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Palladium/Phosphorus-doped Porous Organic Polymer as Recyclable Chemoselective and Efficient Hydrogenation Catalysts under Ambient Conditions

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Abstract. A new type of phosphorus-doped porous organic polymer (POP) has been readily synthesized through Heck reaction, which could be used not only as a support but also a ligand for palladium nanoparticles. The dual-functional material supported palladium nanocatalyst was used for efficient and chemoselective hydrogenation of varieties of nitroarenes and α,β -unsaturated compounds, as well as the synthesis of indoles from 2-nitrophenylacetonitrile under 1 atm hydrogen in green solvents at room temperature. No obvious aggregation and loss of catalytic activity of the new nanocatalyst were observed after 10 times in the reaction.

Keywords: heterogeneous catalysis; palladium nanoparticles; porous organic polymers; hydrogenation, nitroarenes; indoles

Introduction

The chemoselective hydrogenation of nitroarenes and α , β -unsaturated carbonyl compounds when other sensitive functional groups such as carbonyl, carboxyl, ester, amide or nitrile groups are appear in the same substrates represents a cornerstone of modern industrial chemistry. As the former produces aniline and aniline derivatives, which are important feedstocks and key intermediates for the manufacture of many pharmaceutical, polymer, dye, and natural products. The latter obtains ketones and has been extensively applied in the synthesis of functional materials and fine chemicals. Due to the limitation of homogeneous catalysis in the difficult separation of product and catalyst, the heterogeneous catalysts are desperately in demand for industrial applications because of the recovering and recycling of the catalysts.^[1] Nevertheless, to develop heterogeneous catalysts with not only high catalytic activity, but also selectivity towards the nitro group^[2] or C=C bond of compounds^[3] α,β -unsaturated carbonyl is а dominating challenge. For the reduction of nitro group, the hydrogenation process is sometimes

performed under drastic (for example, T > 100 °C,^[4a-g] or $P > 1.0 \text{ atm } \text{H}_2^{\text{[4a-m]}}$) conditions. Furthermore, from the viewpoint of green chemistry, the direct hydrogenation of nitroarenes using H_2 will be more favorable, although other hydrogen sources were used as stoichiometric reducing agents to obtain the high selectivity had also been reported.^[5] For the selective hydrogenation of C=C bonds, great efforts have been made to achieve the aimed products, but high H_2 pressure, high temperature, toxic solvent, or various additives like amines, pyridines and diphenylsulfide are sometimes inevitable.^[6]

Until now, to obtain the advantages of homogeneous and heterogeneous catalysts, immobilizing metal nanoparticles (NPs) onto high surface solids would be an effective approach. A huge number of microporous and mesoporous materials were chosen to be the supports of metal species in hydrogenation reactions, such as zeolite, silica, titania, carbonaceous materials, MOFs and POPs.^[7] Among above mentioned materials, the POPs have received special attention because of their high surface area, tunable pore size distribution. excellent stabilities. modifiable functionality, and flexible synthetic strategy. Recently, kinds of POPs have been used as supports of metal

NPs for hydrogenation reactions.^[8] For instances, Wang and coworkers reported several click-based POP supports of Pd NPs with uniform



Scheme 1. Synthesis of porous organic ligand (POLs) and preparation of different content Pd nanocatalysts

distributions for hydrogenation of nitroarenes and olefins.^[8a-d] Owing to the coordination of the N atom to the Pd NPs, the nanocatalysts could be recycled several times without loss of catalytic activity. Besides, other N,^[8e-f]O,^[8g] and S^[8h]-doped POPs have also been designed and applied to the hydrogenation reactions. Despite these pioneering work, the design and synthesis of new type of support as well as ligand for the metal active site to protect it from leaching and agglomeration is still an exciting yet challenging task.

