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## Palladium-Metalated Porous Organic Polymers as Recyclable Catalysts for Chemoselective Decarbonylation of Aldehydes

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A novel palladium nanoparticles (NPs)-metalated porous organic ligand (Pd NPs/POL-xantphos) has been prepared for chemoselective decarbonylation of aldehydes. The heterogenous catalyst not only has excellent catalytic activity and chemoselectivity, but also hold high activity after 10 runs of reuse. The effective usage of this method is demonstrated through the synthesis of biofuels such as furfuryl alcohol (FFA) via the highly chemoselective decarbonylation of biomass-derived 5-hydroxymethylfurfural (HMF) with a TON up to 1540. More importantly, 9fluorenone could be obtained in one step through the decarbonylation of 2-bromobenzaldehyde by using this heterogeneous catalyst.

It is imperative to search for new sources of both transportation fuels and bulk chemicals due to the increasing environmental concerns and urgent shortages of fossil resources.<sup>1</sup> Biomass-derived sugars are wonderful substitutes for fossil resources due to their structural diversity and abundance.<sup>2</sup> Current strategies for the implementation of biofuels from biomass-derived sugars are mostly directed to the fermentation of cellulose into bioalcohols or the conversion of biomass-derived sugars into synthesis gas with the subsequent formation of synthetic fuels by a Fischer-Tropsch process.<sup>3</sup> As we all know, biomass-derived sugars are significantly more oxygen rich than those frequently-used chemicals and fuels. Thus, the chemoselective deoxygenation of saccharides is central for the valid utilization of biomassderived carbohydrate feedstocks. At present, this goal is mainly achieved by dehydration and decarbonylation/decarboxylation.4

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Scheme 1. Synthesis of POL-xantphos and corresponding Pd nanocatalyst.

Furan derivatives are accessible from furfurals which have already been produced on an industrial scale from biomassderived pentose.<sup>5</sup> For example, 5-hydroxymethylfurfural (HMF) which was obtained through selective dehydration from hexoses or even cellulose<sup>6</sup> can further transform into valueadded furan derivatives such as furfuryl alcohol (FFA) through the decarbonylation by removing a CO moiety. Decarbonylation of HMF was first reported by Lillwitz, which suffered from low chemoselectivity or needed a stoichiometric amount of metal catalysts.<sup>7</sup> To overcome the shortcomings, a series of methods have been developed for effective decarbonylation of HMF.<sup>8</sup> However, high metal loading,<sup>8b</sup> high pressure in supercritical CO<sub>2</sub>,<sup>8a</sup> low chemoselectivity,<sup>8c,8f</sup> or molecular sieves were needed.<sup>8b,8e</sup> According to previous studies, compared with homogeneous catalysts, their heterogeneous counterparts with immobilized metals on high surface solids could be more effective and chemoselective.<sup>9</sup> Thus we intend to use heterogeneous catalysts to improve the reactivity and chemoselectivity of the decarbonylation of HMF.

Porous organic ligands (POLs), a new kind of porous organic polymer (POP) material, which can be synthesized through free-radical polymerization routes from the corresponding vinylfunctionalized diphosphine monomers by using AIBN initiator under solvothermal conditions.<sup>10-12</sup> Compared with other supports, POLs have attracted attention from many chemists due to their high surface area, large pore volume,

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hierarchical porosity, superior stability, high efficiency, and excellent selectivity. More importantly, they have been used not only as a solid support but also a ligand for various metal catalysts.<sup>11</sup> The POLs also can swell in different solvents, and the structure of those swollen polymers could be described as solution. The "quasi-homogeneous" character of Metal/POLs makes them have better catalytic activity than the "real homogeneous" catalysts.<sup>12b</sup> For example, a series of phosphorus-doped porous organic polymers were used as recyclable catalysts in hydroformyl-ation, isonitrile insertion, and hydrogenation reactions by our group and others.<sup>12</sup>Herein, we report a new Pd NPs-metalated porous organic ligand (Pd NPs/POL-xantphos)<sup>13</sup> as recyclable catalysts for the chemoselective decarbonylation of aldehydes.

The new type of porous organic polymer (POL-xantphos) was designed and synthesized by free-radical polymerization reaction using the corresponding vinylfunctionalized diphosphine monomer. After  $Pd(OAc)_2$  loading and  $H_2$  reduction, the POL-xantphos could be turned into palladium nanocatalyst Pd NPs/POL-xantphos (Scheme 1). To study the structure–reactivity relationship, the prepared POL-xantphos and Pd NPs/POL-xantphos were fully characterized.



