Electronic Supplementary Information for

Combining Palladium Complex and Organic Amine on Graphene Oxide for Promoted Tsuji–Trost Allylation

Qingshan Zhao, Yuanzhi Zhu, Zhen Sun, Yang Li, Guoliang Zhang, Fengbao Zhang, and Xiaobin Fan*

State Key Laboratory of Chemical Engineering, School of Chemical Engineering & Technology, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin300072, China

E-mail: xiaobinfan@tju.edu.cn

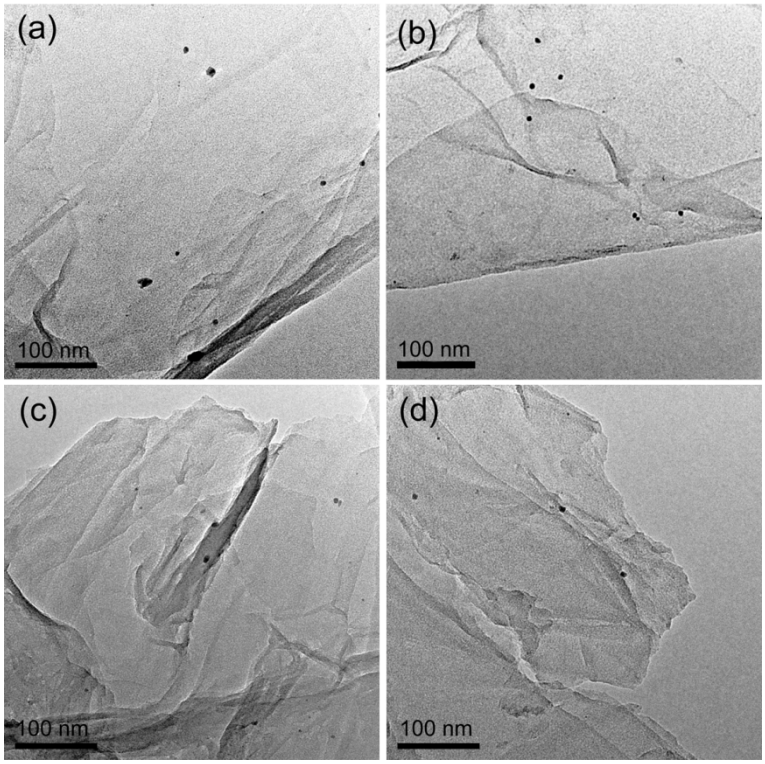

Fig. S1 TEM images of used catalysts with different amount of DEAPMS. (a) 0 equiv. DEAPMS, (b) 1 equiv. DEAPMS, (c) 2 equiv. DEAPMS, and (d) 3 equiv. DEAPMS.

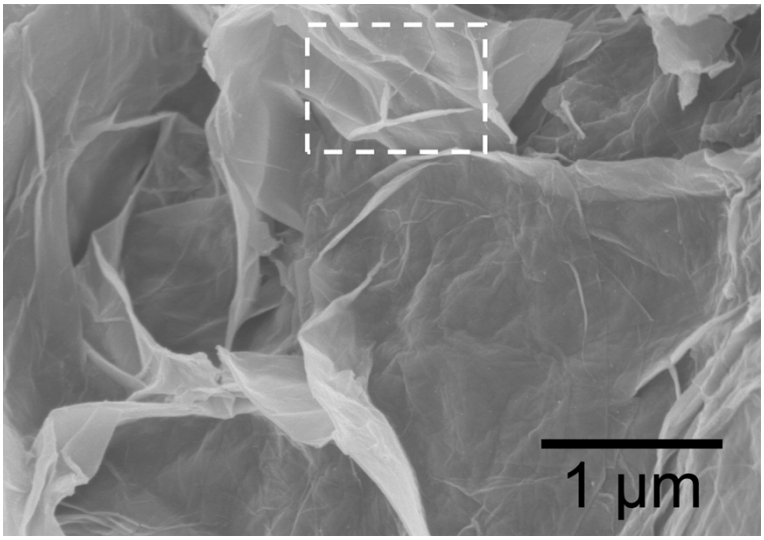

Fig. S2 SEM image of the recycled GO-NEt_2-2N-Pd after five-cycle reuse. In the white box region, some small nanoparticles can be observed.

