Organic Polymers

Prefunctionalized Porous Organic Polymers: Effective Supports of Surface Palladium Nanoparticles for the Enhancement of Catalytic Performances in Dehalogenation

Hong Zhong, Caiping Liu, Hanghui Zhou, Yangxin Wang, and Ruihu Wang*^[a]

Abstract: Three porous organic polymers (POPs) containing H, COOMe, and COO⁻ groups at 2,6-bis(1,2,3-triazol-4-yl)pyr-idyl (BTP) units (i.e., POP-1, POP-2, and POP-3, respectively) were prepared for the immobilization of metal nanoparticles (NPs). The ultrafine palladium NPs are uniformly encapsulated in the interior pores of POP-1, whereas uniform- and dual-distributed palladium NPs are located on the external surface of POP-2 and POP-3, respectively. The presence of carboxylate groups not only endows POP-3 an outstanding

Introduction

Metal nanoparticles (NPs) supported on porous materials have been widely applied in energy conversion, environmental protection, and catalysis.^[1-4] Considerable efforts have been devoted to the fabrication of ultrafine metal NPs in the interior pores based on powerful confinement effect of pore structures,[5-7] but most of the synthetic methods show a lack of generality for porous materials with different structures and functions, because the size, distribution, and location of metal NPs strongly depend on the porous nature of the materials and the reduction method of the metal precursors.^[8-11] The incorporation of functional groups for the customized performances usually decreases the surface area and the pore volume of the porous materials, resulting in the diffusion of metal NPs and their precursors from interior pores to the external surface during preparation and/or catalytic reactions.[12-14] In contrast, metal NPs on the external surface can provide higher catalytic activity than NPs in the interior cavities, owing to acceleration of mass transfer and easy availability of active sites.^[15-18] However, these surface metal NPs have received little attention because they are instable and prone to aggregation. It is desirable but challenging to seek for an effective strategy to immobilize metal NPs on the external surface of porous materials.

 [a] H. Zhong, Dr. C. Liu, H. Zhou, Y. Wang, Prof. R. Wang State Key Laboratory of Structural Chemistry Fujian Institute of Research on the Structure of Matter Chinese Academy of Sciences, Fuzhou, Fujian 350002 (China) Fax: (+ 86) 591-8371-1028 E-mail: ruihu@fjirsm.ac.cn

Supporting information for this article can be found under http:// dx.doi.org/10.1002/chem.201601956. dispersibility in H_2O /EtOH, but also enables the palladium NPs at the surface to show the highest catalytic activity, stability, and recyclability in dehalogenation reactions of chlorobenzene at 25 °C. The palladium NPs on the external surface are effectively stabilized by the functionalized POPs containing BTP units and carboxylate groups, which provides a new insight for highly efficient catalytic systems based on surface metal NPs of porous materials.

As a new class of important porous materials, porous organic polymers (POPs) have captured widespread interest in gas storage and separation, sensing, proton conductivity, drug delivery, and catalysis.^[19-23] It has been demonstrated that the structures and porous properties of POPs could be elegantly tuned through selecting building units with different linking groups.^[23-25] In addition, the modular nature of the synthesis of POPs has allowed the incorporation of various functionalities for a specific purpose.^[26,27] Relative to an extensive research in the functionality of POPs directed at gas sorption and separation,^[28-30] the pre-designable functionalities for immobilization of metal NPs have seldom been explored.

The introduction of suitable functional groups into building units is one of the feasible routes for tailor-made synthesis of functionalized POPs at the molecular level.^[31,32] Carboxylate has been known to possess an outstanding coordination ability to metal species, the incorporation of carboxylate into POPs not only may improve the stability of metal NPs through coordination and electrostatic interactions, but is also favorable for catalytic reactions in polar solvents through increasing the polarity and dispersibility of the POPs. To search for stable palladium NPs on the external surface of POPs, herein, we reported three POPs containing H, COOMe, and COO⁻ groups at 2,6bis(1,2,3-triazol-4-yl)pyridyl (BTP) units, that is, POP-1, POP-2 and POP-3, respectively. The introduction of COOMe and carboxylate groups has exerted crucial effects on the porous nature and functions of the POPs, resulting in variation of the size and location of the palladium NPs from interior pores to the external surface. In comparison with palladium NPs in the interior cavities, a superior catalytic activity, stability, and recyclability in dehalogenation reactions have been demonstrated by the external surface palladium NPs in Pd/POP-3.

Chem. Eur. J. 2016, 22, 1–10 Wiley Online Library These are not the final page numbers! **77**



Results and Discussion

As show in Scheme 1, POP-1 and POP-2 were readily synthesized through a facile click reaction of 1,3,5-tris(4-azidophenyl)benzene with 2,6-diethynylpyridine and methyl 2,6-diethynylisonicotinate, respectively, under standard click reaction condi-



Scheme 1. Schematic illustration for the synthesis of POP-1, POP-2, POP-3, Pd/POP-1, Pd/POP-2, and Pd/POP-3.

tions.^[33–37] Subsequent hydrolysis of POP-2 in aqueous LiOH solution gave rise to POP-3. As expected, POP-1 and POP-2 are hydrophobic, whereas POP-3 shows superior dispersibility in water/ethanol owing to the presence of the carboxylate group (Figure S1 in the Supporting Information). The treatment of POP-1, POP-2, and POP-3 with Pd(OAc)₂ with a 1:1 molar ratio of BTP to Pd^{II}, and subsequent reduction by NaBH₄ gave rise to the Pd/POP-1, Pd/POP-2, and Pd/POP-3 systems, respectively. Inductively coupled plasma (ICP) analyses show palladium contents in Pd/POP-1, Pd/POP-2, and Pd/POP-3 of 0.22, 0.36, and 0.39 mmol q^{-1} , respectively.

