Electronic Supplementary Information

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

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Materials

Graphite (SP-1) was purchased from BAY CARBON Inc. $NaNO_3$, $KMnO_4$, H_2SO_4, H_2O_2 $Pd(NO_3)_2$, toluene, THF, NMP, DMF, Cs_2CO_3, $CH_3COONa•3H_2O$ and 4-methylstyrene were purchased from Wako Pure Chemical Industries, Ltd. Ethylene glycol, EtOH, DMA and *n*-hexane were purchased from Kanto chemical Co., Ltd. $Pd(OAc)_2$ and $PdCl_2$ were purchased from Tanaka Kikinzoku international k.k. Tetramethylammonium bromide (TMAB), tetrabutylammonium bromide (TBAB), hexadecyltrimethylammonium bromide (C_{16}TAB), dimethyldipalmitylammonium bromide (DMDPAB), styrene, iodobenzene, 4-*tert*-butylstyrene, 4-bromostyrene, 4-chlorostyrene and 1,1,2,2-tetrachloroethane were purchased from Tokyo Chemical Industry Co. AcOEt, K_2CO_3, Na_2CO_3, KH_2PO_4, $NaHCO_3$, Et_3N and dodecane were purchased from Nacalai Tesque Co. Ltd. 1-Iodonaphthalene was purchased from Alfa Aesar. All reagents were used directly without further purification.

Methods

Transmission electron microscopy (TEM) images were obtained by using a JEOL JEM-2100F at an acceleration voltage of 200 kV. Gas chromatography (GC) analysis was performed on Shimadzu GC-2014 equipped with FID detector. Fourier transform infrared (FT-IR) was measured by JASCO ATR PRO450-S with Ge. X-ray diffraction (XRD) was measured by PANalytical Co. X' part PRO using Cu K_α radiation (λ =1.541 Å) in the 2θ range of 2.0-75°. The operating tube current and voltage were 40 mA and 40 kV, respectively. The data was collected at the step size of 0.017° and the type of scan was continuous. ^{1}H-NMR spectra were recorded using a JEOL JNM-LA400 spectrometers or Varian NMR System 600. Proton chemical shifts are relative to solvent residual peaks (chloroform: 7.27ppm). Energy dispersive X-ray spectroscopy (EDX) was measured by SHIMADZU. Co. Rayny EDX-700HS. The operating tube current and voltage were 100 μA and 15 kV, respectively. Rh was used as X-ray tube.

Preparation of Pd/GO composite

GO was prepared from natural graphite flakes according to modified Hummers method.[1] Pd/GO composite was prepared following the previously reported method.[2] 20 mL of EtOH and 1.25 mg of $Pd(OAc)_2$ were added to 20 mL of 0.1 wt% GO dispersion in water. Then the mixtures were stirred at 60 °C for 1 h.

Preparation of Pd/GO with surfactants for XRD measurement

Pd/GO was mixed with various surfactants (3.1 mmol) in 50% aq. EtOH at room

temperature for 1 h. Then, the mixture was washed several times by the centrifugation. The precipitate was coated on the sample holder, dried by gentle heating in air, and analyzed by XRD.

General procedure for Heck reaction

The suspension of Pd/GO composite in 50% aq. EtOH was washed with 50% aq. ethylene glycol by centrifugation for 3 times, then dispersed in 50% aq. ethylene glycol. Screw-capped test tube was charged with styrene (**1a**, 0.38 mmol), iodobenzene (**2a**, 0.25 mmol), K_2CO_3 (0.75 mmol) and C_{16}TAB (0.13 mmol), Pd/GO suspension (Pd: 0.09 mol%= 0.00023 mmol), and 50% aq. ethylene glycol (4.5 mL). The reaction mixture was stirred at 80˚C for 24 h. After the reaction, the product yield was determined by GC using dodecane as an internal standard. The isolated product showed complete agreement in ^{1}H NMR with the previous report.[3]

TEM image of the catalyst

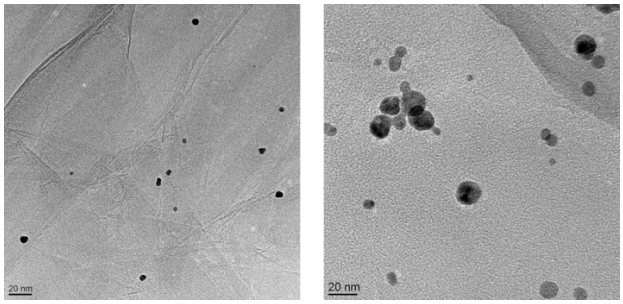

Figure S1. As prepared Pd/GO (left) and recovered Pd/GO after 3rd recycle (right). Partial aggregation of Pd nanoparticle was observed, while only 1.1% of Pd (2.5 nmol) was leached into the mixture analyzed by ICP-AES.

XPS analysis

As prepared Pd/GO is composed of Pd(II) and Pd(0). Complete reduction of Pd to Pd(0) always accompanies reduction of GO to cause aggregation of GO sheets and reduction of catalytic activity[2)] in the absence of surfactant. Therefore, we use the mixture of Pd(II) and Pd(0) as catalyst, although actual catalyst in Heck reaction is Pd(0).

