

Supporting Information

TiO₂ modified montmorillonite supported porous carbon im-mobilized Pd species nanocomposite as an efficient catalyst for Sonogashira reactions

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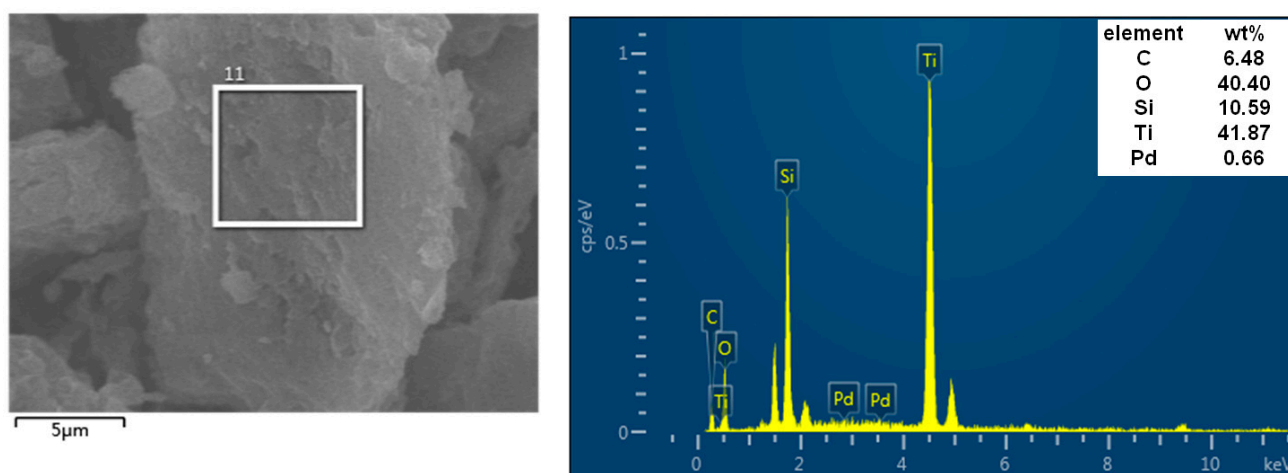


Figure S1. SEM-EDX scanning results of the $\text{TiO}_2\text{-MMT}_{60}/\text{PCN}_{40}@\text{Pd}^0$ nanocomposites.

SEM-EDX tests was performed with scanning electron microscope (JEM-6360, JEOL Ltd. Japan) equipped with an energy dispersive X ray-spectroscopy (Oxford EDX system).

