

Preparation and Oxidation Function of Metallophthalocyanine Complex Encapsulated in the Faujasite Zeolite by the 'Ship-in-bottle' Method

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Metallophthalocyanines (MPc) are known to have similar structure/function to metalloporphyrins which show a high-performance catalytic functions in biological metabolic systems. However, it is very difficult to make MPc appear some catalytically-active functions, because they easily precipitate as stable and inactive aggregates in spite of their high potentialities. In order to obtain MPc as an isolated monomer, we tried to synthesize the MPc compounds encapsulated in the nanopores of Faujasite type zeolite (Z) (MPc-Z; M = Co(II), Cu(II)) by the 'ship-in-bottle' method (Figure 1). Further, another secondary metal ion (M'^{n+}) were introduced into the MPc-Z by the ion-exchange methods. The MPc complex generated in the zeolite makes expect to appear a novel latent ability as catalyst and the multiple functions by changing the secondary metal ion.

MPc- M'^{n+} -X was prepared from the template reaction of phthalonitrile with the metal ion-exchanged zeolite X that was heated at 493 K for 3 hours, and excess M'^{n+} ion which did not react with phthalonitrile in the zeolite were exchanged to M'^{n+} ($M'^{n+} = Na^+$, etc.). The MPc- Na^+ -Z was characterized by elemental and fluorescent X-ray analyses and UV-vis, reflectance and ESR spectroscopic methods and the nitrogen adsorption study. The two bands appeared in the UV-vis and reflectance spectra were assigned to characteristic Q- and B-bands of MPc. Solid state ESR spectra of MPc- Na^+ -X indicate that MPc is located independently in the nanopores of zeolite X, and the coordination plane around metal ion has been distorted by the encapsulation. The oxidative reaction experiments with organic substrates were carried out in the presence of MPc- M'^{n+} -Z and H_2O_2 as oxidant in acetonitrile solvent at 323 K, and the reaction products were analyzed by gas chromatography, which suggested that the reactive oxygen species of MPc-X is different from that of zeolite-free MPc. Interestingly, the TON number of the oxidative reaction by of substrates by MPc- M'^{n+} -X was controlled by the secondary ion M'^{n+} .

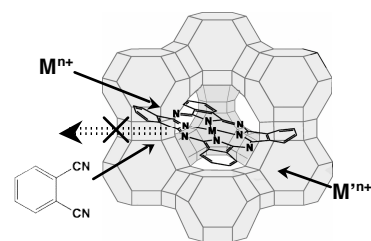


Figure 1.
Schematic structure of MPc-Z
prepared by 'Ship-in-bottle' method