ELECTRONIC SUPPORTING INFORMATION (ESI)

Monolith catalyst design by 3*D* printing: A reusable support for modern palladium-catalyzed cross-coupling reactions

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Mechanical characterization

Compression test on the 3D printed monoliths (Pd-MOT) were performed using mechanical testing equipment (ZwickiLine Z5.0 TS, Zwick-Roell) at a displacement rate of 0.5mmmin^{-1} until crushing. The monolith sample was smoothened at top/bottom surfaces prior analysis to ensure a homogenous distribution of load on the 3D printing mediated structure. Stress-strain data were obtained from the load and displacement data. The compressive strength was calculated from the load at failure and the nominal contact surface area.

Hot filtration test experiment

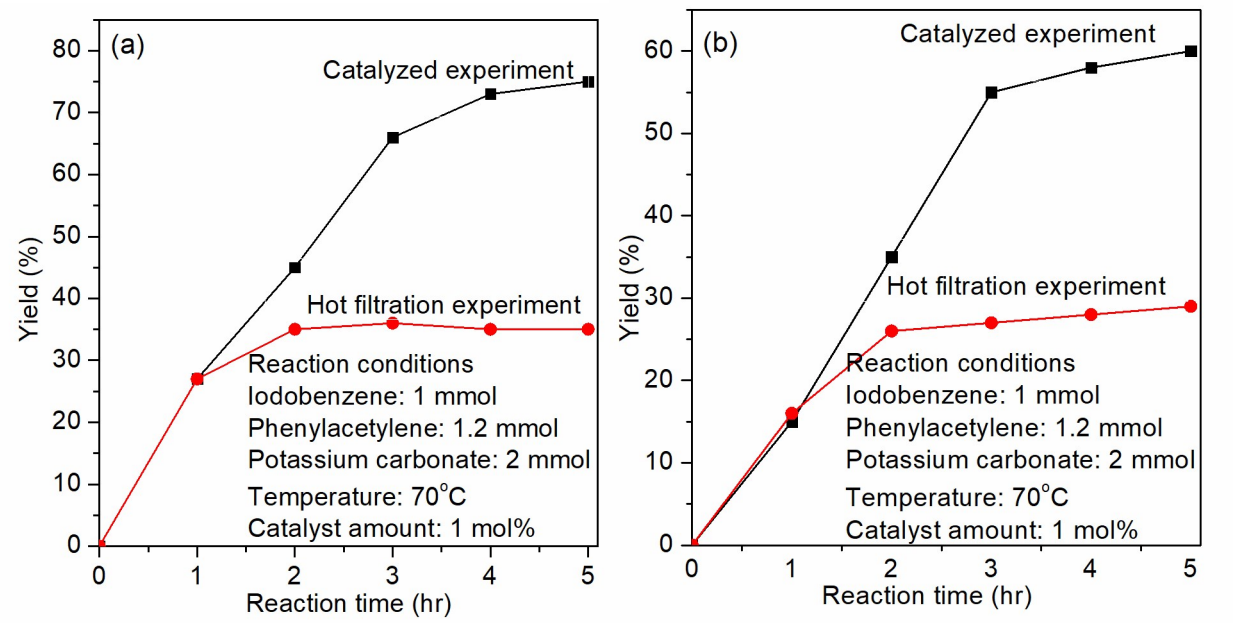

Figure S1: Hot filtration test for Sonogashira-Hagihara reaction (a) with Pd-MOT (b) with Pd/Al_2O_3 catalyst

