Supporting Information

Tuning the Catalytic Performance for the Semi-hydrogenation of Alkynols by Selectively Poisoning the Active Sites of Pd Catalysts

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1. Supplementary Figures S1-S11

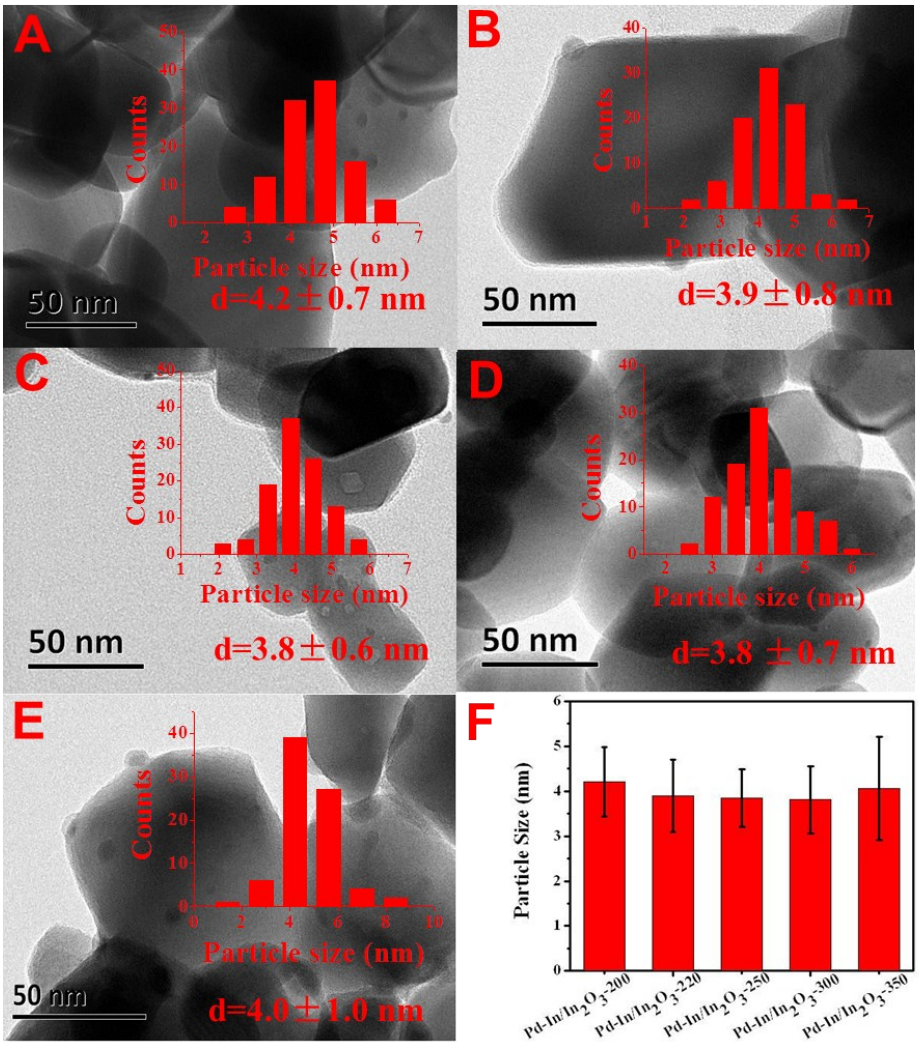

Figure S1. **TEM images of various Pd samples and the corresponding particle size distribution of Pd NPs.** (A) Pd-In/In_2O_3-200, (B) Pd-In/In_2O_3-220, (C) Pd-In/In_2O_3-250, (D) Pd-In/In_2O_3-300, (E) Pd-In/In_2O_3-350; (F) A summary of the particle size distribution of Pd NPs on the corresponding catalyst.