As we know, the phosphine ligands are among the best choice to form the coordination interaction with the metal ions. Lately, we have reported a porous organic ligand (POL-Ph₃P) (see SI, Scheme S1) supported palladium for the Suzuki-Miyaura crosscoupling reactions.^[9] To the best of our knowledge, in spite of so many advantages of these P-doped POPs, attempts to use them to catalyze hydrogenation reactions have not been reported. Herein, a new type of P-doped porous organic polymer POL-1 (Scheme 1, a) was designed and synthesized through Heck reaction, which could turned to POL-2 after loading PdCl₂ and H₂ reduction. The obtained POL-2 could sever as not only a support but also a ligand for Pd nanocatalysts (Scheme 1, b) and we demonstrate the utilization of this new P-doped POP to the room temperature hydrogenation of both nitroarenes and C=C bond of α,β -unsaturated carbonyl compounds with high efficiency, selectivity and recyclability under atmosphere pressure. What's more, the synthesis of indoles by reductive cyclization of 2nitrophenylacetonitrile over the Pd NPs was also carried out.

Results and Discussion

To explore the structure-reactivity relationship, the POL-2 was characterized by thermogravimetry (TG), N_2 adsorption-desorption analysis, and transmission electron micro graph (TEM). The TG shows that POL-2 remains intact at temperatures up to 400 °C, indicating its good thermal stability (SI, Figure S 1). Nitrogen adsorption-desorption analysis (Figure 1, a and b) shows that POL-2 possesses very favorable hierarchical pore size distributions, according to the pore size distribution curves, and the pore sizes were mainly distributed at 0.70, 0.85, 1-10 nm respectively, which was calculated from the method of non-local density functional theory (NLDFT). The BET surface areas and total pore volumes of POL-2 are up to 554.2 m²/g and 0.959 cm³/g respectively. The TEM image shows that the Pd nanoparticles were highly dispersed on the surface of POL-2 (Figure 1, c), and the size mainly range from 2 to 4 nm (Figure 1, d). For the SEM, XRD, XPS, ¹³C and ³¹P MAS data, please see the supporting information.



Figure 1. a) N₂ adsorption-desorption isotherms, b) Pore size distribution curves, c) TEM of Pd@ POL-2, d) Histogram for the Pd particles size distribution of Cat C before use.

We prepared catalysts with different Pd loadings, that is, 1 wt%, 4 wt% and 7 wt% Pd@ POL-2, and the Pd content was determined by ICP-AES. Interestingly, we found the catalytic activity could be regulated by loading different contents of Pd onto POL-2. The reduction of *p*-nitroacetophenone was carried out as the model reaction with different catalysts under 1 atm H₂ in an ethanol solvent and the results were summarized in table 1. Remarkably, Cat C exhibited a high catalytic activity and selectivity towards the nitro group of **1a** to afford **2a** in 91% yield without the reduction of the carbonyl group

Table	1.	Pd-Catalyzed	hydrogenation	of	р-
nitroace	etoph	nenone ^[a]			

0	Catalyst (Pd: 0.5 mol EtOH, r.t., 1 atm H ₂	<u>%)</u> o _∖	NH ₂
1 a			2a
Entry	Catalyst	<i>t/</i> h	Yield (%) ^[b]
1	Pd(PPh ₃) ₄	1	<5
2	Pd@C ^[c]	1	<10
3	Pd@C ^[d]	1	<20
4	Pd@C ^[e]	1	<20
5	Pd@C ^[e, f]	1	68
6	Cat A ^[g]	1	No reaction
7	Cat B ^[g]	1	15
8	Cat C ^[g]	1	91
9	Pd@POL PPh3[h]	1	82

^[a] Reaction conditions: **1a** (2.0 mmol, 330 mg), catalyst (Pd, 0.01 mmol), ethanol (5 ml), r.t., 1 atm H₂.

^[b] Isolated yields.

^[c] 10 wt % Pd@C bought from sigma Aldrich.

^[d] 10 wt % Pd@C bought from Energy Chemical.

^[e] 5 wt % Pd@C bought from Aladdin.

^[f] The amount of catalyst is 1 mol %.

