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PAPER
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Journal Name

COMMUNICATION

Preparation of Bispyridine based Porous Organic Polymer as a New Platform for Cu(II) Catalyst and Its Use in Heterogeneous Olefin Epoxidation

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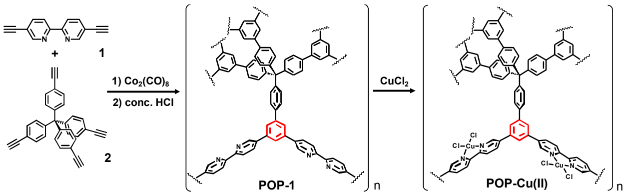
New class of bispyridine (bpy) incorporated POP was prepared via a cobalt-catalyzed acetylene trimerization. Subsequent immobilization of $CuCl_2$ gave POP-Cu(II). This new heterogeneous catalyst displayed outstanding olefin oxidation activity compared to its homogeneous analogue, suggesting that degradation of homogeneous catalysts was successfully inhibited by site isolation.

Preparation of epoxides via olefin oxidation has become one of the most important research areas because the formation of a carbon-oxygen bonding is a very critical process for the production of various fine chemicals and industrial polymers.[1] Although olefin oxidation using stoichiometric amount of toxic reagents such as peracids has been one of the most widely used synthetic methods, potentially explosive and toxic wastes are inevitably produced.[2] Therefore, research efforts have been focused on using transition metal catalysts such as vanadium,[3] manganese,[4] iron,[5] and copper.[6] Such transition metal-based catalysts have demonstrated great potentials with high selectivity and efficiency, but they usually suffer from low stability and separation.[7] Therefore, a new class of catalyst such as heterogeneous system with excellent stability and efficiency is urgently needed. Current research efforts are focused on the development of efficient heterogeneous catalysts.

In this regard, the immobilization of molecular catalysts onto solid supports has attracted much attention,[8] including utilization of well-defined porous solids such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and porous organic polymers (POPs) due to their high surface areas and great structural versatility.[9] In addition, these porous materials may offer a highly tunable platform for various single-site catalytic reactions.[10] Because immobilization of molecular catalysts using traditional catalyst supports often encounters difficulty in maximizing their potential,[11] well-controlled catalyst supports are essential for the development of practical catalysts. Well-defined porous materials have recently considered as one of the most promising methods.[12] Particularly, POPs have become very attractive hybrid supports for various applications despite they have no uniform pores that make it difficult to analyze their structures via X-ray crystallographic studies. This is because POPs have strong covalent bonds, thus providing good chemical stability.[13]

Herein, we report the preparation of bispyridine (bpy) containing POPs and immobilization of $CuCl_2$ complex to fabricate a new heterogeneous catalytic system incorporating (bpy)$CuCl_2$ units for oxidation of various olefins. Of various transition metal-based catalytic systems, Cu based system is of particular interest when taking economic considerations into account, although it has inherently low catalytic activity.[14]

Scheme 1. Preparation of **POP-1** and **POP-Cu(II)**.



New POP incorporated with (bpy)$CuCl_2$ units, **POP-Cu(II)**, can be prepared following modified literature procedure.[15] A cobalt-catalyzed acetylene trimerization copolymerizes 5,5'-diethynyl-2,2'-bipyridine (**1**) and tetra(4-ethynylphenyl)-methane (**2**) to form robust **POP-1**. Subsequent metalation with $CuCl_2$ gives **POP-Cu(II)** (Scheme 1, see Supporting Information (ESI) section for detailed experiments and characterizations). To optimize the copolymerization, various reaction conditions were tested. Two-to-one molar ratio of monomers **1** (69 mg) and **2** (70 mg) in a freshly distilled 1,4-dioxane (15 mL) afforded **POP-1** in high yield (96%), with a

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surface area of about 812 m^2/g and a mean pore diameter of 5.3 nm. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) study indicated that **POP-1** showed negligible amount of Co content (0.1 wt.%) and that cobalt catalyst was successfully removed after washing with HCl solution. Interestingly, when the reaction concentration was doubled by reducing the reaction solvent in half, **POP-2** with a surface area of 659 m^2/g and a mean pore diameter of 6.1 nm was quickly formed within a few minutes (Scheme S2 and Table S1 in ESI). Low solubility of oligomeric intermediates in high reaction concentration might have quickly afforded highly branched polymers with low surface area. On the other hand, when the reaction was conducted with low reaction concentration by tripling the solvent amount, **POP-3** was afforded with very low product yield (5 %) with longer reaction time (~72 h) required. It showed a surface area of 760 m^2/g and a mean pore diameter of 4.9 nm (Fig. S1 and Table S2 in ESI).