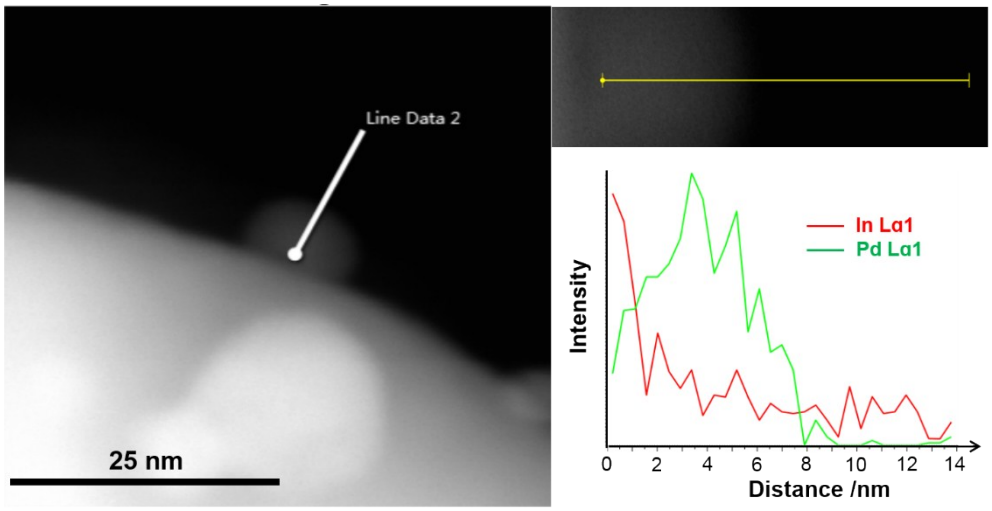

Figure S2. Compositional line profiles of Pd-In/In_2O_3 -250 recorded along the arrow shown in the STEM image.

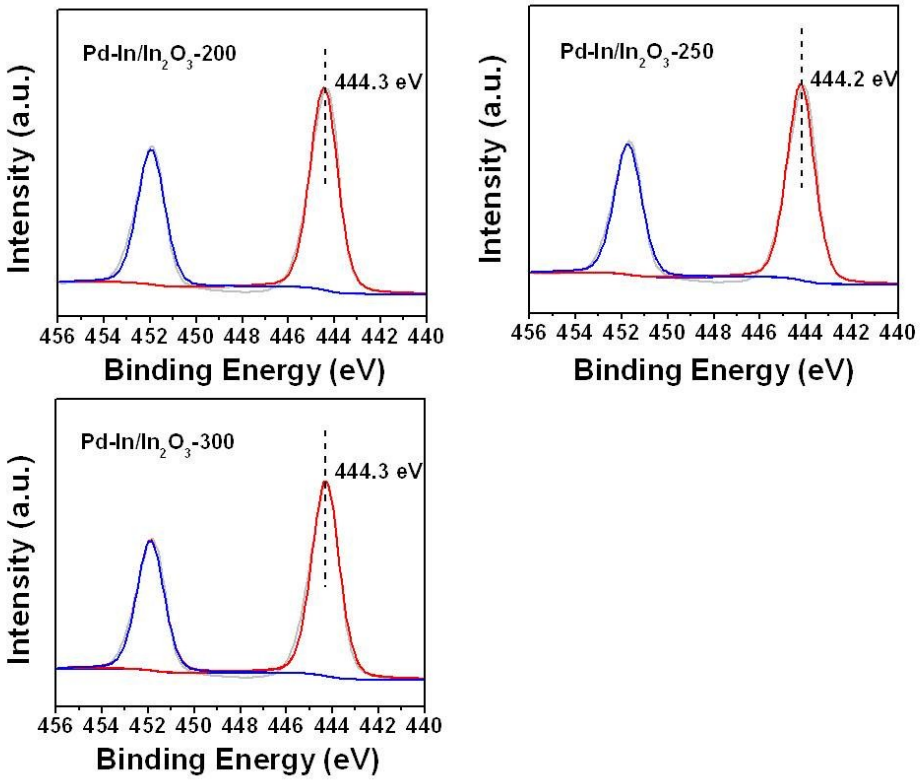

Figure S3. In 3d XPS of Pd-In/In_2O_3-200, Pd-In/In_2O_3-250 and Pd-In/In_2O_3-300 catalysts.