^[g] Cat A, B, C see Scheme 1, b.

^[h] The Pd loading was 7 wt%, the structure of POL-PPh₃, see SI, Scheme S1.

(Table 1, entry 8). In sharp contrast, homogeneous Pd(PPh₃)₄ showed low efficiency (entry 1) and the commercial Pd/C bought from three different companies gave unsatisfactory yields (entries 2-5). Compared with Cat C, Cat A, and Cat B showed lower activity, either did not lead to any detectable product formation or brought lower yield (entries 6 and 7), while Pd@POL PPh₃ had a moderate yield (entry 9). Thus, the optimized reaction conditions for the selective hydrogenation of nitroarenes were determined to be using 0.5 mol % Cat C, under 1 atm H_2 at room temperature in ethanol (Table 1, entry 8).

The general applicability was demonstrated in table 2. A number of nitro compounds were converted into corresponding amines with excellent yields and selectivities. For example, nitrobenzene and those substituted with various groups were all tolerated under the extremely mild conditions (Table 2, 2a-2j, 88-99% yields), and the catalyst showed no effect on the sensitive groups such as acetyl, cyan, formamide, -Cl, and p-OBn groups (2a-2e and 2m). In addition, 2k was also achieved from the reduction of 4-nitro-1H-indole (Table 2, 2k, 99% vield), and nitronaphthalene was converted to naphthylamine smoothly (Table 2, 2l, 98% yield). To our regret, the





^[a] Reaction conditions: 1 (2.0 mmol), Cat C, 15.1 mg (Pd, 0.01 mmol), ethanol (5 ml), r.t., 1 atm H₂.

^[b] Isolated yields.

^[c] Reacted at 60 °C.

catalyst showed no selectivities towards some reducible functional groups, such as N-Cbz protective group, alkene, alkyne and azide, which could be reduced along with nitro groups, albeit with excellent yields (Table 2, 2i and 2n). It is worth mentioning that the reaction still allowed high selectivities when performed at 60 °C (2a, 2c and 2e), and this made it possible for larger scales, since during which heat removal caused by the very high exothermicity of the reaction was difficult.

We next turned our focus on the selective hydrogenation of α,β -unsaturated compounds (Scheme 2). Interestingly, It was found that the optimized conditions used for nitroarenes was not suitable for this transformation, in which Cat C gave a 4:1 (4a : 5a) selectivity, albeit with excellent efficiency. However, Cat B gave almost only 4a in 99% yield, that is, Cat B could realize the chemoselective reduction of the C=C bond in α . β unsaturated compounds under mild reaction conditions.



Scheme 2. The selective hydrogenation of 3a over Cat B and Cat C

Table 3. Pd NPs Catalyzed hydrogenation of various α,β -unsaturated compound.^[a,b]



^[a] Reaction conditions: **3** (2.0 mmol), Cat B, 26.5 mg (Pd, 0.01 mmol), ethanol (5 ml), r.t., 1 atm H_2

^[b] Isolated yields

^[c] The reaction was performed in CH₂Cl₂

 $[d] R^3 = N_3$

The general scope was tested in the hydrogenation of varieties of α , β -unsaturated compounds with the results summarized in table 3. Gratifyingly, in all cases, we got the full conversion of the substrates towards the corresponding products (Table 3, **4a-41**, 83-99% yields). Remarkable chemoselectivity was achieved in the hydrogenation of the C=C bond when other sensitive groups such as carbonyl, ester, cyan, carboxyl, amide, aldehyde, benzyl ether and *N*-Cbz protective groups are appear in the same substrates, except that when R³ was azide (Table 3, **4k**).



