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Hydrodehalogenation of polyhalogenated aromatics catalyzed by NiPd nanoparticles supported on nitrogen-doped graphene

Xuefeng Guo†, Chao Yu†, Zhouyang Yin, Shouheng Sun* and Christopher T. Seto*

Abstract: We report a $Ni_{30}Pd_{70}$/nitrogen-doped graphene (NG) catalyst that hydrodehalogenates halogenated aromatics under mild reaction conditions. It reduces mono- or dichloroarenes to the corresponding dehalogenated arenes in >90% yield in 10% aqueous isopropanol solvent at or below 50°C within 5 hours. Tests on a variety of substrates containing various functional groups show that the catalyst is selective for reduction of C-Cl and C-Br bonds. In addition, this catalyst completely hydrodehalogenates high concentration solutions of dioxin, polychlorinated biphenyls (PCBs), chloroaromatic constituents of the defoliant agent orange, and polybrominated diphenyl ethers (PBDEs) in 12 hours. The catalyst is reusable and shows no morphological or compositional changes after 5 cycles. This methodology offers a powerful, low-cost and safe technology for the degradation of polyhalogenated aromatics, and may be useful for preventing proliferation of these toxins in the environment from causing serious health issues.

Polyhalogenated aromatics (PHAs), such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), are a class of persistent organic pollutants that adversely affect human health. Due to the stability of C_{Ar}-Cl (97.1 kcal/mol) and C_{Ar}-Br (84.0 kcal/mol) bonds,[1] these PHAs are extremely difficult to degrade in the natural environment, and can accumulate and pass from one organism to another through the food chain.[2] Activation of C_{Ar}-X (X = Cl or Br) bonds to achieve full conversion to C_{Ar}-H is the key step in PHA degradation. Conventional methods to accomplish this transformation rely on hydrodehalogenation reactions in the presence of a catalyst with either isopropanol or pressurized H_2 as the hydrogen source. Transition metal complexes of Pd,[3] Rh,[4] Ni,[5] Co,[6] or Fe,[7] are often selected as hydrodehalogenation catalysts under homogeneous reaction conditions, but these complexes often show limited stability and re-usability. For example, a Rh[4a] catalyst requires strong base (*t*BuOK), high temperature (100 °C) and a long reaction time (24 h) to dehalogenate chlorobenzene. Mild biological reagents have also been developed to degrade halogenated pollutants, but these systems require extremely long reaction times, and only work with low concentrations of PHAs. For example, bio-remediation processes using microalgae[8] or cyanobacteria[9] to dechlorinate PHAs require weeks to months to achieve only partial dechlorination of low concentrations of PHAs in soil.

Recently, a nanostructured composite of Fe(0) and Pd(0) was studied as a catalyst to degrade PHAs in water.[10] Fe reacts with water to generate H_2 for the subsequent Pd catalyzed-hydrodechlorination reaction. In this process, Fe(0) is oxidized and must be regenerated by a stronger reducing agent such as sodium borohydride for the catalysis to proceed. Still, the composite catalyst is not efficient for the dechlorination of high concentrations of PHAs. Supported transition metal catalysts have also been developed for hydrodehalogenation reactions.[11] However, these reactions often use pressured hydrogen gas, which makes them difficult to apply outside of the lab to remediate polluted soil or water. As part of the development of the hydrogen economy, ammonia borane (AB, H_3NBH_3) has emerged as an appealing sustainable fuel source because it is a solid with a high hydrogen storage capacity. In addition, energy-efficient chemical processes have been developed to regenerate AB from its dehydrogenation products, making it an attractive alternative to H_2 gas for hydrodehalogenation reactions.[12] Pd-based NPs catalyze the dehydrogenation of AB for subsequent hydrogenation of nitro compounds ($R-NO_2$) to amines (RNH_2).[13] Combining the Pd-catalyzed C_{Ar}-X reduction with the AB-initiated transfer hydrogenation, here we report an efficient NiPd nanoparticle (NP) catalyst for hydrodehalogenation of high concentrations of chlorinated and brominated aromatics to the corresponding aromatics in near quantitative yield. The NP catalyst is comprised of 3 nm NiPd NPs assembled on nitrogen-doped graphene (NG). It catalyzes the one-pot dehydrogenation of AB and subsequent hydrodehalogenation of halogenated aromatics in 10% aqueous isopropanol at or below 50°C. It is effective for converting C_{Ar}-X to C_{Ar}-H, not only for monohalogenated aromatics, but also for PHAs, including PCBs and PBDEs.

