

Preparation of Co-porphyrin catalyst encapsulated in cyclodextrin-based metal-organic framework for coupling reaction

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Abstract. Immobilization of organometallic catalyst were attempted by using cyclodextrin-based metal-organic framework (CD-MOF) with the characteristic nanoporous structure. Water-soluble Co(II)TCPP was prepared as an organometallic catalyst and introduced into hydrophilic nanopores in CD-MOF by co-crystallization method. In order to evaluate the catalytic properties of the obtained Co(II)TCPP/CDMOF, the oxidative coupling reaction of creosol was performed. At a catalyst concentration of 0.2 mol%, the catalytic activity of the heterogeneous Co(II)TCPP/CDMOF catalyst was almost the same as that of the homogeneous Co(II)TCPP catalyst. The conversion for Co(II)TCPP/CD-MOF catalyst reached 92% after 2-hour reaction.

1. Introduction

Organometallic catalysts have been used as homogeneous catalyst in the fields of fine chemical and pharmaceutical industries [1]. The transition metals in organometallic catalyst are expensive, toxic, and belong to the rare metal. Moreover, contamination by the trace metal in the reaction product can cause toxicity in pharmaceutical products and significantly impair the properties of high-performance products. Thus, heterogeneous catalysis has emerged as a promising solution to obtain reusable catalysts [2]. If the organometallic catalyst could be immobilized in the porous materials with a ship-in-a-bottle structure, the resulting heterogeneous catalyst would be reused several times without the metal leakage.

Cyclodextrin-based metal-organic framework (CD-MOF), which are porous organic crystals, have attracted attention [3]. Research on the encapsulation of functional molecules [4] and fluorescent molecules [5], the reaction deposition of noble metal nanocluster [6] and the polymerization [7] in CD-MOF was recently reported. As shown in Figure 1, CD-MOF crystal consists of the body-centered cubic structure of the primary (γ -CD)₆ unit. The interior cavity of γ -CD is hydrophobic, while the exterior side is hydrophilic. Therefore the hydrophobic nanopore can be created by a pair of γ -CD units. The size of the hydrophobic nanopore is approximately 1.0 nm because fullerene C60 with the molecular size of 1.0 nm can be included between the two γ CD cavities. [4,8] The spherical cavities with the

diameter of 1.7 nm are newly formed at the center of (γ -CD)₆ units by the crystallization and are connected to each other through the apertures of the γ -CD along the a, b or c axes. The spherical cavities are hydrophilic due to the free primary 6-OH groups in γ -CD. Transverse channels extended through the triangular nanopores (0.4 nm) oriented along [1,1,1] axis direction of the crystal. When hydrophilic or hydrophobic molecules were introduced into the corresponding nanopores of CD-MOF by the co-crystallization [5] or the chemical conversion [7,8], nanoparticles with the size of larger than 0.8 nm could be isolated from the environment without leakage.

Metalloporphyrin catalysts have been engaged in various organic synthesis. [9, 10] Jiang et al. [11] reported that high efficiency phenol coupling reaction by aerobic oxidation using a Co(II)porphyrin catalyst. According to this, the oxidative coupling reaction proceeds by reacting various phenol derivatives with oxygen using [5,10,15,20-tetrakis (4-methoxyphenyl) porphyrinato] cobalt(II) as a catalyst. In the previous paper [4], we succeeded in preparing the CD-MOF in which water-soluble porphyrin (tetrakis (4-carboxyphenyl) porphyrin, TCPP) was encapsulated in hydrophilic nanopores by methanol vapour diffusion of methanol to the mixed solution of γ CD, KOH and TCPP. If TCPP complexed with Co(II) could be introduced into CD-MOF, the resulting Co(II)TCPP/CD-MOF would be expected as a heterogeneous catalyst for organic synthesis.

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In this study, the synthesized Co(II)TCPP was added to the γ -CD and KOH solution and Co(II)TCPP/CD-MOF was crystallized by vapor diffusion of methanol. This Co(II)TCPP/CD-MOF was used as a heterogeneous catalyst to perform the coupling reaction of 2-methoxy-4methylphenol (creosol), and its catalytic activity was investigated.

