Supporting Information

Decoding structure–selectivity interplay in Pd–Ag nanocatalysts for butadiene semi-hydrogenation

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Table S1. Porosity properties of the representative catalysts derived from N_2 sorption.

Catalysts	S_{BET} [a] / $cm^2\ g^{-1}$	V_t [b] / $cm^3\ g^{-1}$
$Pd_{2.2}$	1007	0.45
$Pd_{3.0}$	993	0.44
$Pd_{11.4}$	1051	0.47
$Ag_{14.6}$	1025	0.46
$PdAg_{2.7}$	1021	0.46
$PdAg_{3.1}$	1087	0.49
$PdAg_{10.8}$	1081	0.49
$PdAg_{76.7}$	1075	0.48

[a]Specific surface area;

[b]Total pore volume.

Table S2. Elemental analysis of Pd and PdAg catalysts based on the XPS.

Catalysts	Element content / at%				Atomic ratio of Pd species / -			Atomic ratio of Ag Species / -	
	C	O	Pd	Ag	Pd^{4+}	Pd^{2+}	Pd^0	Ag^+	Ag^0
$Pd_{2.2}$	88.74	10.8	0.46	-	0.16	0.25	0.59	-	-
$Pd_{3.0}$	87.87	11.74	0.39	-	0.13	0.23	0.64	-	-
$Pd_{11.4}$	89.4	10.34	0.26	-	0.12	0.22	0.66	-	-
$PdAg_{2.7}$	88.27	11.39	0.17	0.17	0.36	0.21	0.43	0.10	0.90
$PdAg_{3.1}$	91.34	8.18	0.24	0.24	0.24	0.28	0.48	0.13	0.87
$PdAg_{10.8}$	92.20	7.38	0.23	0.19	-	0.32	0.68	0.28	0.72
$PdAg_{76.7}$	92.78	6.91	0.17	0.14	-	0.27	0.73	0.30	0.70
$PdAg_{3.6}$’	90.49	8.96	0.15	0.40	-	0.39	0.61	1.00	0.00
$PdAg_{4.2}$’	89.87	9.64	0.22	0.27	-	0.31	0.69	0.82	0.18
$PdAg_{11.7}$’	80.71	19.13	0.01	0.15	-	0.24	0.76	0.55	0.45

Table S3. Representative works in the literature on 1,3-butadiene hydrogenation.

Catalysts	M^a wt.%	T K	H_2:BD	$GHSV$ cm^3 g_{cat}^{-1} h^{-1}	X_{BD} %	$S_{butenes}$ %	S_{1B} %	TOS h	refs.
Pd_1/graphene	0.25	323	2.5:1	33,333	99	95	71	50	[1]
Pd@ZIF-67	1	328	2:1	36,000	100	98.6	62.1	40	[2]
Pd-Cu/Mn_2O_3	1	323	2:1	36,000	99.1	92	58.5	10	[3]
PdNi/SiO_2	0.91	343	4:1	-	95	98	55	-	[4]
Pd-Ag/ES	0.5	318	2:1	36,000	95	95.8	55	30	[5]
30Al/Pd/Al_2O_3	1	373	2.5:1	30,000	99	100	51	62	[6]
Ag_1Pd_3/γ-Al_2O_3	0.5	308	2:1	16,200	100	84.9	42	12	[7]
30Fe/Pd/Al_2O_3	1	311	2.5:1	30,000	99	95	25	-	[8]
PdCuG-523	1.8	293	5:1	-	98	90	23	-	[9]
Pd-Sn/mixed θ/α-Al_2O_3	0.5	343	1;1	120,000	80	100	58	-	[10]
Pd/carbon	0.25	323	2.5:1	33,333	81	85	39	10	[1]
Au/TiO_2	0.96	456	49:1	8000	98	99.7	67	-	[11]
Au/Carbon	1.62	443	73:1	81000	100	100	34	-	[12]
Au/Al_2O_3	1	393	67:1	20,000	100	100	40	-	[13]
PdAg/AC	1	338	10:1	150,000	100	98.7	66	50	this work

[a]M is Pd or Au.

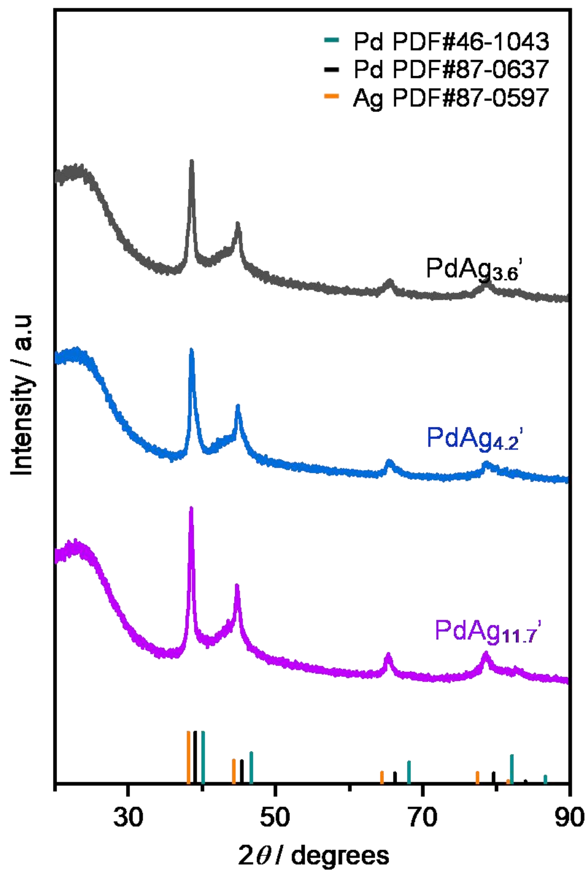

Fig. S1. PXRD of $PdAg_x'$ catalysts.