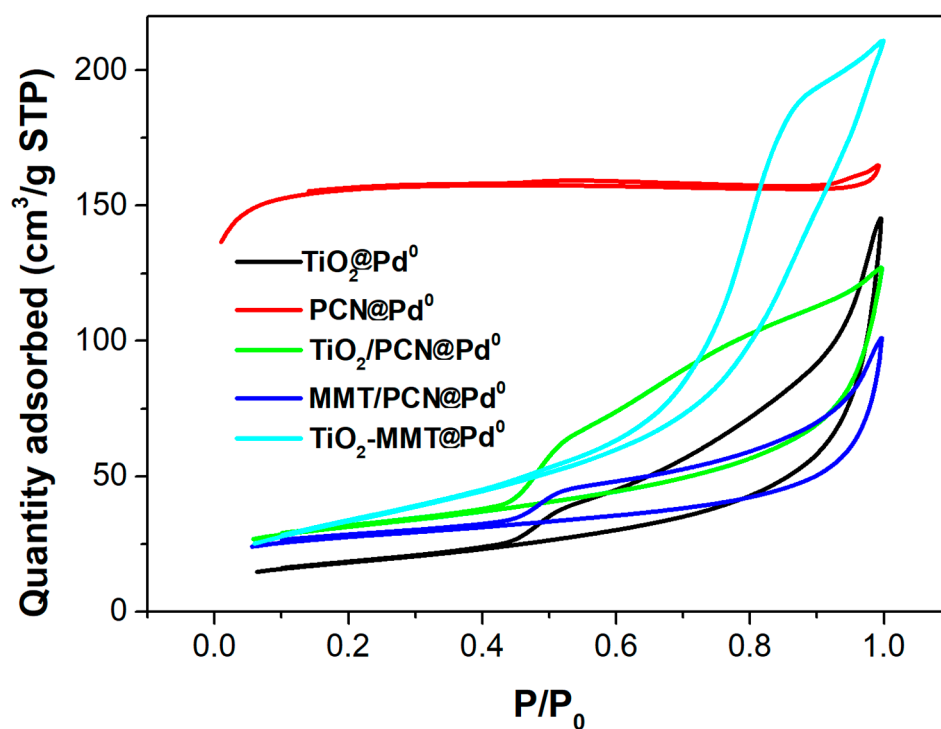


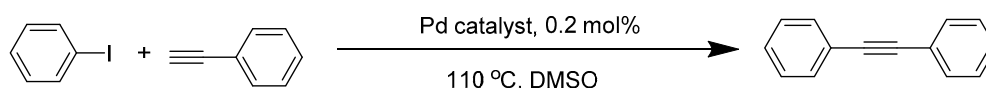
Figure S2. N₂ adsorption/desorption isotherms the heterogeneous catalysts.

Table S1. Structure parameter of heterogeneous catalysts extracted from the isotherms in **Figure S2**.

Sample	S_{BET} (m ² /g)	A_{mic} (m ² /g)	V_{tot} (cm ³ /g)
TiO ₂ -Pd ⁰	63.2	23.9	0.21
PCN-Pd ⁰	521.9	453.9	0.24
TiO ₂ /PCN-Pd ⁰	103.7	53.5	0.19
MMT/PCN-Pd ⁰	89.4	48.1	0.14
TiO ₂ -MMT-Pd ⁰	121.8	34.0	0.33

S_{BET} : specific surface area, by Brumanuer-Emmet-Teller method; A_{mic} : micropores area obtained by t -Polt method; V_{tot} : total volume of pores, the N₂ quantity absorbed at a relative pressure of $P/P_0=0.99$.

Table S2. Model Sonogashira coupling reaction between iodo benzene and phenyl acetylene catalyzed by the heterogeneous catalysts.



Entry	Catalyst	Yield (%)
1	no catalyst	no product
2	TiO ₂ @Pd ⁰	95
3	PCN@Pd ⁰	98
4	TiO ₂ /PCN@Pd ⁰	98
5	MMT/PCN@Pd ⁰	97
6	TiO ₂ -MMT@Pd ⁰	96
7	TiO ₂ -MMT ₆₀ /PCN ₄₀ @Pd ⁰	99

^a GC/MS yield

The preparation process of the heterogeneous catalysts is as follows:

TiO₂@Pd⁰: 2 g of nano TiO₂ particles (sized about 10 nm) were added into the 20 mL of Na₂PdCl₄ solution. Na₂PdCl₄ stock solution was made by dissolving 0.3 g of PdCl₂ and 2 g of NaCl in 100 mL of deionized water. The resulting mixture was allowed to stir at room temperature until the solution turned from brown to colorless. The collected powders were then washed until free of chloride anion, followed by reduction in ethylene glycol at 80 °C for 1 h.

PCN@Pd⁰: 1.33 g of CS was dissolved in 100 mL of 2 wt% CH₃COOH solution. 5 mL of Na₂PdCl₄ solution (contain 0.09 mmol of Pd) was dropped into the CS solution. Then, the CS-Pd²⁺ mixture solution were dried at 60 °C to form blend membranes. Then the blend membrane was carbonized at 800 °C for 4 h under N₂ atmosphere in the tubular muffle furnace. The collected powders were then washed with deionized water, followed by reduction in ethylene glycol at 80 °C for 1 h.