Scheme 3. Catalytic synthesis of indoles from 2nitrophenylacetonitrile

Next, based on the high catalytic activity towards hydrogenation of this porous organic polymer supported Pd NPs, we tried the synthesis of indoles from 2- nitrophenylacetonitrile, as some efforts have been made to this reaction. For example, Makosza^[10] *et al* reported Pd/C catalyzed reductive cyclization of 2-nitrophenylacetonitrile to prepare indole under 3 atm H₂ and acetic acid is a necessary additive (Scheme 3, a). Nagashima^[11] also developed the heterogeneous Pt catalyst [Pt]@SiC₆ could furnish this conversion affording the indole product in 52% yield, however, the reaction require 10 atm of H₂ (Scheme 3, b). Here, we applied our new porous organic P-doped polymer supported Pd NPs to make **Table 4.** Pd NPs Catalyzed reductive cyclization of2-nitrophenylacetonitrile to indoles [a,b]



^[a] Reaction conditions: 6 (0.3 mmol), Cat C, 45 mg (Pd, 0.03 mmol), methanol (3 ml), r.t., 1 atm H₂.
^[b] Isolated yields.

^[c] 40% of **6e** was recovered.

the process more simple and realize the transformation under 1 atm H_2 at room temperature, and there was no need for complicated ligands or additional acids or bases (Scheme 3, c).

Several representative indoles were synthesized over the heterogeneous Pd NPs under 1 atm H_2 at room temperature in CH₃OH (Table 4), good to excellent yields were achieved (**7a-f**, 55-99% yields), which also gave an obvious evidence for the higher activity of Pd@POL -2 than commercial Pd/C catalysts.



Figure 2. a) Reuse of Pd@POL-2 towards hydrogenation of 1-Methoxy-4-nitrobenzene. b) and c) TEM image of Cat C after first use and tenth use.

Finally, the reusability of Pd@POL-2 was examined for the hydrogenation of 1-methoxy-4nitrobenzene **1g** to obtain **2g** (Figure 2). As can be seen, the Pd@POL-2 was recycled ten times without loss of activity, (Figure 2, a). In addition, the TEM images revealed the Pd NPs supported on POL-2^[12] with a mean diameter of about 2.7 nm were formed after first use (Figure 2, b and SI, Figure S6, left), and no obvious aggregation of these nanoparticles occurred up to the 10th run though the mean diameter incraced to 4 nm (Figure 2, c and SI, Figure S6, right). These excellent results benefit from the critical coordination interaction of P atoms and Pd NPs, thus protecting Pd from leaching and agglomeration.

Conclusion

In conclusion, a P-doped porous organic polymer has been readily designed and synthesized and used as not only the support but also the ligand for Pd nanoparticles. By regulating the Pd loading on the polymer, the nanocatalysts could obtain excellent efficiency as well as chemoselectivity towards the hydrogenation reactions. Owing to the coordination interaction of P atoms with the supported Pd NPs, no obvious aggregation and loss of catalytic activity of the new nanocatalyst were observed after 10 times in the reduction of nitro groups.

Experimental Section

General materials and methods

The liquid-state NMR was recorded on a 400 MHz spectrometer. Chemical shifts were reported in ppm. ¹H NMR spectra were referenced to CDCl₃ (7.26 ppm), and ¹³C-NMR spectra were referenced to CDCl₃ (77.0 ppm). All ¹³C NMR spectra were measured with complete proton decoupling. Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. The solid-state NMR was recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP/MAS probehead whose channel was tuned to 400.18 MHz. The samples were packed in the ZrO₂ rotor closed with Kel-F cap which were spun at 12 kHz rate. ¹³C CP/MAS spectra were referenced to adamantane (C10H16) standard (1.63 ppm). ³¹P CP/MAS were referenced to adenosine diphosphate (ADP) (0.0 ppm). Nitrogen sorption isotherms at the temperature of liquid nitrogen were performed on a Quantachrome Autosorb-1 system, and the samples were degassed for 10 h at 393 K before the measurements were obtained. The specific surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The total pore volume at P/Po=0.995. The pore size distribution curves were obtained from the desorption branches using the non-local density functional theory (NLDFT) method. Transmission electron microscope (TEM) images were performed using