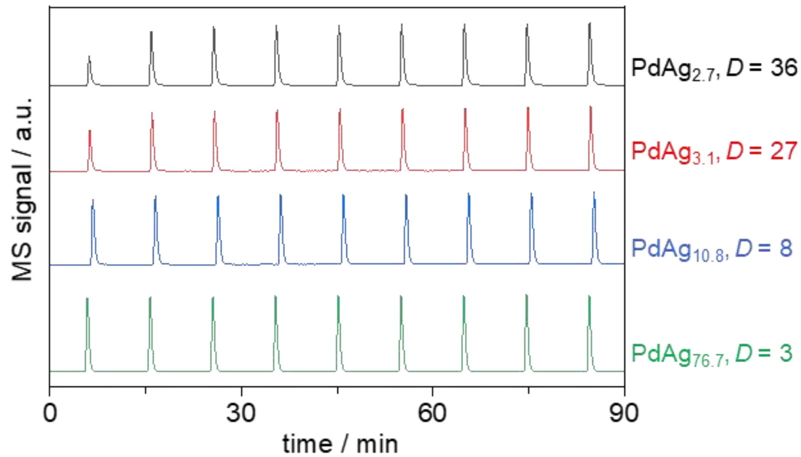

Fig. S2. CO chemisorption on $PdAg_x$ catalysts. D is the estimated percentage metal dispersion.

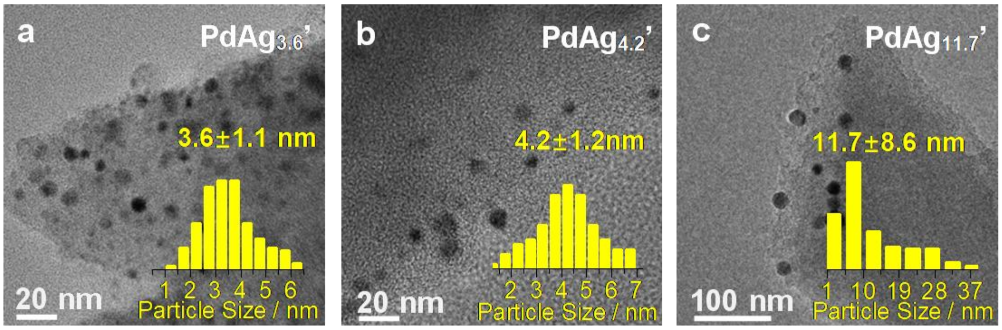

Fig. S3. TEM images of $PdAg_x'$ catalysts.

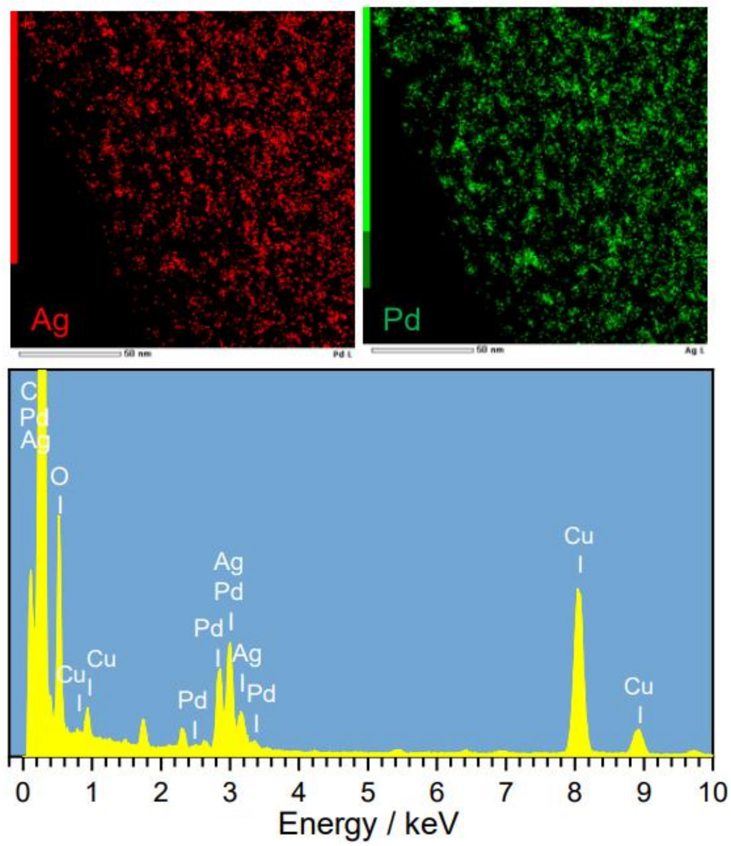

Fig. S4. Elemental mapping images accompanied with the EDX spectrum of the $PdAg_{2.7}$ catalyst.

