

Self-Assembled Poly(imidazole-palladium):

Highly Active, Reusable Catalyst at Parts per Million to Parts per Billion Levels

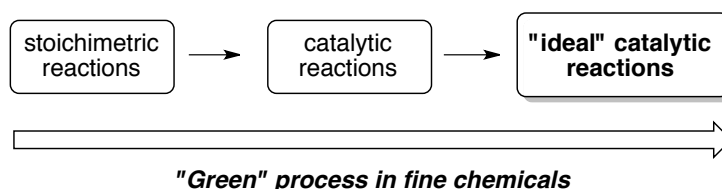
Yamada, Y. M. A.; Sarkar, S. M.; Uozumi, Y. *J. Am. Chem. Soc.*, **2012**, *134*, 3190–3198.

1. Introduction

1-1. “Ideal” catalytic reactions, desired in industrial synthesis

- A goal of chemical process: no waste, low cost and energy, no toxicity => “Green Chemistry”

• Metal-catalyzed reactions (i. e. C–C, C–N bond formation) are extensively used and fundamental process in fine chemicals, but contamination of metals to the product, instruments, is sometimes problem.



“Ideal” catalyst: Easy to remove, low amount (TON, TOF), highly active, recyclable, can be used in water

1-2. Heterogeneous catalysts

- ◆ Recently heterogeneous catalyst has been expected to contribute for achieving “Green Process”.

- Recent developments of heterogeneous catalysis: How to immobilize metal catalyst on a support?

a) Solid-supported metal

- C, Si, HAP (hydroxyapatite) can be used as support.
- Easy to separate from reaction mixture

b) Crosslinked (交差架橋) polymer-supported metal

- PS (polystyrene)-supported Pd is commercially available (Figure 1)

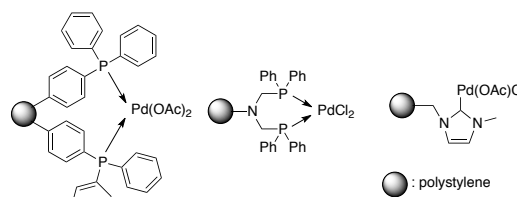


Figure 1. PS-supported catalysts

- Ligand coordination => Better stability

c) Palladium nanoparticle (PdNP)-coated hollow spheres¹

- Recyclable (at least 7 times) without loss of catalytic activity (Figure 2)

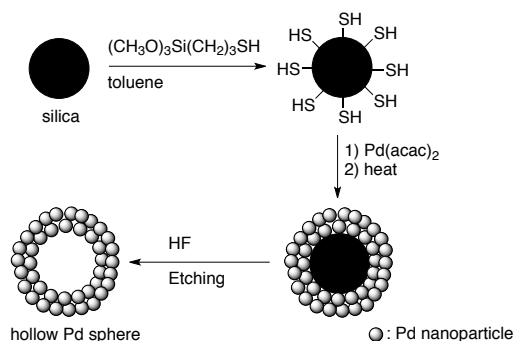


Figure 2. PdNP-coated hollow spheres

Problems:

- Less reactive compared with homogeneous one
- Hard to prepare
- Leaching, solubility, loss of catalytic activity, recyclability

In general, it is difficult to immobilize metal species (soluble) to supports (insoluble).

How can we achieve heterogeneous catalyst with high catalytic activity?

1-3. This work: Metalloenzyme-inspired *non-crosslinked* polymer: “molecular convolution”

- **Metalloenzyme**: Metal-organic hybrids of polypeptides and metal ions, formed via supramolecular chemistry (i.e. Urease, Figure 3)²

- 1) Most thermodynamically-stable manner (non-covalent, ionic, hydrogen bonds, etc.)
- 2) Peptide and metals are self-assembled by non-covalent bonds

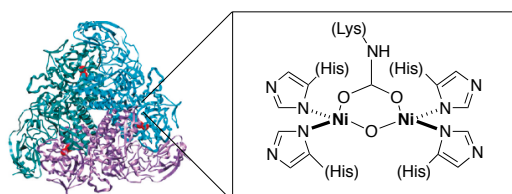


Figure 3. Structure of urease (metalloenzyme)

- The authors original method for preparing heterogeneous catalysts: **Molecular convolution (分子もつれ)**
- Non-crosslinked polymer having multiple ligand => Assembled with metals in supramolecular manner => High activity as catalyst (Figure 4)**³

They designed non-crosslinked polymer having imidazole group, and prepared metalloenzyme-inspired polymeric imidazole palladium (MEPI-Pd).