TiO₂/PCN@Pd⁰: 2 g of nano TiO₂ particles (sized about 10 nm) were added into the above CS-Pd²⁺ mixture solution. Then, the solution was continuously stirred at 60 °C (water bath heating) for 10 h. The TiO₂/CS@Pd²⁺ was separated from the suspension by centrifugation. After washing with deionized water to neutral and naturally drying, the TiO₂/CS@Pd²⁺ were carbonized at 800 °C for 4 h under N₂ atmosphere in the tubular muffle furnace. The collected powders were then washed with deionized water, followed by reduction in ethylene glycol at 80 °C for 1 h.

MMT/PCN@Pd⁰: 2 g of nano MMT were added into the above CS-Pd²⁺ mixture solution. Then, the solution was continuously stirred at 60 °C (water bath heating) for 10 h. The MMT/CS@Pd²⁺ was separated from the suspension by centrifugation. After washing with deionized water to neutral and naturally drying, the MMT/CS@Pd²⁺ were carbonized at 800 °C for 4 h under N₂ atmosphere in the tubular muffle furnace. The collected powders were then washed with deionized water, followed by reduction in ethylene glycol at 80 °C for 1 h.

TiO₂-MMT@Pd⁰: 2 g of nano TiO₂-MMT particles (sized about 10 nm) were added into the 20 mL of Na₂PdCl₄

solution. Na_2PdCl_4 stock solution was made by dissolving 0.3 g of PdCl_2 and 2 g of NaCl in 100 mL of deionized water. The resulting mixture was allowed to stir at room temperature until the solution turned from brown to colorless. The collected powders were then washed until free of chloride anion, followed by reduction in ethylene glycol at 80 °C for 1 h.

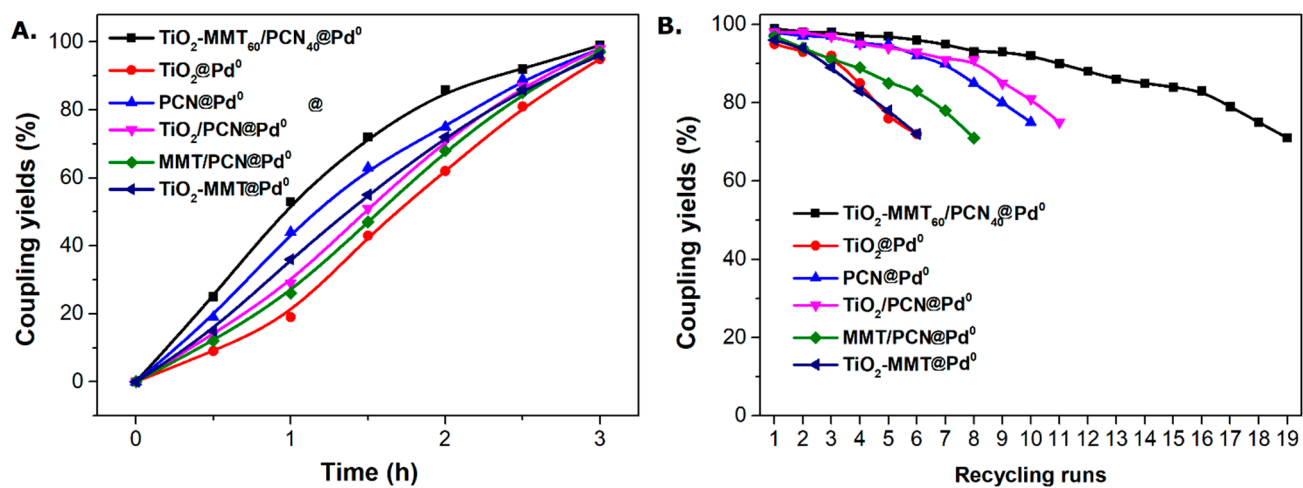


Figure S3. Performances of the heterogeneous catalysts applied in model Sonogashira reaction: **A.** coupling yields vs time; **B.** coupling yields vs recycling runs.

Table S3. A comparison of TiO₂-MMT/PCN@Pd⁰ catalyst with recent reported catalysts for Sonogashira reactions.