The FTIR spectra of POP-1, POP-2, and POP-3 indicate the total consumption of the starting materials due to the disappearance of stretching vibration peaks of the terminal alkynyl

and azido groups at $\tilde{v} = 3262$ and 2126 cm⁻¹, respectively, the characteristic peaks of the triazolyl group occur at $\tilde{\nu} = 1610$ and 3142 cm⁻¹, which suggests complete azide-alkyne cycloaddition (Figure 1 a-c).^[33, 38] Furthermore, the characteristic bands of the COOMe group at $\tilde{\nu} = 1726 \text{ cm}^{-1}$ and the carboxylate group at $\tilde{v} = 1604 \text{ cm}^{-1}$ were observed in the FTIR spectra of POP-2 and POP-3, respectively. In the solid-state ¹³C NMR spectra of POP-1, POP-2, and POP-3 the present resonance of the C4-triazolyl carbon atom around $\delta = 148$ ppm and the absent characteristic peaks of alkynyl carbon atoms in the range of $\delta =$ 70–100 ppm further confirm the successful polymerization (Figures S2a-c in the Supporting Information).^[11,19] The broad signals at $\delta =$ 118–139 ppm correspond to the aromatic carbon atoms. The resonance peaks at $\delta = 166$ and 169 ppm are assigned to carbonyl carbon atoms of POP-2 and POP-3, respectively. Scanning electron microscopy (SEM) images show that POP-1, POP-2, and POP-3 are composed of granular particles with a size of 50-100 nm (Figure S3 in the Supporting Information), which is in agreement with most of the reported POPs.^[39-41] It should be mentioned that the FTIR (Figure 1) and solid-state ¹³C NMR spectra (Figure S2 in the Supporting Information) as well as the SEM images (Figures S3b, e, and h in the Supporting Information) of Pd/POP-1, Pd/POP-2, and Pd/POP-3 are almost identical with those of POP-1, POP-2, and POP-3, respectively, indicating that the structural polymers are well maintained after palladium loading.

In the thermal gravimetric analysis (TGA) curves of POP-1 and POP-2 an initial weight loss of 5.5 and 5.6%, respectively, before 130°C was observed, whereas POP-3 shows a weight loss of 18.4% before 170°C (Figure S4 in the Supporting Information), which is attributed to the hydrophilicity enhancement of the structural framework. The thermal stability of Pd/POP-1, Pd/POP-2, and Pd/POP-3 is lower than that of POP-1, POP-2, and POP-3, respectively (Figure S4 in the Supporting Information). Powder X-ray diffraction (PXRD) analyses indicate that POP-1, POP-2, and POP-3 are amorphous (Figure S5 in the Supporting Information) owing to the irreversibility of the click reaction.^[34,35] No obvious characteristic peaks of palladium particles were observed in the PXRD patterns of Pd/POP-1, Pd/POP-2, and Pd/POP-3.



Figure 1. FTIR spectra of a) the starting materials, POP-1, and Pd/POP-1, b) the starting materials, POP-2, and Pd/POP-2, and c) the starting materials, POP-3, and Pd/POP-3. (DEP = 2,6-diethynylpyridine, DEP-COOMe = methyl-2,6-diethynylisonicotinate, TAPB = 1,3,5-tris(4-azidophenyl)benzene).

2

www.chemeurj.org

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim **K** These are not the final page numbers!



CHEMISTRY A European Journal Full Paper

The porous properties of POP-1, POP-2, and POP-3 were investigated by physisorption of nitrogen at 77 K. The nitrogen adsorption/desorption isotherm of POP-1 exhibits a combination of type I and IV (Figure 2a),^[11] which indicates the existence of both micropores and mesopores in POP-1. However, POP-2 and POP-3 give an isotherm of type IV.^[11] The Brunauer–



Figure 2. a) N_2 adsorption/desorption isotherms for POP-1, POP-2, POP-3, Pd/POP-1, Pd/POP-2, and Pd/POP-3. b) Pore size distribution for POP-1 and Pd/POP-1. c) Pd 3d XPS spectra for Pd/POP-1, Pd/POP-2, and Pd/POP-3. d) N 1s XPS spectra for POP-1, POP-2, POP-3, Pd/POP-1, Pd/POP-2, and Pd/POP-3.

Chem. Eur. J. **2016**, 22, 1–10

www.chemeurj.org

3

Emmett-Teller (BET) surface areas of POP-1, POP-2, and POP-3 are 358, 106, and 79 m²g⁻¹, respectively. POP-1 possesses a narrow pore size distribution of around 1.50 nm (Figure 2b), whereas the micropores in POP-2 and POP-3 are negligible (Figure S6 in the Supporting Information). The contribution of microporosity to these POPs can be calculated as the ratio of the micropore volume $(V_{0,1})$ to the total pore volume (V_{tot}) .^[19] The $V_{0.1}/V_{tot}$ value of POP-1 is 0.160, which is decreased sharply to 0.035 and 0.030 in POP-2 and POP-3, respectively (Table S1 in the Supporting Information). The shapes of the N₂ adsorption/desorption isotherms of Pd/POP-1, Pd/POP-2, and Pd/POP-3 are well preserved (Figure 2a), indicating that the pore systems have not been altered substantially by the palladium NPs. The BET surface areas of Pd/POP-1, Pd/POP-2, and Pd/ POP-3 are decreased to 263, 72, and 50 m^2q^{-1} , respectively, which is attributed to both partial pore filling and mass increment after palladium loading.

Considering significant influences of BTP functionalization on the porous properties of POPs, their effects on the palladium NPs and the catalytic performances were further examined. Transmission electron microscope (TEM) analyses show that ultrafine palladium NPs in Pd/POP-1 are uniformly encapsulated in the interior cavities (Figures 3a and b), and that their aver-



Figure 3. TEM images of a,b) Pd/POP-1, d,e) Pd/POP-2, and g,h) Pd/POP-3. HAADF-STEM and EDX mapping images of c) Pd/POP-1, f) Pd/POP-2, and i) Pd/POP-3.

age size is (1.5 ± 0.3) nm, which is similar to the micropore size of POP-1. It should be mentioned that the average size of palladium NPs in Pd/POP-1 is smaller than those supported on POPs containing mono- or bi-dentate coordination groups.^[5] Moreover, the uniform distribution of the palladium NPs is much different from the reported dual distribution both in the interior pores and on the external surface of POPs when NaBH₄ is used as a reduction agent of the palladium precursors.^[19] These observations are probably ascribed to the strong chelat-



ing coordination ability of the ter-dentate BTP units and a superior confinement effect of the micropores, which restrict the diffusion of the palladium NPs and their precursors from interior pores to the external surface of POP-1 during the preparation of the palladium NPs. In contrast, the palladium NPs in Pd/POP-2 are uniformly located on the external surface with an average size of (3.3 ± 0.3) nm (Figures 3d and e), which is probably ascribed to the filling of the interior cavities by the COOMe groups. Interestingly, the change of the functional groups from the COOMe to the carboxylate group results in the formation of dual-distributed palladium NPs in the interior pores and on the external surface of POP-3 (Figures 3g and h), and the average diameters of the palladium NPs in Pd/POP-3 are (1.6 ± 0.35) and (3.5 ± 0.35) nm, respectively, which are comparable with those in Pd/POP-1 and Pd/POP-2, respectively. The dual distribution of the palladium NPs in POP-3 is probably ascribed to a synergetic effect of the carboxylate groups by electrostatic and/or coordination interactions. The size, location, and distribution of the palladium NPs in the interior pores and the external surface were further demonstrated by highannular dark-field scanning TEM (HAADF-STEM) and energydispersive X-ray (EDX) mapping images of Pd/POP-1, Pd/POP-2, and Pd/POP-3 (Figures 3 c, f, and i as well as Figure S7 in the Supporting Information).