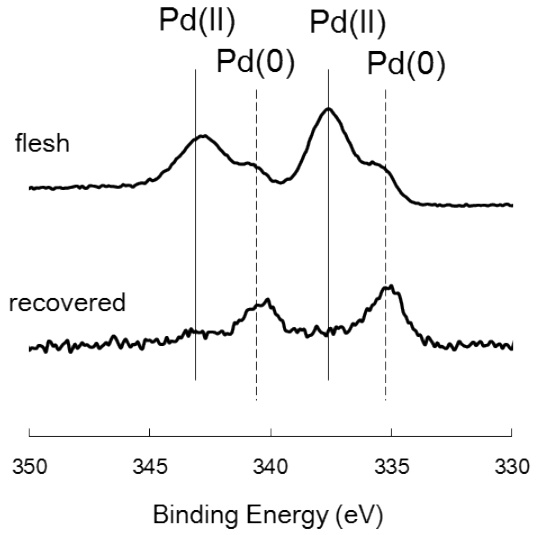

Figure S2. XPS analysis of the catalyst before and after Heck reaction.

Stability test by XRD

Pd/GO is easily aggregated in the presence of base at high temperature. To check the stability and dispersibility of Pd/GO with surfactant, Pd/GO + C_{16}TAB was stirred in 50% aq. ethylene glycol under the presence of K_2CO_3 at 80 °C for 6 h. The interlayer distance did not significantly changed (d = 1.29 nm).

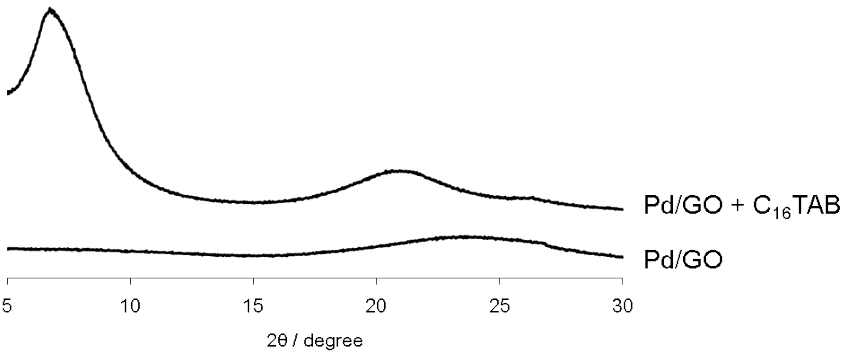

Figure S2. XRD analysis of the catalyst after heating in basic condition.

Preparation of alkene-intercalated Pd/GO for XRD measurement

Alkene (300 μL) and Pd/GO were stirred in 50% aq. EtOH at room temperature for 1 h. Then, the mixture was washed one time by the centrifugation. The precipitate was coated on the sample holder, dried by gentle heating in air, and analyzed by XRD.

Three-component reaction

The suspension of Pd/GO composite in 50% aq. EtOH was washed with 50% aq. ethylene glycol and centrifuged for 3 times, then dispersed in 50% aq. ethylene glycol. Screw-capped test tube was charged with styrene (**1a**, 0.25 mmol), iodobenzene (**2a**, 0.25 mmol), 4-*tert*-butylstyrene (**1e**, 0.25 mmol), K_2CO_3 (0.75 mmol), additive (0.13 mmol), Pd/GO suspension (Pd: 0.09 mol%= 0.00023 mmol), and 50% aq. ethylene glycol (4.5 mL). The reaction mixture was stirred at 80˚C for 24 h. After the reaction, ethyl acetate was added to extract the product. Yields were determined by ^{1}H NMR (in $CDCl_3$) using 1,1,2,2-tetrachloroethane as an internal standard.

Size of substrates

Chemical structures were written by Chem3D Pro 12.0, and minimized energy by MM2 method.

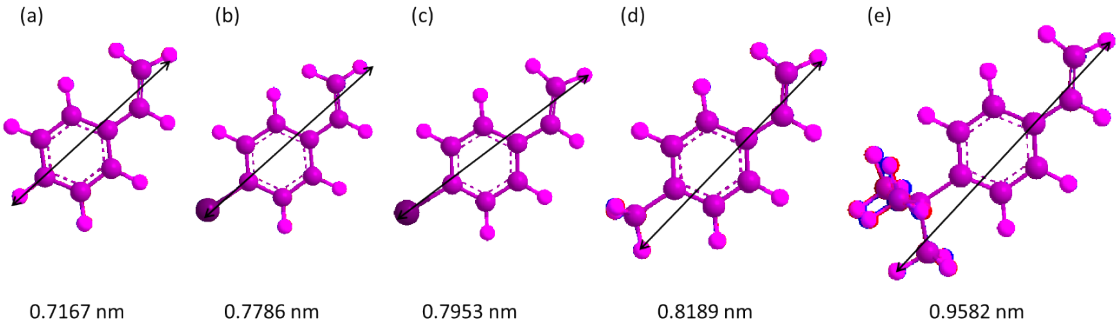

Figure S4. Molecular size of (a) styrene, (b) 4-chlorostyrene, (c) 4-bromostyrene, (d) 4-methylstyrene, and (e) 4-*tert*-butylstyrene.

References

1) Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, *J. Am. Chem. Soc.*, **2008**, *130*, 5856.
2) S. Yamamoto, H. Kinoshita, H. Hashimoto, Y. Nishina, *Nanoscale*, **2014**, *6*, 6501.
3) M. Mahesh , J. A. Murphy, H. P. Wessel, *J. Org. Chem.* **2005**, *70*, 4118.