Figure 1. a) Pore size distribution curves, b)  $N_2$  adsorption-desorption isotherms, c) TG curve of POL-xantphos, d) SEM image of POL-xantphos.

In the <sup>31</sup>P NMR spectrum of fresh Pd NPs/POL-xantphos, the peak at 28.42 ppm can be ascribed to the palladium coordinate with P atom (Supporting Information, Figure S8), and the coordination of Pd nanoparticle with POL-xantphos is further confirmed by XPS (Figure S7). TG curve of POLxantphos shows that the polymer remains intact at temperatures up to 450 °C (Figure 1c). The nitrogen adsorption-desorption analysis (Figure 1b) demonstrates that POL-xantphos and Pd NPs/POL-xantphos have hierarchical porosity, high surface area and large pore volume, which is further confirmed by TEM and SEM images (Figure S2-S6 and Figure 1d). Base on nonlocal density functional theory (NLDFT), the pore sizes of POL-xantphos and Pd NPs/POL-xantphos were primarily distributed between 0.7nm and 3 nm (Figure 1a). The X-ray diffraction (XRD) shows POL-xantphos and Pd/POLxantphos are amorphous, XRD of fresh Pd/POL-xantphos shows a peak at about 40 theta, indicating the appearance of Pd NPs. XRD of used Pd/POL-xantphos demonstrates almost

the same curve as fresh Pd/POL-xantphos, which can be ascribed the stability of Pd NPs in the polymer supported catalysts (Figure S9). These structural characteristics are very desirable for substrate-catalyst interactions. And the ICP-AES shows that palladium loading is 4.81 wt%.

Table 1. Optimization of the reaction conditions.<sup>a</sup>



Entry	Catalyst	Ligand	1b	1c	1d	1e
1	Pd(PPh <sub>3</sub> ) <sub>4</sub>	/	18	23	<1	<1
2	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	34	31	6	<1
3	Pd(OAc) <sub>2</sub>	dppm	26	33	10	5
4	Pd(OAc) <sub>2</sub>	dppe	33	26	4	<1
5	Pd(OAc) <sub>2</sub>	dppb	30	25	9	7
6	Pd(OAc) <sub>2</sub>	xantphos	39	27	12	14
7	Pd NPs/POL-PPh3[b]	/	62	18	<1	<1
8	Pd NPs/POL-xantphos[b]	/	93	2	<1	<1
9	Pd/C <sup>[b,c]</sup>	/	42	<1	<1	<1

<sup> $\alpha$ </sup>Reaction conditions: HMF 1a (0.5 mmol), K<sub>2</sub>CO<sub>3</sub> (0.5 mmol), homogeneous catalyst (5 mol%), ligand (12 mol%), 1,4-dioxane (1.5 mL), 140 <sup> $\circ$ </sup>C, 6 h, under air atmosphere, GC yield. <sup>b</sup>Heterogeneous catalyst (2 mol%). <sup>c</sup>Different Pd/C were tested (See Table S1 in supporting information).

Due to the significance of decarbonylation of 5-hydroxymethylfurfural (HMF) in developing sustainable energy, this reaction was chosen to investigate the reactivity of the Pd NPs/POL-xantphos (Table 1). And the reaction conditions were carefully screened and results were depicted in Table 1. When the reaction was treated with 5 mol% Pd(PPh<sub>3</sub>)<sub>4</sub> in 1,4-dioxane at 140 °C, the target product furfuryl alcohol (FFA) was obtained with a yield of 18% (Table 1, entry 1). Then, ligands were chosen to improve the chemoselectivity of this reaction. Pd(OAc)<sub>2</sub>/xantphos was identified as the optimal homogeneous catalytic system for the reaction, increasing the yield of FFA to 39% with poor chemoselectivity (Table 1, entries 2-6). In order to further increase the yield of FFA, drawing on the experience from preceding studies on metalated porous organic ligands,<sup>12</sup> we synthesized two heterogeneous catalysts, <sup>13</sup> which were used for the decarbonylation of HFM. The yield of FFA was amazingly improved to 93% with excellent chemoselectivity when we used Pd NPs/POL-xantphos (2 mol%) as a catalyst (Table 1, entry 7-8). In the meantime, we chose the commercial catalyst Pd/C as a comparison, but the yield of FFA catalysed by Pd/C was only 40% after 6 hours of reaction (Table 1, entry 9). With this, the optimal conditions to the decarbonylation of HFM were Pd NPs/POL-xantphos (2 mol%) as a catalyst in 1,4-dioxane with  $K_2CO_3(1 \text{ eq.})$  at 140  $^{\circ}C$ under air atmosphere (Table 1, entry 8).