It has been reported that the loading amount of palladium precursors and the reduction methods may influence the structures and properties of the palladium NPs,^[2] however, we failed to obtain uniformly distributed palladium NPs even when half the amount of $Pd(OAc)_2$ with respect to Pd/POP-3 was used under the same conditions, no apparent variation was observed in their TEM images (Figures 4a and d). In addition, the variation of the reduction agent of $Pd(OAc)_2$ from NaBH₄ to H₂ or N₂H₄·H₂O has no detectable effect on the dual distribution of the palladium NPs on the external surface of POP-3, either (Figures 4b, e, c, and f). These results reveal that the introduction of carboxylate groups not only can modulate the properties of the POPs, but also exerts an important effect on the formation and structure of the palladium NPs.



Figure 4. TEM images of Pd/POP-3 prepared a,d) by using half of the theoretical amount of $Pd(OAc)_2$, b,e) by using H_2 as a reducing agent, and c,f) by using N_2H_4 as reducing agent.

The existing state of the surface palladium in Pd/POP-1, Pd/ POP-2, and Pd/POP-3 was investigated by X-ray photoelectron spectroscopy (XPS). As shown in Figure 2c, the Pd 3d spectra present two sets of doublet peaks corresponding to Pd 3d_{5/2} and Pd $3d_{3/2}$. The Pd $3d_{5/2}$ peaks at 335.75, 335.90, and 335.40 eV are attributed to Pd⁰ species of Pd/POP-1, Pd/POP-2, and Pd/POP-3, respectively. In comparison with Pd/POP-1, a positive shift of 0.15 eV and a negative shift of 0.35 eV was observed for Pd/POP-2 and Pd/POP-3, respectively, which exhibits that Pd⁰ species in Pd/POP-2 are more electron-deficient than in Pd/POP-1 because of an electron-withdrawing effect of the COOMe group, whereas an electron-donating effect of the carboxylate group results in more electron-rich Pd⁰ species in Pd/POP-3.^[11,34] The ratio of Pd⁰ to Pd^{II} in Pd/POP-1, Pd/POP-2, and Pd/POP-3 are 0.49, 0.52, and 0.41, respectively. It should be mentioned that the Pd $3d_{5/2}$ binding energy peaks for Pd^{II} species in Pd/POP-1, Pd/POP-2, and Pd/POP-3 shift negatively by 0.65, 0.45, and 0.70 eV, respectively, in comparison with that of 338.4 eV for free Pd(OAc)2,^[4] the negative shift is ascribed to the strong coordination interaction of Pd^{II} with the chelating ter-dentate BTP units, in which election donation from BTP to Pd^{II} makes the Pd^{II} species less electron-deficient.

In order to further confirm the interactions between the supports and the incorporated palladium species, XPS spectra of N 1s in the POPs and the Pd/POPs systems were implemented (Figure 2 d). The peaks at 399.45, 399.60, and 399.70 eV correspond to the N 1s of POP-1, POP-2, and POP-3, respectively. The peaks in Pd/POP-1, Pd/POP-2, and Pd/POP-3 are shifted to 399.65, 399.70, and 399.75 eV, respectively. The shift of the N 1s toward higher binding energies results from coordination of nitrogen atoms to palladium,^[42-44] which further suggests the electron donation from the BTP units to the palladium species after palladium loading.

To have a clear insight into the effects of the functional groups on the electronic properties of POP-1, POP-2, and POP-3, the hybrid Becke three-parameter Lee-Yang-Parr (B3LYP) density functional method in combination with the 6-311+ G(d) basis set were performed based on their model compounds. As shown in Figure 5 and Table S2 in the Supporting Information, the H, COOMe, and COO⁻ groups at the BTP units significantly influence their charge distribution. The charges of the pyridyl nitrogen atom in POP-1, POP-2, and POP-3 are -0.415, -0.393, and -0.438 e, respectively, which are more negative than the nitrogen atoms in 1,2,3-triazolyl. In comparison with POP-1, the electron-withdrawing COOMe group in POP-2 and the electron-donating carboxylate group in POP-3 result in a positive shift of 0.022 e and a negative shift of 0.023 e, respectively, which is consistent with the results of the XPS analyses. The nitrogen atoms of the 1,2,3-triazolyl groups in POP-1, POP-2, and POP-3 all possess negative charges, the charges of the N1 and N3 atoms are almost equal, and are more negative than that of the N2 atom. In view of the charge density of the pyridyl nitrogen atom and the nitrogen atomic arrangement of the 1,2,3-triazolyl group, the BTP unit prefers to coordinate with palladium in a N3-N4-N3' ter-dentate chelating mode, which is the same as those in the BTP-based coordination compounds.^[45-49] HOMO and LUMO analyses reveal

Chem. Eur. J. **2016**, 22, 1 – 10

www.chemeurj.org

4

 $\ensuremath{\mathbb{C}}$ 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

FF These are not the final page numbers!





Figure 6. a) Dehalogenation reaction of chlorobenzene as a function of the time by using 0.5 mmol chlorobenzene and 0.5 mol % palladium at 25 °C. b) Recyclability in the dehalogenation reaction of chlorobenzene for Pd/ POP-1, Pd/POP-2, Pd/POP-3, and Pd/C by using 0.5 mmol chlorobenzene and 1 mol% palladium for 6 h at 25 °C.

