

A Recyclable Heterogeneous Palladium Catalyst Anchored to Modified Metal–Organic Framework for Hydrogenation of Styrene Oxide

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Abstract—A heterogeneous palladium(II) catalyst anchored to modified metal–organic framework has been synthesized and characterized. The performance of the catalyst has been tested for the hydrogenation of styrene oxide at ambient temperature and pressure. The catalyst showed an excellent activity and selectivity for the preparation of 2-phenylethanol from styrene oxide with 100% conversion and 98% selectivity. The catalyst is very stable and easily recyclable for several times without loss of activity.

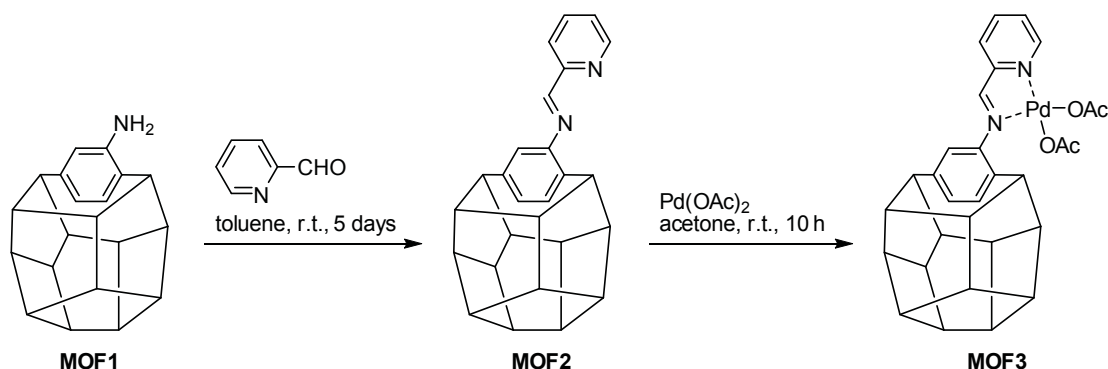
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Metal–organic frameworks (MOFs) have emerged as a promising class of functional materials due to their high surface area, uniform pores, and chemical stability [1–10]. They are successfully employed in heterogeneous catalysis due to their adjustable pore size, high activity, and selectivity. In recent years several research groups reported Pd–MOF catalysts for hydrogenation reaction [11–15]. A common representative of highly porous MOFs is UMCM-1-NH₂ (**MOF1**), which consists of Zn₄O⁶⁺ clusters and 2-aminoterephthalic acid (NH₂–BDC) and 4,4',4''-(benzene-1,3,5-triyl)tribenzoic acid (BTB) linkers forming a hexagonal crystal [5, 16]. Various post-synthetic modifications of this MOF by condensing different functional groups with the amine moiety have also been reported [5, 17, 18].

Herein, we report a heterogeneous Pd(II) catalyst (**MOF3**) and its use in the hydrogenation of styrene oxide to 2-phenylethanol at ambient temperature and pressure with high selectivity. To the best of our knowledge, hydrogenation of epoxides over palladium–MOF catalysts was not described previously. Styrene oxide was used as substrate since selective hydrogenation of this compound to 2-phenylethanol over heterogeneous catalysts has attracted a great deal of interest in recent years. Due to its pleasant floral scent, 2-phenylethanol is commonly used in perfumes, deodorants, cosmetics, soaps, detergents, and foods [19, 20]. Various palladium-based catalysts demonstrated high activity and selectivity in the hydrogenation of styrene oxide [21–24]. However, in most cases high pressure and

Scheme 1.



elevated temperature were needed, which favored formation of by-products. However, even small amounts of impurities may destroy the aroma of 2-phenylethanol. Therefore, it is a challenge to develop more eco-friendly selective methods for this conversion. Our test experiment revealed that **MOF3** is highly efficient to complete the reaction at room temperature and atmospheric pressure of hydrogen in a selective way with 100% conversion. In addition, the catalyst can be recycled several times without loss of performance. The synthetic route for preparing **MOF3** is shown in Scheme 1. Schiff base-functionalized **MOF2** was synthesized according to the known procedure by condensation of pyridine-2-carbaldehyde with amino-functionalized **MOF1** [18]. The palladium catalyst (**MOF3**) was prepared by reacting $\text{Pd}(\text{OAc})_2$ with **MOF2** in acetone for 10 h at room temperature. The obtained solid was washed with chloroform and dried at 50°C.

