Supplementary Material (ESI) for New Journal of Chemistry

SUPPLEMENTARY MATERIAL

Novel polymer-supported ruthenium and iron complexes that catalyze the conversion of epoxides into diols or diol mono-ethers: clean and recyclable catalysts

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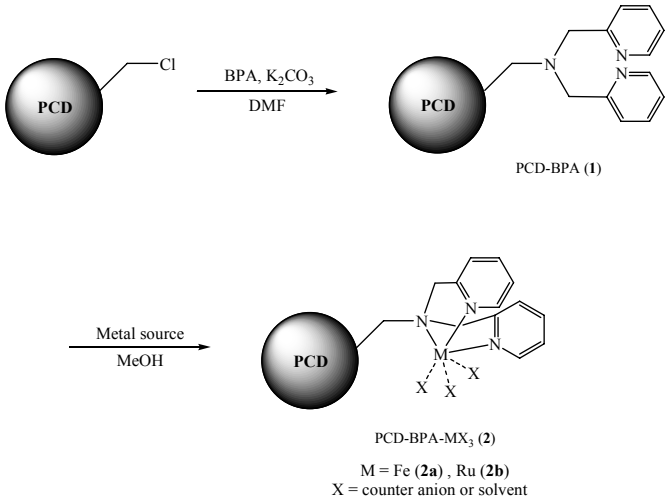
Synthesis and physical properties of poly(chloromethylstyrene-co-divinylbenzene) (PCD) : This polymer was obtained by suspension copolymerization of chloromethylstyrene (7:3 mixture of *m* and *p* isomers) and divinylbenzene with benzoyl peroxide in the presence of cyclohexane and poly(vinyl alcohol) in water as described previously.[1] The crosslinking ratio was about 1% based on the quantity of divinylbenzene as a crosslinker. Actually, the polymer bead named as Merrifield's resin can be obtained from chemical company such as Aldrich. The mesh size was very broad from several μm to several hundred μm. We picked up polymer beads having 200~300 μm diameter by sieve (80~150 mesh). The underivatized chloromethyl groups were uncapped. The PCD was not swollen well in DMF, and thus it may not be porous. The underivatized chloromethyl groups were inside the polymer beads. They could be substituted from the other group in the status of swelling of beads. However, since the polymer bead was not swollen in solvents such as DMF and alcohols that we used, the residual chloromethyl group could not be substituted from picoline residues.



Scheme S1. Synthesis of PCD supported BPA-metal catalysts

Attachment of Bis(2-picolyl)amine(BPA) to PCD, PCD-BPA (1) : The mixture of PCD (0.540 g), bis(2-picolyl)amine (0.917 g, 4.6 mmol), and K_2CO_3 (0.829 g, 6 mmol) in 20 mL DMF was shaken under 50□ for 12 hr. The solid product was filtered and washed with DMF (2 hr with 10 mL), water (2 hr with 10 mL), and acetone (2 hr with 10 mL). Then, it was further washed with acetonitrile (40 mL) for 1 day by shaking to give a yellow solid.

From the elemental analysis result for PCD-BPA (wt%, C 77.02, H 6.41, N 9.06), we can calculate the Cl portion to be 7.49 because PCD-BPA consists of C, H, N, and Cl.

Element	Carbon	Hydrogen	Nitrogen	Chlorine
Wt %	77.02	6.41	9.06	7.49

Because PCD-BPA was prepared by treating PCD and BPA, all the nitrogen detected should come from BPA (Calculated percentages of each elements in BPA are C, 72.33; H, 6.58; N, 21.09). From above table, therefore, elemental contributions of C, H, and N from BPA can be subtracted to give the contributions from PCD.

Element	Carbon	Hydrogen	Nitrogen	Chlorine
Attached BPA portion	31.07	2.83	9.06	0
PCD portion	45.95	3.58	0	7.49

Theoretically, the number ratio of C, H, Cl in PCD is 9 : 9 : 1. The number ratio of C : Cl in PCD-BPA is calculated from wt% (45.95/12.011 : 7.49/35.5) as 9 : 0.495, showing about 49.5% of initial chloromethyl site remained and 50.5% of chloromethyl site is substituted by BPA ligand. Incomplete substitution may be due to the steric bulkiness of BPA compound.

Determination of amount of BPA in 1: The PCD-BPA bead (**1**) consists of Cl-methyl styrene and BPA-methyl styrene. Molecular weights of Cl-methyl styrene and BPA-methyl styrene are 152.67 g/mol and 315.43 g/mol, respectively. In the 1 g of PCD-BPA (**1**), the weight portion of BPA-methyl styrene is 1 g x 315.43/(152.67+315.43) = 0.674 g. Therefore, the 1 g of PCD-BPA (**1**) contains BPA sites of 2.14 mmol (0.674g/315.43g/mol = 2.14 mmol).

Loading of Fe or Ru ions into BPA ligand, PCD-BPA-M (2): PCD-BPA (100 mg; 0.214 mmol for BPA sites) and ten times excess amount of iron(III) perchlorate (779 mg, 2.2 mmol) or $RuCl_3$

(456 mg, 2.2 mmol) were mixed in 30 ml of MeOH and the mixture was shaken for 12 hr at room temperature. The solid product was filtered and washed with MeOH (twice for 12 hr with 30 mL), H_2O (1 hr with 30 mL), and acetone (2 hr with 30 mL), and then air-dried to give a greenish-yellow solid of PCD-BPA-Fe(ClO_4)$_3$ (**2a**) and a black solid for PCD-BPA-$RuCl_3$ (**2b**), respectively.

Determination of amount of metals in 2: 10 mg of **2** was dissolved in a mixture of HNO_3 (3 mL) and HCl (9 mL), and heated to 100 ^oC for 12 hr. The solution was cooled down to room temperature and filtered to remove the unresolved materials. The filtrate was transferred to a volumetric flask and water was added to make 100 mL. Based on the standard solution (0.01, 0.1, 1, and 10 ppm) with ICP Spectrometer, the amount of metals in **2** was determined to be 0.0565 mmol for Fe (**2a**; 26 % of BPA) and 0.0260 mmol for Ru (**2b**; 12 % of BPA), respectively.

Reference

[1] B.-B. Jang, K.-P. Lee, D.-H. Min and J. Suh, *J. Am. Chem. Soc*., 1998, **120**, 12008.