a JEM-2100 with accelerating voltage of 200 kV. Scanning electron microscopy (SEM) was performed using a X-ray photoelectron HITACHI-4800. The spectroscopy(XPS)was conducted using a Thermo Scientific ESCALAB 250Xi with the Al Ka irradiation at θ =90° for X-ray sources, and the spectrometer binding energy was calibrated through the reference C 1s (284.9eV). The samples were pressed to tablet and were pasted on sample stage using conducting resin and the pressure of vacuum chamber was lower than 10-10mbar when testing while the step size of 0.10 eV was employed. Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (NETZSCH STA 449 F3), the sample was heated at the rate of 10K•min⁻¹ from room temperature up to 1073K under a nitrogen atmosphere. Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. All reaction mixtures were stirred with a magnetic bar in flame-dried glassware.

Preparation of POL-PPh₃

Mg turnings (2.40 g, 100 mmol) were added to a round bottom flask under nitrogen, and were activated by treatment with a grain of I2 in THF (80 mL). pbromostyrene (14.64 g, 80 mmol) was slowly added to the flask, and the mixture was stirred for 1 h at room temperature. Next, PCl₃ (3.43 g, 25 mmol) was slowly added to the solution in the ice water bath over 30 min followed by stirring at room temperature for 4 h. The reaction was quenched with aq.NH₄Cl, and the mixture was extracted with ethyl acetate. The organic layer was washed with H₂O twice, dried over NaSO₄, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford tris(4-vinylphenyl)phosphane (5.45 g, 64% yield). Under nitrogen, tris(4-vinylphenyl)phosphane (10.0 g) was dissolved in THF (100 mL), followed by the addition of AIBN (1.0 g) at room temperature. Next, the mixture was transferred into an autoclave at 100 °C for 24 h. After evaporation of THF under vacuum, a white solid (9.6 g, 96% yield) was obtained.

Preparation of POL-1 and Cat A

Tris(4-vinylphenyl)phosphane (6.46 g, 19 mmol, 1.0 eq.), 1,3,5-tribromobenzene (6.58 g, 20.9 mmol, 1.1 eq) , Pd(PPh₃)₄ (1.1 g, 0.95 mmol, 0.05eq.) and K₂CO₃ (18.3 g, 133 mmol, 7.0 eq.) were added to a round bottom flask in super dry DMF (150 mL) under nitrogen. And the mixture was stirred at 120 °C. Gray solid was obtained after 72 h and the mixture was cooled to room temperature, filtration and washed by H₂O, MeOH, THF, EtOAc and DCM 3 times respectively, then the gray solid was dried under vacuum to afford POL-1 4.8 g. As a note, during this process, part of the catalyst Pd(PPh₃)₄ was loaded to POL-1, after reduction under 1 atm H₂ at 180 °C, the Pd loading is determined by ICP-AES to be 1 wt% (Cat A).

Preparation of POL-2, Cat B and Cat C

To a round bottom flask was added POL-1 (1.0 g), MeCN 15 mL, and PdCl₂ (177.3 mg, 1.0 mmol), The reaction mixture was stirred at room temperature for 5 h, the gray solid turned to yellow , the yellow solid was washed using MeOH, EtOAc THF and MeCN 3 times respectively after filtration. Next, the yellow was reduced at 180 °C for 5 h and cooled to room temperature to obtain Cat C (7 wt % Pd NPs@POL-2), During this process, the C=C double bonds of POL-1 were reduced to C-C single bonds to obtain POL-2. Changing PdCl₂ loading to 70 mg could give Cat B (4 wt %NPs@ POL-2). The Pd content was determined by ICP-AES.

General procedure for hydrogenation of various nitroarenes and the recycling experiment

To a three-necked round bottom flask was added nitroarenes 1 (2 mmol), Cat C, 15.1 mg (Pd, 0.01 mmol). The flask was purged with H₂ for 5 minutes, and EtOH (5 mL), was added under H₂. The reaction mixture was stirred at room temperature and the reaction progress was monitored by TLC. Upon completion, the mixture was filtered off Cat C. The EtOH was removed under vacuum, and then the residue was further purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford the corresponding aniline 2.