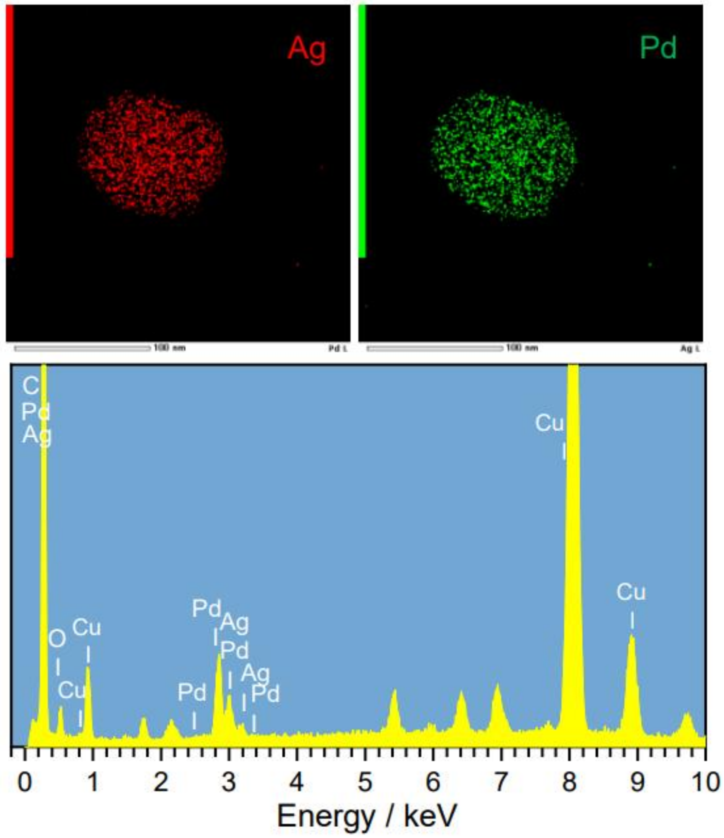

Fig. S5. Elemental mapping images accompanied with the EDX spectrum of the $PdAg_{76.7}$ catalyst.

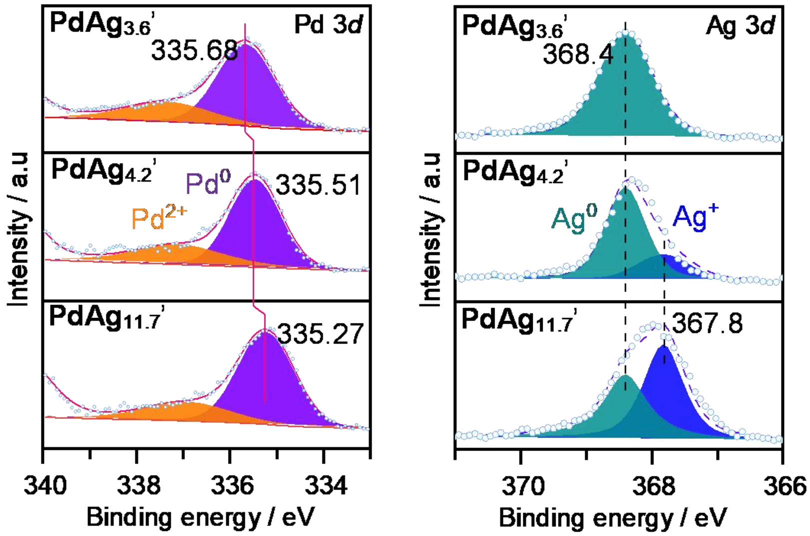

Fig. S6. The core-level Pd 3*d* and Ag 3*d* XPS spectra of $PdAg_x'$ catalysts.

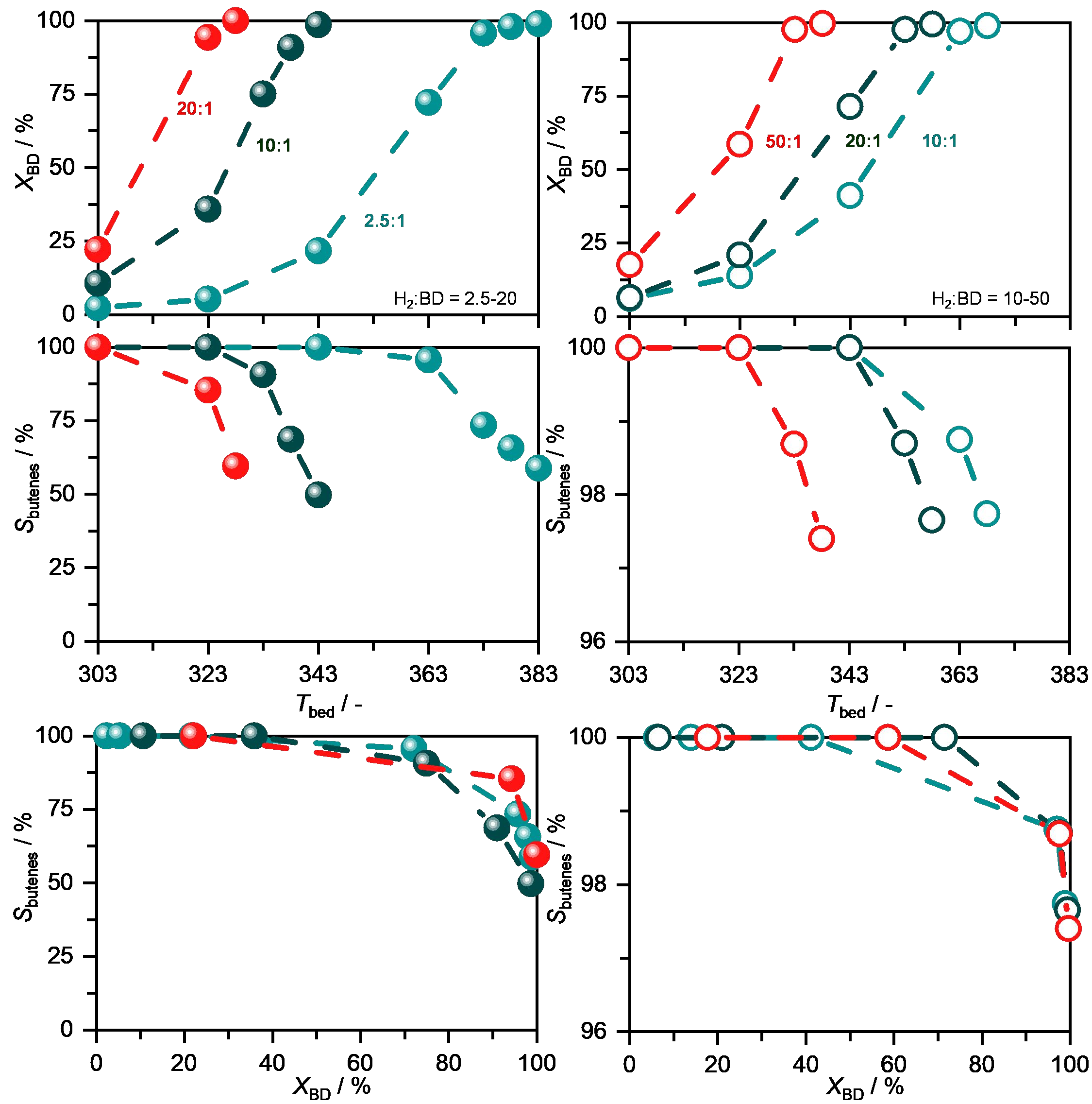

Fig. S7. Conditions : W_{cat} = 30 mg, F_{tota} = 75 $cm^3\ min^{-1}$, *GHSV* = 150000 $cm^3\ g_{cat}^{-1}\ h^{-1}$, $PdAg_{2.7}$ (left), $PdAg_{76.7}$(right).

