Electronic Supplementary Material (ESI) for Nanoscale.

Towards highly active Pd/CeO_2 for alkene hydrogenation by tuning Pd dispersion and surface properties of catalysts

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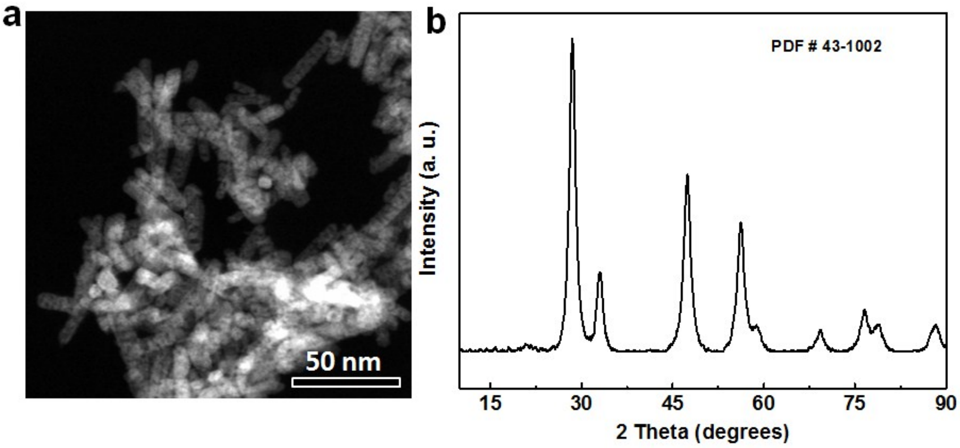

Figure S1. (a) Dark field TEM image and (b) XRD spectrum of *PN*-CeO_2 support.

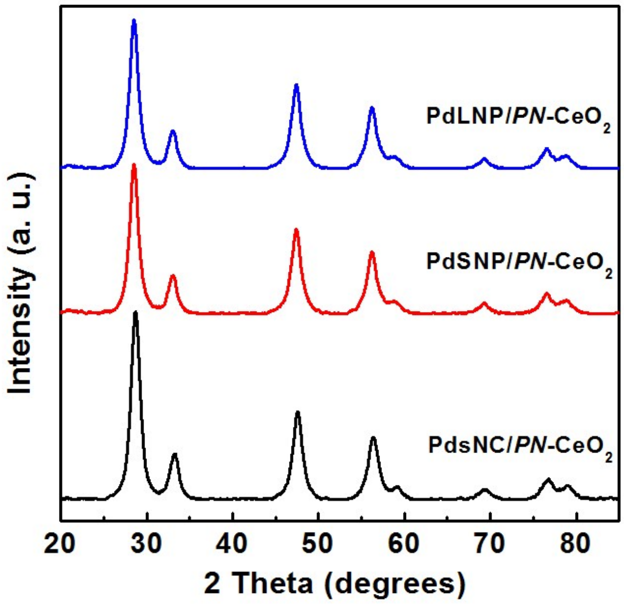

Figure S2. XRD spectrum of various Pd/*PN*-CeO_2 catalysts.

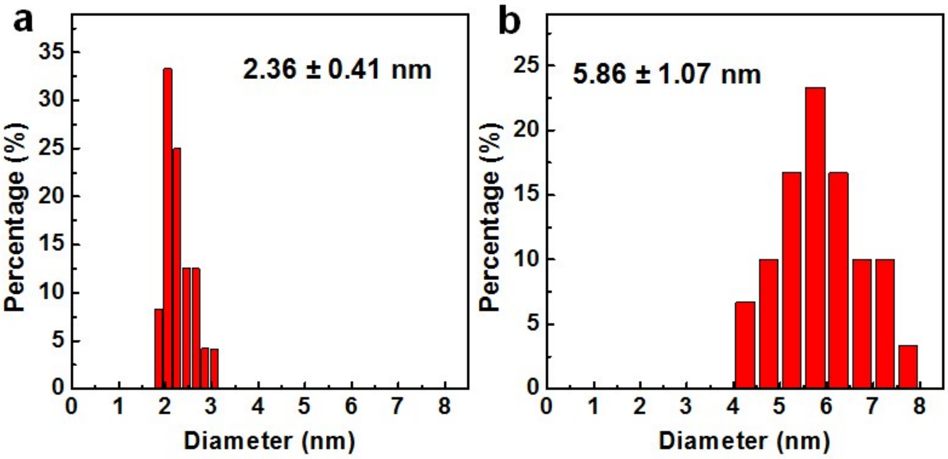

Figure S3. The size distribution of (a) PdSNP/*PN*-CeO_2 and (b) PdLNP/*PN*-CeO_2 catalysts.