Figure 5. Electrostatic potential (ESP)-mapped molecular van der Waals surfaces, highest occupied molecular orbitals, and the lowest unoccupied molecular orbitals for the model compounds of a,b) POP-1, c,d) POP-2, and e,f) POP-3.

that the HOMO and LUMO in POP-1 and the HOMO in POP-2 are shared by BTP and phenyl units, whereas the HOMO in POP-3 is mainly occupied by the carboxylate group. The LUMO in POP-2 is mainly focused on the pyridyl unit, and the LUMO in POP-3 is mainly occupied by the triazolyl and phenyl groups (Figure 5).

Aryl halides are a high risk to environment and our health due to their toxicity and strong bioaccumulation potential, however they are widely used as insect repellents, fungicides, and organic intermediates.^[50-52] The dehalogenation of aryl halides is a significant process for the removal of halogenated organic pollutants and for the synthesis of fine chemicals. Various catalysts, such as TiO₂-Fe₂O₃ mixed-oxides,^[53] phosphinorhodium catalysts,^[54] organometallic complexes,^[55] and palladium NPs,^[56,57] have been reported for dehalogenation reactions. Among them, supported palladium NPs are one of the common catalysts. The use of suitable supports not only can inhibit the agglomeration of palladium NPs through coordination, electrostatic, and/or confinement interactions, but also may accelerate the rate-determining oxidative addition of aryl halides through endowing palladium NPs with steric and electronic effects, resulting in an improvement of the catalytic activity.^[58-60] However, the use of POPs as heterogeneous supports of palladium NPs in this reaction has not been reported hitherto. To distinguish the influences of the COOMe and carboxylate groups on the catalytic performances, the Pd/POP-1, Pd/POP-2, and Pd/POP-3 systems were initially evaluated by the dehalogenation of chlorobenzene with 0.5 mol% palladium in H₂O/EtOH at 25 °C. As shown in Figure 6 a, Pd/POP-3 afforded full conversion of chlorobenzene to benzene in 20 h, whereas the use of Pd/POP-1 and Pd/POP-2 gave 70 and 93% GC yield, respectively. The superior catalytic activity of Pd/POP-3 is attributed to its superior dispersibility in H₂O/EtOH (Figure S1 in the Supporting Information), which facilitates the contact between the active sites and the substrates. The electron-donating effect of the carboxylate group also increases the electron density of the Pd⁰ species in Pd/POP-3, which sufficiently facilitate oxidative addition of the C-X bond.^[60] Apparently, the palladium NPs on the external surface in Pd/POP-2 and Pd/POP-3 possess higher catalytic activity than those encapsulated in the interior cavities in Pd/POP-1. As a comparison, commercial Pd/C was also tested under the same conditions and a conversion of 85% of chlorobenzene was achieved within 20 h, which is lower than that of the palladium NPs on the external surface.

To further explore the catalytic efficiency of this system, a more versatile and practical method was investigated in the dehalogenation reaction by using Pd/POP-3 as a catalyst in the presence of HCOONH₄ at 25 °C. As shown in Table 1, the amount of the catalyst is very important for this reaction. The use of 0.25 mol% palladium catalyst gave only 4% conversion within 24 h (Table 1, entry 1), whereas a quantitative yield was observed when the palladium amount was increased to 0.5 mol% (Table 1, entry 2) with a TON value up to 200, which exceeds those from palladium NPs supported by metal-organic frameworks^[53] and amphiphilic polymers.^[57] Notably, chlorobenzene can be completely transferred into benzene in the presence of 1.0 mol% Pd/POP-3 in 6 h (Table 1, entry 3). The dependence on the catalyst loading amount is probably ascribed to a long induction period of the dehalogenation reaction.^[51] A control experiment was also performed in the pres-

| Chem. Eur. J. 2016, 22, 1 – 10 | www.chemeurj.org | |
|--------------------------------|-----------------------|---|
| These are not the | final page numbers! 7 | 7 |

| Table 1. Dehalogenation reaction of aryl halides catalyzed by Pd/POP-3. ^[a] | | | | | | | | |
|--|---|-------------|-------|-------------------------------|--------------------|--|--|--|
| R CI $\frac{[Pd], HCOONH_4}{H_2O/EtOH, 25 °C}$ R | | | | | | | | |
| Entry | Substrate | [Pd] [mol%] | t [h] | Conversion [%] ^[b] | TON ^[c] | | | |
| 1 | √−cı | 0.25 | 24 | 4 | 16 | | | |
| 2 | CI-CI | 0.5 | 24 | 100 | 200 | | | |
| 3 | CI-CI | 1 | 6 | 100 | 100 | | | |
| 4 ^[d] | CI-CI | - | 6 | 0 | 0 | | | |
| 5 | Br | 1 | 6 | 100 | 100 | | | |
| 6 | ∑—ı | 1 | 6 | 93 | 93 | | | |
| 7 | F ₃ C-Cl | 1 | 6 | 100 | 100 | | | |
| 8 | H ₃ C – Cl | 1 | 6 | 100 | 100 | | | |
| 9 | H3CO-CI | 1 | 6 | 100 | 100 | | | |
| 10 | H ₃ C Cl CH ₃ CH ₃ | 1 | 6 | 87 | 87 | | | |
| 11 | | 1 | 6 | 100 | 100 | | | |
| 12 | CI-CI | 1 | 6 | 100 | 100 | | | |
| 13 | CI CI | 1 | 6 | 92 | 92 | | | |
| 14 | | 1 | 12 | 100 | 100 | | | |
| 15 | CI-CI | 1 | 1 | 32 | 32 | | | |
| 16 ^[e] | Cl-Cl | - | 24 | 32 | 32 | | | |
| [a] Reaction conditions: aryl halide (0.5 mmol), HCOONH ₄ (2.5 mmol), H ₂ O/EtOH (1:1, 2 mL), 25 °C. [b] GC yield. [c] TON = turnover number, that | | | | | | | | |

is, mol product per mol catalyst. [d] POP-3 was used in the absence of palladium. [e] Filtration experiment.

ence of POP-3 only, no dehalogenation product was detected under the same conditions (Table 1, entry 4). It is known that the activation of aryl iodides is easier than of aryl bromides or chlorides due to the order of the C-X bond energy. In fact, chlorobenzene and bromobenzene are more reactive than iodobenzene (Table 1, entries 3, 5, and 6).^[53,59] When aryl chlorides bearing electron-withdrawing and electron-donating groups, such as --CF3, --Me, and --OMe, were used, the corresponding products were obtained in quantitative yields (Table 1, entries 7-9). The use of 2,6-dimethyl-chlorobenzene with bulkier steric hindrance gave an GC yield of 87% (Table 1, entry 10). Interestingly, 1,2-dichlorobenzene and 1,4-dichlorobenzene can be completely dehalogenated under the same conditions (Table 1, entries 11 and 12). The dehalogenation reaction of 1,3,5-trichlorobenzene afforded a conversion of 92% with chlorobenzene (1.8%) and 1,2-dichlorobenzene (3.0%) residues in 6 h (Table 1, entry 13), whereas a GC yield of 100% of the target product was obtained when the reaction time was prolonged to 12 h (Table 1, entry 14).

