

Construction of Covalent Organic Framework for Catalysis: Pd/COF-LZU1 in Suzuki-Miyaura Coupling Reaction

San-Yuan Ding, Jia Gao, Qiong, Wang, Yuan Zhang, Wei-Guo Song, Cheng-Yong Su and Wei Wang

J. Am. Chem. Soc. **2011**, *133*, 19816–19822.

1. Introduction

1-1. Porous material as catalyst

- Porous materials, such as zeolites and metal-organic frameworks (MOFs), possess well-defined and predictable porous structures and have potential for adsorption, gas storage and catalysis.¹³
- These materials have potential as recyclable catalytic system. Indeed, catalytic use of zeolites and MOFs has been reported.²

<Problems>

- The porous structure has poor stability under the reaction conditions (MOF)
- Small pore size prevented efficient diffusion of the reactants to the reactive sites (Zeolite)

1-2. Covalent organic framework (COF)

- COF is a structurally-ordered porous organic polymer.

→ Another candidate as porous material.

- COF was predicted to have potential for catalysis, because:

- (1) Highly stable covalent structure.
- (2) Pore size can be designed.

- Imine ligands are versatile for incorporating metal ions.
- The only reported imine-linked COF was highly stable in water and most organic solvents.³

➤ Imine-linked COF was candidate as catalytic COF.

→ New imine-linked COF (COF-LZU1) was designed.

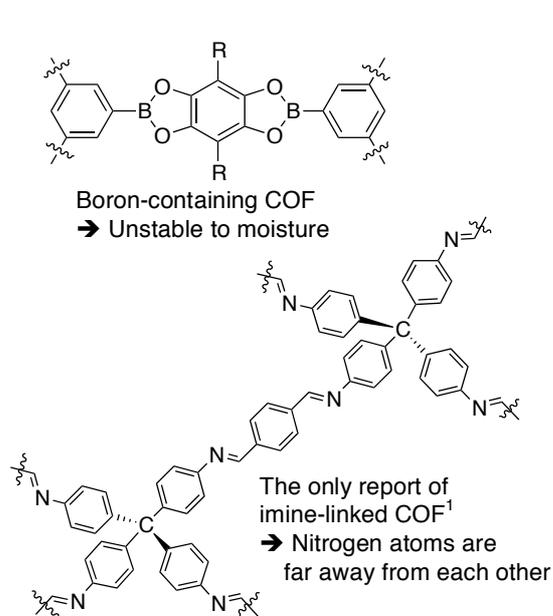


Figure 1. The structure of reported COF

1-3. This work

- Design and synthesis of new imine-linked COF
- First application of COF for catalysis

2. Results and discussion

2-1. Synthesis of COF-LZU1

- COF-LZU1 was synthesized from 1,3,5-triformylbenzene and 1,4-diaminobenzene (Scheme 1).

2-2. Identification of COF-LZU1

2-2-1. Eclipsed structure

- FT-IR spectrum indicated the existence of imine bonds.
- There are two possible structures of COF-LZU1, eclipsed structure and staggered structure.
- Powder X-ray diffraction pattern indicated the eclipsed one (Figure 2).

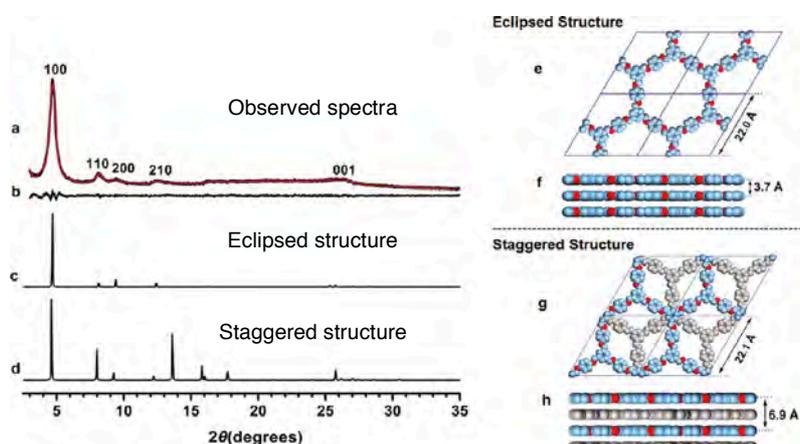


Figure 2. (a-d) Observed and calculated PXRD pattern. (e,f) Construction of eclipsed structure. (g,h) Construction of staggered structure.

2-2-2. Incorporation of Pd

- Pd/COF-LZU1 was prepared by just mixing COF-LZU1 and Pd(OAc)₂ (Scheme 1).
- By ICP analysis, the Pd content was determined as $\sim 7.1 \pm 0.5$ wt %. It corresponds to 0.5 Pd atom per unit cell.
- ¹³C CP/MAS NMR⁴ of Pd/COF-LZU1 was almost identical to that of COF-LZU1, suggesting that the porous structure was preserved well even after incorporation of Pd (Figure 3).
- Using TEM, it was found that the structure was preserved and palladium was well dispersed (Figure 4).
- According to X-ray photoelectron spectroscopy (XPS), coordination of Pd by the imine group was observed (similar to Pd/Phen) (Figure 5).