The catalyst was characterized by X-ray powder diffraction (XRPD), BET surface area measurement, FT-IR spectra, thermogravimetric analysis (TGA), NMR, and elemental analysis. The microanalysis data for **MOF3** suggested the formula $(\text{Zn}_4\text{O})_3[(\text{BDC}-\text{C}_6\text{H}_5\text{N}_2\text{Pd}(\text{OAc})_2)_3(\text{BTB})_4]$. The X-ray powder diffraction pattern of **MOF3** (Fig. 1) showed peaks identical to those previously reported for **MOF1** and **MOF2** [18], indicating that the structural framework remained intact after the complex formation. The BET surface area of **MOF3** was estimated at 1073 m^2/g (Fig. 2); this value is significantly lower than 3900 m^2/g reported for parent **MOF1** [25]. The reduced surface area of **MOF3** is due to the addition of extra mass, $\text{Pd}(\text{OAc})_2$, to the parent MOF. Similar trends were observed for other MOFs after their post-modification with palladium [26, 27]. Figure 3 shows the TG data for the catalyst. ^1H NMR spectrum of **MOF3** showed peaks at δ 1.84 ppm for the methyl protons of acetate group and δ 8–9 ppm for the pyridyl protons, which are consistent with the values reported for other modified MOFs [28, 29].

The hydrogenation of styrene oxide was performed at ambient pressure and temperature in methanol. The progress of the reaction was monitored by TLC and GC analysis which revealed that about 5 h is required to complete the reaction. The formation of 2-phenylethanol was confirmed by FT-IR, ^1H NMR, and GC/MS analysis. The IR spectrum showed a broad peak at 3354.59 cm^{-1} indicating the presence of a hydroxy group in the product molecule. The ^1H NMR spectrum of the crude product was recorded in CDCl_3 after removal of all volatiles in a vacuum at room tem-

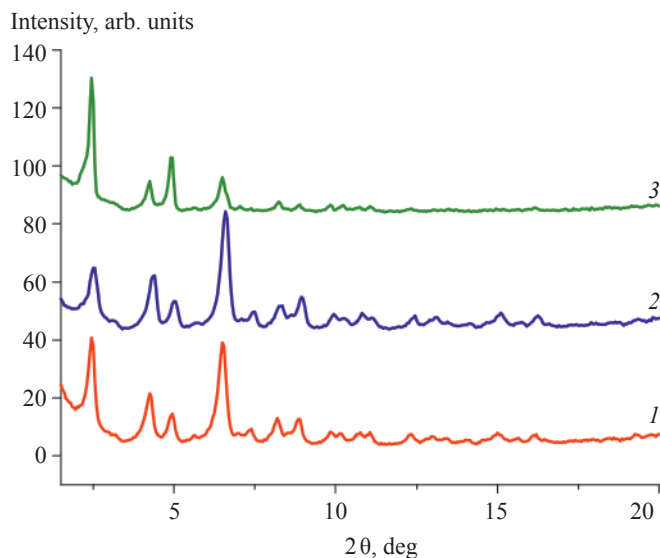


Fig. 1. X-Ray powder diffraction patterns of (1) **MOF-1**, (2) **MOF-2**, and (3) **MOF-3**.