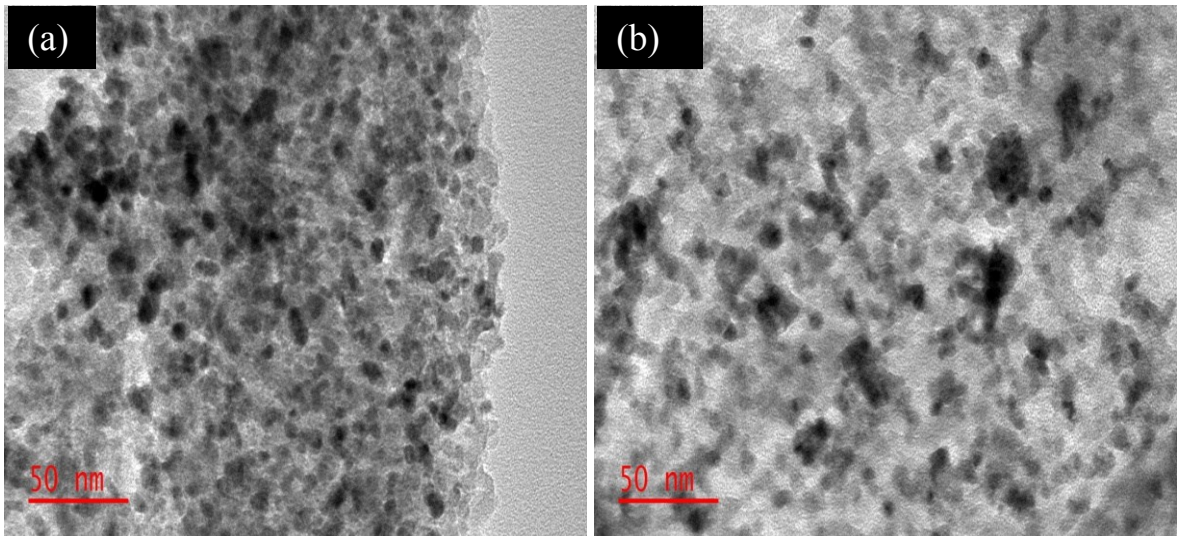

Figure S2: (a) TEM image of used Pd-MOT catalyst (b) TEM image of used Pd/Al_2O_3 catalyst

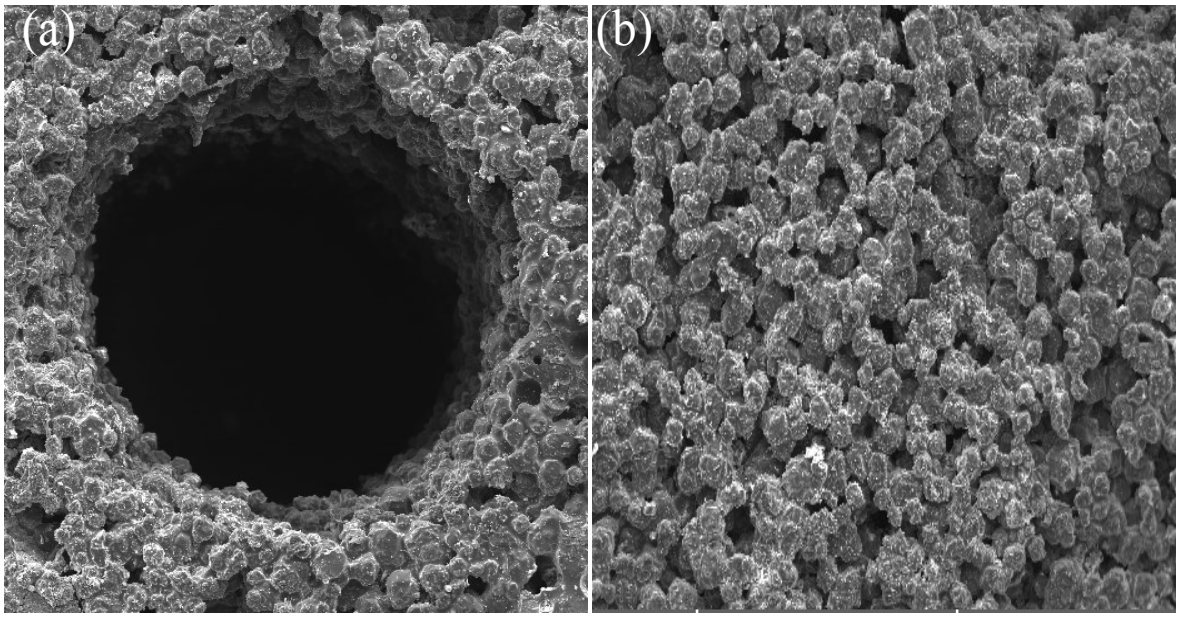

Figure S3: (a) SEM image of reused Pd-MOT catalyst (b) SEM image of reused Pd/Al_2O_3 catalyst

Table S1: Comparative experimental results obtained from the coupling reaction of iodobenzene with butyl acrylate catalyzed by Pd-MOT and Pd/Al_2O_3 [a] at different catalyst amount

Entry	*Catalyst amount*	Pd-MOT		*Pd/Al_2O_3*	
	(g)/Pd content (mol %)	*Yield (%)* [b]	*Selectivity (%)*[b]	*Yield (%)*[b]	*Selectivity (%)*[b]
1	0.5 (0.3)	50	100	40	100
2	1.0 (0.6)	60	100	50	100
3	1.5 (1.0)	85	100	65	100
4	2.0 (1.3)	97	100	78	100
5	2.5 (1.7)	99	100	80	100
6	3.0 (2.0)	99	100	78	100

[a] Reaction conditions: Iodobenzene (1.0 mmol); n-butyl acrylate (1.2 mmol); potassium carbonate (2 mmol); temperature: 80 °C; reaction time: 8 h. [b] Determined from the GC analysis.