The high catalytic activity of Pd/POP-1, Pd/POP-2, and Pd/ POP-3 prompted us to examine their stability and recyclability, which are also important factors in heterogeneous systems. The catalytic recyclability was evaluated by the dehalogenation reaction of chlorobenzene by using 1.0 mol% palladium at 25°C. As shown in Figure 6b, Pd/POP-3 may be used for at least four runs with 100% conversion of chlorobenzene, whereas the conversion decreased to 80 and 43% for Pd/POP-1 and Pd/POP-2, respectively, in the fourth run. When Pd/C was used, the conversion of chlorobenzene decreased to 16 and 5% in the third and fourth run, respectively. The palladium leaching after the first run for Pd/POP-1, Pd/POP-2, and Pd/ POP-3 was 0.78, 1.62, and 0.93 ppm, respectively. Notably, after the reaction was run for 1 h, the palladium-containing catalytic species was quickly removed by filtration, and the filtrate was continued to react for additional 23 h, and no change in the conversion was detected (Table 1, entries 15 and 16), which indicates that the dehalogenation reaction proceeds in a heterogeneous manner in the catalytic system. The recyclability was also investigated by using 0.5 mol% palladium at 25 °C for 12 h. As shown in Figure S8 in the Supporting Information, a conversion of 45% of chlorobenzene was maintained for at least five runs for Pd/POP-3, whereas the conversion of chlorobenzene for Pd/POP-1 and Pd/POP-2 was decreased from 30 to 19 and from 40 to 9%, respectively, under the same conditions, which further reveals a superior stability and recyclability of Pd/POP-3.

After consecutive reaction, the resultant powders were isolated and examined by SEM and TEM. The SEM images (Figure S3 in the Supporting Information) show that the original morphologies of Pd/POP-1, Pd/POP-2, and Pd/POP-3 are intact after consecutive dehalogenation for four runs. However, the average size of the palladium NPs in Pd/POP-1 increases to (2.5 ± 0.35) nm with concomitant formation of a few large palladium NPs after the fourth run (Figures 7a and S9a in the Supporting Information), which may be ascribed to the migration of the palladium NPs from the interior pores and the accumulation on the external surface during the consecutive dehalogenation reaction. In contrast, an obvious agglomeration was observed in Pd/POP-2 after the fourth run (Figures 7d and S9b in the Supporting Information). However, the palladium NPs in Pd/POP-3 are uniformly dispersed on the external surface with a mean size of (4.5 ± 0.35) nm after the fourth run (Figures 7 g and S9c in the Supporting Information). These results signify that the carboxylate group is favorable for the stabilization of the palladium NPs through electrostatic and/or coordination interactions. HAADF-STEM and EDX mapping images further testify the location and distribution of the palladium NPs on the external surface after catalytic recycles (Figure 7).

Conclusion

6

An effective strategy for the functionalization of POPs at the molecular level and for the stabilization of palladium NPs on the external surface of POPs has been presented. The function-

Chem. Eur. J. **2016**, 22, 1 – 10

www.chemeurj.org







Figure 7. TEM and HAADF-STEM images for a-c) Pd/POP-1, d-f) Pd/POP-2, and g-i) Pd/POP-3) after recycling four runs.

alization of BTP unit by using COOMe and carboxylate groups has exerted dominant effects on the structures and properties of the resulting POPs and the palladium NPs. The introduction of carboxylate groups engenders a dual functionality; it not only endows POP-3 am outstanding dispersibility in H₂O/EtOH, but also improves the stabilization of palladium NPs on the external surface of POP-3 through its electrostatic and coordination interactions. The use of POPs as heterogeneous supports of palladium NPs in dehalogenation reactions has been evaluated. Pd/POP-3 shows the highest catalytic activity, recyclability, and no obvious agglomeration of the palladium NPs at the surface was observed after consecutive four runs. The remarkable performances of Pd/POP-3 provide a new and general avenue for the customerization of metal NPs with high catalytic activity and recyclability. Further investigation into the predesignable synthesis of metal NPs on the external surface of functionalized POPs for specific applications is in progress.

Experimental Section

General information: 2,6-Diethynylpyridine,^[61] methyl-2,6-diethynylisonicotinate,^[61] and 1,3,5-tris(4-azidophenyl)benzene^[62] were prepared according to literature methods. Other chemicals were commercially available and used without further purification. Solidstate ¹³C cross-polarization/magic angle spinning (CP/MAS) NMR spectrometry was performed on a Bruker SB Avance III 500 MHz spectrometer with a 4 mm double resonance MAS probe, a sample spinning rate of 7.0 kHz, a contact time of 2 ms, and a pulse delay of 5 s. FTIR spectra were recorded with KBr pellets by using a Perkin–Elmer instrument. Thermal gravimetric analysis (TGA) was carried out on NETZSCH STA 449C by heating samples from 30 to 800 °C under a dynamic nitrogen atmosphere with a heating rate of 10 °Cmin⁻¹. Powder X-ray diffraction (PXRD) patterns were recorded in the range of 2 θ =5–85° on a desktop X-ray diffractometer (RIGAKU-MiniflexII) with Cu_{Ka} radiation (λ =1.5406 Å). Nitrogen adsorption and desorption isotherms were measured at 77 K by using a Micromeritics ASAP2020 system. The samples were degassed at 100 °C for 10 h before the measurements. Surface areas were calculated from the adsorption data by using Brunauer-Emmett-Teller (BET) methods. The pore size distribution curves were obtained from the adsorption branches by using the nonlocal density functional theory (NLDFT) method. Field-emission scanning electron microscopy (SEM) was performed on a JEOL JSM-7500F instrument operated at an accelerating voltage of 3.0 kV. Transmission electron microscope (TEM) images were obtained with a JEOL JEM-2010 instrument operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB250 spectrometer by using non-monochromatic $AI_{K\alpha}$ X-rays as the excitation source and choosing C 1s (284.6 eV) as the reference line. Elemental analyses were performed on an Elementar Vario MICRO elemental analyzer. Inductively coupled plasma spectroscopy (ICP) was measured on a JobinYvonUltima2 spectrometer. Gas chromatography (GC) was performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-5, $30 \text{ m} \times 0.25 \text{ }\mu\text{m}$) by using a flame ionization detector.

