Supplementary Information

Recyclable Pd/Graphene Catalyst: Mechanistic Insights into Heterogeneous and Homogeneous Catalysis

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1. Methods

1-1. TEM measurements For the transmission electron microscope (TEM) analysis, samples were dispersed in methanol solution and dropped on a 200-mesh Cu grid, and images were taken using JEOL JEM 2100F high-resolution transmission electron microscope at an acceleration voltage of 200 kV.

1-2. ESI-MS measurements ESI(+)-MS measurements were performed using Shimadzu LCMS-2020.

1-3. XRD measurements X-ray diffraction patterns were obtained on an X-ray powder diffractometer (Rigaku RINT-2000) using Cu Kα radiation.

1-4. NMR measurements NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are relative to solvent peaks [chloroform: 7.27 (^{1}H), 77.00 (^{13}C)]. The NMR spectra of products showed complete agreement with the known data.

1-5. GC measurements GC analysis was carried out with Shimadzu GC-2014 equipped with FID detector . The chemical yields were determined using dodecane as an internal standard. Calibration curves were prepared using commercially available standard samples.

2. Experimental Details

2-1. Preparation of Catalyst Pd/graphene was prepared by following the reported procedures.[4]

TG analysis in air suggested 10.6wt% of Pd was supported onto the exfoliated graphene.

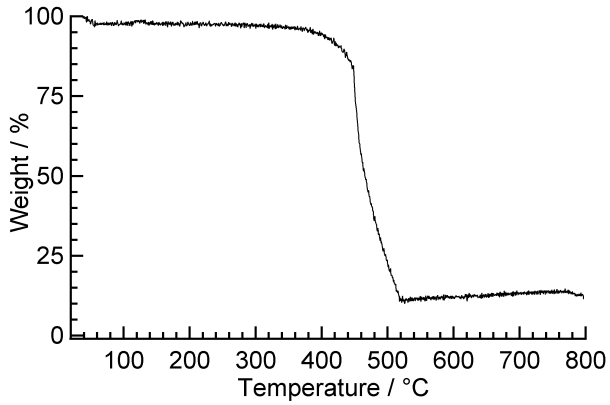

Fig. S1. TG mass loss curve for Pd/Graphene.

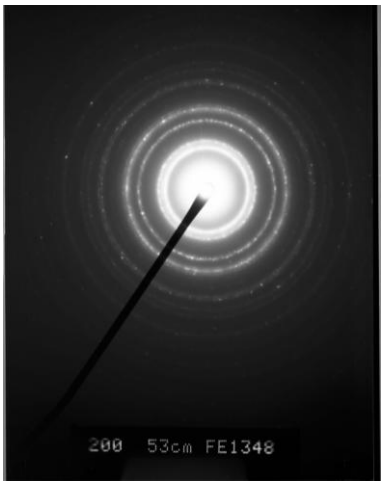

Fig. S2. ED pattern of Pd/Graphene.

2-2. Typical procedure for Suzuki-Miyaura coupling reaction The mixture of bromobenzene (0.20 mmol), phenylboronic acid (0.22 mmol) , K_2CO_3 (0.3 mmol), Pd/graphene (1 mg), EtOH (0.25 mL), H_2O (0.25 mL) was heated at 80°C for 2 h with stirring at 1000 rpm. The yield of the product was determined by GC using dodecane as an internal standard.

2-3. Catalyst recycling method After the reaction, the reaction mixture was filtered with Millipore membrane filter (0.2 μm). The recovered solid material was used for the next reaction without any activation procedure. When the activity of the catalyst decreased, it was heated at 300°C for 30 min in air to remove some impurities adsorbed onto the catalyst.

2-4. ESI-MS experiment Pd/graphene (5 mg) and bromobenzene (2 mg) were heated in EtOH: H_2O= 1: 1 at 80°C for 30 min. The reaction mixture was filtered, and the liquid phase was injected into MS apparatus using MeOH as an eluent.

2-5. Hydrogenation of alkyne The mixture of diphenylacetylene (0.20 mmol) and Pd/graphene (1 mg) in EtOH (0.5 mL) was connected with a hydrogen balloon, and stirred for 15 h. The reaction mixture was purified by passing through a pad of silica. The NMR spectra of the product showed complete agreement with the known data.[5]

2-6. Hydrothiolation of alkyne The mixture of diphenylacetylene (0.20 mmol), thiophenol (2.1 mmol) and Pd/graphene (1 mg) in toluene (0.5 mL) was heated at 100°C for 15 h. The reaction mixture was purified by passing through a pad of silica. The NMR spectra of the product showed complete agreement with the known data. [6]

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