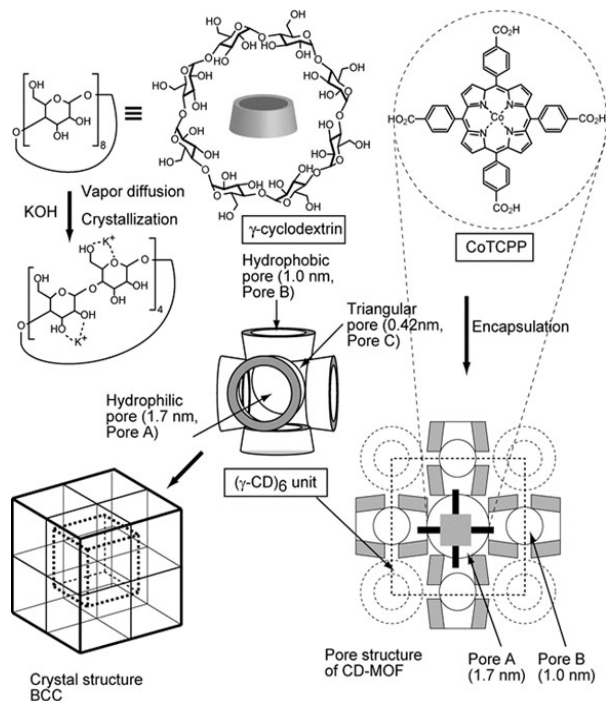


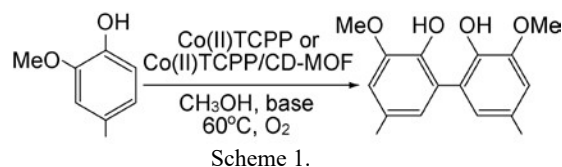
Fig. 1. Crystal structure and pore structure of CD-MOF

2. Experimental

γ -CD (Tokyo Chemical Industry Co., Ltd., Japan) was used for the crystallization of CD-MOF. Anhydrous methanol, dichloromethane, N,N-dimethylformamide (DMF), 2-methoxy-4methylphenol (creosol), cobalt(II) acetate tetrahydrate ($\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) and potassium hydroxide were purchased from FUJIFILM Wako Pure Chemical Co., Japan. TCPP was purchased from Sigma-Aldrich Co. These reagents were used without purification.

The synthesis of Co(II)TCPP was performed as described in literature [12]. TCPP(0.2 g, 0.253 mmol) and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.64 g, 2.53 mmol) were dissolved in 60 mL DMF and heated reflux for 5 h. CD-MOF was crystallized by methanol vapor diffusion method according to a previous paper [4]. The Co(II)TCPP/CD-MOF was prepared by co-crystallization method [5]. γ -CD (0.163 g, 0.125 mmol) and Co(II)TCPP (0.063 mmol, 0.053g) were dissolved in 5 mL of KOH solution (200 mmol/L). The crystallization period by vapor diffusion of methanol was 3 days at room temperature. The oxidative coupling of creosol was carried out by using homogeneous Co(II)TCPP or heterogeneous Co(II)TCPP/CD-MOF catalyst in methanol (Scheme 1). Creosol, base (NaOH or Na_2CO_3), and methanol were added to an eggplant flask with reflux condenser in air.

The air was removed by vacuum, and O_2 was introduced at a pressure of 101 kPa. The eggplant flask was then sealed, and the resulting mixture was stirred at 60°C under an atmosphere of oxygen. After prescribed periods, the concentrations of creosol and biphenyl compounds were measured with HPLC. The catalyst concentration was defined as the molar fraction of Co(II)TCPP for both homogeneous Co(II)TCPP and heterogeneous Co(II)TCPP/CD-MOF catalyst.