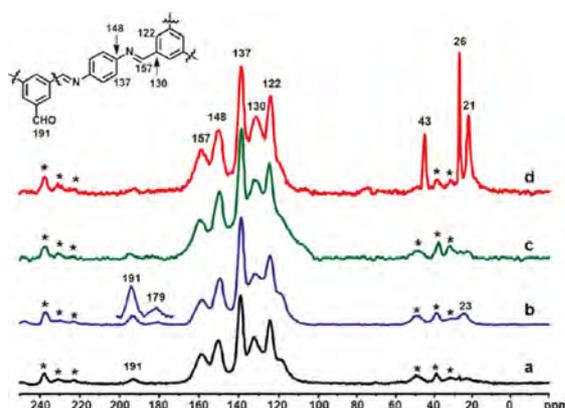


Figure 3. ¹³C CP/MAS NMR spectra of COF-LZU1 (a), Pd/COF-LZU1 (b), Pd/COF-LZU1 after the first cycle use (c) and Pd/COF-LZU1 after the fourth cycle use (d). 23 and 179 ppm (b) were assigned to the acetate group of Pd(OAc)₂.

→ Pd(OAc)₂ was supposedly located between two adjacent layers and coordinated by two nitrogen atoms (Scheme 1).

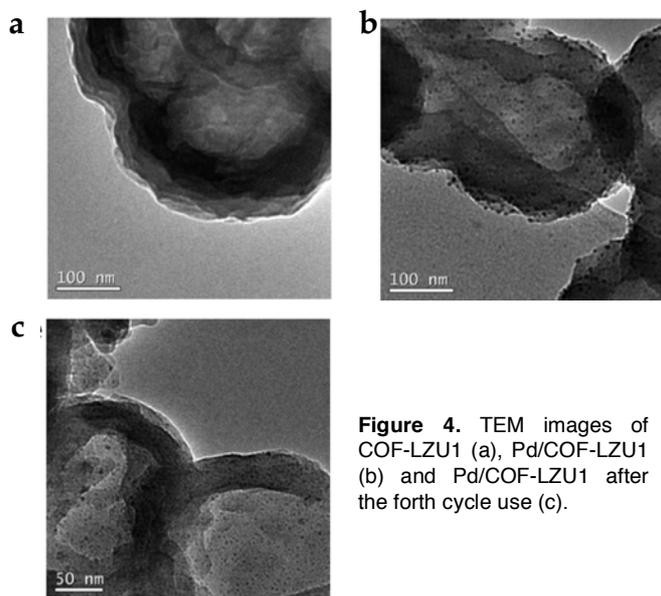


Figure 4. TEM images of COF-LZU1 (a), Pd/COF-LZU1 (b) and Pd/COF-LZU1 after the fourth cycle use (c).

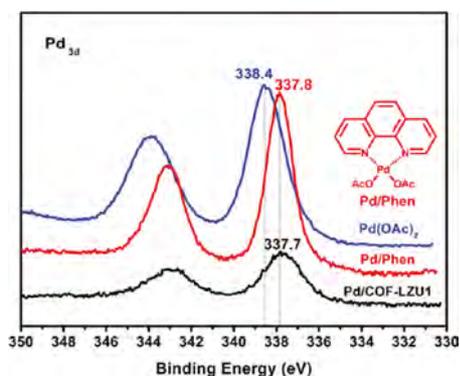


Figure 5. XPS spectra of Pd(OAc)₂, Pd/Phen and Pd/COF-LZU1.

➤ From these observations, the structures of COF-LZU1 and Pd/COF-LZU1 were proposed (Figure 6).

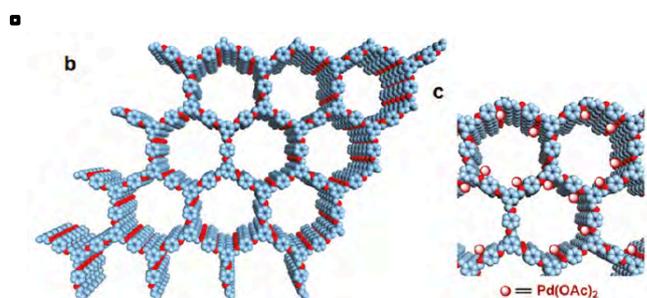
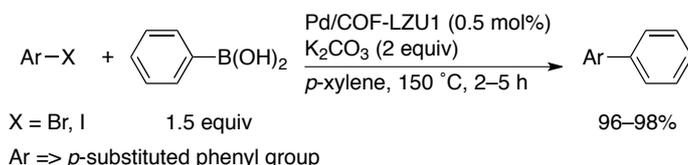


Figure 6. Proposed structure of COF-LZU1 and Pd/COF-LZU1

2-3. Suzuki-Miyaura coupling reaction catalyzed by COF-LZU1

2-3-1. Catalytic ability

- Pd/COF-LZU1 showed excellent catalytic ability (Scheme 2).
- Reactivity was high compared to Pd(II)-containing MOF (when ArX = anisyl bromide, MOF⁵ → 85%, COF → 96%).