We first tested MPd (M = Ni, Co, Fe) NP catalysts for AB-initiated C_{Ar}-Cl conversion to C_{Ar}-H. 3-4 nm MPd NPs were first prepared as shown in Figure S1.[14] We deposited these NPs onto the common carbon (C) or graphene (G) supports (Figure S2) and studied their roles in catalyzing AB-initiated hydrodechlorination of chlorobenzene. We found NiPd NPs to be more active than either CoPd or FePd. To further enhance NiPd catalysis, we deposited these NPs on nitrogen-doped graphene (NG)[15] for NPs to be better anchored against aggregation via pyridine-N coordination. In the catalytic reaction, the NG serves as a NP anchor, while NG and AB neutralize the HCl generated during the reaction, enhancing catalysis and stabilizing the catalyst. We assembled 3 nm $Ni_{30}Pd_{70}$ NPs on NG by mixing and sonicating a hexane dispersion of NPs and NG. We tested the assembly conditions and used a 1:1 w/w mixture of NPs/NG to form a well-dispersed monolayer of NPs on the NG surface (Figure 1a). We further prepared $Ni_{30}Pd_{70}$/C, $Ni_{30}Pd_{70}$/G, $Ni_{54}Pd_{46}$/NG, $Ni_{67}Pd_{33}$/NG and Pd/NG (Table 1 and Figure 1b-1d). After testing the AB-initiated transfer hydrogenation and hydrodechlorination of chlorobenzene and dichlorobenzene, we found $Ni_{30}Pd_{70}$/NG to be the most efficient catalyst for the hydrodechlorination reaction (Table 1).

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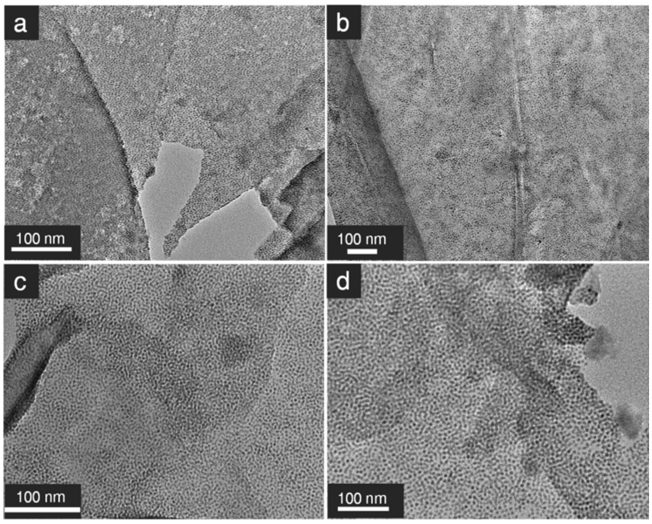
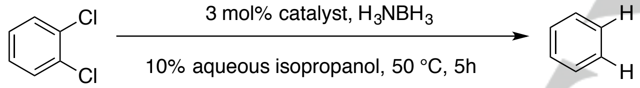


Figure 1. a) TEM image of 3.0 ± 0.1 nm $Ni_{30}Pd_{70}$/NG, b) TEM image of 3.4 ± 0.3 nm $Ni_{54}Pd_{46}$/NG, c) TEM image of 3.8 ± 0.2 nm $Ni_{67}Pd_{33}$/NG, d) TEM image of 4.0 ± 0.2 nm Pd/NG. These NiPd/NG samples were prepared by mixing hexane dispersions of NiPd NPs and NG in 1:1 mass ratios. Each TEM sample was prepared by adding a drop of hexane dispersion of NiPd/NG on an amorphous carbon coated Cu grid followed by hexane evaporation under ambient conditions.