Absorption spectra of TCPP and Co(II)TCPP were measured with a UV-VIS spectrophotometer (V-550, JASCO Co.). Scanning electron microscope (SEM VE-9800, Keyence) was used in visualization of crystal shape of Co(II)TCPP/CD-MOF. The crystal structures of CD-MOFs were determined from powder X-ray diffractometer (X'Pert-PRO, Malvern Panalytical). Nitrogen sorption isotherms were measured with a liquid N_2 bath (-196°C) using a surface area and porosity analyzer (Shimadzu TriStar II, Japan). After Co(II)TCPP/CD-MOF was dissolved in water, the cobalt concentration in the solution was measured with an induction plasma emission spectrometer (Thermo Scientific iCAP 7000 Plus), and the cobalt content per CD-MOF was determined. HPLC (Shimadzu Corp.) with a reverse phase column (InertSustainTM AQ-C18, GL Sciences Inc.) was used for the analysis of the coupling reaction products.

3. Results and Discussion

3.1. Co(II)TCPP/CD-MOF

Fig. 1 shows the UV-Vis absorption spectrum of TCPP and synthesized Co(II)TCPP. The absorption spectrum of a typical porphyrin consists of a strong transition at about 400 nm (the Soret band) and a weak transition at about 550 nm (the Q band). TCPP had an absorption maximum at a wavelength of 416 nm and weak absorption at 513 nm, 547 nm, 589 nm, and 647 nm in the Q band. Co(II)TCPP shifted the absorption maximum of the Soret band to the longer wavelength side to 430 nm, the four absorption peaks in the Q band disappeared, and absorption appeared at a wavelength of 543 nm [12].

Co(II)TCPP/CD-MOF was a cubic crystal as shown in Figure 3 and had a maximum size of 150 μm . The crystallization yield of Co(II)TCPP/CD-MOF was 76%, which was almost the same as that of CD-MOF crystallization [5,13]. The Co(II)TCPP content in Co(II)TCPP/CD-MOF could be controlled by changing the opening area of the vessel used for methanol vapor diffusion. We prepared two-types of Co(II)TCPP/CD-MOF of which the catalyst loadings were 5.1wt% and

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9.8wt%. When these values were converted to the number of Co(II)TCPP molecules per $(\gamma\text{-CD})_6$ unit constituting CD-MOF, they were 0.49 and 0.94, respectively. When TCPP was introduced into CD-MOF [4], there were 2.1 TCPP molecules per $(\gamma\text{-CD})_6$ unit. This suggested that a pair of TCPP molecules might be located in the hydrophilic nanopore. Thus, when CD-MOF was used as a support for organometallic catalysts, a heterogeneous catalyst having high catalyst dispersibility and a high catalyst loading could be realized.

The crystallinity of Co(II)TCPP/CD-MOF was evaluated using X-ray diffraction. Figure 4 shows the XRD patterns of CD-MOF and Co(II)TCPP/CD-MOF. The peaks at $2\theta = 5.17^\circ$ and 6.95° derived from the (200) plane and the (211) plane of the CD-MOF were observed, respectively, confirming that the crystal structure was maintained even when Co(II)TCPP was introduced. The

BET specific surface area of the synthesized CD-MOF is $970 \text{ m}^2/\text{g}$, whereas the Co(II)TCPP/CDMOF has a BET specific surface area of $682 \text{ m}^2/\text{g}$.

