RSC Advances

This article can be cited before page numbers have been issued, to do this please use: Y. Nishina, A. Saito and S. Yamamoto, *RSC Adv.*, 2014, DOI: 10.1039/C4RA10512E.

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

RSC Advances

www.rsc.org/advances

ROYAL SOCIETY OF CHEMISTRY

View Article Online
DOI: 10.1039/C4RA10512E

Chemical Communications

RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Fine Tuning of Sheet Distance of Graphene Oxide that Affect the Activity and Substrate Selectivity of Pd/Graphene Oxide Catalyst in Heck Reaction

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Akinori Saito,[a] Shun-ichi Yamamoto,[b] and Yuta Nishina[b,c*]

Interlayer distance of graphene oxide (GO) of Pd/GO composite could be tuned using cationic surfactants. The distance becomes larger when a large surfactant is used. The catalytic activity in Heck reactions dramatically improved using the surfactant-modified Pd/GO catalyst. Substrate selectivity could also be improved by adjusting the size of the surfactant to increase accessibility of substrates to the active catalytic centre.

Graphene oxide (GO), prepared by oxidation of graphite using potassium permanganate or another strong oxidizing reagent,[1-4] has a large theoretical surface area of > 2,000 m^2/g, derived from its 2-dimensional sheet structure with one-carbon atom thickness. A promising application of GO is to make graphene by reduction; however, it has been difficult to remove oxygen functional groups (-COOH, -OH, and C-O-C) completely.[5] Recent advances in the efficient reduction of GO and its application as energy storage electrode materials[6] has strongly attracted much attention. In addition, preparation of composite materials of GO with polymers,[7] metals,[8] and organic molecules[9] has also been well developed. Among these applications, we have focused on the preparation of metal nanoparticle-GO composites and the application of catalysts in organic reactions. Palladium (Pd) is one of the most frequently used metals in catalysis,[10] therefore, many Pd/GO composites have been prepared and used as a catalyst.[11] GO is quite resistant to acidic and oxidative conditions, on the other hand, tend to aggregate under high temperature, basic, and reductive conditions by elimination of its oxygen functional groups.[12] The aggregation of GO dramatically reduces its surface area, therefore, the catalytic activity of a Pd/GO composite also decreases under harsh conditions. To prevent the aggregation of GO, functionalization with surfactants,[13] esters,[14] amides,[9a,15] or silane coupling agents[16] has often been proposed. Among these methods, functionalization with a surfactant is readily applicable to tune the sheet distance of GO.[13a] We have developed Pd/GO and Pd/graphene composites as efficient catalysts in Suzuki-Miyaura reactions and selective hydrogenation reactions.[11d,17] Suzuki-Miyaura reactions can proceed under mild reaction conditions, therefore, significant aggregation of GO does not occur to keep high catalytic activity.[17a] On the other hand, Heck reactions require higher reaction temperatures, leading to the aggregation of GO to decrease the catalytic activity (Table 1, entry 1), therefore, Pd on activated carbon (Pd/C) showed higher catalytic activity in Heck reaction than Pd/GO.[18] We applied surfactant-modification to a Pd/GO catalyst to improve catalytic activity,[19] as well as substrate selectivity in Heck reactions.

Initially, sheet distance of Pd/GO[20] and its surfactant-modified Pd/GO composites was analysed by X-ray diffraction (XRD) using Bragg's equation. A cationic surfactant (ammonium) with different lengths of alkyl chains was investigated. The interlayer distance of Pd/GO was 0.87 nm, slightly larger than the original GO (d = 0.86 nm). As the size of alkyl chain of ammonium ion increased, the distance also increased; tetramethylammonium (Pd/GO + TMAB, d = 0.92 nm), tetrabutylammonium (Pd/GO + TBAB, d = 1.00 nm), hexadecyltrimethylammonium (Pd/GO + C_{16}TAB, d = 1.19 nm), dimethyldipalmitylammonium (Pd/GO + DMDPAB, d = 2.80 nm) (Figure 1).

