Visible-light photoredox catalysis mediated by rationally-designed metal–organic framework photocatalysts

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Abstract: The present research spotlights the designability of metal–organic frameworks (MOFs) for the development of heterogeneous photoredox catalysts. A photoredox-active dye molecule, tetrakis(4-carboxyphenyl)porphyrin (TCPP), has been incorporated into MOF framework as a bridging organic ligand for connecting zirconium-oxo clusters. The resultant MOF, Zr-MOF-TCPP, promoted oxidative hydroxylation of phenylboronic acid under green LED irradiation to afford phenol in good yield and selectivity. Moreover, its particle size could be controlled by using inorganic salts as modulators during the MOF formation; as a result, Zr-MOF-TCPP with reduced particle size showed improved reactivity due to the increasing number of accessible active sites.

Keywords: Photoredox catalysis, Heterogenization, Metal–organic framework.

1. Introduction

In recent years, visible-light photoredox catalysis has been the focus of much attention due to its environmentally-friendly aspects. This photocatalytic process mediated by one electron redox cycle realizes organic transformation under visible light at room temperature. Thanks to such mild reaction conditions, highly controlled reaction where side reactions are inhibited can be designed, and also the use of readily available and inexhaustible visible light enables us to save energy. However, the current photoredox catalysts are dominated by homogeneous ones, such as metal complexes and dyes, and suffer from limited recyclability and weak stability. These situations stimulate our interests in the development of heterogeneous photoredox catalysts.

Metal–organic frameworks (MOFs) are a new class of organic–inorganic hybrid porous materials formed via self-assembly between metal-oxo clusters and bridging organic ligands. Their framework compositions and porous structures can be tuned by various combinations of metal-oxo clusters and bridging organic ligands. This unique feature, so-called framework designability, simultaneously provides catalytic active sites and molecular-sized reaction space and thus makes MOFs attractive platforms for designing efficient heterogeneous catalysts. Herein, a photoredox-active dye molecule, tetrakis(4-carboxyphenyl)porphyrin (TCPP), has been selected and used as a promising organic ligand to develop MOF-based heterogeneous photoredox catalysts. The potential application of the resultant MOF as photoredox catalysts has been evaluated by oxidative hydroxylation of phenylboronic acid to afford phenol under green LED irradiation. Moreover, the effect of particle size control using inorganic salts as modulators on photocatalytic activity has been investigated.

2. Experimental

The synthesis of a Zr-based MOF containing TCPP unit, denoted as Zr-MOF-TCPP, was performed by a solvothermal method in DMF at 338 K using zirconium(IV) chloride and TCPP molecule as starting materials. The thus-obtained Zr-MOF-TCPP was characterized by XRD, FE-SEM, N_2 adsorption–desorption, and DRUV–vis measurements. Photoredox activity was evaluated with oxidative hydroxylation of phenylboronic acid. Typically, a mixture of photocatalyst (10 mg), phenylboronic acid (0.6 mmol), triethylamine (3.0 mmol), and solvent (4 mL), whose pH was adjusted to 7 by using H_2SO_4, was loaded in a

Pyrex reaction vessel, bubbled with O_2, and then irradiated with green LED light (λ = 523 nm) at room temperature. The progression of the reaction was monitored by a GC with a flame ionization detector.

3. Results and discussion

The successful introduction of TCPP into the MOF framework was confirmed by XRD measurements, where typical peaks corresponding to MOF-525 type structure containing TCPP unit were observed. Also, the FE-SEM image of Zr-MOF-TCPP demonstrated the formation of highly crystalline particles with a cuboctahedral morphology. DRUV–vis measurements revealed that Zr-MOF-TCPP possessed visible-light absorption property extending to wavelength of around 800 nm. Zr-MOF-TCPP was then applied to oxidative hydroxylation of phenylboronic acid under green LED irradiation. The reaction efficiently proceeded on Zr-MOF-TCPP to give phenol in high yield and selectivity. Noted that the reaction rate of Zr-MOF-TCPP was higher than that of the homogeneous counterpart, TCPP molecule. This fact would reflect the effectiveness of forming MOF structure to avoid aggregation of TCPP molecules. Moreover, Zr-MOF-TCPP could be recycled at least five cycles without significant loss of its reactivity.

Subsequently, in order to investigate the effect of particle size of Zr-MOF-TCPP on photocatalytic activity, a coordination modulation approach has been applied to the MOF synthesis process. The addition of inorganic salts as modulator to the precursor solution led to decrease particle size of synthetic Zr-MOF-TCPP, and the smallest Zr-MOF-TCPP particle was formed when Li_2CO_3 was used as the modulator among various inorganic salts explored in this study. The photocatalytic activity of Zr-MOF-TCPP improved by decreasing in the particle sizes due to the increasing number of accessible active sites (**Figure 1**).

Finally, estimation of the mechanism of the photoredox reaction mediated by Zr-MOF-TCPP was carried out using laser flash photolysis measurements. The results emanating from the LFP data showed that the photo-excited TCPP incorporated within Zr-MOF-TCPP would be subjected to reductive quenching by TEA and then reacts with O_2 to give active $O_2^{\bullet-}$ species.

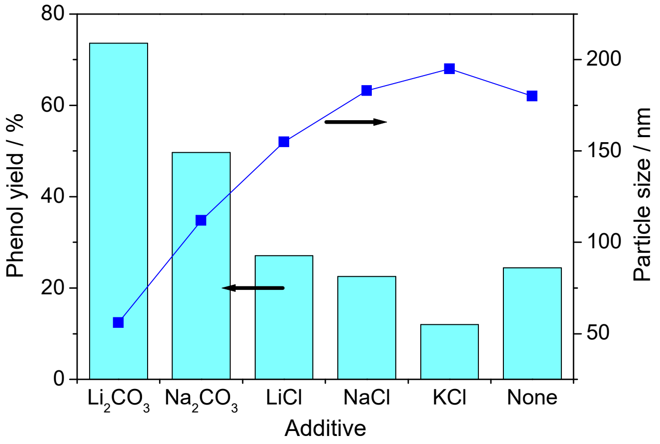

Figure 1. Relationship between the catalytic activities for oxidative hydroxylation of phenylboronic acid and the particle sizes of Zr-MOF-TCPPs prepared using various additives.

4. Conclusions

In summary, a visible-light-responsive MOF photocatalyst was designed by utilizing a photofunctional molecule, TCPP, as the bridging organic ligand. The synthesized MOF, Zr-MOF-TCPP, was found to efficiently promote hydroxylation of phenylboronic acid under green LED irradiation and possess high stability and recyclability. In addition, particle size control of Zr-MOF-TCPP was achieved by using inorganic salts as modulator, and consequently, the thus-obtained small sized-MOF showed improved photoredox activity.

References

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