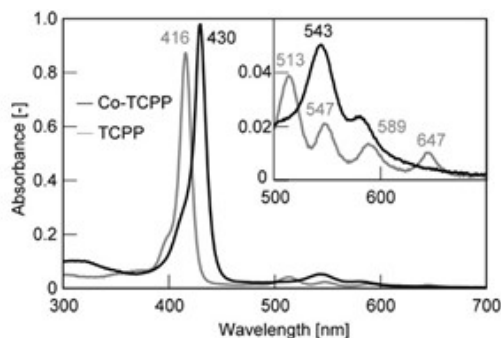


Fig. 2. UV-Vis spectrum of TCPP and Co(II)TCPP

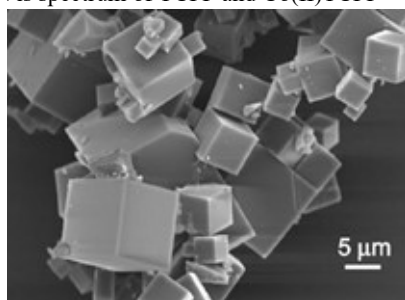


Fig. 3. SEM image of Co(II)TCPP/CD

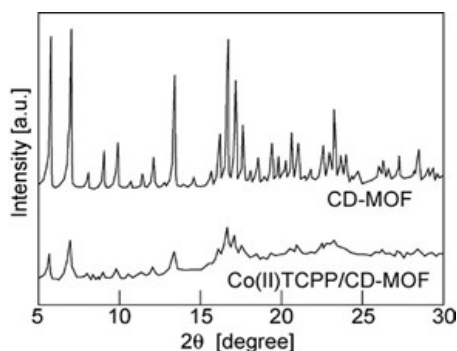


Fig. 4. XRD pattern of CD-MOF and Co(II)TCPP/CD-MOF

3.2 Oxidative coupling of creosol

The coupling reactions were proceeded easily by using the homogeneous Co(II)TCPP catalyst in O_2 atmosphere, but no reaction occurred in N_2 atmosphere. As shown in Figure 5, Na_2CO_3 and NaOH were used as bases at the catalyst concentration of 0.045 mol%, but there was no difference in the conversion. The reaction rate increased when the catalyst concentration became 0.2 mol%. The conversion after 24-hour reaction was almost 100% regardless of the basicity and the catalyst concentration. Jiang et al. [11] performed a creosol coupling reaction using meso-tetra (4methoxyphenyl) porphyrin cobalt (II) [T(p-OMe)PPCo] and stated the conversion of 99% and the yield of 98% after 15 hours reaction under the same experimental conditions. These results indicate that Co(II)TCPP also shows almost the same catalytic activity as T(p-OMe)PPCo.

Figure 6 shows a comparison of the conversion of Co(II)TCPP catalyst and Co(II)TCPP/CDMOF catalyst at the catalyst concentration of 0.2 mol%. The Co(II)TCPP/CD-MOF crystal having a catalyst particle size of 5-20 μm as shown in Figure 3 was used. By clathrate crystallization of Co(II)TCPP into CD-MOF, the reaction rate was slightly reduced and the conversion was 92%. It was found that Co(II)TCPP exhibited the high catalytic activity even in the limited space of hydrophilic nanopores formed in CD-MOF. In addition, the reaction behaviors of Co(II)TCPP/CD-MOF catalysts with different catalyst loadings were found to be unchanged at the same catalyst concentration (0.2 mol%).

Figure 7 shows the effect of catalyst concentration on the conversion for Co(II)TCPP/CD-MOF catalyst. When the catalyst concentration was changed from 0.2 mol% to 0.38 mol%, the reaction rate became slightly higher, and the conversions after 24-hour reaction were consistent. When the catalyst concentration was reduced to 0.045 mol% and 0.01 mol%, the reaction rate and the conversion were greatly reduced.

Figure 8 shows that the conversion of a Co(II)TCPP/CD-MOF catalyst with a particle size of 100200 μm is significantly lower than that of a Co(II)TCPP/CD-MOF catalyst with a particle size of 5-20 μm . In the case of the large catalyst particles, it was suggested that the intraparticle diffusion resistance of the reaction product, diphenyl, affected the reaction. Further research is needed to analyze the influence of the diffusion on the reaction.

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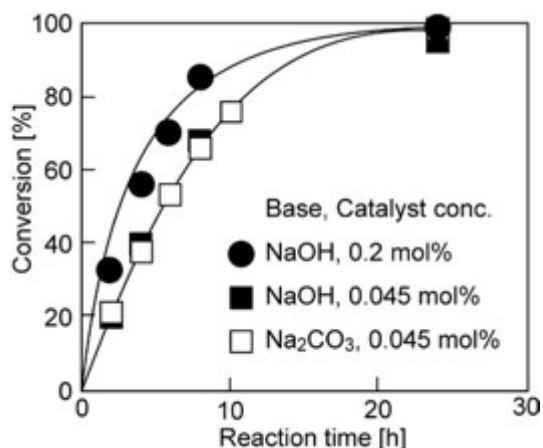


Fig. 5. Catalytic performance of Co(II)TCPP in oxidative coupling.