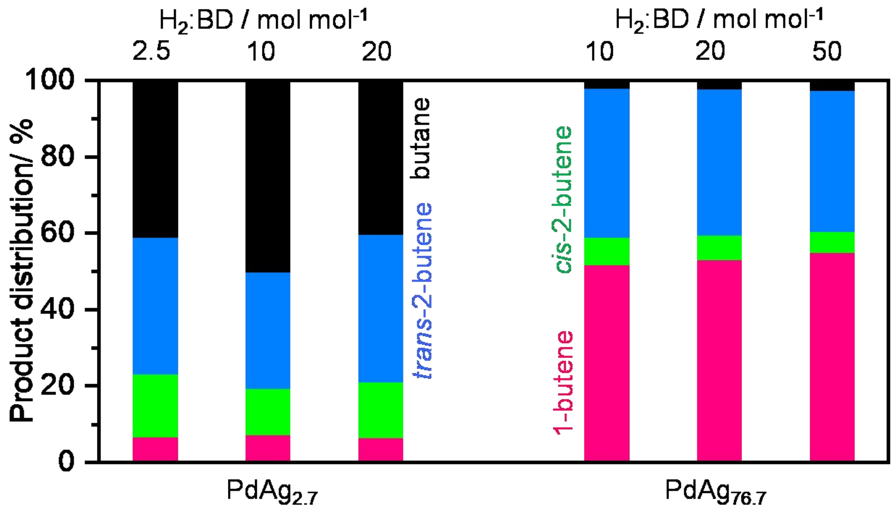

Fig. S8. Comparison on the product distributions at near complete conversion at different H_2:BD ratios on $PdAg_{2.7}$ and $PdAg_{76.7}$.

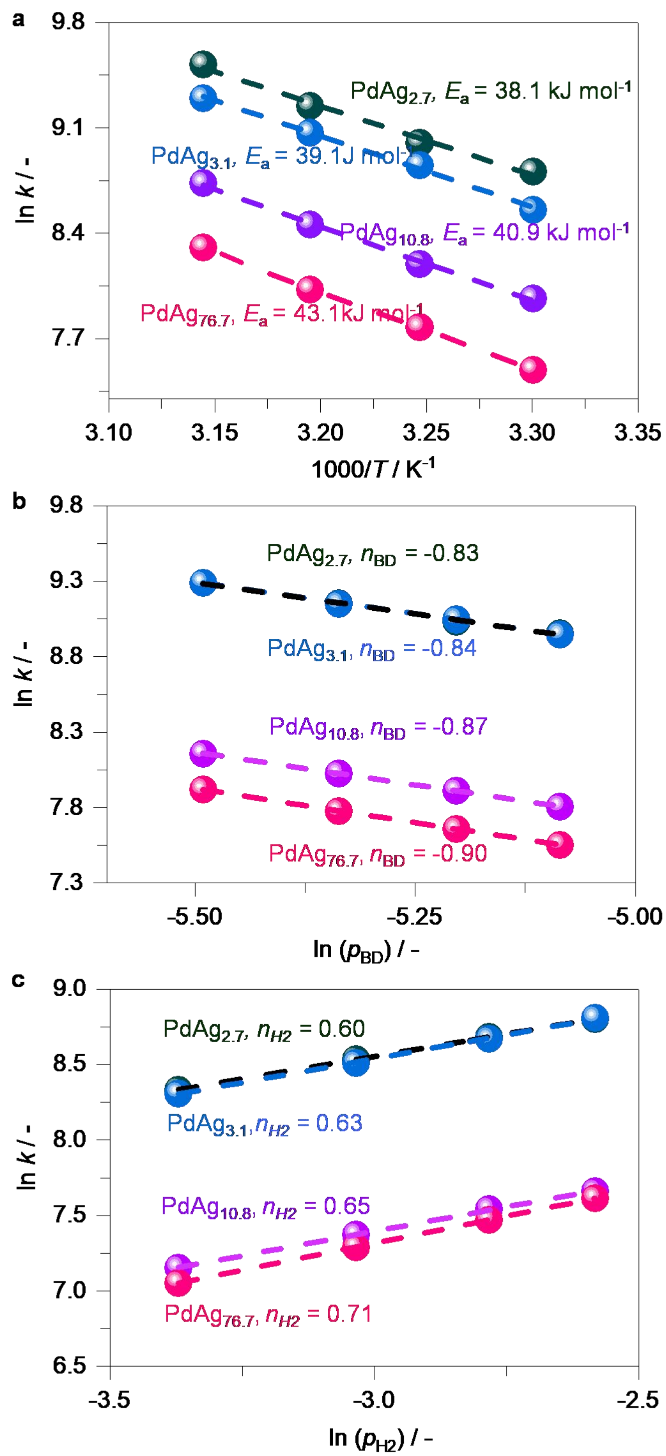

Fig. S9. The reaction kinetics of butadiene hydrogenation on $PdAg_x$. **a**, The apparent activation energies, and the reaction orders of **b**, butadiene, **c**, H_2.