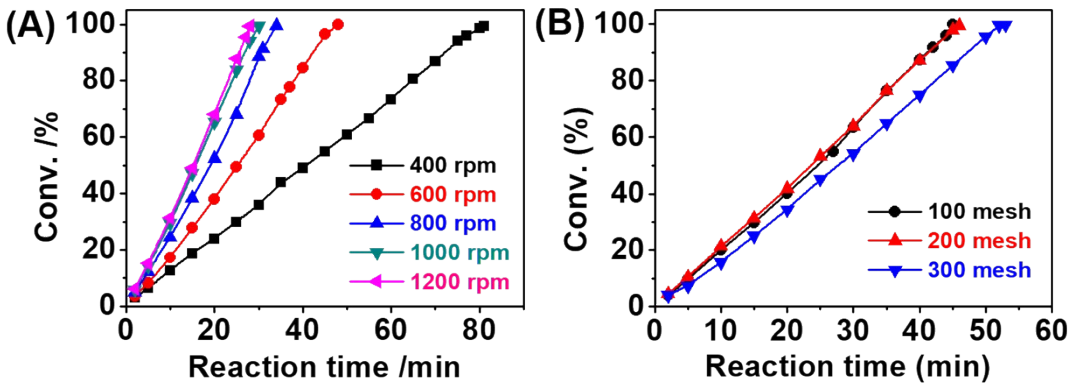

Figure S4. Kinetic studies for the semi-hydrogenation of MBY on Pd-In/In_2O_3-150. The effect of (A) stirring rates and (B) the agglomerative sizes of the catalysts on the activity. Reaction condition: 20 mg catalysts, 120 uL substrate, 5 mL ethanol, 30ºC, 1atm H_2.

As shown in Figure S4, the external diffusion could be elimitated when the stirring rate exceeded 1000 rpm. And for the internal diffusion, it took more time to realize the full conversion on catalyst with 300 meshes compared to that with 200 meshes. The reason lies in the fact that the heavy nano-size In_2O_3 would stick to the wall of the three-neck bottles if the agglomerative sizes of the catalysts is too small, which decreased the activity of the catalysts. This means catalysts with smaller agglomerative sizes are harder to exclude the internal diffusion due to the catalyst deposition. Actually, the internal diffusion may have been eliminated by the ultra-small particle size of In_2O_3 as seen in Figure S1 (~50 nm). And this can be confirmed in Figure 4B. Catalyst with only 100 meshes showed the same activity as that with 200 meshes.

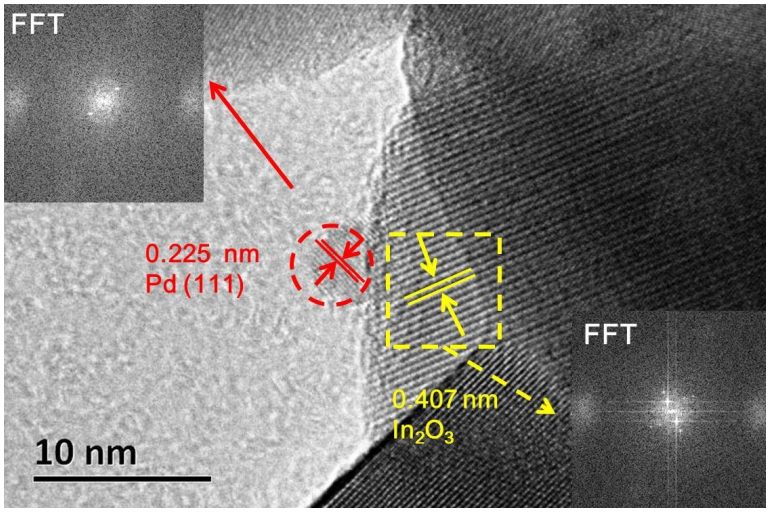

Figure S5. HRTEM image of Pd/In_2O_3.

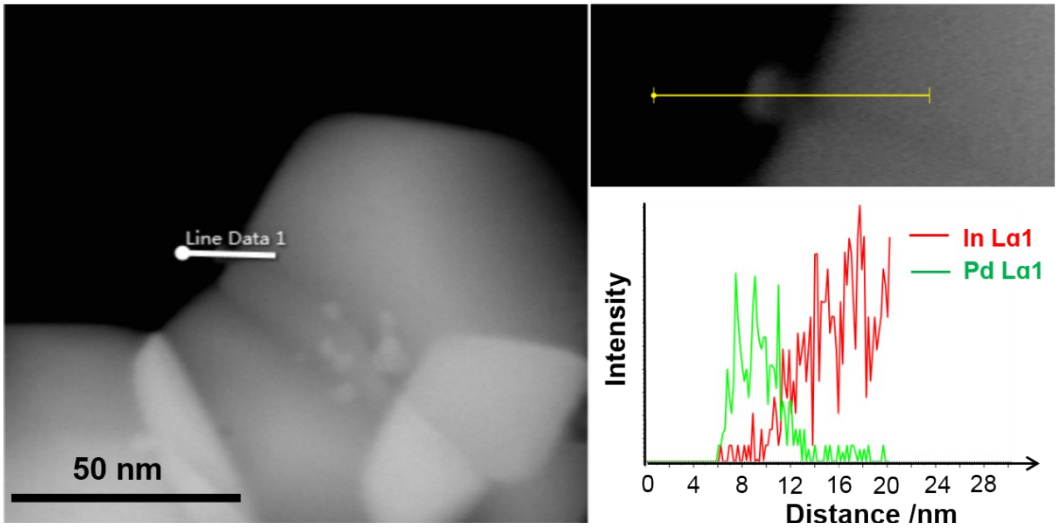

Figure S6. Compositional line profiles of Pd/In_2O_3 recorded along the arrow shown in the STEM image.