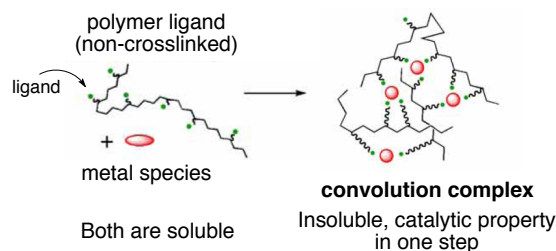


Figure 4. Molecular convolution method

2. Results and Discussion

2-1. Preparation of MEPI-Pd

- ◆ Poly-(*N*-isopropylacrylamide)-based imidazole-bearing polymer and **MEPI-Pd** was prepared (Figure 5).⁴

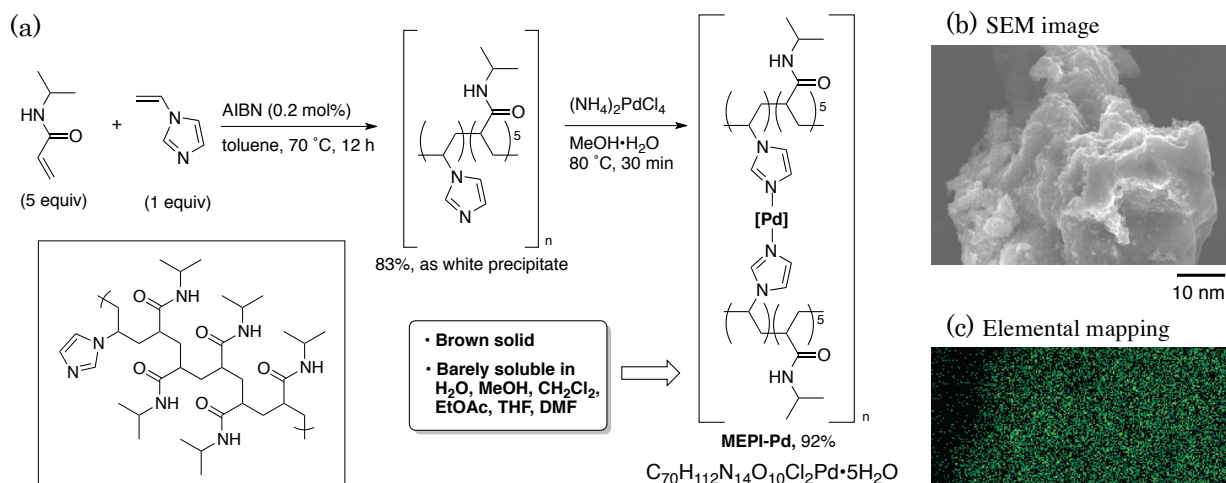
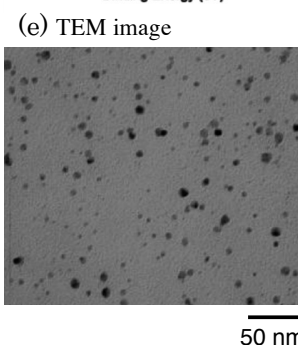
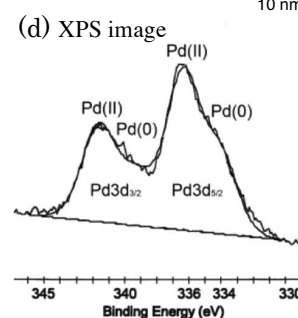


Figure 5. (a) Preparation of MEPI-Pd (b) SEM image of MEPI-Pd

(c) SEM image of elemental mapping (Pd) (d) XPS image (e) TEM image

- Easy to prepare and isolate (only filtration) (Figure 5a)
- Self-assembled, globular and porous structure (Figure 5b)
- Palladium is well dispersed (Figure 5c)
- MEPI-Pd contains Pd(II) as major species, and Pd(0) including nanoparticle as minor species (Figure 5d and 5e)
- IR measurement of C–N stretching absorption: $1548\text{ cm}^{-1} \Rightarrow 1530\text{ cm}^{-1}$
=> Imidazole unit coordinates to Pd

• **Pd should act as cross-linkers between polymeric imidazole through Pd-imidazole coordination (imidazole as Lewis base)**



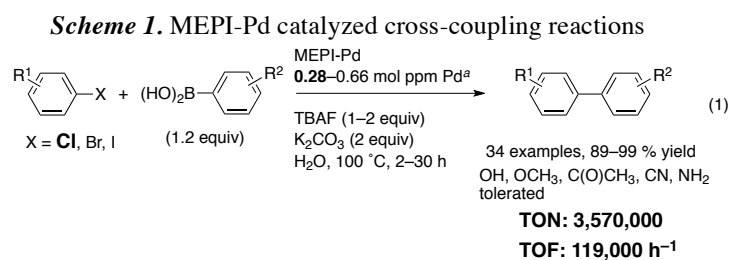
2-2. MEDI-Pd-catalyzed cross coupling reactions

◆ With MEDI-Pd, several palladium-catalyzed cross-coupling reactions were performed (Scheme 1).