Infrared (IR) and solid state nuclear magnetic resonance (NMR) spectroscopic analysis can clearly confirm the formation of polymer.[16] In IR analysis, stretches of terminal alkynes at 3300 cm^{-1} are strongly reduced compared to those of its parent monomers, strongly suggesting that acetylene trimerization has taken place (Fig. 1). In the ^{13}C-CPMAS NMR spectrum, a peak for quaternary carbon of tetraphenylmethane moiety appeared at 64 ppm. Several overlapping peaks between 120-150 ppm were associated with aromatic carbons. No peak for the terminal alkyne was observed around 80 ppm (Fig. S2 in ESI). Results of NMR along with IR studies strongly support near-completion of acetylene trimerization.[17]

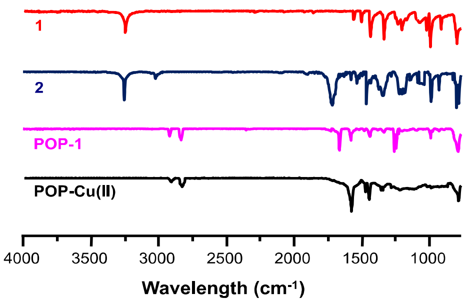

Fig. 1. FT-IR spectra of **1, 2, POP -1,** and **POP-Cu(II)**.

Subsequent metalation of **POP-1** with a solution of CuCl$_2$ in distilled DMF afforded **POP-Cu(II)** in high yield (83 %) with a surface area of 462 m^2/g. The small decrease in specific surface area is consistent with the addition of CuCl$_2$ by metalation (Table S2 in ESI). ICP-AES analysis of digested **POP-Cu(II)** indicated Cu content of 8.3 wt.%.

To investigate thermal stabilities of polymers, thermogravimetric analysis (TGA) was performed. As shown in Fig. S3 in ESI, they are thermally stable up to 300 °C with small continuous weight loss at low temperature region due to free solvent molecules. The thermal decomposition range is slightly broadened due to collapse of polymer networks caused by degradation of irregular network structures.[18]

Liquid phase catalytic oxidation of various olefins was carried out. Briefly, a solution of olefin (1.2 mmol), *tert*-butyl hydroperoxide (TBHP, 70 % solution in water, 0.17 mL, 1.2 mmol), and acetonitrile (1 mL) was stirred at 85 °C with 2 mg of **POP-Cu(II)** (2.6 μmol of Cu) in powder form. The progression of reaction was monitored by using a gas chromatography with a flame ionization detector (GC-FID). Dodecane was used as an internal standard and TBHP was chosen as an oxidant. Various olefins were tested as shown in Table 1.

Table 1. Investigation of olefin epoxidation by **POP-Cu(II)**[a,b,c]

Entry	Substrate	Conversion (%)[d]	TON[e,f]
1	cyclooctene	80.2 ± 6.3	373 ± 20
2	cyclohexene	92.5 ± 6.1	431 ± 17
3	cyclopentane	91.2 ± 6.7	436 ± 23
4	1-octene	78.8 ± 5.3	365 ± 12
5	1-hexane	75.7 ± 6.2	351 ± 18
6	styrene	96.7 ± 2.8	447 ± 9
7	*cis*-stilbene	42.8 ± 5.4	195 ± 12
8	*trans*-stilbene	33.4 ± 5.6	154 ± 14

[a]Reaction conditions; Olefin (1.2 mmol), **POP-Cu(II)** 2 mg (2.6 μmol of Cu), TBHP 0.17 mL (70 % in H$_2$O), acetonitrile 1 mL, 85 °C. [b]Conversions were quantified by GC-FID and dodecane was used as internal standard. [c]Standard deviations are based on four runs. [d]Conversion is based on olefin consumption towards products. [e]TON = mmol product/mmol catalyst. [f]The products; 2-cyclohexene-1-one (cyclohexene), 2-cyclohexene-1-ol (cyclohexene), phenylacetaldehyde (styrene), phenylacetaldehyde (styrene), benzaldehyde (styrene), 2-phenylacetophenone (*cis*- and *trans*-stilbene), epoxides (all substrates) and unidentified products.