To study the recyclability of Pd@POL-2, the hydrogenation of 1-methoxy-4-nitrobenzene was conducted in the same conditions as described above. After reaction, the catalyst was separated through centrifugal, diethyl phthalate was added to the supernatant liquid as an internal standard, and the mixture was filtered under vacuum, the yield was determined by NMR and the catalyst was washed with EtOH, and reused in a next run.

General procedure for hydrogenation of various α,β unsaturated compounds

To a three-necked round bottom flask was added nitroarenes **3** (2 mmol), Cat B, 26.5 mg (Pd, 0.01 mmol). The flask was purged with H_2 for 5 minutes, and EtOH (5 mL), was added under H_2 . The reaction mixture was stirred at room temperature and the reaction progress was monitored by TLC. Upon completion, the mixture was filtered off Cat B. The EtOH was removed under vacuum, and then the residue was further purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford the corresponding ketones **4**.

General procedure for reductive cyclization of 2nitrophenylacetonitriles to indoles

To a three-necked round bottom flask was added nitroarenes **6** (0.3 mmol), Cat C, 45 mg (Pd, 0.03 mmol). The flask was purged with H₂ for 5 minutes, and MeOH (3 mL), was added under H₂. The reaction mixture was stirred at room temperature and the reaction progress was monitored by TLC. Upon completion, the mixture was filtered off Cat C. The MeOH was removed under vacuum, and then the residue was further purified by silica gel column chromatography (petroleum ether and ethyl acetate) to afford the corresponding indols **7**.