View Article Online
DOI: 10.1039/C4RA10512E

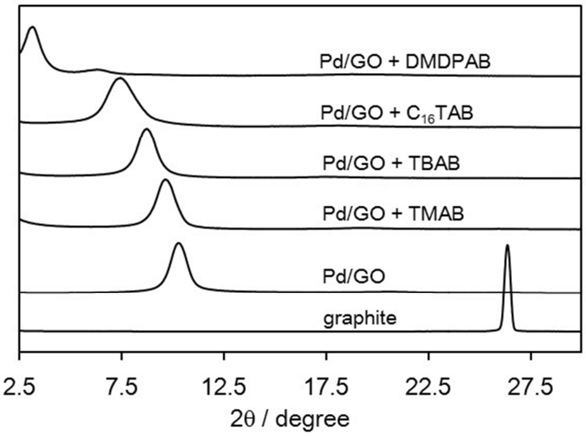
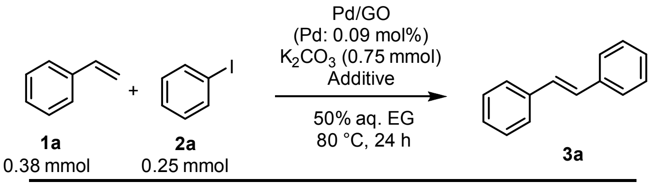


Figure 1 XRD spectra of Pd/GO with surfactants.

Having achieved the fine tuning of the sheet distance of Pd/GO composites by surfactant, we next investigated the catalytic activity in Heck reactions using styrene (**1a**) and iodobenzene (**2a**) as substrates. As a result of the screening of additives, hexadecyltrimethylammonium bromide (C_{16}TAB) was optimum (Table 1, entries 2-6) and the required amount was 0.13 mmol for 0.25 mmol of **2a** (Table 1, entries 4, and 7-9). When the reaction was performed at low temperature (60 °C), the yield of **3a** dramatically decreased (Table 1, entry 10); on the other hand, the yield was almost the same when performed at 100 °C (Table 1, entry 11). As a Pd precursor, $Pd(OAc)_2$ was found to be the best; $PdCl_2$ and $Pd(NO_3)_2$ gave **3a** in 41% and 44% yields, respectively. As a result of solvent screening, toluene, *n*-hexane, THF, and ethyl acetate did not provide the product at all. The optimum base was K_2CO_3, and other bases decreased the product yield; Na_2CO_3 (70%), Cs_2CO_3 (22%), AcONa (16%), and Et_3N (3%). The catalytic activity was slightly decreased when reused; 1st recycle (84% yield), 2nd recycle (74% yield), and 3rd recycle (75% yield). The recovered catalyst was analyzed by Transmission Electron Microscope (TEM) and X-ray Photoelectron Spectroscopy (XPS) (Figure S1 and S2), and leaching of Pd was measured by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). After the Heck reaction, Pd(0) species predominantly formed and partial aggregation of Pd particles were observed, while only 2.5 nmol of Pd (1.1% of the loaded Pd) was leached into the reaction solution.

Table 1 Screening of additives[a]



Entry	Additive	Yield of **3a** (%)[b]
1	-	29
2	TMAB (0.13 mmol)[c]	30
3	TBAB (0.13 mmol)[d]	42
4	C_{16}TAB (0.13 mmol)[e]	90
5	DMDPAB (0.13 mmol)[f]	65
6	SDS (0.13 mmol)[g]	20
7	C_{16}TAB (0.06 mmol)	74
8	C_{16}TAB (0.19 mmol)	89
9	C_{16}TAB (0.25 mmol)	83
10[h]	C_{16}TAB (0.19 mmol)	31
11[i]	C_{16}TAB (0.19 mmol)	84

a; Reaction conditions: styrene (**1a**, 0.38 mmol), iodobenzene (**2a**, 0.25 mmol), Pd/GO (Pd: 0.09 mol%), K_2CO_3 (0.75 mmol) and additive were mixed in 50% aq. ethylene glycol at 80 °C for 24 h. b; Yields were determined by GC using dodecane as an internal standard. c; tetramethylammonium bromide. d; tetrabutylammonium bromide. e; hexadecyltrimethylammonium bromide. f; dimethyldipalmitylammonium bromide. g; sodium dodecyl sulfate. h; 60 °C. i; 100 °C.

Fourier-transfer infrared (FT-IR) spectroscopy (Figure 2) and energy dispersive X-ray (EDX) spectroscopy of C_{16}TAB-modified Pd/GO composites were measured to clarify the interaction between C_{16}TAB and GO. FT-IR spectra showed no significant change other than the appearance of an alkyl group at 2740-2980 cm^{-1}. When ionic interaction between ammonium and carboxylate occurs, the peak of C=O bond at 1730 cm^{-1} shifts to a smaller wavenumber,[13a] therefore, the alkyl chain of C_{16}TAB is supposed to interact with GO. EDX analysis showed the presence of Br (5.3 wt%), which also supports that ionic interaction did not occur between C_{16}TAB and GO. From the EDX result of Br content, the surfactant- modified Pd/GO composite contained its 24 wt% of C_{16}TAB.