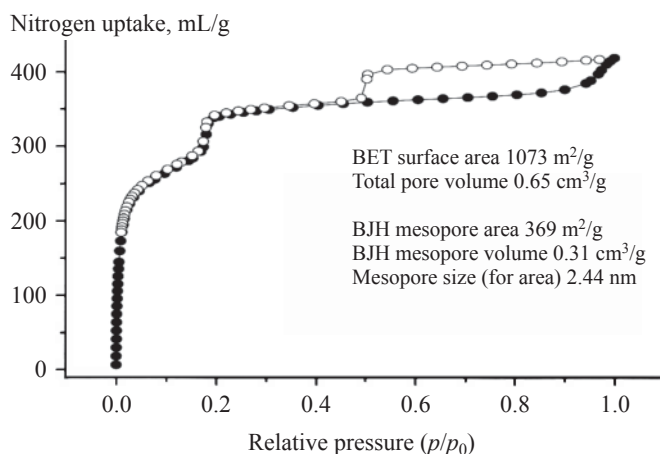


Fig. 2. Nitrogen adsorption (dark circles) and desorption (light circles) isotherms of **MOF-3** at -196°C .

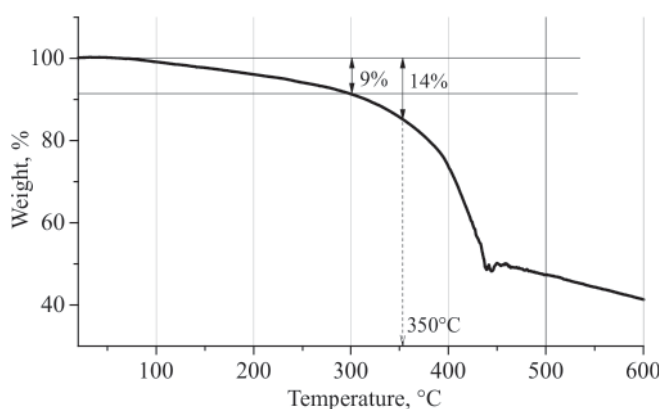


Fig. 3. Thermogravimetric analysis curve of **MOF-3**.

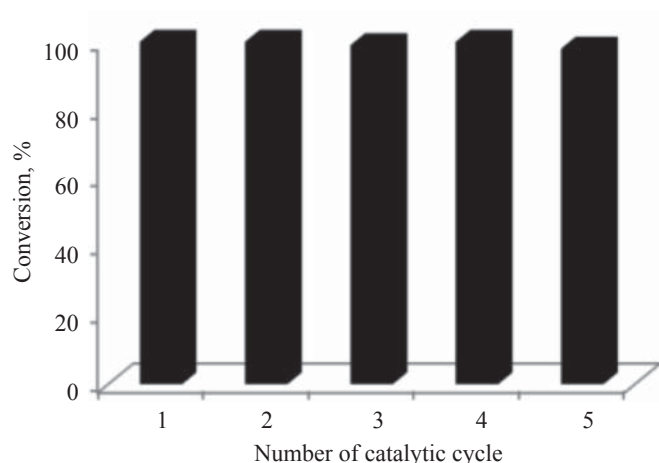


Fig. 4. Recyclability chart of the catalyst **MOF-3** for five consecutive catalytic runs.

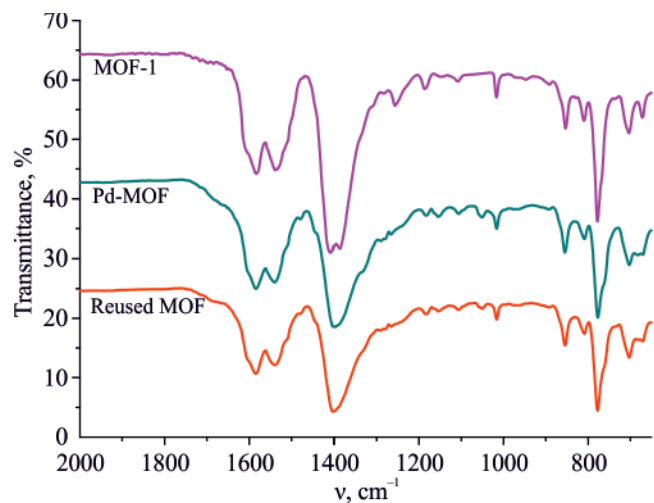


Fig. 5. FTIR spectra of **MOF-1** (UMCM-1-NH₂), **MOF-3**, and **MOF-3** after 5th run in the reduction of styrene oxide

perature. The ¹H NMR spectrum confirmed the formation of 2-phenylethanol and a trace amount of phenylacetaldehyde (δ 9.74 ppm, CHO). The GC/MS analysis also revealed two products which showed peaks at m/z 122 for 2-phenylethanol (98%) and 119.9 for phenylacetaldehyde (2%).