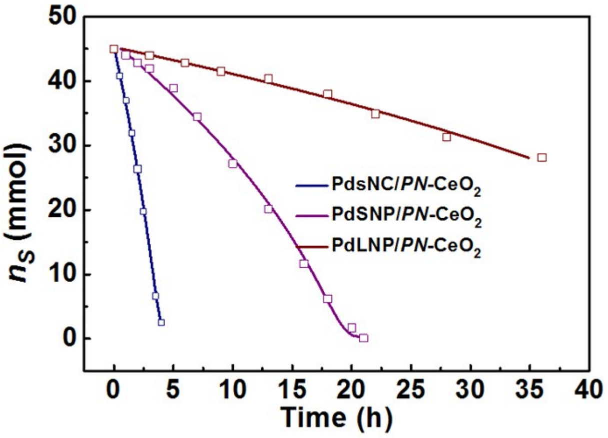

Figure S4. Experimental data of various catalysts and prediction curves obtained with Equation (1).

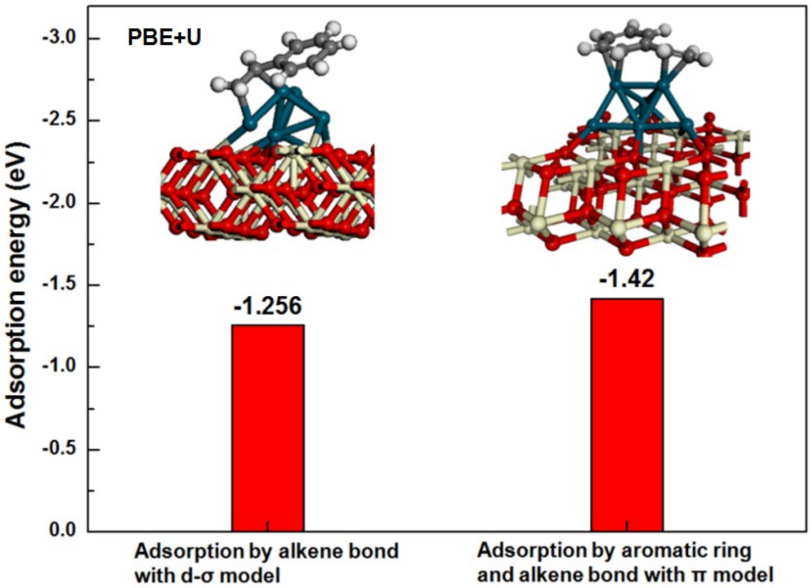

Figure S5. The adsorption energy of styrene on Pd$_6$-CeO$_2$ with various adsorption models.

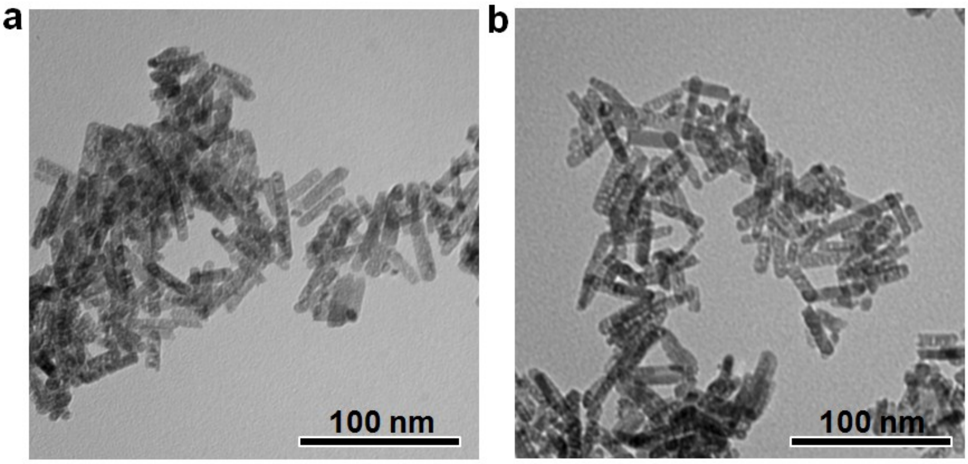

Figure S6. TEM images of the PdsNC/*PN*-CeO$_2$-300 and PdsNC/*PN*-CeO$_2$-500 catalysts.