Computational methods: The hybrid Becke three-parameter Lee Yang Parr (B3LYP)^[63,64] density functional method in combination with 6-311 + G(d) basis set was employed to study the equilibrium geometries and electronic properties for POP-1, POP-2, and POP-3. All geometries were fully optimized and confirmed as minima by analytical frequency calculations at the same level of theory. The natural population analyses were performed by the NBO 3.1 module embedded in the Gaussian 09 $\operatorname{program}^{[65]}$ The atomic charges produced by fitting to the electrostatic potential at points were evaluated by using the ChelpG scheme.^[66] The wavefunction analyses were performed by using the Multiwfn software, which is a multifunctional wavefunction analysis program developed by Lu and Chen, and can be freely downloaded.^[67] During the calculation processes, the default settings were used for all programs. All isosurface maps including the frontier molecular orbitals and the electrostatic potential on van der Waals surface were rendered by using the VMD program.^[68]

Synthesis of POP-1: A mixture of 2,6-diethynylpyridine (0.191 g, 1.50 mmol), 1,3,5-tris(4-azidophenyl)benzene (TAPB) (0.429 g, 1.00 mmol), CuSO₄·5 H_2O (0.038 g, 0.150 mmol), and sodium ascorbate (0.030 g, 0.15 mmol) in dry DMF (60 mL) was stirred under a nitrogen atmosphere at 100°C for 72 h to afford a dark yellow powder. The solid was isolated by filtration, and subsequently washed with an aqueous solution of EDTA-2Na (EDTA = ethylenediaminetetraacetic acid) (0.250 g in 200 mL H₂O), ethanol, and CH₂Cl₂ to remove any unreacted monomers or residues. The deep yellow powder was further treated by Soxhlet extraction in CH₂Cl₂ overnight and dried in vacuo at 60°C for 12 h. Yield: 0.603 g (97%); FTIR (KBr): $\tilde{\nu}$ = 3430 (s), 3142 (m), 1608 (s), 1574 (s), 1517 (s), 1446 (m), 1392 (m), 1232 (m), 1035 (s), 829 cm⁻¹ (s); elemental analysis calcd (%) for $C_{25}H_{19}N_7$: C 71.19, H 4.56, N 23.50; found: C 64.73, H 4.57, N 20.38.

Synthesis of POP-2: A mixture of methyl-2,6-diethynylisonicotinate (0.278 g, 1.50 mmol), 1,3,5-tris(4-azidophenyl)benzene (0.429 g, 1.00 mmol), CuSO₄•5 H₂O (0.038 g, 0.15 mmol), and sodium ascorbate (0.030 g, 0.15 mmol) in dry DMF (70 mL) was stirred under a nitrogen atmosphere at 100 °C for 72 h to afford a dark yellow powder. The solid was isolated by filtration, and subsequently washed with an aqueous solution of EDTA-2 Na (0.250 g in 200 mL H₂O), ethanol, and CH₂Cl₂ to remove any unreacted monomers or residues. The deep yellow powder was further treated by Soxhlet extraction in CH₂Cl₂ overnight and dried in vacuo at 60 °C for 12 h. Yield: 0.678 g (96%); FTIR (KBr): $\tilde{\nu}$ =3356 (s), 3077 (w), 1726 (m),

Chem. Eur. J. 2016, 22, 1 – 10

www.chemeurj.org

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers! **77**



1610 (m), 1568 (s), 1516 (s), 1436 (m), 1236 (s), 1033 (s), 987 (m), 825 cm $^{-1}$ (s); elemental analysis calcd (%) for $C_{27}H_{22}N_7O_2\colon$ C 68.07, H 4.62, N 20.59; found: C 61.16, H 4.53, N 19.18..

Synthesis of POP-3: POP-2 (140 mg) was added to an aqueous solution of LiOH (140 mL, 0.701 g, 29.41 mmol) and the mixture was stirred at 60 °C for 24 h. Subsequently, the solid was collected by filtration, washed with water for several times to completely remove LiOH residues, and dried in vacuo to produce a yellow powder. Yield: 0.572 g (81%); FTIR (KBr): $\tilde{\nu} = 3431$ (s), 3081 (m), 1605 (s), 1548 (s), 1516 (s), 1394 (s), 1335 (m), 1242 (m), 1049 (s), 989 (m), 829 cm⁻¹ (s); elemental analysis calcd (%) for C₂₆H₁₉N₇O₂Li: C 66.67, H 4.06, N 20.94; found: C 54.34, H 4.70, N 16.02.

Synthesis of Pd/POP-1: POP-1 (0.200 g) was added into a solution of palladium acetate (0.163 g, 0.726 mmol) in CH₂Cl₂ (200 mL) and the mixture was vigorously stirred at 60 °C for 24 h. The resultant product was washed thoroughly with CH₂Cl₂ to remove excess palladium acetate and dried in vacuo at 80 °C for 12 h. A 10-fold excess of an aqueous solution of NaBH₄ was added to the suspension of the palladium polymer in water (200 mL), the mixture was stirred at room temperature for 3 h. The resultant black powder was collected by filtration, washed with water for several times, and dried in vacuo at 60 °C for 12 h. Yield: 0.238 g (86%); FTIR (KBr): $\vec{\nu}$ = 3057 (w), 1604 (s), 1574 (s), 1516 (s), 1446 (m), 1396 (m), 1232 (m), 1038 (s), 991 (m), 829 cm⁻¹ (s).

Synthesis of Pd/POP-2: Pd/POP-2 was prepared by using a similar method to the synthesis of Pd/POP-1 except that POP-1 was replaced by POP-2. Yield: 0.216 g (89%); FTIR (KBr): $\tilde{\nu} = 3057$ (w), 1604 (s), 1574 (s), 1516 (s), 1446 (m), 1396 (m), 1232 (m), 1038 (s), 991 (m), 829 cm⁻¹ (s).