The reusability is another significant characteristic of the heterogeneous catalyst. We repeated the decarbonylation of HMF with Pd NPs/POL-xantphos (Figure 2a) up to 10 times. After each run, the nanocatalyst was recovered by vacuum evaporation and washed sequentially with ethyl acetate, water,

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and acetone. We were surprised to find that the nanocatalyst could be used for at least 10 runs without losing any catalytic activity. TEM images show Pd NPs were formed with no notable aggregation after the 10th run (Figure 2b and Figure 2c).



Figure 2. a) Recycling studies of Pd NPs/POL-xantphos for the decarbonylation of HMF, b) TEM image of fresh Pd NPs/POL-xantphos, c) TEM image of used Pd NPs/POL-xantphos.

In order to study the industrial application of this catalyst, we reduced the amount of heterogeneous catalyst to 0.05 mol%. The decarbonylation of 3.78 g of HMF produced the corresponding product FFA with a yield of 77% and the TON up to 1540 (Scheme 2).



 $\label{eq:scheme 2. Industrial studies of Pd NPs/POL-xantphos for the decarbony-lation of HMF.$ 

To expand the scope of application of this catalytic system, we examined the decarbonylation of other aldehydes. The aldehydes bearing various aromatic substituents reacted successfully. The electron-donating and electron-accepting groups (R<sup>1</sup> = 4-NMe<sub>2</sub>, 4-t-Bu, 4-NO<sub>2</sub>, 4-CN, 4-OMe, 4-COMe, 4-COOH, 4-Ph, 3-Ph, 2-Ph, 4-vinyl, 4-acetylene) on the benzene ring of the benzaldehyde all reacted smoothly (Table 2, entries 1-12). Ketonic carbonyl and carboxyl groups did not undergo decarbonylation under this condition, indicating the nanocatalyst has high chemoselectivity (Table 2, entries 6-7). Due to the steric effect, probably, the yield of 3i was much lower (Table 2, entry 10). Two molecules of CO can also be successfully removed from the [1,1'-biphenyl]-4,4'-dicarbaldehyde with two formyl groups to give the decarbonylated product 3m (Table 2, entry 13). And fused-ring aryl aldehydes such as naphthaldehydes (2n), 9-anthraldehyde (2o) and pyrene-1-aldehyde (2p) have all reacted smoothly in removing one molecule of CO to give the decarbonylated products with good yields (Table 2, entries 14-16). Various five and six membered nitrogen-containing heterocyclic compounds (2q-2t) afforded the products (3q-3t) with good to satisfactory yields

### **Table 2.** The decarbonylation of aldehydes.<sup>a</sup>

	R—CHO Pd/PC	DL-xantphos ► R-H	
Entry	Aldehyde	Prouduct	Yield
	R <sup>1</sup> = 4-NMe <sub>2</sub> 2a	$R^1 = 4 - NMe_2$ 3a	87%
2	4— <b>t</b> -Bu, <b>2b</b>	4—t-Bu, <b>3b</b>	81%
3	4-NO <sub>2</sub> , 2c	4-NO <sub>2</sub> , 3c	78%
4	4-CN, 2d	4-CN, 3d	76%
5	4–OMe, <b>2e</b>	4-OMe, <b>3e</b>	92%
6	4-COOH, 2f	4-COOH, 3f	83%
7	R <sup>1</sup> [] 4–COMe, <b>2g</b>	R <sup>1</sup>	71%
8	4–Ph, <b>2h</b>	4–Ph, <b>3h</b>	97% <sup>b</sup>
9	3–Ph, <b>2i</b>	3–Ph, <b>3i</b>	91% <sup>b</sup>
10	2–Ph <b>2</b> j	2–Ph <b>3</b> j	37% <sup>b</sup>
11	CHO 2k	H 3k	90%, 61% <sup>c</sup>
12	CHO 21	<u>з</u> і	89%
13		H	95% <sup>b</sup>
14	2n	3n	96%
15	20 CHO 20		94%
16	2p	<b>зр</b>	92%
17	CHO 2q	N 3q	81%
18	CHO CHO CHO 2r	H N H	94%
19	N 2s	N 35	86%
20	OHC 2t	H 3t	91%
21	CHO Su	S 3u	73%
22	СНО 2	[н зv	99%
23	2w	Н Зw	51%, 39% <sup>c</sup>



(Table 2, entries 17-20). Furan or benzothiophene derivatives can also be decarbonylated smoothly by this method (Table 2, entries 21-22). The long chain alkyl aldehydes (**2w**) did not get a satisfactory yield, maybe because of the influence of  $\beta$ -H eliminating (Table 2, entries 23). Interestingly, several liquid starting materials can also react without the involvement of solvents to give the decarbonyla-ted products (Table 2, entry 11 and entry 23).