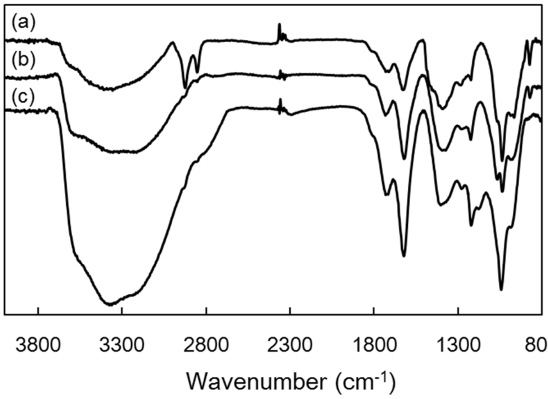


Figure 2 FT-IR spectra of (a) Pd/GO with C_{16}TAB, (b) Pd/GO, and (c) GO.

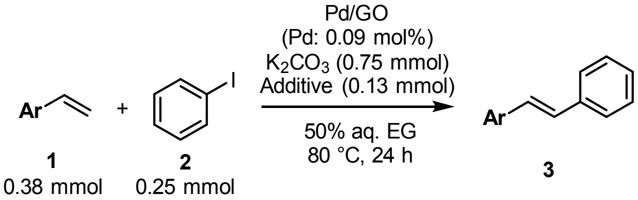
Next, the relationship between the additives that affect interlayer distance and the substrate size was investigated. We focused on C_{16}TAB and DMDPAB as additives that increased sheet distance of GO to 1.19 nm and 2.80 nm, respectively. Non-substituted styrene (**1a**) gave **3a** in 90% yield when C_{16}TAB was added, while DMDPAB was less effective (Table 2, entry 1). The same tendency was observed when 4-chlorostyrene (**1b**) was used as the substrate (Table 2, entry 2). For larger substrates, such as 4-bromostyrene (**1c**), 4-methylstyrene (**1d**), and 4-*tert*-butylstyrene (**1e**), DMDPAB provided the product in higher yield (Table 2, entries 3-5). When 1-iodonaphthalene (**2b**) was used instead of iodobenzene (**2a**), the addition of DMDPAB also gave high yield (Table 2, entry 6). These results suggest that the substrate selectivity in Pd/GO catalysis can be tuned by changing the molecular size of the surfactant; when the size of **1** was smaller than 0.78 nm (**1a** and

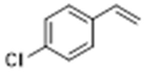
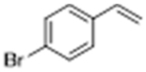
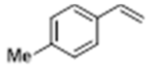
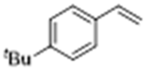
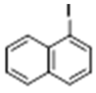
View Article Online
DOI: 10.1039/C4RA10512E

1b), C_{16}TAB showed better performance, on the other hand, DMDPAB was suitable for large-sized substrates (**1c** and **1d**) (See, Figure S4). Since Pd/C does not have sheet structure, the obvious size effect of the surfactant was not observed (Table 2, entries 7 and 8).

XRD measurement of Pd/GO mixed with styrenes provided more convincing evidence for the sheet distance effect. The molecular size of styrene (**1a**) and 4-*tert*-butylstyrene (**1e**) were estimated to be 0.72 nm and 0.96 nm, respectively (Figure S4). The XRD spectra of Pd/GO intercalated by **1a** and **1e** showed two distinctive peaks; one between 2θ = 10.16° (○, the peak of Pd/GO) and 7.46° (△, the peak of Pd/GO + C_{16}TAB), and the other between 2θ = 7.46° (△) and 3.16° (□, the peak of Pd/GO + DMDPAB), and the peak of Pd/GO + **1e** showed low angle shift compared with that of Pd/GO + **1a** (Figure 3). These results suggest that the Heck reaction can occur inside of GO layers, although outerlayer reaction would also be involved.

Table 2 The effect of additives[a]



Entry	1	2	Yield (%)[b]	
			C_{16}TAB[c]	DMDPAB[d]
1	**1a**	**2a**	90	65
2	 **1b**	**2a**	91	87
3	 **1c**	**2a**	72	>99
4	 **1d**	**2a**	60	88
5	 **1e**	**2a**	47	95
6	**1a**	 **2b**	48[e]	71[e]
7[f]	**1a**	**2a**	96[g]	93[g]
8[f]	**1a**	**2b**	63[g]	66[g]

a; Reaction conditions: alkene (**1**, 0.38 mmol), iodobenzene (**2**, 0.25 mmol), Pd/GO (Pd: 0.09 mol%), K_2CO_3 (0.75 mmol) and additive (0.13 mmol) were mixed in 50% aq. ethylene glycol at 80 °C for 24 h. b; Yields were determined by ^{1}H NMR (in $CDCl_3$) using 1,1,2,2-tetrachloroethane as an internal standard. c; C_{16}TAB was used as the additive. d; DMDPAB was used as the additive. e; Isolated yield. f; Pd/C was used as the catalyst instead of Pd/GO. g; Yields were determined by GC using dodecane as an internal standard.