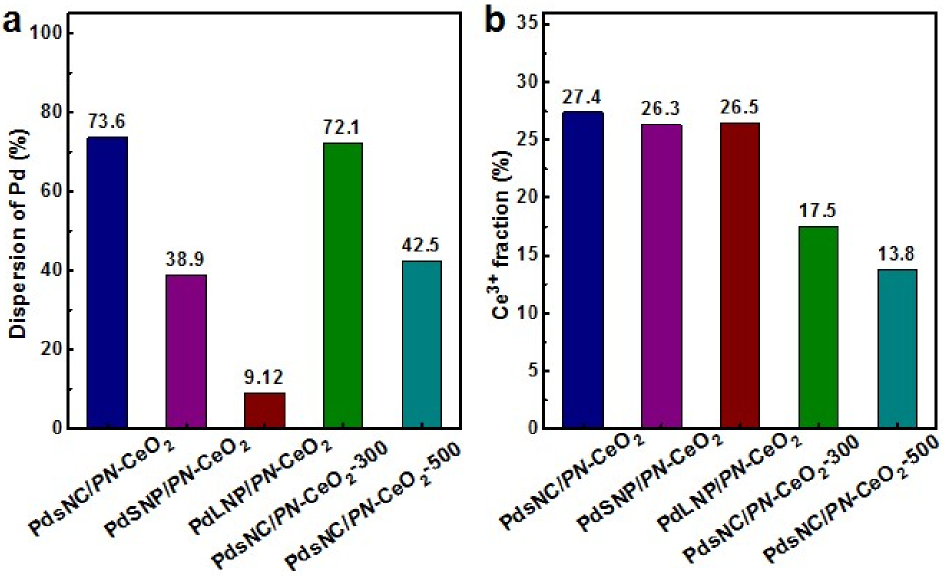

Figure S7. Summary of the Pd dispersion and surface properties of various Pd/*PN*-CeO$_2$ catalysts.

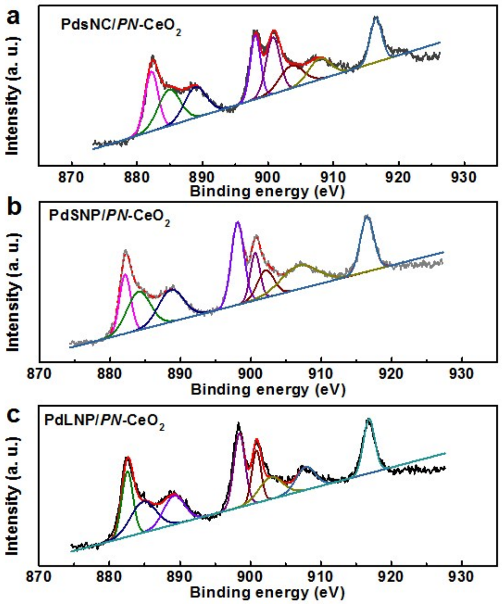

Figure S8. XPS spectra of Ce elements for (a) PdsNC/*PN*-CeO$_2$, (b) PdSNP/*PN*-CeO$_2$ and (c) PdLNP/*PN*-CeO$_2$ catalysts.

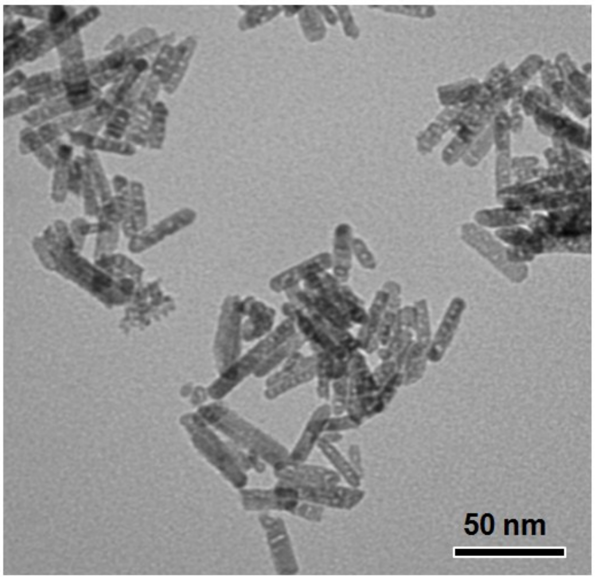

Figure S9. TEM image of the PdsNC/PN-CeO$_2$ catalysts after 3 cycles of styrene hydrogenation.

Table S1. The TOFs of previous studies for hydrogenation reaction.