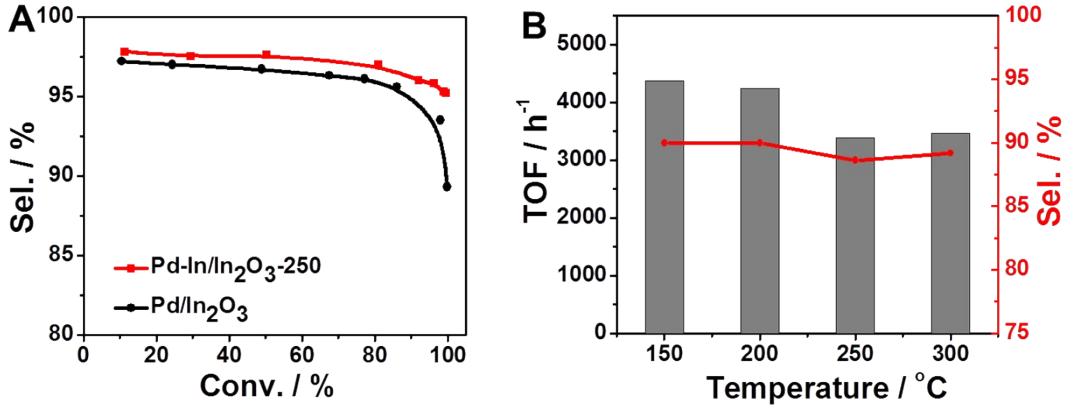

Figure S7. Controlling experiments about the interactions between Pt NPs and the supports. (A) Comparison of selectivity versus conversion of Pd-In/In_2O_3-200, Pd-In/In_2O_3-250, Pd-In/In_2O_3-300 and Pd/In_2O_3. (B) Comparison of catalytic performance of Pd/SiO_2 reduced at different temperatures, which donated as Pd/SiO_2-150, Pd/SiO_2-200, Pd/SiO_2-250 and Pd/SiO_2-300.

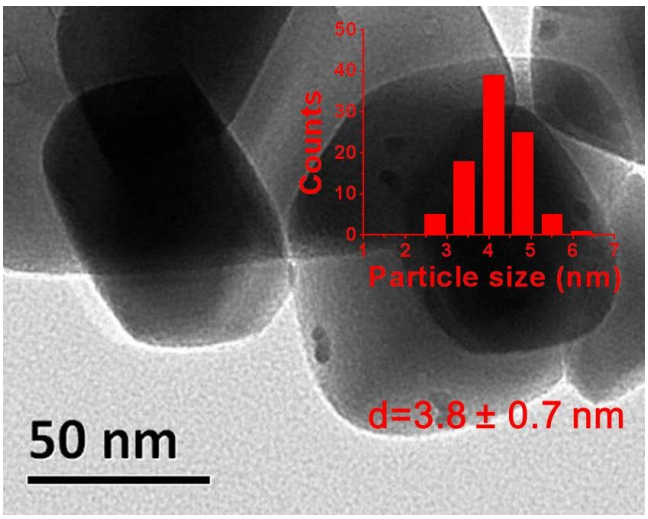

Figure S8. Pd NPs size distribution of Pd/In_2O_3.

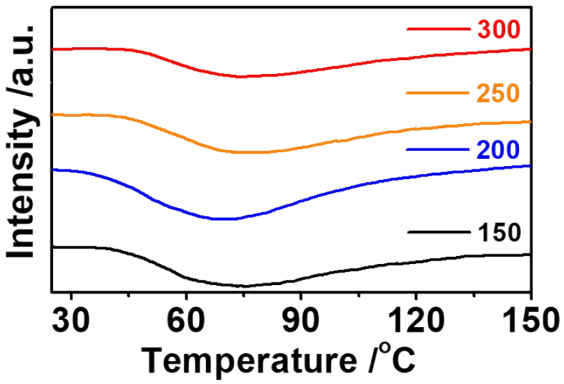

Figure S9. H_2-TPD profiles of the Pd-based catalysts with various reduction temperatures.

