

PREPARATION AND CATALYTIC BEHAVIOUR OF POLYMER-BOUND METALLOPORPHYRIN IN HYDROGENATION OF OLEFIN

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Abstract The meso-tetraarylporphyrin has been anchored to styrene-divinylbenzene copolymers by reaction of meso-tetra(4-hydroxyphenyl) porphyrin with chloromethylated resin under mild condition. A number of polymer transition metal complexes have been prepared with the polymer ligand and metal salts. The polymeric ligand and its complexes have been characterized by electronic spectra, and vibrational spectra. Cyclohexene can be hydrogenated with the polymeric porphyrin palladium complex(P-THPPPd) as catalyst, and its catalytic activity was influenced by the polarity of solvents, the contents of water in ethanol or reaction temperature. However, its catalytic activity was lower for nitro groups, carbonyl groups and olefins with steric hindrance substituents, and showed no activity for aromatic rings under these conditions.

Keywords Polymer-bound catalyst; Metalloporphyrin; Hydrogenation

INTRODUCTION

The synthesis of polymer-bound transition metal complexes and their use in catalytic reaction have received much attention^[1,2]. Such polymeric catalysts have the advantage of being easily separated after reaction, and they can often be recovered and reused. In addition, an increase in stability, activity and selectivity^[3,4] was often observed.

Metalloporphyrins and polymer-bound metalloporphyrins catalyst have been mainly used in the epoxidation of alkenes and the hydroxylation of saturated hydrocarbons^[5-8] as synthetic model of cytochrome P-450^[9-11]. In this paper, we report the synthesis of polystyrene-supported porphyrin (Fig.1) with copper, cobalt, zinc and palladium complexes, which are based on preparation of low molecular model porphyrin^[12]. The catalytic activity for the hydrogenation of olefins was studied.

* This work was supported by the National Natural Science Foundation of China.

Received April 8, 1997

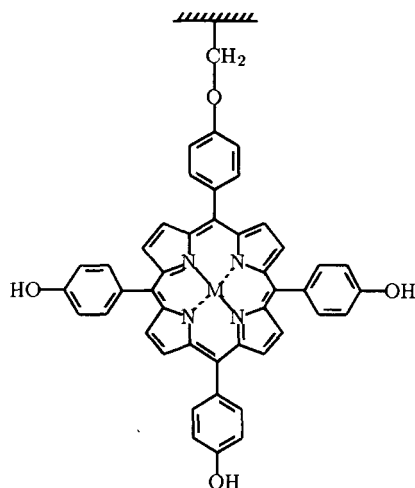


Fig.1 The structure of P-THPPM ($M = \text{Cu}, \text{Co}, \text{Zn}, \text{Pd}$)

EXPERIMENTAL

Materials and equipments

Chloromethylated polystyrene was donated by Institute of Molecular Chemistry, Nankai University, China (contains 4.96 mmol/g chlorine and 2% crosslinked with divinylbenzene). Anhydrous potassium carbonate, N,N-dimethylformamide, anhydrous alcohol and metal salts were obtained available commercially. meso-Tetra (p-hydroxylphenyl) porphyrin (THPPH₂) was synthesized according to the following literature procedure^[14].

The electronic spectra of the pellet of the polymer in KBr, were recorded on a Hitachi U-3400 spectrophotometer using pure KBr tablet as reference. The IR spectra of the samples in KBr pellet were recorded on an Alpha-centauri FT-IR spectrophotometer. All metal ion contents were measured on a Labtam-8401 ICP Emission Spectrometer. Analytical GLC was performed with a Shimadzu GC-16A gas chromatography using 3 m×3 mm PEG-20000 column.

Preparation of polymer-bound porphyrin (P-THPPH₂)

Chloromethylated polystyrene (1.37 g) was swelled in N,N-dimethylformamide (5 ml) for 24 h. To this, a DMF (50 ml) solution of THPPH₂ (0.5 g, 0.74 mmol) was added followed by anhydrous potassium carbonate (0.5 g, 3.62 mmol). After stirring for 5 h at 80°C, the color of solution changed from deep greenish blue to very light purple. The purple polymer formed was filtered after cooling, washed thoroughly with water, ethanol and chloroform until the filtrate was colorless, and dried in vacuum at 80°C to yield polymer-supported porphyrin (P-THPPH₂).

Preparation of metal complexes of P-THPPM ($M = \text{Cu}^{\text{II}}, \text{Co}^{\text{II}}, \text{Zn}^{\text{II}}$)

The appropriate metal compound ($\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ or $\text{Co}(\text{OAc})_2$

$\cdot 4\text{H}_2\text{O}$) (1 mmol) was added to the resin (P-THPPH₂) (200 mg) in DMF (35 ml). After stirring for 5 h at 80°C, the complexes were filtered off, washed with distilled water and alcohol respectively, and dried under vacuum.