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References

- [1] a) R. K. Rai, A. Mahata, S. Mukhopadhyay, S. Gupta, P.-Z. Li, K. T. Nguyen, Y. Zhao, B. Pathak, S. K. Singh, *Inorg. Chem.* 2014, 53, 2904-2909; b) M. Zhao, K. Yuan, Y. Wang, G. Li, J. Guo, L. Gu, W. Hu, H. Zhao and Z. Tang, *Nature* 2016, 539, 76-80; c) G.-H. Wang, J. Hilgert, F. H. Richter, F. Wang, H.-J. Bongard, B. Spliethoff, C. Weidenthaler, F. Schüth, *Nature Mater.* 2014, *13*, 293-300;. d) D. Astruc, F. Lu and J. R. Aranzaes, *Angew. Chem. Int. Ed.* 2005, *44*, 7852-7872.
- [2] a) R. V. Jagadeesh, A.-E. Surkus, H. Junge, M.-M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner, M. Beller, *Science* 2013, 342, 1073-1076; b) A. Corma, P. Serna, *Science* 2006, 313, 332-334; c) H.-U. Blaser, H. Steiner, M. Studer, *ChemCatChem* 2009, 1, 210-221; d) I. Sorribes, L. Liu, A. Corma, ACS Catal. 2017, 7, 2698-2708; e) G. Hahn, J.-K. Ewert, C. Denner, D. Tilgner, R. Kempe, *ChemCatChem* 2016, 8, 2461-2465.
- [3] a) N. Mahata, A. F. Cunha, J. J. M. Órfão, J. L. Figueiredo, *Chem. Eng. J.* 2012, *188*, 155-159; b) Z. Wei, Y. Gong, T. Xiong, P. Zhang, H. Li, Y. Wang, *Catal. Sci. Technol.* 2015, *5*, 397-404; c) S. Jagtap, Y. Kaji, A. Fukuoka, K. Hara, *Chem. Commun.* 2014, *50*, 5046-5048; d) A. Nagendiran, V. Pascanu, A. Bermejo Gomez, G. Gonzalez Miera, C.-W. Tai, O. Verho, B. Martin-Matute, J.-E. Baeckvall, *Chem. Eur. J.* 2016, *22*, 7184-7189.
- [4] For selected examples: a) D. He, H. Shi, Y. Wu, B.-Q. Xu, Green Chem. 2007, 9, 849-851; b) K.-i. Shimizu, Y. Miyamoto, A. Satsuma, J. Catal. 2010, 270, 86-94; c) Y. Chen, J. Qiu, X. Wang, J. Xiu, J. Catal. 2006, 242, 227-230; d) M. Boronat, P. Concepción, A. Corma, S. González, F. Illas, P. Serna, J. Am. Chem. Soc. 2007, 129, 16230-16237; e) Z. Wei, J. Wang, S. Mao, D. Su, H. Jin, Y. Wang, F. Xu, H. Li, Y. Wang, ACS Catal. 2015, 5, 4783-4789; f) G. Fan, W. Huang, C. Wang, Nanoscale 2013, 5, 6819-6825; g) F. A. Westerhaus, R. V. Jagadeesh, G. Wienhoefer, M.-M. Pohl, J. Radnik, A.-E. Surkus, J. Rabeah, K. Junge, H. Junge, M. Nielsen, A. Brueckner, M. Beller, Nat. Chem. 2013, 5, 537h) A. Corma, P. Serna, H. García, J. Am. 543: Chem. Soc. 2007, 129, 6358-6359; i) A. Indra, N. Maity, P. Maity, S. Bhaduri, G. K. Lahiri, J. Catal. **2011**, 284, 176-183; j) X. Wang, Y. Li, J. Mol. Catal. A: Chem. **2016**, 420, 56-65; k) M. Makosch, W.-I. Lin, V. Bumbálek, J. Sá, J. W. Medlin, K. Hungerbühler, J. A. van Bokhoven, ACS Catal. 2012, 2, 2079-2081; 1) M. Takasaki, Y. Motoyama, K. Higashi, S.-H. Yoon, I. Mochida, H. Nagashima, Org. Lett. 2008, 10, 1601-1604; m) A. Corma, P. Serna, Nat. Protocols 2006, 1, 2590-2595;
- [5] a) K. Layek, M. L. Kantam, M. Shirai, D. Nishio-Hamane, T. Sasaki, H. Maheswaran, *Green Chem.* 2012, 14, 3164-3174; b) X. Lin, M. Wu, D. Wu, S. Kuga, T. Endo, Y. Huang, *Green Chem.* 2011, 13, 283-287; c) D. Cantillo, M. Baghbanzadeh, C. O. Kappe, *Angew. Chem. Int. Ed.* 2012, 51, 10190-10193; d) U. Sharma, P. K. Verma, N. Kumar, V. Kumar, M. Bala, B. Singh, *Chem. -Eur. J.* 2011, 17,

5903-5907; e) R. V. Jagadeesh, G. Wienhofer, F. A. Junge, M. Beller, Chem. Commun. 2011, 47, 10972-10974; f) Q. Shi, R. Lu, K. Jin, Z. Zhang, D. Zhao, Green Chem. 2006, 8, 868-870; g) Z. Zhao, H. Yang, Y. Li, X. Guo, *Green Chem.* **2014**, *16*, 1274-1281; h) M. B. Gawande, A. K. Rathi, P. S. Branco, I. D. Nogueira, A. Velhinho, J. J. Shrikhande, U. U. Indulkar, R. V. Jayaram, C. A. A. Ghumman, N. Bundaleski, O. M. N. D. Teodoro, *Chem. -Eur. J.* 2012, 18, 12628-12632; i) R. Dey, N. Mukherjee, S. Ahammed, B. C. Ranu, Chem. Commun. 2012, 48, 7982-7984; j) Y. Li, Y.-X. Zhou, X. Ma, H.-L. Jiang, Chem. Commun. 2016, 52, 4199-4202.