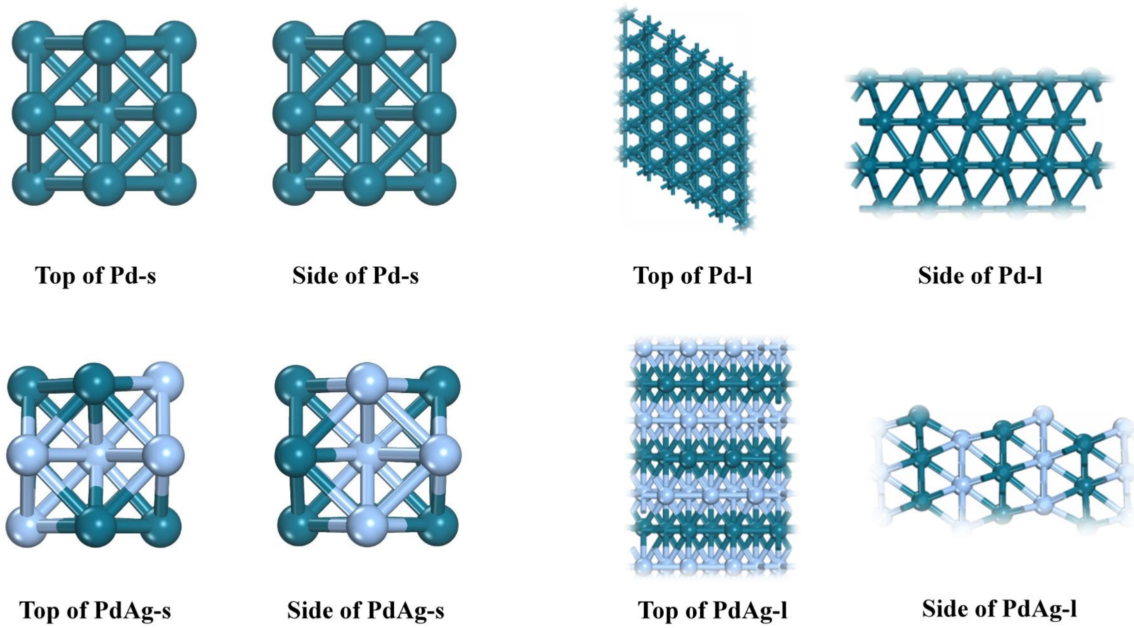

Fig. S10. The side and top views of the DFT models for the Pd and PdAg catalysts. The model of Pd-s uses three layers with thirteen Pd atoms, the model of PdAg-s uses three layers with seven Pd atoms and six Ag atoms, the model of Pd-l uses six layers on the Pd(111), and the model of PdAg-l uses six layers on the Pd_1Ag_1.

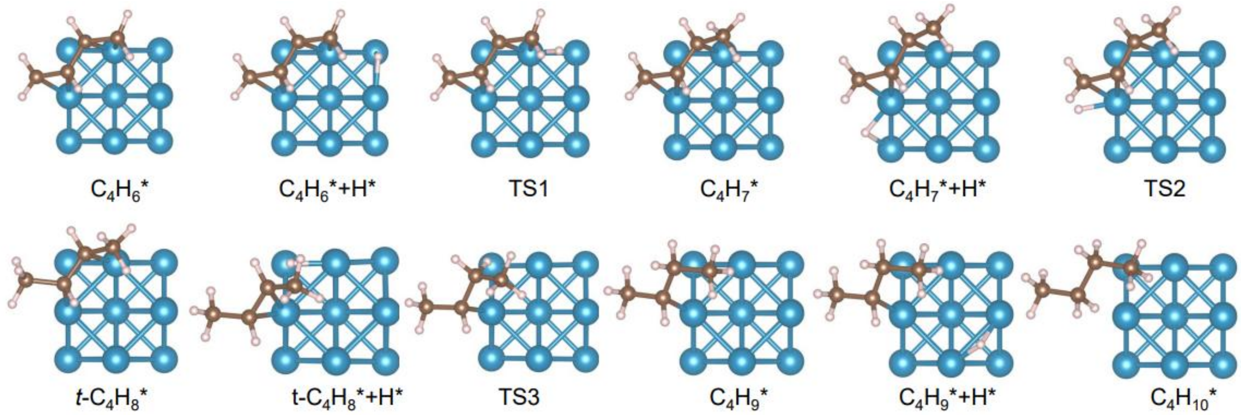

Fig. S11. Illustrations of the catalyst models of BD hydrogenation through BD→*trans*-2B→butane on small Pd ensembles Pd-s.

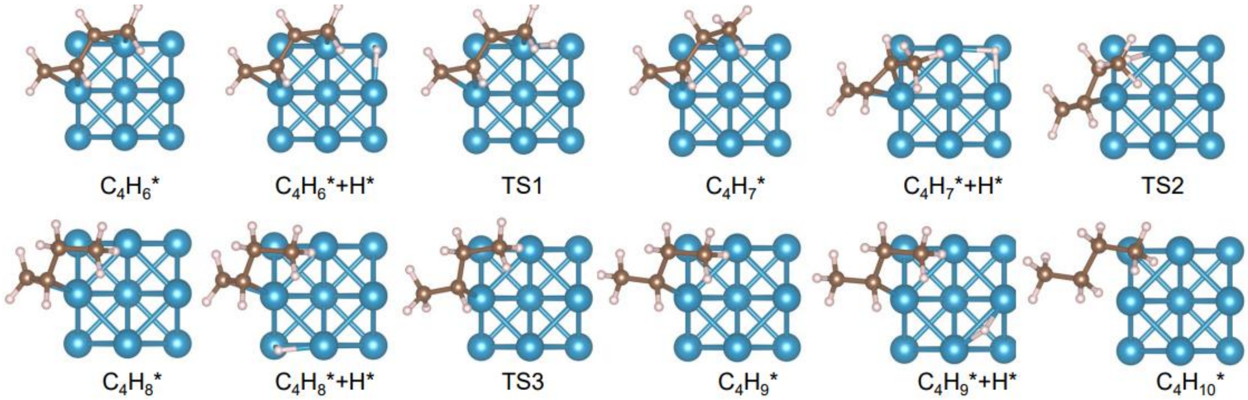

Fig. S12. Illustrations of the catalyst models of BD hydrogenation through BD→1B→butane on small Pd ensembles Pd-s.