The stability and recyclability of **MOF3** were investigated by performing repeated reaction cycles under the same conditions. At the end of each cycle, the catalyst was recovered by filtration, washed with methanol, and dried at 50°C. The results are shown in Fig. 4. The yield and selectivity were identical irrespective of the number of cycles performed. The performance of **MOF3** was further confirmed by a hot filtration experiment. The reaction was stopped after 2 h, the catalyst was removed by filtration, and the reaction was allowed to continue for next 10 h under the same conditions without catalyst. No further increase of conversion of styrene oxide was observed. The IR and ¹H NMR spectra of the reused solid catalyst were indistinguishable from those of a freshly prepared sample (Fig. 5), indicating that no structural deterioration occurred during the catalytic reaction.

Table 1 compares the performance of some reported palladium catalysts and **MOF3** in the hydrogenation of styrene oxide. It is seen that **MOF3** can work at ambient conditions and is superior to other catalysts in terms of selectivity and reactivity. Furthermore, **MOF3** could be reused several times without loss of activity.

In summary, we have described the synthesis of a highly efficient heterogeneous catalyst where Pd(II) is bonded by bidentate iminopyridine ligand anchored to metal-organic framework (MOF) for selective hydrogenation of styrene oxide to 2-phenylethanol. The catalyst showed high activity and selectivity at ambient conditions without any basic promoter. Moreover, the catalyst can be recycled several times without loss of activity and selectivity.

EXPERIMENTAL

The X-ray powder diffraction patterns were recorded on a Rigaku diffractometer (Cu K_{α} radiation, $\lambda = 1.54 \text{ \AA}$). Nitrogen adsorption/desorption isotherms were measured on a Micromeritics ASAP 2020 surface

Table 1. Hydrogenation of styrene oxide using different palladium catalysts

Catalyst; load, %	Conditions (temperature, pressure, agitation speed)	Conversion, %	Selectivity for 2-phenylethanol, %	Reference
Pd/C; 5%	40°C, 2.0 MPa	93	84	[24]
Pd/C; 5%	28°C, 15 atm, 1100 rpm	96	97–98	[30]
Pd/MgO; 2%	100°C, 10000 h ⁻¹	99	98	[22]
Pd-AFCTS; 3%	40°C, 2.0 MPa	85	97	[24]
MOF3 ; 2%	Room temperature, 1 atm	100	98	This work

analyzer at -196°C . Prior to the measurement, a sample was degassed at 50°C under reduced pressure for 12 h. Thermogravimetric analysis was carried out in the range $25\text{--}600^{\circ}\text{C}$ on a Scinco S-1000TGA system under nitrogen flow at a heating rate of 10.0 deg/min . The FT-IR spectra were obtained on a Thermo Scientific Nicolet iS10 FTIR spectrometer at ambient temperature. The ^1H NMR spectra were recorded on a Varian Unity Inova instrument at 400 MHz from solutions prepared by digesting 10 mg of a sample in a mixture of $\text{DMSO-}d_6$ ($0.750\ \mu\text{L}$) and dilute DCl ($120\ \mu\text{L}$, 35% DCl in D_2O). The metal content of the catalyst was determined by inductively coupled plasma mass spectrometry using a Perkin Elmer Elan 6100 ICP/MS system. The elemental analyses (C, H, N) were performed using a Flash EA 1112 elemental analyzer (Thermo Electron Corporation) from samples preliminarily dried at 50°C in a vacuum for 12 h. The GC/MS data were obtained using a Bruker 3800 GC/1200L MS instrument.

Synthesis of MOF3. An equimolar mixture of **MOF2** [18] and $\text{Pd}(\text{OAc})_2$ in acetone was kept for 10 h at room temperature. Prior to drying, the solvated catalyst was soaked in chloroform for three days, and the solvent was changed every 24 h during this process.