POP-Cu(II) was found to be a good catalyst for most olefins, generating oxide products. In the reaction of cyclooctene (entry 1), the conversion rate after 24 h of reaction period reached about ~80 % while cyclohexene (entry 2) and cyclopentane (entry 3) gave higher conversion rates of 93% and 91 %, respectively. Clearly, cyclohexene is more reactive than other cycloolefins with **POP-Cu(II)** because of its better diffusion profile.[19] In cases of 1-octene (entry 4) and 1-hexene (entry 5), the reaction showed conversion rates of ~79% and ~76 %, respectively, whereas oxidation of styrene (entry 6) gave a conversion rate of ~97 %. Variation in conversion rate might be due to conformation of double bond. In cyclo-olefins, both double bond epoxidation and allylic oxidation may occur simultaneously. Since cyclohexene contains a double bond located in the plane of allylic carbons (Fig. S4 in ESI), it might have facilitated oxidation at all positions, resulting in high conversion. In case of cyclooctene, the double bond is located at different plane from other carbons[20] which is presumably responsible for the relatively lower conversion. For styrene, although the reaction would

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take place primarily only at the double bond with low conversion since there is no allylic hydrogen, it is highly activated in the presence of phenyl ring. In addition, highly opened reaction site might have facilitated catalyst access, resulting in high conversion.[20] In case of linear olefins, relatively low conversion is probably due to its steric hindrance arisen from long alkyl chain.[21] Size-selectivity was also found when bigger substrates were employed (entry 7 and 8). Access to metal centers of the larger olefins might have been less facilitated due to structural disadvantage, resulting in smaller conversion found in *trans*-stilbene.

It is expected that the reaction would proceed via formation of copper-peroxo species using TBHP as an oxidant.[22] As shown in Fig. S5 in ESI, the activation of catalytic Cu-site by TBHP may follow Haber-Weiss-type decomposition process. Both *t*-BuO and *t*-BuOO are possible reactive species responsible for olefin oxidations.[23] Further study was carried to investigate the function of oxidant. The oxidations were carried out with the addition of diphenylamine as a radical inhibitor (Table S3 in ESI). Conversions were decreased significantly, supporting that *t*-BuO and *t*-BuOO might be effectively consumed by radical inhibitor before catalytic oxidation takes place.[24]

As a control, the reaction mixture was investigated by removing all solid suspension after the reaction was completed in order to verify the stability of **POP-Cu(II)**.[25] No leaching of catalysts into reaction solution was found after performing the ICP-AES study, showing a negligible amount of Cu content (0.02 wt.%). Encouraged by this result, catalyst reusability was tested. After each reaction cycle, the catalyst was isolated, washed three times with methanol in air, dried at room temperature, and reused for the next run. Remarkably, it showed no significant catalytic activity change even after five times of re-use (Table 2). It also retained its morphology after multiple catalytic reactions. This was confirmed by SEM analysis (Fig. S6 in ESI).

Table 2. Investigation of the recyclability of styrene oxidation[a,b,c]

Cycle	Conversion (%)[d]	TON[e]
1	96.3 ± 3.8	446 ± 12
2	94.0 ± 3.5	437 ± 10
3	95.2 ± 6.2	438 ± 25
4	95.8 ± 3.6	441 ± 9
5	94.5 ± 3.5	438 ± 10

[a] Reaction conditions; Styrene (0.14 mL,1.2 mmol), POP-Cu(II) 2 mg (2.6 μmol of Cu), TBHP 0.17 mL (70 % in H_2O), acetonitrile 1 mL, 85 °C. [b] Conversions were quantified by GC-FID and dodecane was used as internal standard. [c] Standard deviations are based on three runs of POP-Cu(II). [d] Conversion is based on olefin consumption towards products. [e] TON = mmol product/mmol catalyst. [f] The products; phenylacetaldehyde, benzaldehyde, epoxide, and unidentified products.