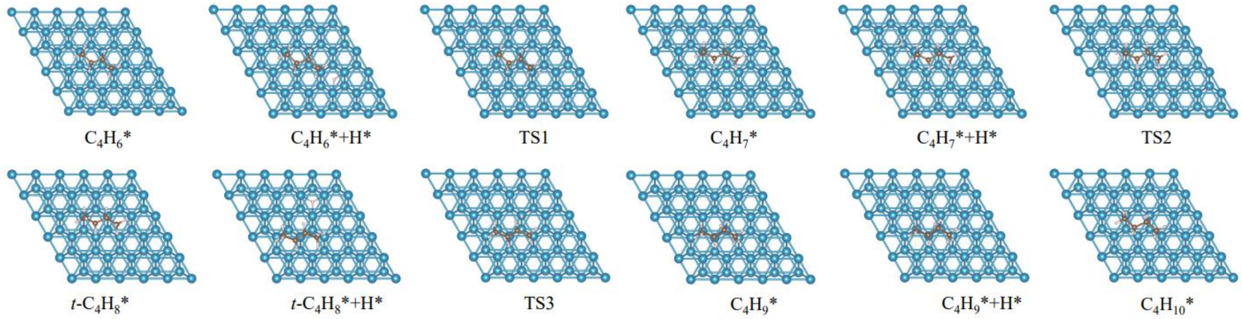

Fig. S13. Illustrations of the catalyst models of BD hydrogenation through BD→*trans*-2B→butane on large Pd ensembles Pd-l.

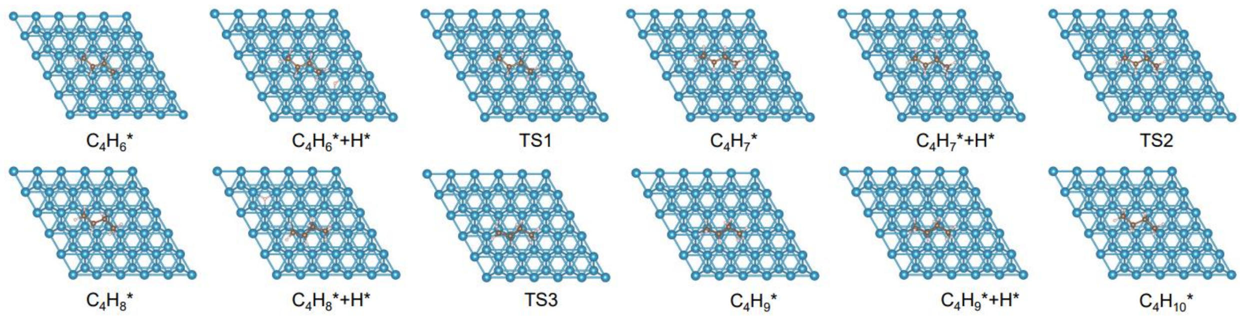

Fig. S14. Illustrations of the catalyst models of BD hydrogenation through BD→1B→butane on large Pd ensembles Pd-l.

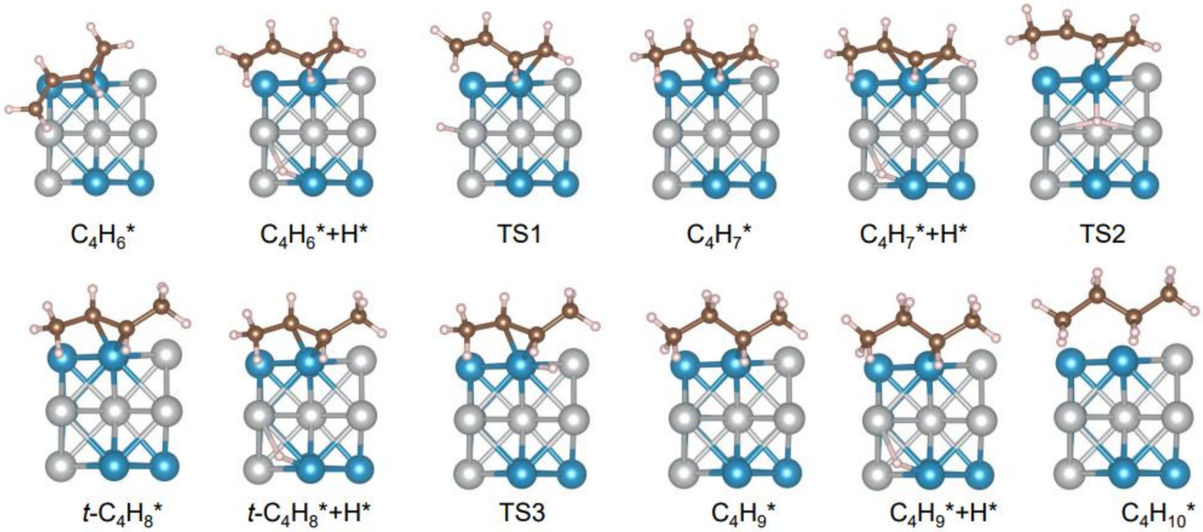

Fig. S15. Illustrations of the catalyst models of BD hydrogenation through BD→*trans*-2B→butane on small Pd-Ag ensembles PdAg-s.