Table 1. Hydrodehalogenation of dichlorobenzene catalyzed by Pd-based catalysts on different carbon supports[a]



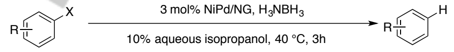
Entry	Catalyst	Yield[b] (%)
1	$Ni_{30}Pd_{70}$/C	81
2	$Ni_{30}Pd_{70}$/G	84
3	**$Ni_{30}Pd_{70}$/NG**	**99**
4	Pd/NG	69
5	$Ni_{54}Pd_{46}$/NG	72
6	$Ni_{67}Pd_{33}$/NG	44

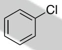
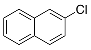
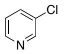
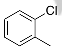
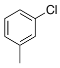
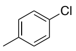
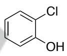
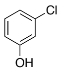
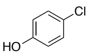
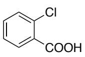
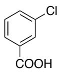
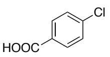
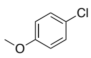
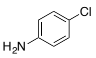
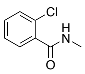
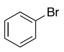
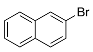
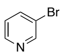
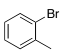
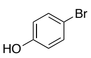
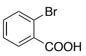
[a] Reaction conditions: dichlorobenzene (1 mmol), ammonia borane (6 mmol), 10% aqueous isopropanol (3.0 mL) and catalyst (3 mol %) for 5 h at 50 °C. [b] Yields determined by GC-MS.

To demonstrate that AB is the source of hydrogen in the reactions, and not isopropanol, we performed the hydrodechlorination of dichlorobenzene in 10% aqueous isopropanol without adding AB and found the yield of dechlorinated products to be less than 3%. We also tested the reaction in aqueous AB solution without adding isopropanol as a cosolvent, and obtained a 76% yield of benzene. The reduction in yield from 99% (10% aqueous isopropanol solvent) to 76% (pure water as the solvent) is likely caused by the poor solubility of dichlorobenzene in pure water. When 10% isopropanol was added to improve the dichlorobenzene solubility, the reaction was completed within 5 hours and all the dichlorobenzene was converted to benzene. AB serves as both the hydrogen source, and as a base to neutralize the hydrochloric acid generated during the reaction, which is key to maintaining the pH of the reaction mixture and to stabilizing the NiPd/NG catalyst.

Using $Ni_{30}Pd_{70}$/NG (abbreviated as NiPd/NG) as the catalyst, we studied the time-dependent AB initiated hydrodechlorination of chlorobenzene at 40°C. Figure S4 shows the concentration changes of chlorobenzene and benzene over time in the presence of 3 mol% NiPd/NG. The disappearance of chlorobenzene and growth of benzene follows the exponential concentration changes of a first order reaction, indicating that the reaction proceeds without formation of other detectable intermediates. Using these reaction conditions, we examined a series of other mono-halogenated aromatic compounds (Table 2). NiPd/NG is an efficient and selective hydrodechlorination catalyst for these substrates. Chlorobenzene, 2-chloronaphthylene and 3-chloropyridine are reduced in greater than 94% yield (entries 1-3). The reaction is effective for substrates with either electron-donating (entries 4-9, 13-14) or electron-withdrawing groups (entries 10-12, 15). The conversion is not sensitive to the position of the halogen atom relative to other functional groups (entries 4-12). Hydroxyl, amine, amide, and carboxylic acid groups are not reduced under the reaction conditions. Furthermore, the reaction can be extended to brominated substrates (entries 16-21).

Table 2. Hydrodehalogenation of mono-halogen substituted compounds[a]

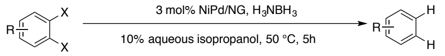


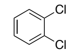
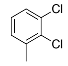
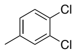
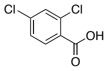
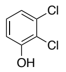
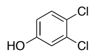
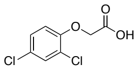
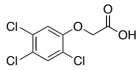
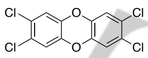
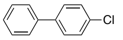
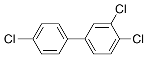
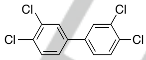
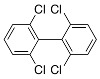
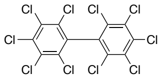
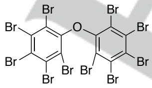
Entry	Ar-X	Yield[b] (%)	Entry	Ar-X	Yield[b] (%)	Entry	Ar-X	Yield[b] (%)
1		99[c]	2		94[c]	3		98[c]
4		98[c]	5		99[c]	6		99[c]
7		91	8		91	9		93
10		97	11		97	12		98
13		87	14		90	15		92
16		99[c]	17		97[c]	18		99[c]
19		99[c]	20		96	21		97

[a] Reaction conditions: aryl halides (1 mmol), ammonia borane (2 mmol), 10% aqueous isopropanol (3.0 mL) and NiPd/NG (3 mol%) for 3 h at 40 °C. [b] Isolated yield except where noted otherwise. [c] Yield determined by GC−MS.