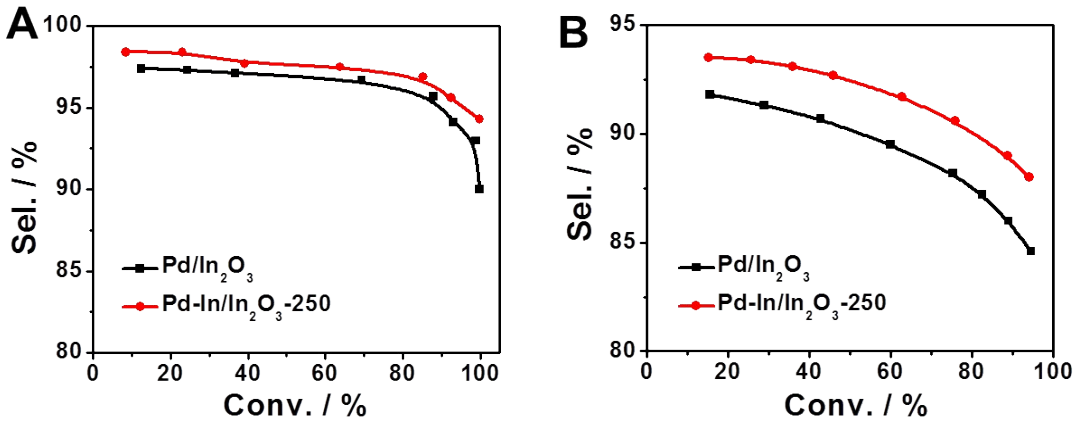

Figure S10. Comparison of selectivity versus conversion of Pd-In/In_2O_3-250 and Pd/In_2O_3 for the semi-hydrogenation of (A) dehydrolinalool and (B) dehydronerolidol.

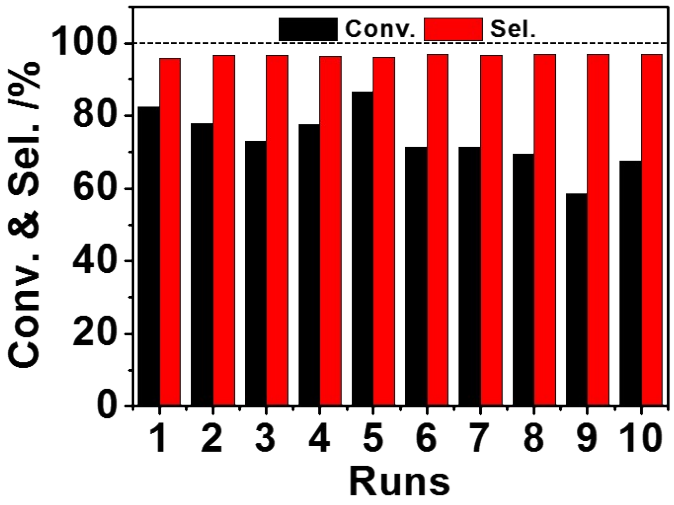

Figure S11. The reusability of Pd-In/In_2O_3-250 at lower conversions. Reaction condition: 20 mg catalysts, 120 uL substrate, 5 mL ethanol, 30°C, 1atm H_2, stirring rate of 1000 rpm.

2. Supplementary Tables Tables S1-S2

Table S1. Adsorption energy of substrates on different active sites of Pd.[1]

Active sites (eV)	E_{ads1}[a] (eV)	E_{ads2}[b] (eV)	ΔE (eV)
Pd111	-1.30	-0.39	-0.91
Pd100	-2.04	-0.53	-1.51
Pd211	-1.48	-0.59	-0.90
Pd-edge	-1.40	-0.92	-0.48
Pd-corner	-1.14	-0.88	-0.26

[a] Adsorption energy of MBY.

[b] Adsorption energy of MBE.

Table S2. Results of ICP-AES measurements.

Entry	Catalysts	Pd Content/wt %
1	Pd-In/In_2O_3-100	0.27
2	Pd-In/In_2O_3-150	0.27
3	Pd-In/In_2O_3-200	0.28
4	Pd-In/In_2O_3-250	0.26
5	Pd-In/In_2O_3-300	0.23
6	Pd/In_2O_3	0.28
7	Pd/SiO_2	0.28
8	Pd-In/In_2O_3-250 (after recycling)	0.26

References

1. L. Shen, S. Mao, J. Li, M. Li, P. Chen, H. Li, Z. Chen and Y. Wang, *J. Catal.*, 2017, **350**, 13-20