Hydrogenation of styrene oxide. A small vial was charged with **MOF3** (11 mg, 2 mol %), 1 mL of methanol was added, and styrene oxide (0.4 mmol) was then added. The vial was capped with a rubber stopper, and the mixture was stirred at room temperature in a hydrogen atmosphere at ambient pressure using a hydrogen-filled balloon. After completion of the reaction (5 h), the mixture was centrifuged, and the supernatant solution was separated for analysis.

Catalyst recycling. After completion of the reaction, the mixture was centrifuged, and the solution containing product was decanted. The catalyst was washed with methanol ($2 \times 2\ \text{mL}$), separated by centrifugation, and dried at 50°C for the next run.

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CONFLICT OF INTERESTS

The authors declare the absence of conflict of interests.

REFERENCES

- Chae, H.K., Siberio-Perez, D.Y., Kim, J., Go, Y., Eddaoudi, M., Matzger, A.J., O'Keeffe, M., and Yaghi, O.M., *Nature*, 2004, vol. 427, p. 523. <https://doi.org/10.1038/nature02311>
- Koh, K., Wong-Foy, A.J., and Matzger, A.J., *Angew. Chem., Int. Ed.*, 2008, vol. 47, p. 677. <https://doi.org/10.1002/anie.200705020>
- Murray, L.J., Dinca, M., and Long, J.R., *Chem. Soc. Rev.*, 2009, vol. 38, p. 1294. <https://doi.org/10.1039/b802256a>
- Li, J.R., Kuppler, R.J., and Zhou, H.C., *Chem. Soc. Rev.*, 2009, vol. 38, p. 1477. <https://doi.org/10.1039/B802426J>
- Tanabe, K.K. and Cohen, S.M., *Inorg. Chem.*, 2009, vol. 49, p. 6766. <https://doi.org/10.1021/ic101125m>
- Yuan, S., Chen, Y-P., Qin, J., Lu, W., Wang, X., Zhang, Q., Bosch, M., Liu, T-F., Lian, X., and Zhou, H.C., *Angew. Chem., Int. Ed.*, 2015, vol. 54, p. 14696. <https://doi.org/10.1002/anie.201505625>
- Li, Z., Peters, A.W., Bernales, V., Ortuno, M.A., Schweitzer, N.M., DeStefano, M.R., Gallington, L.C., Platero-Prats, A.E., Chapman, K.W., Cramer, C.J., Gagliardi, L., Hupp, J.T., and Farha, O.K., *ACS Cent. Sci.*, 2017, vol. 3, p. 31. <https://doi.org/10.1021/acscentsci.6b00290>
- Kim, I.S., Li, Z., Zheng, J., Platero-Prats, A.E., Mavrandonakis, A., Pellizzeri, S., Ferrandon, M., Vjunov, A., Gallington, L.C., Webber, T.E., Vermeulen, N.A., Penn, R.L., Getman, R.B., Cramer, C.J., Chapman, K.W., Camaioni, D.M., Fulton, J.L., Lercher, J.A., Hupp, J.T., Farha, O.K., and Martinson, A.B.F., *Angew. Chem., Int. Ed.*, 2018, vol. 57, p. 909. <https://doi.org/10.1002/anie.201708092>
- Metzger, E.D., Brozek, C.K., Comito, R.J., and Dinca, M., *ACS Cent. Sci.*, 2016, vol. 2, p. 148. <https://doi.org/10.1021/acscentsci.6b00012>
- Manna, K., Ji, P., Lin, Z., Greene, F.X., Urban, A., Thacker, N.C., and Lin, W., *Nat. Commun.*, 2016, vol. 7, p. 12610. <https://doi.org/10.1038/ncomms12610>
- Opelt, S., Türk, S., Dietzsch, E., Henschel, A., Kaskel, S., and Klemm, E., *Catal. Commun.*, 2008, vol. 9, p. 1286. <https://doi.org/10.1016/j.catcom.2007.11.019>
- Llabrés i Xamena, F.X., Abad, A., Corma, A., and Garcia, H., *J. Catal.*, 2007, vol. 250, p. 294. <https://doi.org/10.1016/j.jcat.2007.06.004>
- Chen, G., Wu, S., Liu, H., Jiang, H., and Li, Y., *Green Chem.*, 2013, vol. 15, p. 230. <https://doi.org/10.1039/C2GC36618E>