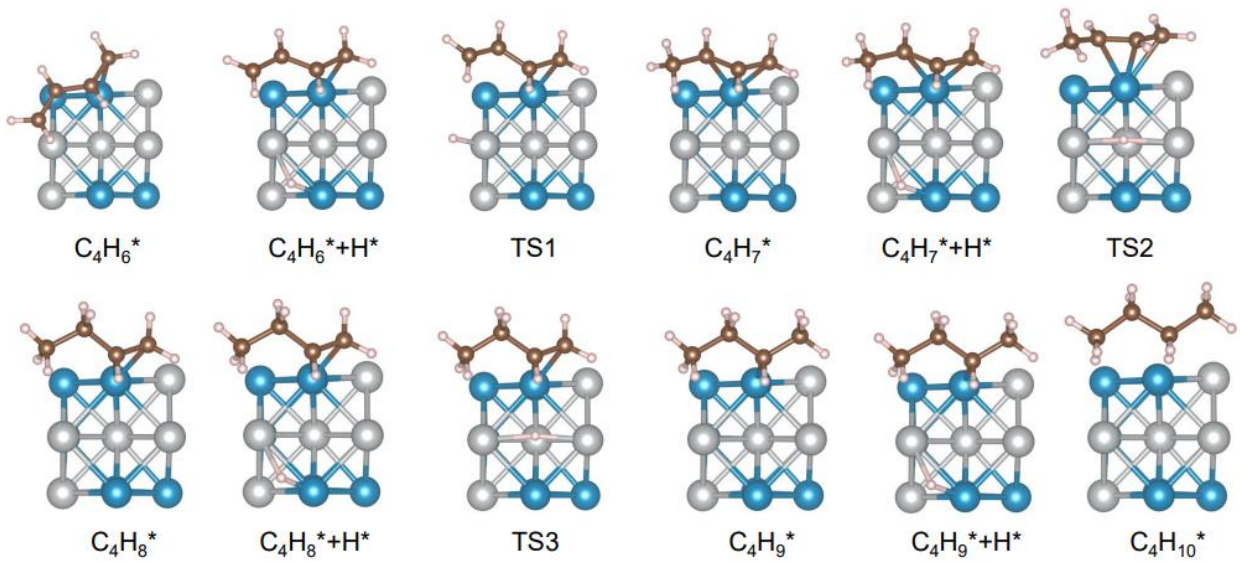

Fig. S16. Illustrations of the catalyst models of BD hydrogenation through BD→1B→butane on small Pd-Ag ensembles PdAg-s.

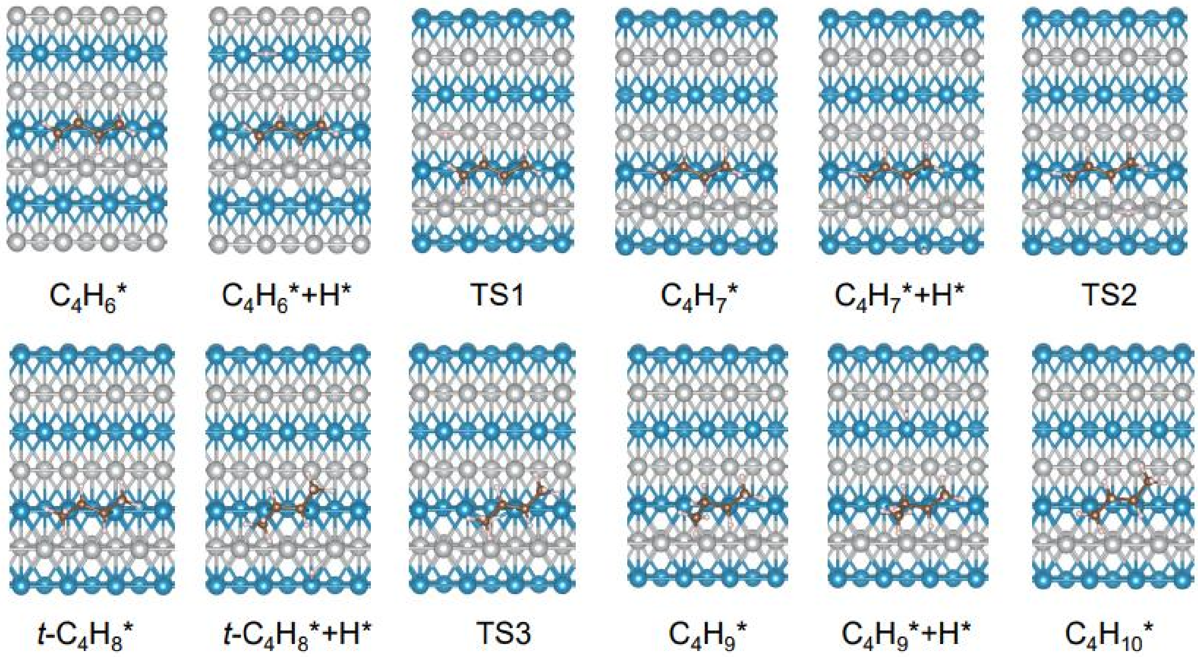

Fig. S17. Illustrations of the catalyst models of BD hydrogenation through BD→*trans*-2B→butane on large Pd-Ag ensembles PdAg-l..