4



Scheme 3. The applications of Pd NPs/POL-xantphos in decarbonylation of 4-halobenzaldehydes.

Moreover, some special substrates could be converted into interesting products using this nanocatalyst. For example, when we used 4-halobenzaldehydes as the raw materials, fluorobenzaldehyde **4a** can be decarbonylated to fluorobenzene **4b** (Scheme 3, eq 1). But when we used 4-bromobenzaldehyde **4c** as the substrate, we found that [1,1'-biphenyl]-4,4'dicarbaldehyde **4f**, [1,1'-biphenyl]-4-carbaldehyde **4e**, and biphenyl **4d** can be obtained. And the yields of the products were dependent on the reaction time (Scheme 3, eq 2). Another interesting finding is that the amount of produced 9fluorenone **4h** was more than that of decarbonylated product when we used 2-bromobenzaldehyde **4g** as a substrate in standard conditions in one step (Scheme 3, eq 3). And this is the first time that 9-fluorenone **4h** was synthesized through the Pd-catalyzed dimerization of 2-bromobenzaldehyde.

In summary, we have developed a highly chemoselective and efficient method for decarbonylation of aldehydes with a novel recyclable and highly stable heterogeneous nanocatalyst. To study their structure-reactivity relationships, the prepared POL-xantphos and Pd NPs/POL-xantphos were fully character-rized. TEM images show that the Pd NPs are highly discretely distributed in this porous polymer, which results in the high activity of this nanocatalyst. More importantly, this nanocatalyst can be reused in the decarbonylation of HMF, which makes upgrading of this significant biomass into biofuels possible for industrial application.

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### Notes and references

4 | J. Name., 2012, 00, 1-3

- (a) R. A. Kerr and R. F. Servise, *Science*, 2005, **309**, 78-102; (b)
   A. Corma, S. Lborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411-2502; (c) G. W. Huber, J. N. Chheda, C. J. Barret and J. A. Dumesic, *Science*, 2005, **308**, 1446-1450.
- 2 C. Li, X. Zhao, A. Wang, G. W. Huber and T. Zhang, Chem. Rev., 2015, 115, 11559-11624.
- 3 (a) G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2016, 106, 4044-4098; (b) C. Li, X. Zhao, A. Wang, G. W. Huber and T. Zhang, *Chem. Rev.* 2015, 115, 11559-11624.

(a) C. Wang, L. Wang, J. Zhang, H. Wang, J. P. Lewis and F.-S. Xiao, J. Am. Chem. Soc., 2016, **138**, 7880-7883; (b) L. R. Baker, G. Kennedy, M. V. Spronsen, A. Hervier, X. Cai, S. Chen, L.-W. Wang and G. A. Somorjai, J. Am. Chem. Soc., 2012, **134**, 14208-14216; (c) E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gärtner and J. A. Dumesic, *Science*, 2008, **322**, 417-421; (d) S. Wang, V. Vorotnikov and D. G. Vlachos, ACS Catal., 2015, **5**, 104-112; (e) M.-Y. Chen, C.-B. Chen, B. Zada and Y. Fu, Green Chem., 2016, **18**, 3858-3866; (f) L. Luo, H. S. Yun, A. V. Mironenko, K. Goulas, L. D.