Encouraged by the general applicability of NiPd/NG to mono-halogenated substrates, we extended the study to substrates containing multiple Cl or Br atoms. Using 1,2-dicholorobenzene as an example, we examined its time-dependent hydrodechlorination at 50°C. As shown in Figure S5, the first hour of the reaction gives exponential decay of dichlorobenzene accompanied by an increase in both the chlorobenzene and benzene concentrations. This pattern is typical of a stepwise process in which the two chlorine atoms are reduced sequentially. The chlorobenzene concentration reaches a maximum at two hours, and subsequently decreases with a corresponding increase in the concentration of the benzene final product. The reaction is complete after 5 hours. During the course of the reaction we do not detect any other intermediates by GC-MS. Using these reaction conditions, we examined other polyhalogenated substrates (Table 3). Dichlorinated substrates (entries 1-6) are dehalogenated to their parent compounds in high yield. The environmental pollutants 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid and 2,3,7,8-tetrachlorodibenzodioxin (entries 7-9) are all completely dechlorinated in high yield under the reaction conditions. We also examined five chlorinated biphenyl substrates (entries 10-14). Compounds 10-12 that contain chlorine atoms meta and/or para to the biphenyl bond are fully reduced under the standard conditions. In contrast, substrates with chlorine atoms ortho to the biphenyl bond are reduced more slowly (entries 13 and 14). These are the most sterically hindered positions in the molecule, and the ortho chlorine substituents enforce a perpendicular geometry of the two phenyl rings. These substrates require 12 hours to achieve complete reduction of all of the C-Cl bonds. In a similar manner, the four bromine atoms in PBDE (entry 12) that are ortho to the ether oxygen reside in sterically hindered positions, and PBDE also requires 12 hours for full dehalogenation.

Table 3. Hydrodehalogenation of multi-halogen substrates[a]



Entry	Ar-X	Yield[b] (%)	Entry	Ar-X	Yield[b] (%)	Entry	Ar-X	Yield[b] (%)
1		98[c]	2		97[c]	3		98[c]
4		97	5		90	6		93
7		90	8		87	9		92[c,d]
10		99[c]	11		99[c]	12		98[c]
13		97[c,e]	14		94[c,e,f]	15		97[c,e]

[a] Reaction conditions: organic halides (1 mmol), ammonia borane (3.0 equiv with respect to halogen atoms), 10% aqueous isopropanol (3.0 mL) and NiPd/NG (3 mol%) at 50 °C. [b] Isolated yield except where noted. [c] Yield determined by GC−MS. [d] 0.003 mmol (1 mg) of dioxin was used in the reaction. [e] Reaction was run for 12 h. [f] 0.04 mmol of decachlorobiphenyl was used in the reaction.

We have also examined if the NiPd/NG catalyst can be recycled through several sequential hydrodehalogenation reactions. We measured the stability of the catalyst by observing NiPd NP morphology and composition changes before and after the hydrodechlorination of dichlorobenzene. After the first reaction was complete, we separated the catalyst from the reaction solution by filtration, and washed it with water and isopropanol. We then re-used it in the next hydrodehalogenation reaction. Our tests showed that after the 5th reaction/separation cycle, the catalyst had no obvious loss in activity and the product yield remained >91% (Table S1). TEM and ICP-AES analyses of the catalyst after the 5th reaction cycle showed that the NPs display no obvious morphology changes or aggregation (Figure S6), and the NP composition is stabilized at $Ni_{28}Pd_{72}$. These results suggest that NG offers the necessary anchoring sites to stabilize NiPd NPs against aggregation. The combination of NG and AB neutralizes the hydrochloric acid generated during the reaction, and prevents Ni from leaching out of the NiPd NPs.

In conclusion, the NiPd/NG catalyst reported here shows superior performance for the hydrodehalogenation of PHAs under mild and environmentally friendly reaction conditions. Dehalogenation reactions often require strong bases, strong reducing agents and harsh reaction conditions including high temperatures. In contrast, this NiPd/NG system uses ammonia borane as the hydrogen source and base, and an aqueous solvent system. The reaction is compatible with a variety of functional groups including hydroxyl groups, amines, amides and carboxylic acids. Under these mild conditions, the NiPd/NG catalyst promotes the complete dehalogenation of several severe environmental contaminants including the components of agent orange, dioxins, PCBs and PBDEs, which are extremely difficult to decontaminate using conventional methods. This concept of exploiting nanoparticles for green chemistry applications may provide a promising avenue for the rational design and assembly of nanostructured catalysts for solving long-standing problems in environmental chemistry.