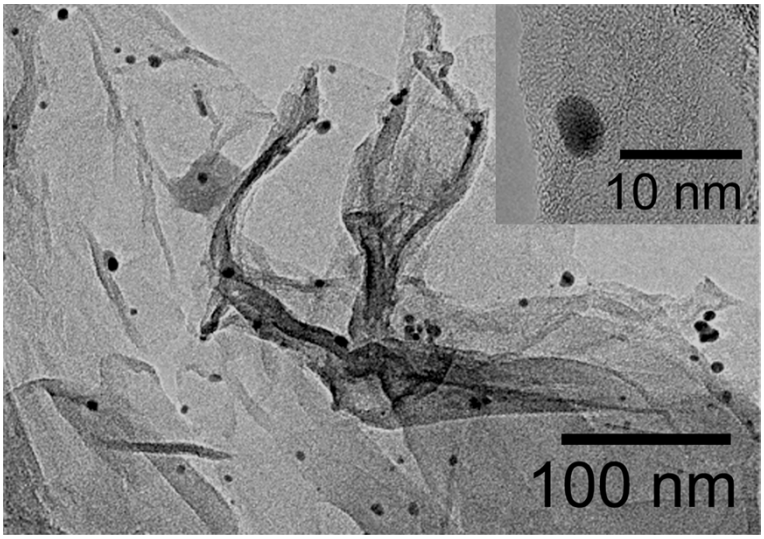

Fig. S3 TEM image of the recycled GO-NEt_2-2N-Pd after five-cycle reuse. As can be seen, a number of nanoparticles are distributed on the GO surface.

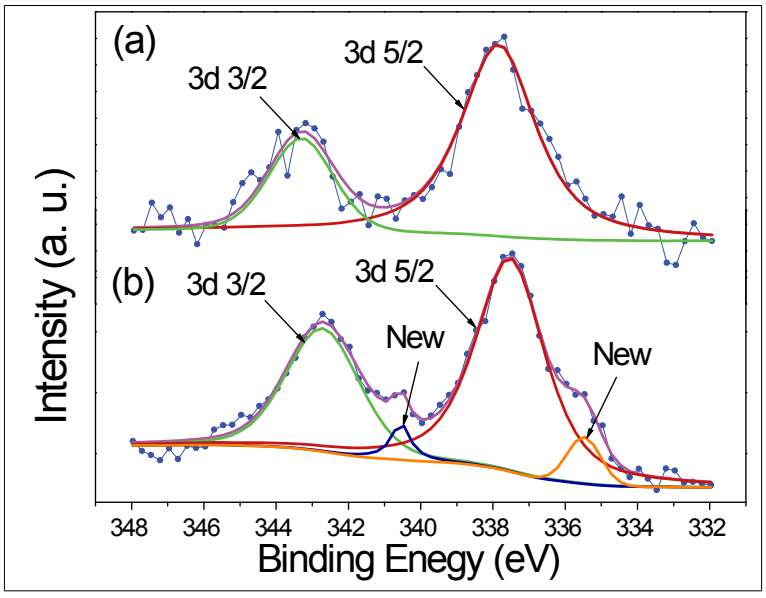

Fig. S4 Pd 3d XPS spectra of (a) fresh GO-NEt_2-2N-Pd and (b) recycled GO-NEt_2-2N-Pd. After the reaction, two small new peaks of Pd $3d_{5/2}$ (at 335. 5 eV) and Pd $3d_{3/2}$ (at 340.6 eV) corresponding to Pd(0) appear.

Table S1 The ICP result for GO-NEt_2-2N-Pd.

Sample	Pd (mg/L)	Pd loading (wt%)
GO-NEt_2-2N-Pd	3.929	0.98

ICP analysis was measured with 50 mL solution of palladium ions from 20 mg of solid sample. Through calcining, dissolving, and filtrating processes, the sample were detected by inductively coupled plasma optical emission spectroscopy (ICP-OES).

(Pd loading (wt%) = $\frac{3.929\ mg/L\ *\ 0.05\ L}{20\ mg}$ = 0.98%)

Additional experiments:

To explore the influence of Pd(0) nanoparticle size on the catalytic results, a series of additional experiments were carried out as follows.

Preparation of GO-NEt_2-2N supported Pd(0) nanoparticles.

Pd(0) nanoparticles were deposited on modified GO (GO-NEt_2-2N) by employing two different reductants: hydrazine hydrate and hydroge. GO-NEt_2-2N was firstly prepared through the procedure as described. Typically, 8.8 mg of $PdCl_2$ powder (0.05 mmol) and GO-NEt_2-2N (50 mg) were dispersed in 50 mL water. The mixture was stirred for 1 h at room temperature. Pd(0) nanoparticles reduced by hydrazine hydrate (Pd-MGO-N_2H_4) was synthesized by adding 156 mg (80 wt%, 2.5 mmol, 50 equiv. of Pd) of hydrazine hydrate, and the mixture was stirred at 90 ^oC for 1h. Pd(0) nanoparticles reduced by hydrogen (Pd-MGO-H_2) was obtained by bubbling hydrogen for 1 h with a flow of 40 mL min^{-1}. After the reaction, the resulting mixtures were filtered and washed with water multi times until no palladium ions were detected in the filtrate, followed by freeze-drying.