Table S2: Comparative experimental results obtained from the coupling reaction of iodobenzene with phenylboronic acid catalyzed by Pd-MOT and Pd/Al_2O_3 at different reaction time.

Entry	*Reaction time*	Pd-MOT		*Pd/Al_2O_3*	
	(hr)	*Yield (%)* [b]	*Selectivity (%)*[b]	*Yield (%)*[b]	*Selectivity (%)*[b]
1	0	0	0	0	0
2	1	36	100	36	100
3	2	50	100	52	100
4	3	62	100	62	100
5	4	70	100	64	100
6	5	75	100	66	100
7	6	78	100	69	100

[a] Reaction conditions: Iodobenzene (1 mmol); phenylboronic acid (1.2 mmol); potassium carbonate (2 mmol); temperature: 70 °C; [b] Determined from the GC analysis.

Table S3: Comparative experimental results obtained from the coupling reaction of iodobenzene with phenylboronic acid catalyzed by Pd-MOT and Pd/Al_2O_3 [a] at different catalyst amount

Entry	*Catalyst amount*	Pd-MOT		*Pd/Al_2O_3*	
	(g)/Pd content mol%)	*Yield (%)* [b]	*Selectivity (%)*[b]	*Yield (%)*[b]	*Selectivity (%)*[b]
1	0.5 (0.3)	50	100	51	100
2	1.0 (0.6)	73	100	60	100
3	1.5 (1.0)	85	100	70	100
4	2.0 (1.3)	90	100	78	100
5	2.5 (1.7)	93	100	79	100

[a] Reaction conditions: Iodobenzene (1 mmol); phenylboronic acid (1.2mmol); potassium carbonate (2 mmol); temperature: 70 °C; reaction time 6 hr [b] Determined from the GC analysis

Table S4: Comparative experimental results obtained from the coupling reaction of iodobenzene with phenylacetylene catalyzed by Pd-MOT and Pd/Al_2O_3 [a] using different solvent.

Entry	*Catalyst*	*Solvent*	*Temperature (*°C)	*Yield%*	*Selectivity%*
1	Pd-MOT	EtOH	60	28	100
2	Pd/Al_2O_3	EtOH	60	29	100
3	Pd-MOT	$EtOH/H_2O$	70	75	100
4	Pd/Al_2O_3	$EtOH/H_2O$	70	60	100
5	Pd-MOT	DMF	100	46	-
6	Pd/Al_2O_3	DMF	100	46	-

[a] Reaction conditions: iodobenzene (1 mmol); phenylacetylene (1.2mmol); potassium carbonate (2 mmol); temperature: 70 °C; reaction time 5 hr [b] Determined from the GC analysis

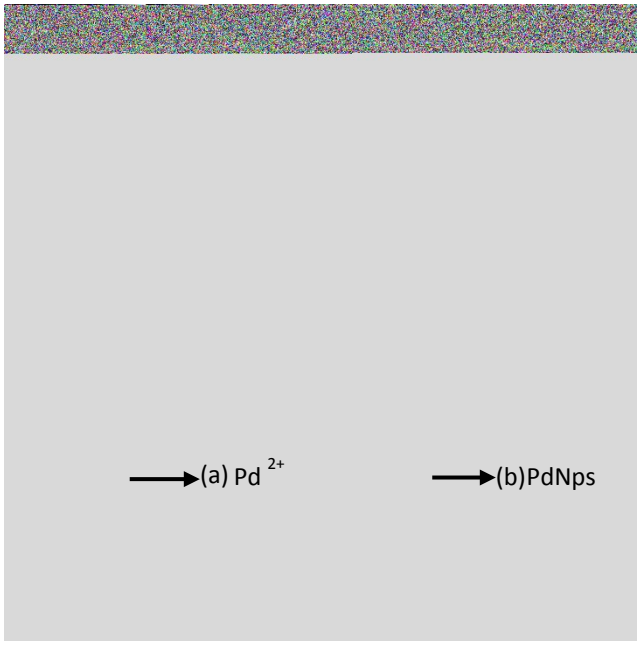

Figure S4: (a) Uv-vis spectra of the fresh catalyst (b) Uv-vis spectra of the reused catalyst