Preparation of metal complexes of P-THPPPd

An ethanol solution (20 ml) of palladium dichloride (0.43 mmol) was added to polymer ligand (P-THPPH₂). The mixture was refluxed and stirred for 15 h. After cooling, the complex was filtered off, washed thoroughly with water and ethanol, then dried under vacuo.

Hydrogenation of alkenes

General procedure: The substrate cyclohexene (1 mmol) was added into ethanol (10 ml) and the system was heated to appropriate temperature. The polymer catalyst (5 mg) was added and the system was purged with hydrogen. Since stirring of the mixture was started, the hydrogen consumption was monitored using a gas burette. After the reaction, the catalyst was filtered. The products were identified by GLC.

RESULTS AND DISCUSSION

Characterization of polymer-bound porphyrin and its complexes

The IR spectra of the polymer ligand and (P-THPPH₂) and its complexes (P-THPPM) exhibits an absorption band at 1262 cm^{-1} due to the $\nu(\text{C}-\text{O}-\text{C})$ of ether bond between polystyrene and porphyrin, and several bands near 2920, 1607, 1576, 1470, and 1354 cm^{-1} due to $\nu(-\text{CH}_2-)$, $\nu(\text{C}=\text{C})$ of phenyl, $\nu(\text{C}=\text{C})$ of pyrrole, $\nu(\text{C}=\text{N})$, and $\nu(\text{C}-\text{N})$, respectively. The polymer ligand exhibits bands at 3327, 965, and 735 cm^{-1} due to the $\nu(\text{N}-\text{H})$ and $\delta(\text{N}-\text{H})$ which disappears in the spectra of polymer complexes (P-THPPCu, P-THPPCo, P-THPPZn) indicates that the most parts of P-THPPH₂ convert to P-THPPM [$\text{M} = \text{Cu}(\text{II})$, $\text{Co}(\text{II})$, $\text{Zn}(\text{II})$]. The polymer palladium complex exhibits a broad band (compared with ligand) at 984 cm^{-1} due to the folding characteristic band of polymer ligand with that of metal complex of

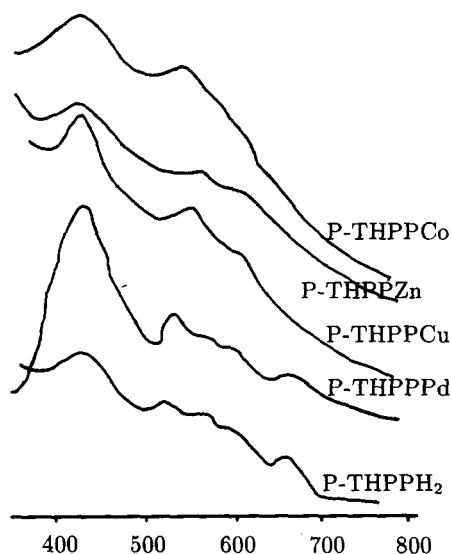


Fig.2 Electronic spectra of P-THPPH₂ and its complexes P-THPPM ($\text{M} = \text{Cu}$, Co , Zn , Pd)

to the folding characteristic band of polymer ligand with that of metal complex of

porphyrin (near 1000 cm^{-1})^[13], and it indicates that P-THPPH₂ is partly complexed with palladium.

The electronic spectrum of the polymer ligand (P-THPPH₂) exhibits bands at 427.5 nm (Soret band), 517.4 nm (QY(1-0)), 559.4 nm (QY(0-0)), 597.4 nm (Qx(1-0)), 657.3 nm (Qx(0-0)) (Fig. 2). For polymeric copper, cobalt, and zinc complexes the number of bands decrease, which indicates that the P-THPPH₂ was more completely complexed with metal respectively. However, the polymer palladium complex exhibits bands at 436.5, 533.8, 564.8, 600.0 and 658.9 nm. These suggest that the Soret band hyperchromic shift, the number of bands (compared with that of ligand) has not decreased, but the absorption intensity of the Soret band have increased, and bands have shifted. This also indicates that the complex reaction has not been completed. The content of porphyrin ligand determined by elemental analysis was 0.95 mmol THPP/g·(P-THPPH₂). The amount of metal incorporated was determined by Labtam-8401 Inductively Coupled Plasma-atomic Emission Spectrometry. The metal ratios of the complexes vary with the different metals: 0.94 mmol Cu/g·(P-THPPCu), 0.70 mmol Co/g·(P-THPPCo), 0.4 mmol Pd/g·(P-THPPPd).