(a) Suzuki–Miyaura reaction (eq. 1)

• The highest TON and TOF to date (i.e. **1000 mol** of product => **0.28 mmol** of catalyst is enough)

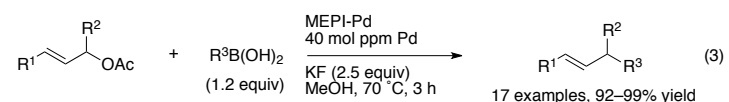
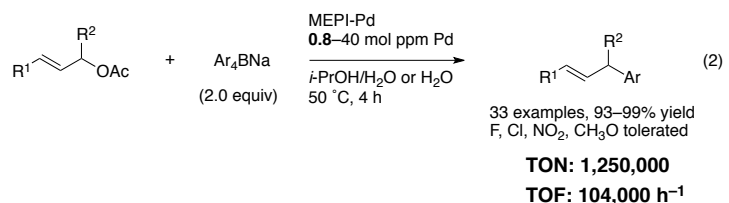
• High reactivity, broad functional group tolerance



(b) Allylic arylation/alkenylation (eqs. 2, 3)

• Little had been known for alkenes synthesis with heterogeneous catalyst.

• Highest TON and TOF was also achieved.



R³ = aryl, vinyl

^a 1 mol ppm = 10⁻⁴ mol% = 10⁻⁶ equiv

=> A variety of compounds can be prepared with MEPI-Pd.

2-3. High reactivity and recyclability of MEPI-Pd and why

1) Recyclability

MEDI-Pd can be used at least 6 times. (After 7 times: not mentioned)

eq. 1) 1st use: 99% 6th use: 99%

eq. 2) 1st use: 98% 6th use: 97%

TEM, XPS images (Figure 5d, 5e) did not changed after 6th use => Catalytic activity is not lost

2) Leaching test

• Reactions did not proceed after hot filtration.

• ICP-AES analysis (detection limit: 5 ppb of Pd) => No detection of Pd species (at least 99.95% of Pd are retained in MEPI-Pd.)

3) Efficient “dissociation–transformation–association” process

• They speculated that MEPI-Pd was formed the most thermodynamically-stable manner, which might result in high catalytic activity.

1) Imidazole unit can readily dissociate from Pd (A to B)

2) Transmetalation (B to C)

3) Imidazole unit can associate with Pd (C to A)