Characterization and catalytic tests.

The samples were characterized by TEM and ICP. As shown in **Fig. S5** below, images reveal that Pd-MGO-N_2H_4 and Pd-MGO-H_2 exhibit nanoparticle size of 25 $\pm$ 5 nm and 3 $\pm$ 1 nm, respectively. The Pd contents of Pd-MGO-N_2H_4 and Pd-MGO-H_2 amount to 4.98% and 3.72%, respectively.

The efficiency tests of the catalysts towards Tsuji–Trost allylation were conducted under the same conditions as described. The results are summarized in **Table S2**. As a control, the catalytic result of commercial Pd/C catalyst is also listed in the table.

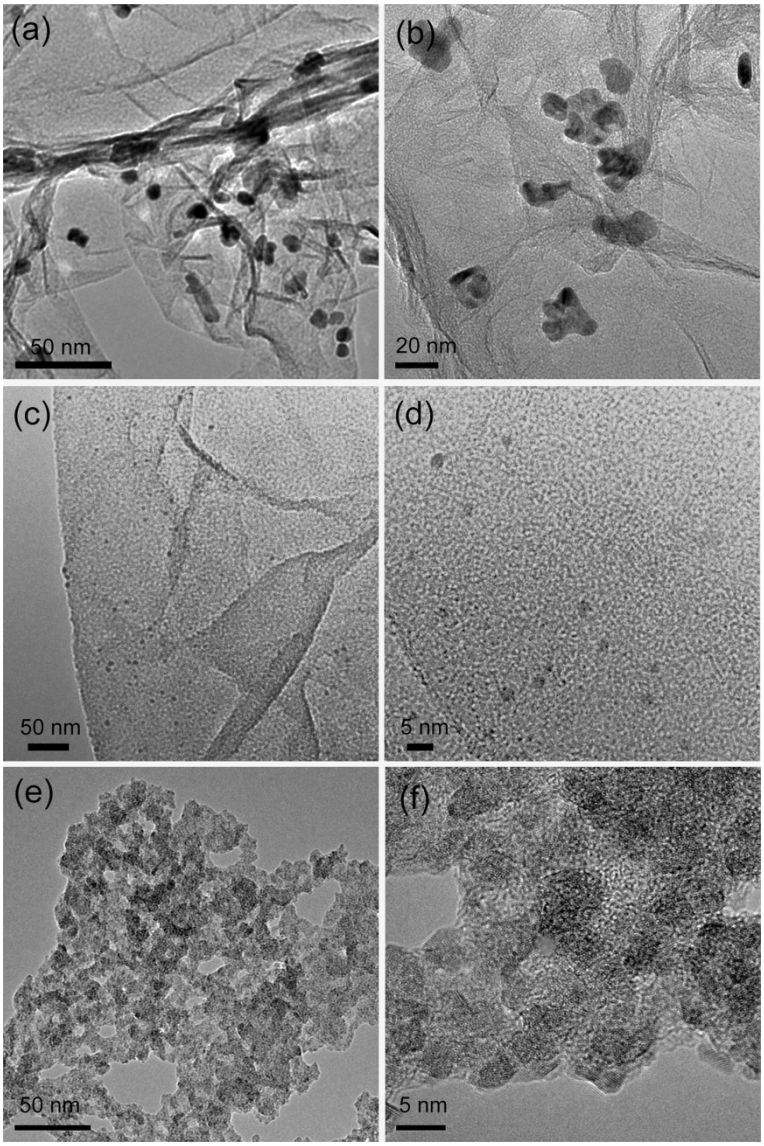

Fig. S5. TEM images of (a) (b) Pd-MGO-N_2H_4, (c) (d) Pd-MGO-H_2, and (e) (f) commercial Pd/C catalyst.

Table 2S Tsuji–Trost allylation catalyzed by Pd(0) catalysts.

Entry	Catalyst	Particle size (nm)	Pd content (wt %)	Conversion (%)	Yield (%)	
					3	**4**
1	Pd-MGO-N_2H_4	25 ± 5	4.98%	43.12	42.34	0.78
2	Pd-MGO-H_2	3 ± 1	3.72%	52.51	51.41	1.10
3	Pd/C	5 ± 2	5.00%	54.93	54.34	0.59

Discussion and conclusion.

As seen in **Table 1**, all of the samples exhibit good efficiency towards the Tsuji–Trost allylation. Pd-MGO-H_2 shows a comparable activity with the commercial Pd/C catalyst, while Pd-MGO-N_2H_4 gives a lower conversion compared with Pd-MGO-H_2 and commercial Pd/C catalyst. Therefore, Pd(0) is also an effective species towards the Tsuji–Trost allylation, and smaller nanoparticle size of Pd(0) tends to give a higher catalytic activity.