DOI: 10.1039/C8CC03109F

**Journal Name** 

- 3866; (f) J. Luo, H. S. Yun, A. V. Mironenko, K. Goulas, J. D. Lee, M. Monai, C. Wang, V. Vorotnikov, C. B. Murray, D. G. Vlachos, P. Fornasiero and R. J. Gorte, *ACS Catal.*, 2016, 6, 4095-4104; (g) Y. Yang, Z. Du, Y. Huang, F. Lu, F. Wang, J. Gao and J. Xu, *Green Chem.*, 2013, **15**, 1932-1940.
- 5 (a) P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538-1558; (b) S.
   H. Pang, C. A. Schoenbaum, D. K. Schwartz and J. W. Medlin, *ACS Catal.*, 2014, **4**, 3123-3131.
- 6 (a) Y. Roman-Leshkov, J. N. Chheda and J. A. Dumesic, Science, 2006, **312**, 1933-1937; (b) H. B. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, Science, 2007, **316**, 1597-1600; (c) T. Wang, M. W. Nolte and B. H. Shanks, Green Chem., 2014, **16**, 548-572.
- 7 L.D. Lillwitz, US4089871 (A), 1973.
- 8 (a) F. M. A. Geilen, T. V. Stein, B. Engendahl, S. Winterle, M. A. Liauw, J. Klankermayer and W. Leitner, Angew. Chem. Int. Ed., 2011, 50, 6831-6834; (b) J. Dai, X. Fu, L. Zhu, J. Tang, X. Guo and C. Hu, ChemCatChem, 2016, 8, 1379-1385; (c) J. Mitra, X. Zhou and T. Rauchfuss, Green Chem., 2015, 17, 307-313; (d) Q. Meng,; C. Qiu, G. Ding, J. Cui, Y. Zhu and Y. Li, Catal. Sci. Technol., 2016, 6, 4377-4388; (e) Y.-B. Huang, Z. Yang, M.-Y. Chen, J.-J. Dai, Q.-X. Guo and Y. Fu, ChemSusChem, 2013, 6, 1348-1351; (f) M. Chatterjee, T. Ishizaka, A. Chatterjeeb and H. Kawanami, Green Chem., 2017, 19, 1315-1326.
- 9 (a) Y.-B. Zhou, Y.-Q. Wang, L.-C. Ning, Z.-C. Ding, W.-L. Wang, C.-K. Ding, R.-H. Li, J.-J. Chen, X. Lu, Y.-J. Ding and Z.-P. Zhan, J. Am. Chem. Soc., 2017, 139, 3966-3969; (b) S. Lin, C. S. Diercks, Y.-B. Zhang, N. Kornienko, E. M. Nichols, Y. Zhao, A. R. Paris, D. Kim, P. Yang, O. M. Yaghi and C. J. Chang, Science, 2015, 349, 1208-1213; (c) L. Chen, Y. Yang, Z. Guo and D. Jiang, Adv. Mater., 2011, 23, 3149-3154; (d) B. Li, Z. Guan, W. Wang, X. Yang, J. Hu, B. Tan and T. Li, Adv. Mater. 2012, 24, 3390-3395; (e) T. T. Adint and C. R. Landis, J. Am. Chem. Soc., 2014, 136, 7943-7953.
- 10 (a) P. Bhanja, S. Chatterjee and A. Bhaumik, *ChemCatChem.*, 2016, **8**, 3089-3098; (b) P. Bhanja, R. Gomes and A. Bhaumik, *RSC Adv.*, 2015, **5**, 74916-74923.
- 11 (a) Q. Sun, Z. Dai, X. Meng and F.-S. Xiao, *Chem. Soc. Rev.*, 2015, **44**, 6018-6034; (b) Q. Sun, Z. Dai, X. Meng, L. Wang and F.-S. Xiao, *ACS Catal.*, 2015, **5**, 4556-4567.
- (a) W. Tong, W.-H. Li, Y. He, Z.-Y. Mo, H.-T. Tang, H.-S. Wang and Y.-M. Pan, Org. Lett., DOI: 10.1021/acs.orglett.8b00886;
  (b) Q. Sun, Z. Dai, X. Liu, N. Sheng, F. Deng, X. Meng and F.-S. Xiao, J. Am. Chem. Soc., 2015, **137**, 5204-5209;
  (c) C. Li,; K. Sun, W. Wang, L. Yan, Y. Sun, Y. Wang, K. Xiong, Z. Zhan, Z. Jiang and Y. Ding, J. Catal., 2017, **353**, 123-132;
  (d) C. Li, L. Yan, L. Lu, K. Xiong, W. Wang, M. Jiang, J. Liu, X. Song, Z. Zhan, Z. Jiang and Y. Ding, J. Catal., 2017, **353**, 123-132;
  (d) C. Li, L. Yan, L. Lu, K. Xiong, W. Wang, M. Jiang, J. Liu, X. Song, Z. Zhan, Z. Jiang and Y. Ding, Green Chem., 2016, **18**, 2995-3005;
  (e) R. Cai, X. Ye, Q. Sun, Q. He, Y. He, S. Ma and X. Shi, ACS Catal., 2017, **7**, 1087-1092;
  (f) W. Wang, C. Li, L. Yan, Y. Wang, M. Jiang and Y. Ding, ACS Catal., 2016, **6**, 6091-6100;
  (g) Y.-B. Zhou, C.-Y. Li, M. Lin, Y.-J. Ding and Z.-P. Zhan, Adv. Synth. Catal., 2015, **357**, 2503-2508;
  (h) Z.-C. Ding, C.-Y. Li, J.-J. Chen, J.-H. Zeng, H.-T. Tang, Y.-J. Ding and Z.-P. Zhan, Adv. Synth. Catal., 2017, **359**, 2280-2287.
- 13 General procedures for the synthesis of POL-xantphos and Pd NPs/POL-xantphos are depicted in supporting information (Experimental Section).