Experimental Section

General Procedure for the Hydrodehalogenation Reactions: The aryl halide (1 mmol), NPs/NG (10 mg, 3 mol %), NH_3BH_3 (3 mmol) and 10% aqueous isopropanol (3 mL) were stirred in a 10 mL sealed tube at 50 °C for 5 hours. After the reaction was complete, the catalyst was filtered and the mixture was extracted with ethyl acetate. The organic phase was evaporated under vacuum and purified by flash column chromatography (hexane/ethyl acetate = 8:1) to give the final product.

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Keywords: Dehalogenation • Heterogeneous catalyst • Nanoparticles • Hydrogen Transfer • Ammonia Borane •

[1] S. J. Blanksby, G. B. Ellison, *Accounts Chem. Res.* **2003**, *36*, 255-263.
[2] a) A. J. Jamieson, T. Malkocs, S. B. Piertney, T. Fujii, Z. Zhang, *Nat. Ecol. Evol.* **2017**, *1*, 51; b) M. Bartrons, J. Catalan, J. Penuelas, *Sci. Rep.* **2016**, *6*, 25446; c) B. C. Kelly, M. G. Ikonomou, J. D. Blair, A. E. Morin, F. A. P. C. Gobas, *Science* **2007**, *317*, 236-239.
[3] a) A. Pyo, S. Kim, M. R. Kumar, A. Byeun, M. S. Eom, M. S. Han, S. Lee, *Tetrahedron Lett.* **2013**, *54*, 5207-5210; b) N. Iranpoor, H. Firouzabadi, R. Azadi, *J. Organomet. Chem.* **2010**, *695*, 887-890; c) O. Navarro, N. Marion, Y. Oonishi, R. A. Kelly, S. P. Nolan, *J. Org. Chem.* **2006**, *71*, 685-692.
[4] a) T. J. You, Z. R. Wang, J. J. Chen, Y. Z. Xia, *J Org Chem* **2017**, *82*, 1340-1346; b) G. Lazaro, V. Polo, F. J. Fernandez-Alvarez, P. Garcia-Orduna, F. J. Lahoz, M. Iglesias, J. J. Perez-Torrente, L. A. Oro, *Chemsuschem* **2015**, *8*, 495-503; c) K. Fujita, M. Owaki, R. Yamaguchi, *Chem. Commun.* **2002**, 2964-2965.
[5] K. Mochizuki, M. Suzuki, *Inorg. Chem. Commun.* **2011**, *14*, 902-905.
[6] K. S. Chan, C. R. Liu, K. L. Wong, *Tetrahedron Lett.* **2015**, *56*, 2728-2731.
[7] a) W. M. Czaplik, S. Grupe, M. Mayer, A. Jacobi von Wangelin, *Chem. Commun.* **2010**, *46*, 6350-6352; b) H. Q. Guo, K. Kanno, T. Takahashi, *Chem. Lett.* **2004**, *33*, 1356-1357.
[8] a) A. Papazi, K. Kotzabasis, *Plos One* **2013**, *8*; b) A. Papazi, E. Andronis, N. E. Ioannidis, N. Chaniotakis, K. Kotzabasis, *Plos One* **2012**, *7*; c) M. Cvancarova, Z. Kresinova, A. Filipova, S. Covino, T. Cajthaml, *Chemosphere* **2012**, *88*, 1317-1323.
[9] a) H. J. Zhang, X. J. Jiang, L. P. Lu, W. F. Xiao, *Plos One* **2015**, *10*; b) H. J. Zhang, C. M. Hu, X. Y. Jia, Y. Xu, C. J. Wu, L. N. Chen, F. P. Wang, *J. Appl. Phycol.* **2012**, *24*, 221-225.

[10] a) F. D. Kopinke, *Environ. Sci. Technol.* **2012**, *46*, 11467-11468; b) Y. Zhuang, S. Ahn, A. L. Seyfferth, Y. Masue-Slowey, S. Fendorf, R. G. Luthy, *Environ. Sci. Technol.* **2011**, *45*, 4896-4903.

