Applied Catalysis A: General 515 (2016) 164–169

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Synthesis of conjugated Mn porphyrin polymers with *p*-phenylenediamine building blocks and efficient aerobic catalytic oxidation of alcohols

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ARTICLE INFO

Article history:
Received 27 October 2015
Received in revised form 31 January 2016
Accepted 5 February 2016
Available online 8 February 2016

Keywords:
N-Heterocyclic carbene
Aromatic amination
Conjugated metalloporphyrin polymer
Alcohol oxidation
Catalysis

ABSTRACT

A series of conjugated metalloporphyrin polymers (MnP-AMPs) were synthesized based on Buchwald-Hartwig aromatic amination with *p*-phenylenediamine and manganese tetraphenylporphyrin as building blocks, and N-heterocyclic carbene-palladium complex as catalyst. Brunauer–Emmett–Teller surface area analysis, scanning electron microscopy and transmission electron microscopy showed that MnP-AMPs had large surface areas and uniform pore sizes. The stable porous and superreticular conjugated structure of MnP-AMP further activated manganese ions in the porphin ring compared with those in the original monomanganeseporphyrin. Moreover, introducing C—N bonds in MnP-AMP increased its polarity and affinity to alcohols, so MnP-AMP exhibited high catalytic activity when applied to aerobic oxidation of alcohols. For the catalysis of selective oxidation of benzyl alcohol to benzaldehyde with air, the conversion and aldehyde selectivity both reached up to 100% under mild condition in acetonitrile at 40 °C. MnP-AMP also remained stable in oxidation reaction system and still had high catalytic activity after several recycles.

1. Introduction

Metalloporphyrins, as excellent biomimetic catalysts for C—H bond activation [1,2], can also be used in catalytic oxidation of alcoholic hydroxyl group with high selectivity [3,4]. However, they are generally responsible for catalysis in homogeneous systems and prone to self-oxidation and degradation, rendering recycle and reuse rather difficult [5]. The existing problems can mainly be solved by utilizing metalloporphyrins in a multiphase process, immobilization in most cases [6–8]. New bonds form in metalloporphyrin immobilization, which are generally unstable and easily breakable, so the performance in reuse is limited [9]. Self-oxidization, degradation, or difficulty in reuse cannot be circumvented by metalloporphyrin immobilization [10]. Aggregating metalloporphyrin to special insoluble polymer is a new method for the heterogeneous catalysis of metalloporphyrins [11–13].

Metalloporphyrin polymerization can be mainly divided into four categories: hydrogen-bonding association [14,15], axial polymerization [16], metal-organic frameworks [17,18], and para-covalent polymerization [19,20]. Para-covalent polymerization connects metalloporphyrin monomers through covalent bonds. Such polymers can form different kinds of covalent polymers by changing the coupling groups [21,22]. Since para-covalent polymerization hardly occurs in four para positions of metalloporphyrin, only phenylene- and alkynyl-coupling conjugated polymers have been successfully synthesized till now [23,24]. Synthesis of phenylimine-coupling metalloporphyrin polymer and application of it in the catalytic oxidation of alcohol have not been reported yet. In this study, we designed a conjugated metalloporphyrin polymer coupled with phenylimine, which had a porous network structure with hyperconjugation, further activating center manganese ions compared with those in monometalloporphyrin. A large number of C—N bridging groups enhanced the polarity of the polymer, so it showed high affinity to alcohols and superb catalytic performance for the oxidation of alcohols into aldehydes.

The coupling reaction between phenylimine and metalloporphyrin polymer could not be catalyzed by common palladium catalysts such as tetrakis(triphenylphosphine) palladium(0), Pd(dba)$_2$, and tetrakis (triphenylphosphine) palladium(0)/CuI. N-Heterocyclic carbene palladium complex is a new coupling catalyst for Buchwald-Hartwig aromatic amination [25,26]. *N*,*N*-(2,4,6)-Methylimidazolium chloride, a N-heterocyclic carbene precursor, was herein synthesized. It exhibited high catalytic activity when combined with palladium acetate in four-directional coupling polymerization with *p*-phenylenediamine and T(p-Br)PPMnCl.