14. Huang, Y., Zheng, Z., Liu, T., Lü, J., Lin, Z., Li, H., and Cao, R., *Catal. Commun.*, 2011, vol. 14, p. 27. <https://doi.org/10.1016/j.catcom.2011.07.004>
15. Kong, G.Q., Ou, S., Zou, C., and Wu, C.D., *J. Am. Chem. Soc.*, 2012, vol. 134, p. 19851. <https://doi.org/10.1021/ja309158a>
16. Li, Y. and Yang, R.T., *Langmuir*, 2007, vol. 23, p. 12937. <https://doi.org/10.1021/la702466d>
17. Wang, Z., Tanabe, K.K., and Cohen, S.M., *Inorg. Chem.*, 2009, vol. 48, p. 296. <https://doi.org/10.1021/ic801837t>
18. Doonan, C.J., Morris, W., Furukawa, H., and Yaghi, O.M., *J. Am. Chem. Soc.*, 2009, vol. 131, p. 9492. <https://doi.org/10.1021/ja903251e>
19. Mookherjee, B.D. and Wilson, R.A., *Kirk-Othmer Encyclopedia of Chemical Technology*, New York: Wiley, 1994, 4th ed., vol. 17.
20. Bauer, K., Garbe, D., and Surburg, H., *Common Fragrance and Flavor Materials: Preparation, Properties, and Uses*, Weinheim: VCH, 1990, 2nd ed.
21. Rode, C.V., Telkar, M.M., and Chaudhari, R.V., *J. Mol. Catal. A: Chem.*, 2003, vol. 200, p. 279. [https://doi.org/10.1016/S1381-1169\(03\)00094-3](https://doi.org/10.1016/S1381-1169(03)00094-3)
22. Kirm, I., Medina, F., Rodriguez, X., Cesteros, Y., Salagre, P., and Sueiras, J.E., *J. Mol. Catal. A: Chem.*, 2005, vol. 239, p. 215. <https://doi.org/10.1016/j.molcata.2005.06.032>
23. Bergada, O., Salagre, P., Cesteros, Y., Medina, F., and Sueiras, J.E., *Appl. Catal., A*, 2007, vol. 331, p. 19. <https://doi.org/10.1016/j.apcata.2007.07.017>
24. Dabbawala, A.A., Sudheesh, N., and Bajaj, H.C., *Dalton Trans.*, 2012, vol. 41, p. 2910. <https://doi.org/10.1039/C2DT11924B>
25. Tanabe, K.K. and Cohen, S.M., *Angew. Chem., Int. Ed.*, 2009, vol. 48, p. 7424. <https://doi.org/10.1002/anie.200903433>
26. Ding, S.Y.D., Gao, J., Wang, Q., Zhang, Y., Song, W.G., Su, C.Y., and Wang, W., *J. Am. Chem. Soc.*, 2011, vol. 133, p. 19816. <https://doi.org/10.1021/ja206846p>
27. Bloch, E.D., Britt, D., Lee, C., Doonan, C.J., Uribe-Romo, F.J., Furukawa, H., Long, L.R., and Yaghi, O.M., *J. Am. Chem. Soc.*, 2010, vol. 132, p. 14382. <https://doi.org/10.1021/ja106935d>
28. Wang, Z. and Cohen, S.M., *Angew. Chem., Int. Ed.*, 2008, vol. 120, p. 4777. <https://doi.org/10.1002/ange.200800686>
29. Oisaki, K., Li, Q., Furukawa, H., Czaja, A.U., and Yaghi, O.M., *J. Am. Chem. Soc.*, 2010, vol. 132, p. 9262. <https://doi.org/10.1021/ja103016y>
30. Yadav, V.G. and Chandalia, S.B., *Org. Process Res. Dev.*, 1998, vol. 2, p. 294. <https://doi.org/10.1021/op980027r>