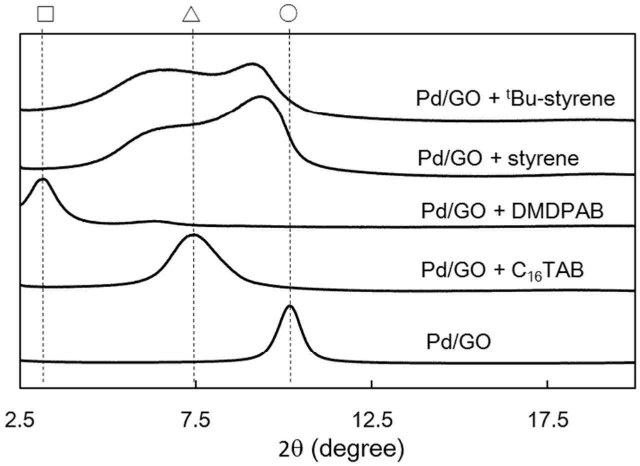
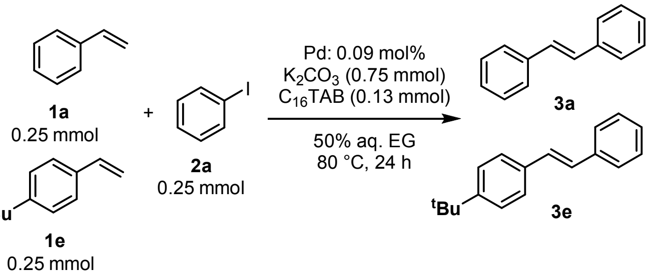


Figure 3 XRD spectra of Pd/GO with **1** or surfactants.

To confirm the effect of surfactant to tune substrate selectivity, we performed the three-component reaction, in which styrene (**1a**), 4-*tert*-butylstyrene (**1e**), and iodobenzene (**2a**) were employed (eq 1). When Pd/GO was used as a catalyst, the product ratio **3a**/**3e** was 1.6, while Pd/C gave the product mixture with **3a**/**3e** ratio of 1.1.



Conclusions

We have developed the surfactant-modified Pd/GO catalyst system for Heck reactions. The role of the surfactant is to increase the dispersibility of Pd/GO as well as to tune the interlayer distance of GO that affected the substrate selectivity. We are still facing a challenge to improve the selectivity by fine tuning of the size of the surfactant and applying the system to packed-bed reactor not only for Heck reaction, but also other metal-catalysed reactions.

Notes and references

[a] Graduate School of Natural Science and Technology, Okayama University, 3-1-1, Tsushimanaka, Kita-ku, Okayama 700-8530.
[b] Research Core for Interdisciplinary Sciences, Okayama University, 3-1-1, Tsushimanaka, Kita-ku, Okayama 700-8530.
[c] Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012.

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

DOI: 10.1039/C4RA10512E

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

1 D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* **2010**, *39*, 228.

2 W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339.

3 B. C. Brodie. *Phil. Trans. R. Soc. Lond*. **1859**, *149*, 249.

4 L. Staudenmaier, *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 1481.

5 S. Pei, H. M. Cheng, *Carbon* **2012**, *50*, 3210.

6 a) T. Kuila, A. K. Mishra, P. Khanra, N. H. Kim, J. H. Lee, *Nanoscale* **2013**, *5*, 52. b) C. K. Chua, M. Pumera, *Chem. Soc. Rev.* **2014**, *43*, 291.

7 a) T. Kuilla, S. Bhadra, D. Yao, N. H. Kim, S. Bose, J. H. Lee, *Prog. Polym. Sci.* **2010**, *35*, 1350. b) M. Cano, U. Khan, T. Sainsbury, A. O'Neill, Z. Wang, I. T. McGovern, W. K. Maser, A. M. Benito, J. N. Coleman, *Carbon* **2013**, *52*, 363.