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http://dx.doi.org/10.1016/j.apcata.2016.02.003
0926-860X/

2. Experimental

2.1. Reaction reagents

Palladium acetate (47.5% Pd) and potassium *tert*-butoxide (95%) were obtained from J&K Chemicals. (p-Br)PPMnCl was synthesized in our group according to documented procedures and characterized by IR, UV–vis, ^{1}H NMR and MS spectroscopies [27] (Supporting information). *P*-Phenylenediamine, chloromethyl ethyl ether and other reagents were purchased from Alfa Aesar Corp. and Aldrich Corp., and were all analytical grades without special treatment.

2.2. Synthesis of (Pd(IMes)Cl$_2$)$_2$ catalyst

2.2.1. Synthesis of glyoxal-bis (2,4,6-trimethylphenyl)-imine

Typical procedures: 2,4,6-Trimethylaniline (2.7042 g, 0.02 mmol) and *n*-propanol (12 mL) were added to a three-neck flask, into which a mixture of 40% glyoxal (0.01 mol, 1.4510 g), 8 mL *n*-propanol and 4 mL water was then slowly added. After 4 h of reaction at 25 °C and another 2 h of reaction at 60 °C, the reactants were removed into ice water to allow full evaporation. The precipitate was collected by filtration, thoroughly washed with *n*-propanol and then dried in vacuum with a yield of 71.2% (2.0790 g). The products were identified on the basis of ^{1}H NMR and ^{13}C NMR spectral data.

^{1}H NMR (CDCl$_3$): δ 2.19 [s, 12H, *ortho*-CH$_3$], 2.32 [s, 6H, *para*-CH$_3$], 6.93 [s, 4H, *meta*-CH], 8.13 [s, 2H, CH]. ^{13}C NMR (CDCl$_3$): δ 18.2 [s, *ortho*-CH$_3$], 20.7 [s, *para*-CH$_3$], 126.5 [s, *ortho*-C], 128.9 [s, *meta*-C], 134.1 [s, *para*-C], 147.4 [s, *ipso*-C], 163.0 [s, HC=N].

2.2.2. Synthesis of IMes·HCl

Typical procedures: The above obtained glyoxal-bis(2,4,6-trimethylphenyl)-imine (0.4382 g, 1.50 mmol) was added to a three-neck flask, degassed by three freeze-pump-thaw cycles, and purged with argon. Afterwards, 5 mL THF was added to the flask via a syringe until the solid completely dissolved at 45 °C. Then chloromethyl ethyl ether and 1 mL THF were dropwise added to the flask after the temperature was cooled to 15 °C. Finally, the reactants were stirred at 20 °C for 1 h. After reaction, the precipitate was collected by filtration, thoroughly washed with THF and then dried in vacuum with a yield of 62.0% (0.3169 g). The obtained solid was characterized as N,N-(2,4,6-trimethylphenyl) imidazolium chloride (IMes·HCl) on the basis of ^{1}H NMR spectral data.

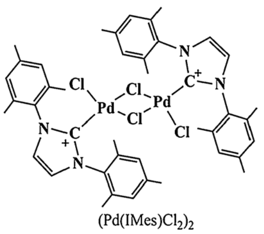

Fig. 1. Structure of (Pd(IMes)Cl$_2$)$_2$.

^{1}H NMR (CDCl$_3$): δ 2.08 [s, 12H, *ortho*-CH$_3$], 2.27 [s, 6H, *para*-CH$_3$], 6.95 [s, 4H, *meta*-CH], 7.61 [s, 2H, im-H$^{4.5}$], 10.06 [s, 1H, im-H^2].