[11] a) A. Goswami, A. K. Rathi, C. Aparicio, O. Tomanec, M. Petr, R. Pocklanova, M. B. Gawande, R. S. Varma, R. Zboril, *Acs Appl. Mater. Inter.* **2017**, *9*, 2815-2824; b) H. P. Rong, S. F. Cai, Z. Q. Niu, Y. D. Li, *Acs. Catal.* **2013**, *3*, 1560-1563; c) Y. Shiraishi, Y. Takeda, Y. Sugano, S. Ichikawa, S. Tanaka, T. Hirai, *Chem. Commun.* **2011**, *47*, 7863-7865.

[12] a) A. D. Sutton, A. K. Burrell, D. A. Dixon, E. B. Garner, J. C. Gordon, T. Nakagawa, K. C. Ott, P. Robinson, M. Vasiliu, *Science* **2011**, *331*, 1426-1429; b) B. L. Davis, D. A. Dixon, E. B. Garner, J. C. Gordon, M. H. Matus, B. Scott, F. H. Stephens, *Angew. Chem. Int. Ed.* **2009**, *48*, 6812-6816; c) S. Hausdorf, F. Baitalow, G. Wolf, F. O. Mertens, *Int. J. Hydrogen. Energ.* **2008**, *33*, 608-614

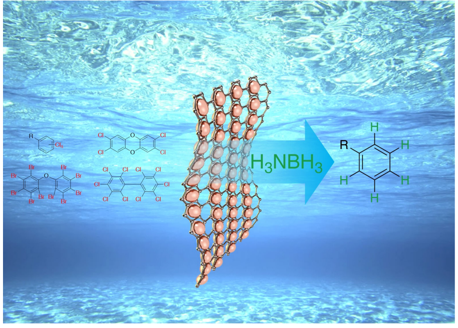
[13] a) C. Yu, J. J. Fu, M. Muzzio, T. L. Shen, D. Su, J. J. Zhu, S. H. Sun, *Chem. Mater.* **2017**, *29*, 1413-1418; b) W. W. Zhan, Q. L. Zhu, Q. Xu, *Acs. Catal.* **2016**, *6*, 6892-6905; c) H. Goksu, S. F. Ho, O. Metin, K. Korkmaz, A. M. Garcia, M. S. Gultekin, S. H. Sun, *Acs. Catal.* **2014**, *4*, 1777-1782. d) C. Yu, X. F. Guo, Z. Xi, M. Muzzio, Z. Y. Yin, B. Shen, J. R. Li, C. T. Seto, S. H. Sun, *J. Am. Chem. Soc.* **2017**, *139*, 5712-5715; e) C. Yu, X. Guo, M. Shen, B. Shen, M. Muzzio, Z. Yin, Q. Li, Z. Xi, J. Li, C. T. Seto, S. Sun, *Angew. Chem. Int. Ed.*, **2018**, *57*, 451-455.

[14] a) O. Metin, A. Mendoza-Garcia, D. Dalmizrak, M. S. Gultekin, S. H. Sun, *Catal. Sci. Technol.* **2016**, *6*, 6137-6143; b) S. F. Ho, A. Mendoza-Garcia, S. Guo, K. He, D. Su, S. Liu, Ö. Metin, S. Sun, *Nanoscale* **2014**, *6*, 6970-6973.

[15] a) H. B. Yang, J. W. Miao, S. F. Hung, J. Z. Chen, H. B. Tao, X. Z. Wang, L. P. Zhang, R. Chen, J. J. Gao, H. M. Chen, L. M. Dai, B. Liu, *Sci. Adv.* **2016**, *2*, e1501122; b) J. L. Shui, M. Wang, F. Du, L. M. Dai, *Sci. Adv.* **2015**, *1*, e1400129.

COMMUNICATION

A NiPd/NG catalyst was developed for the hydrodehalogenation of polyhalogenated aromatics under mild and environmentally friendly conditions. The catalyst promotes the complete dehalogenation of several severe environmental contaminants including the components of agent orange, dioxins, PCBs and PBDEs.



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Page No. – Page No.

Hydrodehalogenation of polyhalogenated aromatics catalyzed by NiPd nanoparticles supported on nitrogen-doped graphene