Synthesis of Pd/POP-3: Pd/POP-3 was prepared by using a similar method to the synthesis of Pd/POP-1 except that POP-1 was replaced by POP-3. Yield: 0.221 g (85%); FTIR (KBr): $\bar{v} = 3424$ (s), 1609 (s), 1549 (s), 1516 (s), 1394 (s), 1375 (s), 1242 (m), 1049 (m), 829 cm⁻¹ (s).

General procedures for the dehalogenation of aryl chorides: Pd/ POP-1, Pd/POP-2, or Pd/POP-3 was added to a mixture of aryl halides (0.5 mmol) and ammonium formate (2.5 mmol) in water/ethanol (1:1, 2.0 mL). The mixture was stirred at 25 °C for the appropriate time. After the reaction was completed, the product was extracted with diethyl ether (3×5 mL). The conversion was determined by GC.

General procedures for the recyclability test: After dehydrogenation of chlorobenzene, the product was extracted with diethyl ether (3×5 mL). The organic layer was analyzed by GC. The black powder in the aqueous phase was separated by centrifugation and washed with water, followed by centrifugation. The procedures were repeated twice, and the resultant solid was directly used for the next run with the addition of fresh chlorobenzene, HCOONH₄, H₂O, and EtOH.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21273239 and 21471151) and by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB20000000).

Keywords: chelating effect · dehalogenation · heterogeneous catalysis · palladium nanoparticles · porous organic polymers

- [1] C. Perego, R. Millini, Chem. Soc. Rev. 2013, 42, 3956-3976.
- [2] Y. Zhang, S. N. Riduan, Chem. Soc. Rev. 2012, 41, 2083-2094.
- [3] S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. G. Song, C. Y. Su, W. Wang, J. Am. Chem. Soc. 2011, 133, 19816–19822.

CHEMISTRY A European Journal

Full Paper

- [4] L. Li, Z. Chen, H. Zhong, R. Wang, *Chem. Eur. J.* 2014, *20*, 3050–3060.
 [5] R. Palkovits, M. Antonietti, P. Kuhn, A. Thomas, F. Schuth, *Angew. Chem. Int. Ed.* 2009, *48*, 6909–6912; *Angew. Chem.* 2009, *121*, 7042–7045.
- [6] J. Mondal, S. K. Kundu, W. K. H. Ng, R. Singuru, P. Borah, H. Hirao, Y.
- Zhao, A. Bhaumik, *Chem. Eur. J.* **2015**, *21*, 19016–19027. [7] W. Wang, A. Zheng, P. Zhao, C. Xia, F. Li, *ACS Catal.* **2014**, *4*, 321–327.
- [8] S. Agarwal, J. N. Ganguli, *RSC Adv.* 2014, *4*, 11893–11898.
- [9] J. Mondal, A. Biswas, S. Chiba, Y. Zhao, Sci. Rep. 2015, 5, 8294.
- [10] Y. Chi, L. Zhao, Q. Yuan, X. Yan, Y. Li, N. Li, X. Li, *J. Mater. Chem.* **2012**,
- 22, 13571-13577. [11] H. Zhong, Y. Gong, F. Zhang, L. Li, R. Wang, J. Mater. Chem. A **2014**, 2,
- 7502-7508. [12] Y. Z. Chen, Q. Xu, S. H. Yu, H. L. Jiang, *Small* **2015**, *11*, 71-76.
- [13] H. Zhong, C. Liu, Y. Wang, R. Wang, M. Hong, Chem. Sci. 2016, 7, 2188– 2194.
- [14] A. M. Doyle, S. K. Shaikhutdinov, H. J. Freund, Angew. Chem. Int. Ed. 2005, 44, 629–631; Angew. Chem. 2005, 117, 635–637.
- [15] N. Huang, Y. Xu, D. Jiang, Sci. Rep. 2014, 4, 7228.
- [16] Y. H. Kim, S. K. Hwang, J. W. Kim, Y. S. Lee, Ind. Eng. Chem. Res. 2014, 53, 12548–12552.
- [17] H. X. Zhang, M. Liu, X. Bu, J. Zhang, Sci. Rep. 2014, 4, 3923.
- [18] B. S. Choi, S. M. Kim, J. Gong, Y. W. Lee, S. W. Kang, H. S. Lee, J. Y. Park, S. W. Han, *Chem. Eur. J.* 2014, *20*, 11669–11674.
- [19] B. G. Hauser, O. K. Farha, J. Exley, J. T. Hupp, Chem. Mater. 2013, 25, 12– 16.
- [20] L. Li, H. Zhao, J. Wang, R. Wang, ACS Nano 2014, 8, 5352-5364.
- [21] W. Lu, Z. Wei, D. Yuan, J. Tian, S. Fordham, H. C. Zhou, Chem. Mater. 2014, 26, 4589–4597.
- [22] H. Xu, X. Chen, J. Gao, J. Lin, M. Addicoat, S. Irle, D. Jiang, Chem. Commun. 2014, 50, 1292–1294.
- [23] P. Arab, M. G. Rabbani, A. K. Sekizkardes, T. İslamoğlu, H. M. El-Kaderi, *Chem. Mater.* 2014, 26, 1385–1392.
- [24] F. M. Wisser, K. Eckhardt, D. Wisser, W. Bohlmann, J. Grothe, E. Brunner, S. Kaskel, *Macromolecules* 2014, 47, 4210–4216.
- [25] H. Ma, H. Ren, X. Zou, S. Meng, F. Sun, G. Zhu, Polym. Chem. 2014, 5, 144–152.
- [26] Z. Xie, C. Wang, K. E. deKrafft, W. Lin, J. Am. Chem. Soc. 2011, 133, 2056–2059.
- [27] N. B. McKeown, P. M. Budd, *Macromolecules* **2010**, *43*, 5163–5176.
- [28] J. X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak, A. I. Cooper, Angew. Chem. Int. Ed. 2007, 46, 8574–8578; Angew. Chem. 2007, 119, 8728– 8732.
- [29] L. Li, H. Zhao, R. Wang, ACS Catal. 2015, 5, 948-955.
- [30] A. P. Katsoulidis, S. M. Dyar, R. Carmieli, C. D. Malliakas, M. R. Wasielewski, M. G. Kanatzidis, J. Mater. Chem. A 2013, 1, 10465-10473.
- [31] X. Liu, Y. Xu, D. Jiang, J. Am. Chem. Soc. 2012, 134, 8738-8741.
- [32] C. Shen, H. Yu, Z. Wang, Chem. Commun. 2014, 50, 11238-11241.
- [33] P. Pandey, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, M. G. Kanatzidis, T. H. Joseph, S. T. Nguyen, J. Mater. Chem. 2011, 21, 1700–1703.
- [34] J. R. Holst, E. Stöckel, D. J. Adams, A. I. Cooper, *Macromolecules* **2010**, *43*, 8531-8538.
- [35] D. J. V. C. van Steenis, O. R. P. David, G. P. F. van Strijdonck, J. H. van Maarseveen, J. N. H. Reek, Chem. Commun. 2005, 4333–4335.
- [36] T. Muller, S. Bräse, Angew. Chem. Int. Ed. 2011, 50, 11844–11845; Angew. Chem. 2011, 123, 12046–12047.
- [37] O. Plietzsch, C. I. Schilling, T. Grab, S. L. Grage, A. S. Ulrich, A. Comotti, P. Sozzani, T. Muller, S. Bräse, New J. Chem. 2011, 35, 1577-1581.
- [38] A. Devadoss, C. E. Chidsey, J. Am. Chem. Soc. 2007, 129, 5370-5371.
- [39] V. M. Suresh, S. Bonakala, H. S. Atreya, S. Balasubramanian, T. K. Maji,
- ACS Appl. Mater. Interfaces **2014**, *6*, 4630–4637. [40] H. Zhao, Z. Jin, H. Su, X. Jing, F. Sun, G. Zhu, Chem. Commun. **2011**, *47*, 6389–6391.
- [41] O. Buyukcakir, S. H. Je, J. Park, H. A. Patel, Y. Jung, C. T. Yavuz, A. Coskun, Chem. Eur. J. 2015, 21, 15320 – 15327.
- [42] H. H. Zhang, Q. S. Hu, K. Hong, Chem. Commun. 2015, 51, 14869– 14872.