Hydrogenation with polymer-bound palladium porphyrin

The polymer-bound palladium porphyrin complex (P-THPPPd) is a catalyst precursor for the hydrogenation of olefins at ambient temperature and pressure, but its activity for nitro groups (nitrobenzene), carbonyl groups (acetaldehyde) and olefins with steric hindrance substituents (methyl methacrylate) are lower, and for aromatic rings (bromobenzene) is none under these conditions. Reduction of cyclohexene in ethanol (10 ml) using P-THPPPd as a catalyst (5 mg) gave cyclohexane in a yield of near 100% (requiring 90 min for reduction of 1 mmol of substrate at 30°C). But P-THPP-Cu, P-THPP-Co and P-THPP-Zn showed no activity for the hydrogenation of cyclohexene.

The rate of reduction is strongly influenced by the polarity of solvent. For example, in the case of cyclohexene, if the relative rate of hydrogenation in THF is 9.3 ml H₂/min·g cat (using 1 mmol of substrate and 10 ml of solvent at 30°C), while the relative rates for hydrogenation in methanol, anhydrous ethanol and 95% alcohol are 34.3, 23.5 and 24.0 (ml H₂/min·g cat.) respectively. The catalytic activity of P-THPPPd is influenced by the contents of water in alcohol. Fig. 3 shows the optimal ratio of C₂H₅OH/H₂O is 80% and the activity of P-THPPPd decreases when the contents of ethanol increase or decrease in the solvent. It is considered that the polarity of solvent increases when the water is added into the ethanol, and the activity increases too. The reason may be that the oxygen atom of the polar molecule is easy to insert into the active center of the catalyst as the fifth ligand. The solubility of substrates and catalysts in the solvent will decrease if the water is in excess, because substrate is difficult to contact with the active center of the

catalyst. Therefore, the substrate cannot be reduced in water.

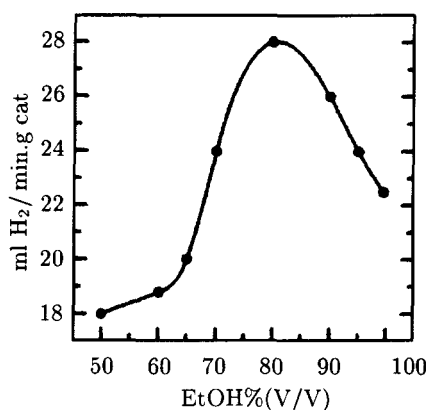


Fig.3 Effect of the concentration of EtOH on the catalytic activity of hydrogenation of P-THPPd

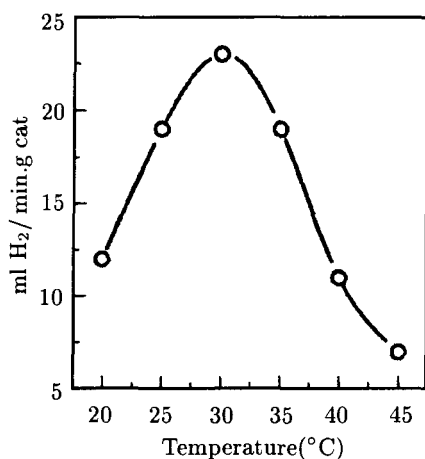


Fig.4 Effect of the reaction temperature on the activity of P-THPPd in hydrogenation of cyclohexene in ethanol

The rate of reduction is influenced by the reaction temperature. Fig. 4 shows the variation of the catalytic activity of P-THPPd with the temperature.

The catalyst can be reused for at least five times without any loss in activity (Fig. 5). The catalyst was not dried before the next catalytic run. The rate of reduction was lower in the first run than that of the other runs. After the first catalytic cycle,

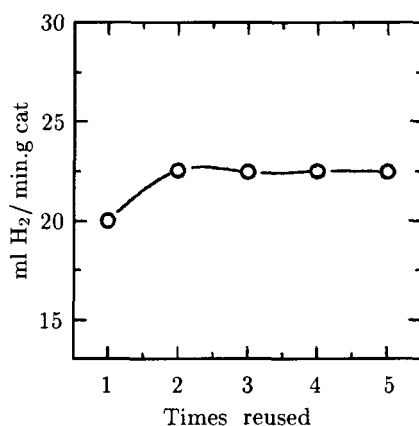


Fig.5 Relationship between the catalytic activity of P-THPPd and times reused in hydrogenation of cyclohexene

the catalyst was characterized by the UV-Vis and IR spectra, which showed no

obvious change. It was considered that the catalyst was drier in first cycle, its active centers could not wholly contact with substrates, therefore, its activity is lower than that in later cycle.

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