2.2.3. Synthesis of (Pd(IMes)Cl$_2$)$_2$ catalyst

Potassium *tert*-butoxide (33.6 mg, 0.30 mmol), potassium chloride (44.7 mg, 0.60 mmol), palladium acetate (27.0 mg, 0.12 mmol) and IMes·HCl (102.0 mg, 0.30 mmol) were added to a three-neck flask which had been purged thoroughly with argon. Deoxygenated, anhydrous THF (12 mL) was added via a syringe under stirring, and the solution was heated at reflux for 16 h after all the reaction reagents dissolved. After reaction, the solution was evaporated under argon at 30 °C, and the orange red solid complex was purified by silica gel chromatography (Et$_2$O/hexanes, 1:1) with a yield of 38%. The products were identified on the basis of ^{1}H NMR, ^{13}C NMR and MS spectral data (Fig. 1).

(Pd(IMes)Cl$_2$)$_2$: MS: *m*/*z* 964; ^{1}H NMR (CDCl$_3$): *δ* 6.85 [s, 4H], 6.13 [s, 4H], 2.31 [s, 12H], 2.05 [s, 24H]; ^{13}C NMR (CDCl$_3$): δ 18.5 [ortho-CH$_3$], 21.6 [para-CH$_3$], 121.3 [C=C], 127, 136.1, 136.9, 137.3 [aryl-C], 195.3 [N—C—N]; Elemental analyses: C, H, Cl, N and Pd was 52.45, 4.98, 14.65, 5.88, and 22.04 wt% respectively.

2.3. Synthesis of MnP-AMP

A mixture of (Pd(IMes)Cl$_2$)$_2$ (96.4 mg, 0.10 mmol), T(p-Br)PPMnCl (100.2 mg, 0.10 mmol), *p*-phenylenediamine (27.0 mg, 0.25 mmol), potassium *tert*-butoxide (56.0 mg, 0.50 mmol) and anhydrous m-xylene (8 mL) was added to a reaction flask, degassed by three freeze-pump-thaw cycles, purged with argon, and stirred

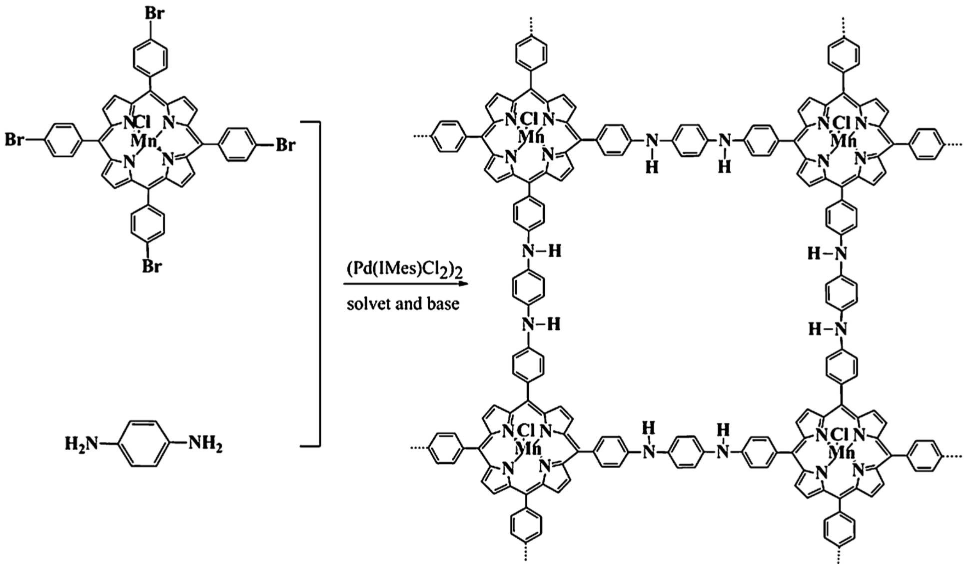

Fig. 2. Schematic representation of the synthesis of MnP-AMP.