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

KK These are not the final page numbers!



CHEMISTRY A European Journal **Full Paper**

- [43] P. K. Chow, G. Cheng, G. S. M. Tong, W. P. To, W. L. Kwong, K. H. Low, C. C. Kwok, C. Ma, C. M. Che, Angew. Chem. Int. Ed. 2015, 54, 2084-2089; Angew. Chem. 2015, 127, 2112-2117.
- [44] L. Li, C. Zhou, H. Zhao, R. Wang, Nano Res. 2015, 8, 709-721.
- [45] Y. Li, J. C. Huffman, A. H. Flood, Chem. Commun. 2007, 2692-2694.
- [46] M. Ostermeier, M. A. Berlin, R. M. Meudtner, S. Demeshko, F. Meyer, C.
- Limberg, S. Hecht, Chem. Eur. J. 2010, 16, 10202-10213. [47] R. M. Meudtner, M. Ostermeier, R. Goddard, C. Limberg, S. Hecht, Chem.
- Eur. J. 2007, 13, 9834-9840. [48] J. D. Crowley, P. H. Bandeen, Dalton Trans. 2010, 39, 612-623.
- [49] S. N. Chen, W. Y. Wu, F. Y. Tsai, Green Chem. 2009, 11, 269-274. [50] Y. Noma, M. Ohno, S. Sakai, Fresenius Environ, Bull. 2003, 12, 302-308.
- [51] S. Loiselle, M. Branca, G. Mulas, G. Cocco, Environ. Sci. Technol. 1997, 31, 261-265.
- [52] G. Yuan, M. A. Keane, Chem. Eng. Sci. 2003, 58, 257-267.
- [53] A. K. Patra, A. Dutta, A. Bhaumik, ACS Appl. Mater. Interfaces 2012, 4, 5022 - 5028.
- [54] A. A. Peterson, K. A. Thoreson, K. McNeill, Organometallics 2009, 28, 5982-5991.
- [55] A. F. Littke, G. C. Fu, Angew. Chem. Int. Ed. 2002, 41, 4176-4211; Angew. Chem. 2002, 114, 4350-4386.
- [56] Y. Huang, S. Liu, Z. Lin, W. Li, X. Li, R. Cao, J. Catal. 2012, 292, 111-117.
- [57] R. Nakao, H. Rhee, Y. Uozumi, Org. Lett. 2005, 7, 163-165.
- [58] O. Navarro, H. Kaur, P. Mahjoor, S. P. Nolan, J. Org. Chem. 2004, 69, 3173-3180
- [59] F. Alonso, I. P. Beletskaya, M. Yus, Chem. Rev. 2002, 102, 4009-4091.
- [60] R. B. Bedford, C. S. J. Cazin, D. Holder, Coord. Chem. Rev. 2004, 248, 2283-2321.

- [61] S. Leininger, M. Schmitz, P. J. Stang, Org. Lett. 1999, 1, 1921-1923.
- O. Plietzsch, C. I. Schilling, M. Tolev, M. Nieger, C. Richert, T. Muller, S. [62] Brase, Org. Biomol. Chem. 2009, 7, 4734-4743.
- [63] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.
- [64] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. 1994, 98, 11623-11627.
- [65] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc. Wallingford CT, 2009.
- [66] C. M. Breneman, K. B. Wiberg, J. Comput. Chem. 1990, 11, 361-373.
- [67] T. Lu, F. W. Chen, J. Comput. Chem. 2012, 33, 580-592.
- [68] W. Humphrey, A. Dalke, K. Schulten, J. Mol. Graph. 1996, 14, 33-38.

Received: April 27, 2016 Published online on



FULL PAPER



H. Zhong, C. Liu, H. Zhou, Y. Wang, R. Wang*

Prefunctionalized Porous Organic Polymers: Effective Supports of Surface Palladium Nanoparticles for the Enhancement of Catalytic Performances in Dehalogenation



POP out: The introduction of carboxylate groups not only endows porous organic polymers (POPs) a superior dispersibility in $H_2O/EtOH$, but also results in the variation of the size and location of palladium nanoparticles (NPs) from the interior pores to the external surface (see figure). Surface palladium NPs show a superior catalytic activity, stability, and recyclability in the dehalogenation of aryl halides.

CHEMISTRY A European Journal

Full Paper