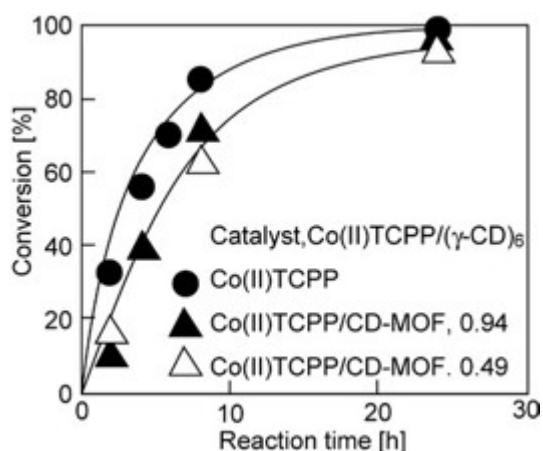


Fig. 6. Comparison of conversion between the Co(II)TCPP catalyst and the Co(II)TCPP/CD-MOF catalyst.

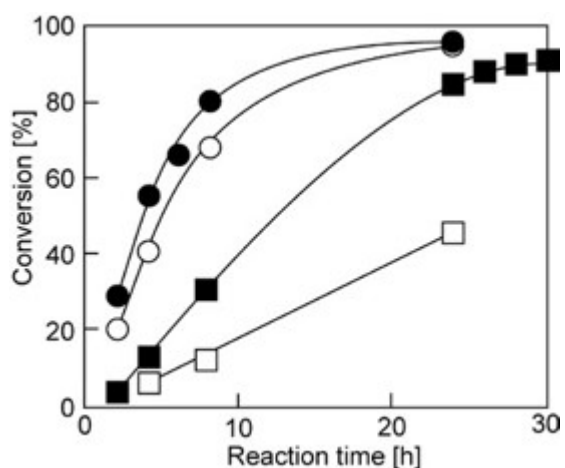


Fig. 7. Effect of Co(II)TCPP catalyst concentration on the conversion for Co(II)TCPP/CD-MOF catalyst: Catalyst concentration ●: 0.38 mol%, ○: 0.2 mol%, ■: 0.045 mol%, □: 0.01 mol%.

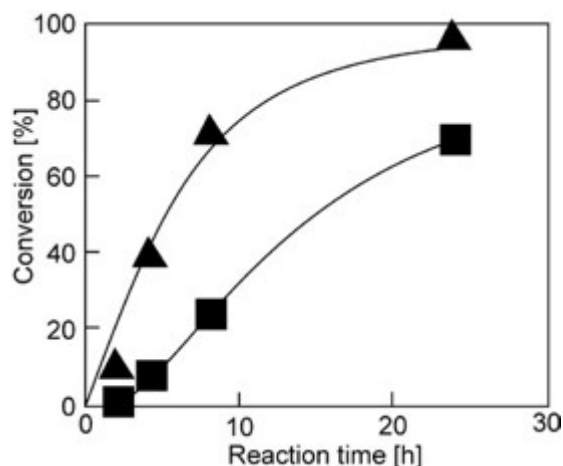


Fig. 8. Effect of crystal size on conversion for Co(II)TCPP/CD-MOF catalyst: Particle size ▲: 5-20 μm , ■: above 100-200 μm : Catalyst concentration 0.2 mol%.

4. Conclusion

Co(II)TCPP could be introduced into the hydrophilic nanopore in CD-MOF crystal by cocrystallization method. One hydrophilic nanopore existed at the center of (CD)₆ unit constituting CDMOF and there were 0.94 molecules of Co(II)TCPP in a hydrophilic nanopore according to the calculation. This value was converted to a catalyst loading to be 9.8 wt%. Thus, when CD-MOF was used as the support material for the organometallic catalyst, a heterogeneous catalyst having a high dispersibility and a high loading could be obtained.

In order to evaluate the catalytic activity of the prepared Co(II)TCPP/CD-MOF, the oxidative coupling of creosol was performed. As a result, for the Co(II)TCPP/CD-MOF with a particle size of 5-20 μm at the catalytic concentration of 0.2 mol%, almost the same performance as the homogeneous Co(II)TCPP catalyst was obtained. When Co(II)TCPP/CD-MOF crystals with a particle size of 100-200 μm were used, the reaction rate was found to decrease due to the influence of intraparticle diffusion resistance.

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