	Catalysts	**Temperature (^oC)**	**Pressure (MPa)**	**TOF (h^{-1})**	**Ref.**
Homogeneous	$[ReBr_2(NO)(PR_3)_2(\eta^2\text{-}H_2)]$	90	1	36,000	1
	$(P{-}P)Co\text{-}(CH_2SiMe_3)_2$	25	4	20	2
	$(Me{-}DuPhos)_3Ni_3(OAc)_5I$	50	5	280	3
	$RuH(OSO_2CF_3)(CO)(SIMes)$	25	2	18,400	4
	Co	22	4	20	5
Heterogeneous	Pd	20	1	1,812	6
	Pd	25	1	4,800	7
	Pt	25	1	2,430	8
	Rh	60	3	1,339	9
	Pd	25	1	5,000	10
	Pd	27	0.1	1,848	11
	Pd (111)	60	0.3	55,080	12

Complete Langmuir-Hinshelwood mechanism for the hydrogenation of styrene

Hydrogenation kinetics were analyzed by Langmuir-Hinshelwood model, assuming only one type of Pd active sites on various catalysts for the dissociative hydrogen adsorption and bimolecular reactions between the adsorbed species.[13] Series of elementary steps comprising styrene hydrogenation are listed in Table S2. The kinetic constant or reaction rate expression of each step is also included.

Table S2. Langmuir-hinshelwood mechanism for hydrogenation of styrene assuming only one types of Pd active sites for various Pd catalysts.

Reaction	Step		Kinetic expression
$Styrene \rightarrow Ethylbenzene$ $S \rightarrow E$	1	$S+\sigma \xleftrightarrow{K_S} S\sigma$	$K_S = \dfrac{\theta_S}{n_s \times \theta}$
	2	$H_2 + 2\sigma \xleftrightarrow{K_{H_2}} 2(H\sigma)$	$K_{H_2} = \dfrac{\theta_H^2}{n_{H_2} \times \theta^2}$
	3	$S\sigma + H\sigma \xleftrightarrow{K_S^*} S^*\sigma + \sigma$	$K_S^* = \dfrac{\theta_{S^*} \times \theta}{\theta_S \times \theta_H}$
	4^*	$S^*\sigma + H\sigma \xrightarrow{k} E\sigma + \sigma$	$r = k \times \theta_{S^*} \times \theta_H$
	5	$E\sigma \xleftrightarrow{K_E} E + \sigma$	$K_E = \dfrac{\theta_E}{n_E \times \theta}$

A surface balance of active sites must be performed in order to express site vacancies in terms of measurable parameters. The coverage of the intermediate species was neglected:

$$\theta + \theta_S + \theta_H + \theta_E = 1 \qquad \text{(S1)}$$

If coverages are expressed in terms of adsorption constants and bulk concentrations (obtained from Table S1):

$$\theta = \frac{1}{1 + K_S n_S + K_E n_E + \sqrt{K_{H_2} n_{H_2}}} \qquad \text{(S2)}$$

Thus, the reaction rate expressions for all four paths of the mechanism can be developed and are presented in Equation S3.

$$r = \frac{k K_S^* K_S n_S K_{H_2} n_{H_2}}{(1 + K_S n_S + K_E n_E + \sqrt{K_{H_2} n_{H_2}})^2} \qquad \text{(S3)}$$

Where r is the reaction rate, k is rate constant of hydrogenation styrene, K_S is the adsorption constant of styrene, K_{H2} is the adsorption constant of hydrogen, K_E is the adsorption constant of ethylbenzene, n_S, n_{H2} and n_E are the mole of styrene, hydrogen and ethylbenzene, respectively.

Since the large excess amount of hydrogen and poor adsorption of alkane on catalysts, Equation (S3) can be simplified by neglecting the influences of hydrogen and ethylbenzene.[12, 14] Thus, kinetic expression can be further simplified in Equation (S4) for the catalytic hydrogenation:

$$r = \frac{k^* K_S n_S}{(1 + K_S n_S)^2} \qquad \text{(S4)}$$

Thus, the reaction rate equation is given as Equation (S5):

$$\frac{dn_S}{dt} = -r = -\frac{k^* K_S n_S}{(1 + K_S n_S)^2} \qquad \text{(S5)}$$

The kinetics of hydrogenation of styrene can be further expressed as Equation (S6) by integrating the Equation (S5):

$$-k^* t = \frac{1}{K_S} Ln(n_S) + \frac{1}{2} K_S n_S^2 + 2n_S + B \qquad \text{(S6)}$$

Where k* is the kinetic constant; t is reaction time; B is a constant. Therefore, these constants (k* and K_S) can be obtained by fitting the n_S and t in Equation (S6).

TOFs are calculated based on *each exposed Pd atom*:

$$TOF = \frac{n_0 \times C}{t \times n_{cat}}$$

$$n_{cat} = \frac{m_{cat} \times w}{Mr_{Pd}} \times Dis_{Pd}$$

Where n_0 is the initial molar of alkenes, C is the conversion of alkenes at the reaction of t, n_{cat} is the molar of exposed Pd atoms, w is the mass fraction of Pd in catalysts, Mr_{Pd} is molar mass of Pd and Dis_{Pd} is the dispersion of Pd of various Pd/CeO_2 catalysts.

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