addition of inorganic salts to precursor solutions led to the decrease in the particle sizes of synthesized MOFs. The size reducing effect was observed most especially when Li_2CO_3 was used as modulator, resulting in the formation of fine particles of 56 nm size. Suppressing crystal growth of MOFs by the ionic species generated via electrolytic dissociation of the inorganic salt in the solvent

as capping agents would be responsible for such a controlling of particle sizes.

Oxidative hydroxylation of phenylboronic acid was performed in the presence of triethylamine (TEA) under green LED light irradiation ($\lambda = 523$ nm). Highly selective conversions of phenylboronic acid to phenol were achieved by using Zr-MOF-TCPPs as heterogeneous photoredox catalysts. Moreover, as shown in Fig. 1, the photocatalytic activity of Zr-MOF-TCPPs improved with decreasing the particle sizes. This finding would be explained by the increasing number of active sites where the reaction substrates can approach easily. On the other hand, the mechanism of the photocatalytic reaction was investigated by laser flash photolysis. The resultant data indicated that the photo-excited TCPP incorporated within the MOF framework is subject to reductive quenching by TEA and subsequently reacts with O_2 to give active $O_2^{\cdot -}$ species during the reaction.

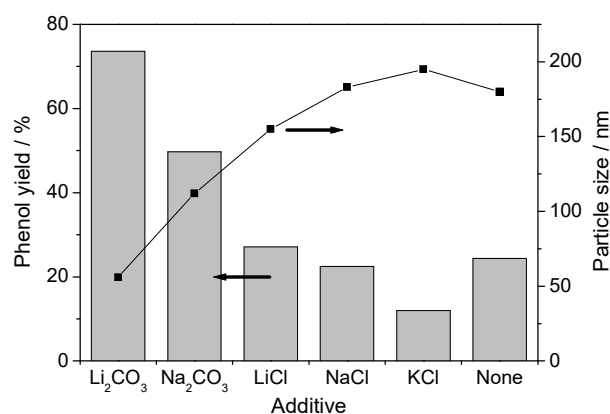


Fig. 1 Relationship between the catalytic activities for oxidative hydroxylation of phenylboronic acid and the particle sizes of various Zr-MOF-TCPPs.

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