- [6] a) Y.-C. Hong, K.-Q. Sun, G.-R. Zhang, R.-Y. Zhong, B.-Q. Xu, Chem. Commun. 2011, 47, 1300-1302; b) D. B. Bagal, Z. S. Qureshi, K. P. Dhake, S. R. Khan, B. M. Bhanage, *Green Chem.* 2011, 13, 1490-1494; c) W. Lin, H. Cheng, L. He, Y. Yu, F. Zhao, J. Catal. 2013, 303, 110-116; d) A. Mori, Y. Miyakawa, E. Ohashi, T. Haga, T. Maegawa, H. Sajiki, Org. Lett. 2006, 8, 3279-3281; e) B. P. S. Chauhan, J. S. Rathore, T. Bandoo, J. Am. Chem. Soc. 2004, 126, 8493-8500; f) T. Gallert, M. Hahn, M. Sellin, C. Schmöger, A. Stolle, B. Ondruschka, T. F. Keller, K. D. Jandt, ChemSusChem 2011, 4, 1654-1661.
- [7] a) J. Su, J.-S. Chen, Microporous Mesoporous Mater. **2017**, *237*, 246-259; b) T. Takahashi, M. Yoshimura, H. Suzuka, T. Maegawa, Y. Sawama, Y. Monguchi, H. Sajiki, *Tetrahedron* **2012**, *68*, 8293-8299; c) T. Maegawa, T. Takahashi, M. Yoshimura, H. Suzuka, Y. Monguchi, H. Sajiki, Adv. Synth. Catal. 2009, 351, 2091-2095

Westerhaus, A.-E. Surkus, M.-M. Pohl, H. Junge, K.

- [8] a) L. Li, H. Zhao, J. Wang, R. Wang, ACS Nano 2014, 8, 5352-5364; b) L. Li, C. Zhou, H. Zhao, R. Wang, Nano Research 2015, 8, 709-721; c) H. Zhong, Y. Gong, F. Zhang, L. Li, R. Wang, *J. Mater. Chem. A.* **2014**, *2*, 7502-7508; d) L. Li, H. Zhao, R. Wang, *ACS Catal.* **2015**, *5*, 948-955; e) Z. Z. Yang, H. Zhang, B. Yu, Y. Zhao, G. Ji, Z. Liu, *Chem Commun.* **2015**, *51*, 1271-1274; f) J. Mondal, S. K. Kundu, W. K. Hung Ng, R. Singuru, P. Borah, H. Hirao, Y. Zhao, A. Bhaumik, *Chem. –Eur. J.* 2015, 21, 19016-19027; g) J. Camacho-Bunquin, N. A. Siladke, G. Zhang, J. Niklas, O. G. Poluektov, S. T. Nguyen, J. T. Miller, A. S. Hock, *Organometallics* **2015**, *34*, 947-952; h) J. Schmidt, J. Weber, J. D. Epping, M. Antonietti, A. Thomas, Adv. Mater. 2009, 21, 702-705; i) J. Mondal, Q. T. Trinh, A. Jana, W. K. H. Ng, P. Borah, H. Hirao, Y. Zhao, ACS Appl. Mater. Interface. 2016, 8, 15307-15319; j) L. Li, Z. Chen, H. Zhong, R. Wang, Chem. -Eur. J. 2014, 20, 3050-3060.
- [9] Y.-B. Zhou, C.-Y. Li, M. Lin, Y.-J. Ding, Z.-P. Zhan,
- *Adv. Synth. Catal.* **2015**, *357*, 2503-2508. [10] M. Mąkosza, W. Danikiewicz, K. Wojciechowski, Liebigs Ann. Chem. 1988, 203-208.
- [11] Y. Motoyama, K. Kamo, H. Nagashima, Org. Lett. **2009**, *11*, 1345-1348.
- [12] When the obtained POL was grinded to grey powders, and crushed into 200-300 mush through a sample sieve, the similar catalytic activities were shown in the reaction of 1a, 3a, and 6a as those without size control, thus confirming the size of the POLs had little impact on the catalytic activity.

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Pd/P-doped Porous Organic Polymer as Recyclable Chemoselective and Highly Efficient Hydrogenation Catalysts under Ambient Conditions

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