Entry	Catalyst	Metal (mol%)	Number of cycles	Reaction conditions	Ref.
1	<i>h</i> -Fe ₃ O ₄ @TiO ₂ -NH ₂ /Pd	0.18%	5	DMF, 90 °C, 3 h	75
2	TiO ₂ @ Pd (II)[PATA-NH ₂]	0.35%	5	H ₂ O, 3 h, r.t.	76
3	K10@Pd(II)APTES	0.3%	4	DMF, 7 h, 80°C	77
4	MMT/CS@Pd, Cu	1%	6	PPh ₃ , H ₂ O/DME, 8 h, 80 °C	78
5	CHT@Pd	0.23%	4	DMF, 10 h, 80 °C	79
6	Hal-pDA-NPC@Pd	0.5%	10	H ₂ O, 50 min, r.t.	80
7	TiO ₂ -MMT ₈₀ /PCN ₂₀ -Pd ⁰	0.2%	16	DMSO, 3 h, 110°C	this work
8	TiO ₂ -MMT ₆₀ /PCN ₄₀ -Pd ⁰	0.2%	19	DMSO, 3 h, 100 °C	this work

¹H NMR of the coupling products

Diphenylacetylene ¹H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.44 (m, 4H), 7.32 (dd, *J* = 5.1, 2.1 Hz, 6H).

1-Methyl-2-phenylthynyl-benzene ¹H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.44 (m, 2H), 7.44 – 7.24 (m, 5H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 2.31 (s, 3H).

1-Methyl-3-phenylthynyl-benzene ¹H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.50 (m, 2H), 7.49 (dt, *J* = 7.4, 1.1 Hz, 1H), 7.42 – 7.23 (m, 3H), 7.23 – 7.17 (m, 2H), 7.17 – 7.08 (m, 1H), 2.50 (s, 3H).

1-Methyl-4-phenylethynyl benzene ¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.62 (m, 2H), 7.58 – 7.53 (m, 2H), 7.48 – 7.38 (m, 3H), 7.25 (d, *J* = 7.9 Hz, 2H), 2.46 (s, 3H).

1-Chloro-2-phenylthynyl-benzene ¹H NMR (400 MHz, Chloroform-*d*) δ 7.59–7.50 (m, 3H), 7.40–7.36 (m, 1H), 7.31 (qd, *J* = 3.7, 1.5 Hz, 3H), 7.23–7.15 (m, 2H).

1-Bromo-3-phenylthynyl-benzene ¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 (t, *J* = 1.8 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.48 – 7.38 (m, 2H), 7.38 – 7.26 (m, 3H), 7.25 – 7.11 (m, 1H).

1-Fluoro-4-phenylthynyl-benzene ¹H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.39 (m, 4H), 7.39 – 7.09 (m, 3H), 7.09 – 6.85 (m, 2H).

1-Methoxy-3-phenylthynyl-benzene ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74–7.57 (m, 2H), 7.41 (qd, *J* = 4.9, 1.7 Hz, 3H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.23 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.16 (dd, *J* = 2.5, 1.4 Hz, 1H), 6.96 (dt, *J* = 8.3, 1.7 Hz, 1H), 3.86 (s, 3H).

1-Methoxy-4-(phenylethynyl)benzene ¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.62 (m, 2H), 7.58 – 7.53 (m, 2H), 7.48 – 7.38 (m, 3H), 7.25 (d, *J* = 7.9 Hz, 2H), 2.46 (s, 3H).

1-Fluoro-3-phenylthynyl-benzene ¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.34 (q, *J* = 3.0 Hz, 3H), 7.28 (dd, *J* = 6.9, 4.4 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.02 (ddt, *J* = 9.3, 4.4, 2.6 Hz, 1H).

1-Phenylethynyl-naphthalene ¹H NMR (400 MHz, Chloroform-*d*) δ 8.49 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.89 (ddt, *J* = 9.5, 8.4, 1.0 Hz, 2H), 7.81 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.76 – 7.54 (m, 4H), 7.54 – 7.36 (m, 4H).

4-Phenylethynyl-9H-fluorene ¹H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.70 (m, 3H), 7.69 – 7.50 (m, 4H), 7.39 (dt, *J* = 15.2, 7.6 Hz, 5H), 3.94 (s, 2H).