• Porous structure => Effective reaction field

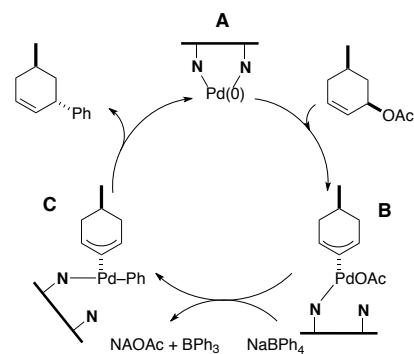


Figure 6. Plausible catalytic cycle

3. Another demonstration: Amphiphilic self-assembled polymeric copper catalyst ⁵

3-1. Preparation of the catalyst

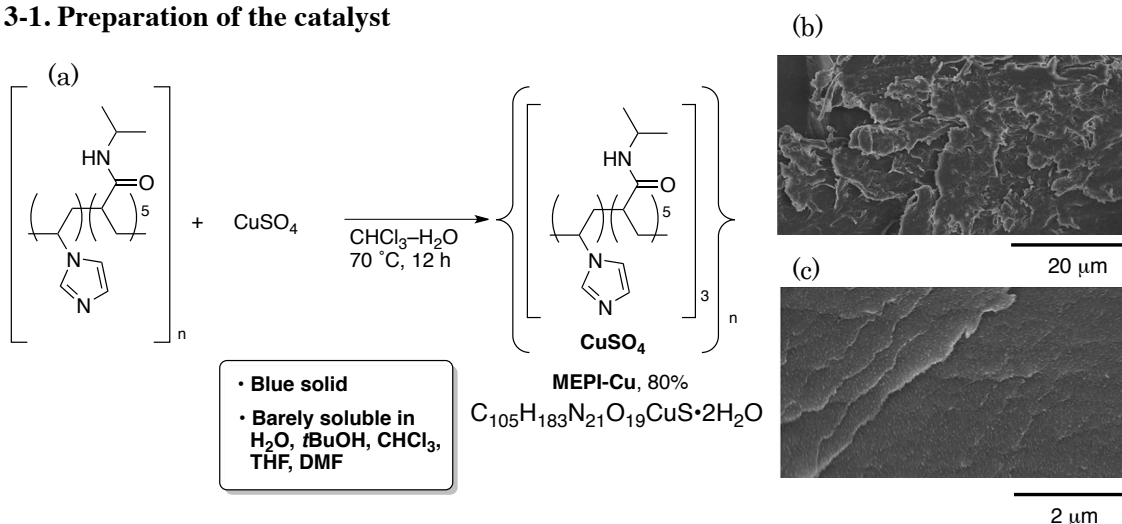
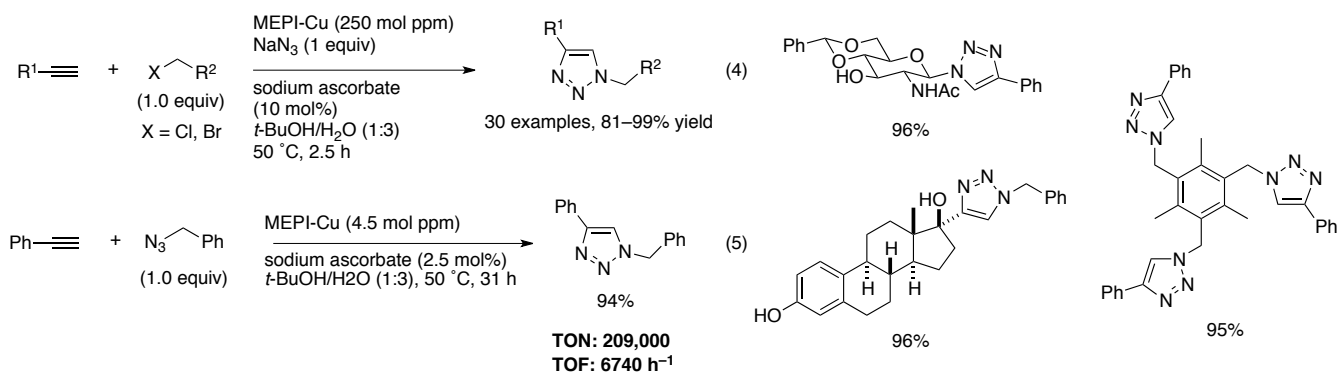


Figure 7. (a) Preparation of MEPI-Cu (b, c) SEM images of MEPI-Cu

- Sheet-like structure: different from MEPI-Pd => **Structure can be changed according to metal species.**

3-2. Application: Click chemistry

Scheme 2. MEPI-Cu catalyzed Huisgen reaction (left) and its application toward functional molecules (right)



- Highest TON and TOF was achieved with no leaching (hot filtration test and ICP), recyclability (6 times).

4. Conclusion

- Non-crosslinked polymers bearing imidazole groups can be prepared, and self-assembled with metal ions.
- They were assembled to form the most thermodynamically stable state, which results high catalytic ability.
- Highest TON, TOF, and recyclability was achieved without leaching and loss of catalytic activity.
- This flexible linkers can be also applied to copper, which assemble to form the most thermodynamically-stable manner.

(1) Kim, S.-W.; Kim, M.; Lee, W. Y.; Hyeon, T. *J. Am. Chem. Soc.* **2002**, *124*, 7642–7643.

(2) Zanbelli, B.; Musiani, F.; Benini, S.; Ciurli, S. *Acc. Chem. Res.* **2011**, *44*, 520–530.

(3) Mattiasson, B.; Kumar, A.; Ivanov, A. E.; Galaev, I. Y. *Nature Protocols*, **2007**, *2*, 213–220.

(4) Schild, H. G. *Progress in Polymer Science*, **1992**, *17*, 163–249.

(5) Yamada, Y. M. A.; Sarkar, S. M.; Uozumi, Y. *J. Am. Chem. Soc.*, **2012**, *134*, 9285–9290.