Scheme 2. Catalytic activity test of Pd/COF-LZU1 in the Suzuki-Miyaura coupling reaction

☆ This superior reactivity may be caused by the unique structure of COF-LZU1:

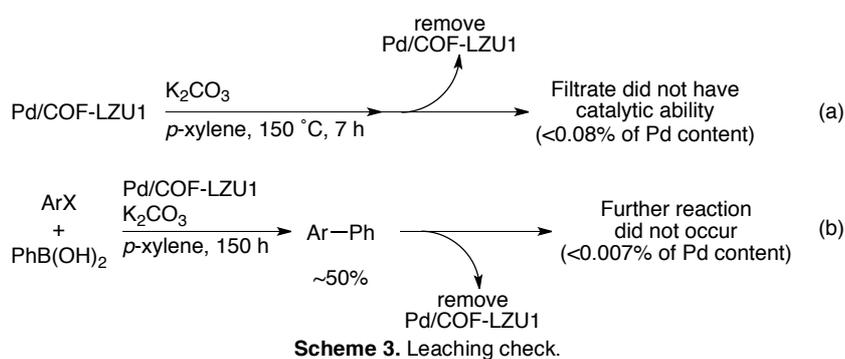
- (1) Pd was strongly coordinated by the nitrogen atoms of the imine group. This coordination ability was derived from eclipsed structure (see Scheme 1 and Figure 2).
- (2) easy access to catalytic active site because of relatively big pores (~1.8 nm, Scheme 1).

2-3-2. Leaching check

- Without reactant, the reaction mixture was stirred at 150 °C for 7 h. The filtrate could not catalyze the reaction (Scheme 3a).

- In the presence of reactants, after 50% conversion, catalyst was removed. Remaining solution did not exhibit further reactivity (Scheme 3b).

→ Coordination of COF-LZU1 to Pd was strong and trace amount of Pd leaching out could not catalyze the reaction.



2-3-3. Recycle test

- Recycling of Pd/COF-LZU1 (1 mol%) was examined.

- Catalyst could be used at least 4 times without decrease of reactivity.

- TEM showed that Pd was highly dispersed even after four cycles (Figure 4c).

- However, PXRD spectra indicated that structural regularity decreased due to the harsh conditions (Figure 7).

- In contrast, ¹³C CP/MAS NMR indicated that backbone structure of the polymer was maintained (Figure 3).

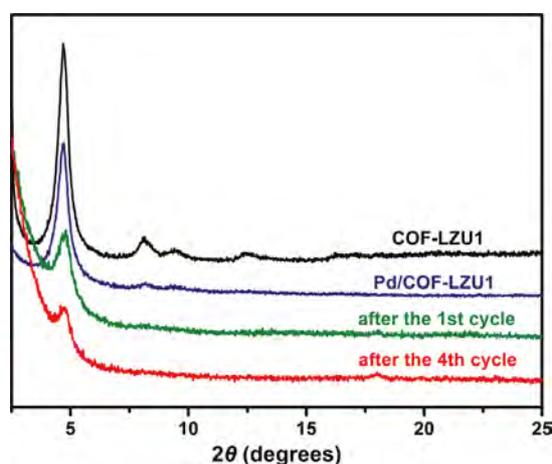


Figure 7. PXRD patterns of COF-LZU1, Pd/COF-LZU1, Pd/COF-LZU1 after the first cycle and after the fourth cycle.

3. Conclusions

- New imine-linked COF for catalytic use (COF-LZU1) was synthesized.
- Pd/COF-LZU1 showed excellent catalytic activity caused by its unique structure.
- The catalyst (Pd/COF-LZU1) was easily recyclable.

→ COF showed excellent heterogeneous catalytic ability. It worked as good ligand and robust support of Pd.

¹ Lanni, L. M.; Tilford, R. W.; Bharathy, M.; Lavigne, J. J. *J. Am. Chem. Soc.* **2011**, *133*, 13975.

² Corma, A.; Garcia, H.; Xamena, F. X. L. *Chem. Rev.* **2010**, *110*, 4606.

³ Uribe-Romo, F. J.; Hunt, J. R.; Furukawa, H.; Klock, C.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2009**, *131*, 4570.

⁴ CP/MAS = Cross Polarization/Magic Angle Spinning. A method for solid state NMR.

⁵ Xamena, F.; Abad, A.; Corma, A.; Garcia, H. *J. Catal.* **2007**, *250*, 294.