For a further control, molecular catalyst (bpy)$CuCl_2$ was prepared[26] and its catalytic activity in styrene oxidation was compared with **POP-Cu(II)** using identical reaction conditions. However, oxidation with (bpy)$CuCl_2$ did not proceed as effective as that with **POP-Cu(II)**. Although the initial catalytic activity of (bpy)$CuCl_2$ was greater than that of **POP-Cu(II)**, it was slowly reduced after 5 h of the reaction time. No further reaction took place after 8 h. This might be due to deactivation of homogeneous catalyst by the formation of less active dimer and/or aggregated species[27] and oxidation of ligand.[28] Thus, successful site isolation strategy via immobilization of catalysts is effective for obtaining higher catalytic activity and stability. Immobilization of $CuCl_2$ might be able to facilitate the accessibility of substrate to catalytically active centers while reducing the potential of catalyst deactivation process.[29]

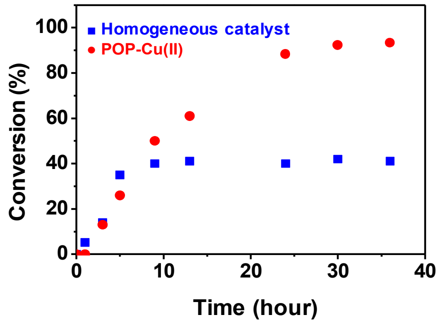

Fig. 2. Comparison of conversions and catalytic stability of **POP-Cu(II)** (red) and its homogeneous analogue (bpy)$CuCl_2$ (blue). Molar ratio of styrene:oxidant:catalyst = 670:670:1, 85 °C. *tert*-Butyl hydroperoxide was used as an oxidant.

In summary, we prepared a new class of heterogeneous catalytic porous organic polymer, **POP-Cu(II)**, based on incorporation of (bpy)$CuCl_2$ unit into **POP-1** made of 5,5'-diethynyl-2,2'-bipyridine (**1**) and tetra(4-ethynylphenyl)methane (**2**) via cobalt-catalyzed acetylene trimerization. The employment of heterogeneous catalyst, **POP-Cu(II)**, for oxidation of various olefins was successfully demonstrated. Particularly, **POP-Cu(II)** showed outstanding catalytic activity compared to its homogeneous analogue, suggesting that degradation of catalysts via oxidation of ligand and aggregation of active catalysts was successfully inhibited or substantially reduced by effective site isolation via immobilization of catalysts on POP based platform. Finally, this heterogeneous catalyst showed good re-usability without significant losing its activity.

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Conflicts of interest

There are no conflicts to declare.

References

1 (*a*) K. C. Gupta and A. K. Sutar, *Cood. Chem. Rev.*, 2008, **252**, 1420.; (*b*) B. S. Lane and K. Burgess, *Chem. Rev.*, 2003, **103**, 2457.

2 A. S. Sharma and H. Kaur, *Appl. Catal. A Gen.* 2017, **546**, 136.

3 C. Cordelle, D. Agustin, J.-C. Daran and R. Poli, *Inorganica Chim. Acta* 2010, **364**, 144.

4 J. Brinksma, R. Hage, J. Kerschner and B. L. Feringa, *Chem. Commun.,* 2000, 537.

5 F. G. Gelalcha, B. Bitterlich, G. Anilkumar, M. K. Tse and M. Beller, *Angew. Chem. Int. Ed.*, 2007, **46**, 7293.

6 R. Bera, C. Adhikary, S. Ianelli, S. Chaudhuri and S. Koner, *Polyhedron*, 2010, **29**, 2166.

7 L. Yin and L. Liebscher, *J. Chem. Rev.*, 2007, **107**, 133.

8 (*a*) K. Ariga, Y. Yamauchi, G. Rydzek, Q. Ji, Y. Yonamine, K. C.-W. Wu and J. P. Hill, *Chem. Lett.*, 2014, **43**, 36.; (*b*) R. Cai, X. Ye, Q. Sun, Q. He, Y. He, S. Ma and X. Shi, *ACS Catal.,* 2017, **7**, 1087; *(c)* S. Fukuzumi, Y.-M. Lee, W. Nam, *ChemCatChem*, 2018, **10**, 1686.