8 a) B. F. Machado, P. Serp, *Catal. Sci. Technol*. **2012**, *2*, 54. b) H. Chang, H. Wu, *Energy Environ. Sci*. **2013**, *6*, 3483. c) X. Huang, X. Qi, F. Boey, H. Zhang, *Chem. Soc. Rev*. **2012**, *41*, 666.

9 a) Z. B. Liu, Y. F. Xu, X. Y. Zhang, X. L. Zhang, Y. S. Chen, J. G. Tian, *J. Phus. Chem. B* **2009**, *113*, 9681. b) Y. Yang, J. Wang, J. Zhang, J. Liu, X. Yang, H. Zhao, *Langmuir* **2009**, *25*, 11808. c) S. Stankovich, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Carbon* **2006**, *44*, 3342. d) D. Chen, H. Feng, J. Li, *Chem. Rev*. **2012**, *112*, 6027.

10 a) *Handbook of Organopalladium Chemistry for Organic Synthesis,* ed. by E. Negishi, Wiley, **2002**, Vol. 1 and 2. b) *Palladium Reagents and Catalysts*, ed. by J. Tsuji, Wiley, **2004**.

11 a) G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mülhaupt, *J. Am. Chem. Soc*. **2009**, *131*, 8262. b) L. Rumi, G. M. Scheuermann, R. Mülhaupt, W. Bannwarth, *Helv. Chim. Acta.* **2011**, *94*, 966. c) Y. Li, X. Fan, J. Qi, J. Ji, S. Wang, G. Zhang, F. Zhang, *Nano Res*. **2010**, *3*, 429. d) S. Yamamoto, H. Kinoshita, H. Hashimoto, Y. Nishina, *Nanoscale* **2014**, *6*, 6501. e) C. Xu, X. Wang, J. Zhu, *J. Phys. Chem. C* **2008**, *112*, 19841. f) S. Moussa, A. R. Siamaki, B. F. Gupton, M. S. El-Shall, *ACS Catal*. **2012**, *2*, 145. g) S. Santra, P. K. Hota, R. Bhattacharyya, P. Bera, P. Ghosh, S. K. Mandal, *ACS Catal*. **2013**, *3*, 2776.

12 a) M. Acik, G. Lee, C. Mattevi, A. Pirkle, R. M. Wallace, M. Chhowalla, K. Cho, Y. Chabal, *J. Phys. Chem. C* **2011**, *115*, 19761. b) X. Fan, W. Peng, Y. Li, X. Li, S. Wang, G. Zhang, F. Zhang, *Adv. Mater*. **2008**, *20*, 4490.

13 a) Y. Matsuo, T. Niwa, Y. Sugie, *Carbon* **1999**, *37*, 897. b) Z. H. Liu, Z. M. Wang, X. Yang, K. Ooi, *Langmuir* **2002**, *18*, 4926. c) Y. Liang, D. Wu, X. Feng, K. Müllen, *Adv. Mater*. **2009**, *21*, 1679. d) Y. Matsuo, K. Hatase, Y. Sugie, *Chem. Commun*. **1999**, 43. e) Á. Mastalir, Z. Király, M. Benkő, I. Dékány, *Catal. Lett.* **2008**, *124*, 34.

14 C. Xu, J. Wang, L. Wan, J. Lin, X. Wang, *J. Mater. Chem*. **2011**, *21*, 10463.

15 N. Shang, C. Feng, H. Zhang, S. Gao, R. Tang, C. Wang, Z. Wang, *Catal. Commun*. **2013**, *40*, 111.

16 a) Y. Matsuo, T. Fukunaga, T. Fukutsuka, Y. Sugie, *Carbon*. **2004**, *42*, 2875. b) Y. Matsuo, T. Tabata, T. Fukunaga, T. Fukutsuka, Y. Sugie, *Carbon* **2005**, *43*, 2875. c) J. Maruyama, S. Akita, Y. Matsuo, Y. Muramatsu, *Carbon* **2014**, *66*, 327.

17 a) Y. Nishina, J. Miyata, R. Kawai, K. Gotoh, *RSC Adv*. **2012**, *2*, 9380. b) N. Morimoto, S. Yamamoto, Y. Takeuchi, Y. Nishina, *RSC Adv.* **2013**, *3*, 15608.

18 R. G. Heidenreich, K. Köhler, J. G. E. Krauter, J. Pietsch, *Synlett* **2002**, *7*, 1118.

19 It has been reported that the addition of surfactant in Pd/C catalyzed Heck reaction efficiently promote the reaction: *Journal of Dispersion Science and Technology* **2012**, *33*, 117.

20 Detailed preparation method and structure characterization of Pd/GO used in this manuscript is shown in ref 11d.