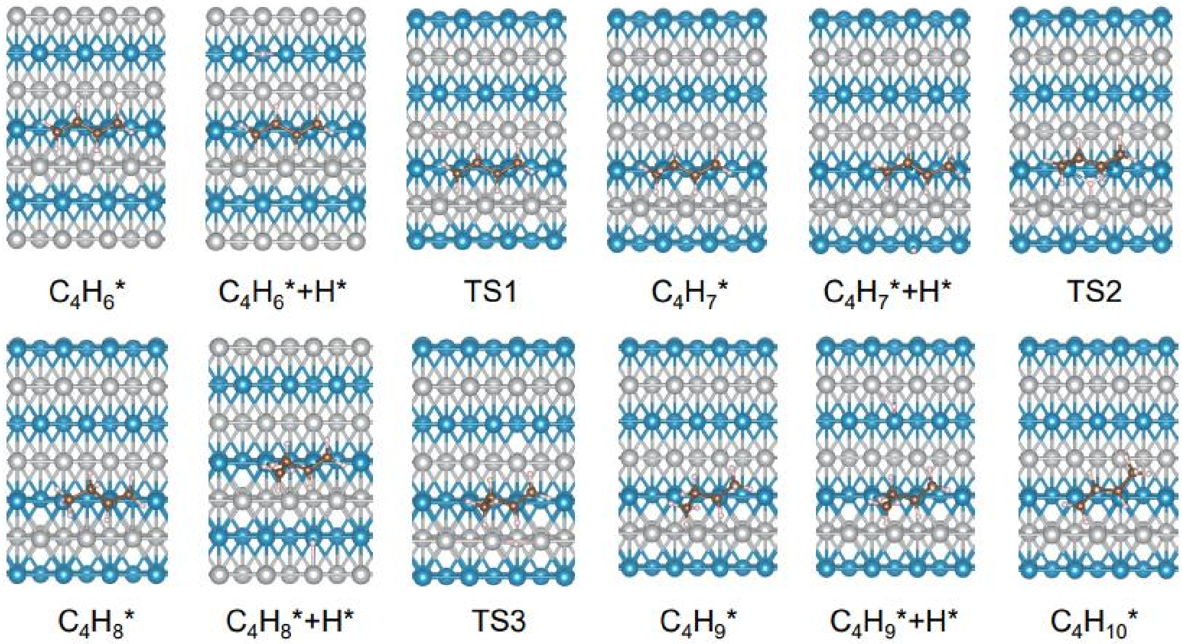

Fig. S18. Illustrations of the catalyst models of BD hydrogenation through BD→1B→butane on large Pd-Ag ensembles PdAg-l.

Supplementary references

[1] H. Yan, H. Cheng, H. Yi, Y. Lin, T. Yao, C. Wang, J. Li, S. Wei, J. Lu, Single-Atom Pd1/Graphene Catalyst Achieved by Atomic Layer Deposition: Remarkable Performance in Selective Hydrogenation of 1,3-Butadiene, J. Am. Chem. Soc., 137 (2015) 10484-10487.

[2] L. Qi, J. Dai, Y. Liao, J. Tian, D.J.C.S. Sun, Technology, Tuning the electronic property of Pd nanoparticles by encapsulation within ZIF-67 shells towards enhanced performance in 1, 3-butadiene hydrogenation, Catal. Sci. Technol., 12 (2022) 2519-2530.

[3] T. Odoom-Wubah, Q. Li, M. Chen, H. Fang, B.B. Asare Bediako, I. Adilov, J. Huang, Q. Li, Influence of Preparation Methods on the Catalytic Activity of Pd–Cu/Mn_2O_3 Catalyst in the Hydrogenation of 1,3-Butadiene, ACS Omega, 4 (2019) 1300-1310.

[4] R. Hou, M.D. Porosoff, J.G. Chen, T. Wang, Effect of oxide supports on Pd–Ni bimetallic catalysts for 1,3-butadiene hydrogenation, Appl. Catal. A, 490 (2015) 17-23.

[5] H. Huang, J. Dai, X. Liu, K.B. Tan, J. Huang, G. Zhan, Q. Li, Waste Eggshell with naturally-functionalized sulfonic groups as excellent support for loading Pd and Ag nanoparticles towards enhanced 1,3-butadiene hydrogenation, Mol. Catal., 510 (2021) 111689.

[6] H. Yi, H. Du, Y. Hu, H. Yan, H.-L. Jiang, J. Lu, Precisely Controlled Porous Alumina Overcoating on Pd Catalyst by Atomic Layer Deposition: Enhanced Selectivity and Durability in Hydrogenation of 1,3-Butadiene, ACS Catal., 5 (2015) 2735-2739.

[7] F. Lu, D. Sun, J. Huang, M. Du, F. Yang, H. Chen, Y. Hong, Q. Li, Plant-Mediated Synthesis of Ag–Pd Alloy Nanoparticles and Their Application as Catalyst toward Selective Hydrogenation, ACS Sustain. Chem. Eng., 2 (2014) 1212-1218.

[8] H. Yi, Y. Xia, H. Yan, J. Lu, Coating Pd/Al_2O_3 catalysts with FeO_x enhances both activity and selectivity in 1,3-butadiene hydrogenation, Chin. J. Catal., 38 (2017) 1581-1587.

[9] A. Cooper, B. Bachiller-Baeza, J.A. Anderson, I. Rodríguez-Ramos, A. Guerrero-Ruiz, Design of surface sites for the selective hydrogenation of 1,3-butadiene on Pd nanoparticles: Cu bimetallic

formation and sulfur poisoning, Catal. Sci. Technol., 4 (2014) 1446-1455.

[10] K. Pattamakomsan, E. Ehret, F. Morfin, P. Gélin, Y. Jugnet, S. Prakash, J.C. Bertolini, J. Panpranot, F.J.C.S. Aires, Selective hydrogenation of 1,3-butadiene over Pd and Pd–Sn catalysts supported on different phases of alumina, Catal. Today, 164 (2011) 28-33.

[11] Okumura M , Akita T , Haruta M .Hydrogenation of 1,3-butadiene and of crotonaldehyde over highly dispersed Au catalysts, Catal. Today, 2002, 74(3):265-269.

[12] Zhang X , Guo Y C , Zhang Z C ,et al. High performance of carbon nanotubes confining gold nanoparticles for selective hydrogenation of 1,3-butadiene and cinnamaldehyde, J. Catal., 292 (2012) 213-226.

[13] Hugon A , Delannoy L , Louis C .Supported gold catalysts for selective hydrogenation of 1,3-butadiene in the presence of an excess of alkenes[J].Gold Bull., 41 (2008) 127-138.