9 (*a*) S. Furukawa, J. Reboul, S. Diring, K. Sumida and S. Kitagawa, *Chem. Soc. Rev.*, 2014, **43**, 5700.; (*b*) T. Yamada, K. Otsubo, R. Makiura and H. Kitagawa, *Chem. Soc. Rev.*, 2013, **42**, 6655.; (*c*) A. Schneemann, B. Bon, I. Schwedler, I. Senkovska, S. Kaskel and R. A. Fischer, *Chem. Soc. Rev.*, 2014, **43**, 6062.; (*d*) C. K. Brozek and M. Dincă, *Chem. Soc. Rev.*, 2014, **43**, 5456.

10 A. Corma, H. García and F. X. L. Xamena, *Chem. Rev.*, 2010, **110**, 4606.

11 (*a*) L.-X. Dai, *Angew. Chem. Int. Ed.,* 2004, **43**, 5726.; (*b*) D. C. Bailey and S. H. Langer, *Chem. Rev.*, 1981, **81**, 10.

12 (*a*) H. G. T. Nguyen, M. H. Weston, A. A. Sarjeant, D. M. Gardner, Z. An, R. Carmieli, M. R. Wasielewski, O. K. Farha, J. T. Hupp and S. T. Nguyen, *Cryst. Growth Des.*, 2013, **13**, 3528.; (*b*) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105.

13 (*a*) P. Kaur, J. T. Hupp and S. T. Nguyen, *ACS Catalysis*, 2011, **1**, 819.; (*b*) J. Weber, J. Schmidt, A. Thomas and W. Böhlmann, *Langmuir*, 2010, **26**, 15650.

14 S. E. Allen, R. R. Walvoord, R. P. Salinas and M. C. Kozlowski, *Chem. Rev.,* 2013, **113**, 6234.

15 M. H. Weston, Y. J. Colón, Y.-S. Bae, S. J. Garibay, R. Q. Snurr, O. K. Farha, J. T. Hupp and S. T. Nguyen, *J. Mater. Chem. A*, 2014, **2**, 299.

16 Z. Xie, C. Wang, K. E. deKrafft and W. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 2056.

17 R. K. Totten, Y.-S. Kim, M. H. Weston, O. K. Farha, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2013, **135**, 11720.

18 A. Dani, V. Crocellà, C. Magistris, V. Santoro, J. Yuan and S. Bordiga, *J. Mater. Chem. A*, 2017, **5**, 372.

19 Q. Zhao, C. Bai, W. Zhang, Y. Li, G. Zhang, F. Zhang and X. Fan, *Ind. Eng. Chem. Res.*, 2014, **53**, 4232.

20 M. Sarkheil and M. Lashanizadegan, *Appl. Organometal. Chem.*, 2017, **31**, 3726.

21 M. Masteri-Farahani, F. Farzaneh and M. Ghandi, *J. Mol. Catal. A.: Chem.*, 2006, **248**, 53.

22 J. Sun, Q. Kan, Z. Li, G. Yu, H. Liu, X. Yang, Q. Huo and J. Guan, *RSC Adv.*, 2014, **4**, 2310.

23 L. Saussine, E. Brazi, A. Robine, H. Mimoun, J. Fischer and R. Weiss, *J. Am. Chem. Soc.*, 1985, **107**, 3534.

24 (a) U. Junghans, C. Suttkus, J. Lincke, D. Lassig, H. Krautscheid and R. Glaser, *Micropor. Mesopor. Mater.*, 2015, **216**, 151.; (b) F. Farzaneh, J. Taghavi, R. Malakooti and M. Ghandi, *J. Mol. Catal. A: Chem.*, 2006, **244**, 252.

25 D. H. Lee, S. Kim, M. Y. Hyun, J.-Y. Hong, S. Huh, C. Kim and S. J. Lee, *Chem. Commun.*, 2012, **48**, 5512.

26 D. A. Martins, L. R. Gouvea, D. Gama Jean Batista, P. B. Silva, S. R. W. Louro, M. N. C. Soeiro and L. R. Teixeira, *Biometals*, 2012, **25**, 951.

27 A. Schiller, R. Scopelliti and K. Severin, *Dalton Trans.*, 2006, 3858.

28 S. Kim, K. Y. Lee, Y. S. Lee, H. G. Jang, J. K. Lee and S. J. Lee, *J. Porphyrins Phthalocyanines* 2014, ***18***, 579.

29 K. Manna, T. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 6566.

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Preparation of Bispyridine based Porous Organic Polymer as a New Platform for Cu(II) Catalyst and Its Use in Heterogeneous Olefin Epoxidation

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