Supplementary Materials

Heterogeneous catalytic aldehyde-water shift of benzaldehyde into benzoic acid and hydrogen

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MAIN TEXT (optional)

1. Materials

$Ce(NO_3)_3$, H_2PtCl_6, benzaldehyde, benzoic acid, benzyl alcohol, NaOH, KOH, Na_3PO_4, Na_2CO_3, DBU, DMAP, $IrCl_3$, $RhCl_3$, $HAuCl_4$, $PdCl_2$, $RuCl_3$, D_2O, PhCDO, 2-methylbenzaldehyde, 3-methylbenzaldehyde, p-tolualdehyde, 4-fluorobenzaldehyde, 2-bromobenzaldehyde, 1, 4-dioxane were purchased from Energy Chemical. All the reagents were of analytical grade and used directly without any further purification before the experiments.

2. Catalytic tests of catalysts

The conversion of benzaldehyde was calculated by:

$$Conv.(PhCHO) = \frac{n_{PhCOOH}+n_{PhCH_2OH}}{n_{PhCHO}} \times 100\% \quad (1)$$

Where n_{PhCOOH}, n_{PhCH_2OH} represented the moles of the generated PhCOOH, $PhCH_2OH$, respectively. n_{PhCHO} represented the moles of PhCHO.

The selectivity of benzoic acid and benzyl alcohol were calculated by:

$$Sel.(PhCOOH) = \frac{n_{PhCOOH}}{n_{PhCOOH}+n_{PhCH_2OH}} \times 100\% \quad (2)$$

$$Sel.(PhCH_2OH) = \frac{n_{PhCH_2OH}}{n_{PhCOOH}+n_{PhCH_2OH}} \times 100\% \quad (3)$$

Where n_{PhCOOH}, n_{PhCH_2OH} represented the moles of generated PhCOOH, $PhCH_2OH$, respectively.

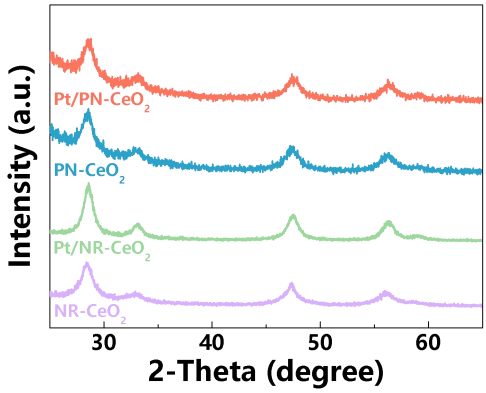
The yield of benzoic acid was calculated by:

$$Yield\ (PhCOOH) = Conv.(PhCOOH) \times Sel.(PhCOOH) \quad (4)$$

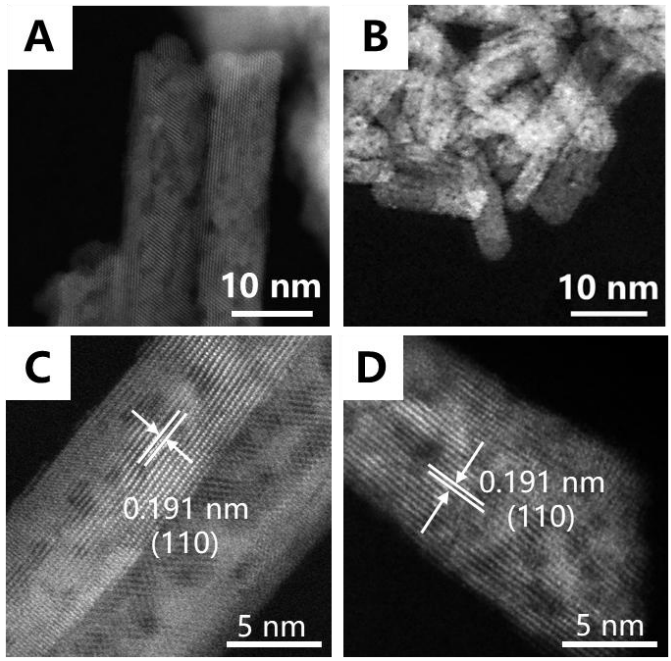
The yield of H_2 was calculated by:

$$Yield\ (H_2) = \frac{amount\ of\ generated\ H_2\ (mol)}{theoretical\ generated\ H_2\ (mol)} \times 100\% \quad (5)$$

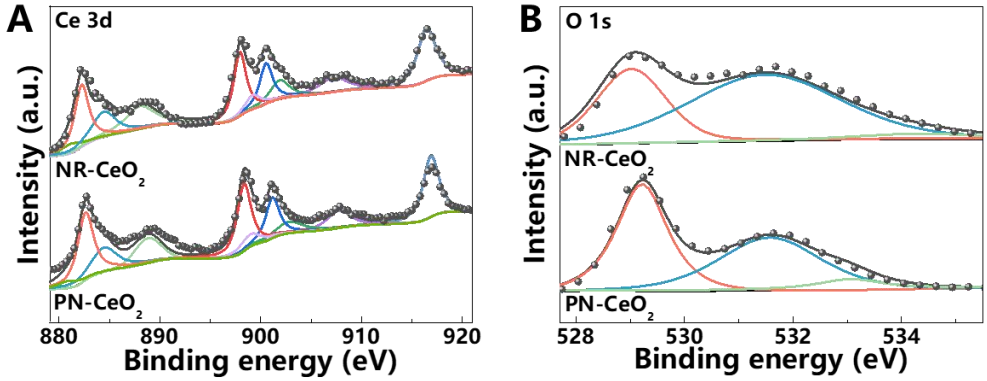
Where the theoretical amount of H_2 was equal to the initial moles of PhCHO.



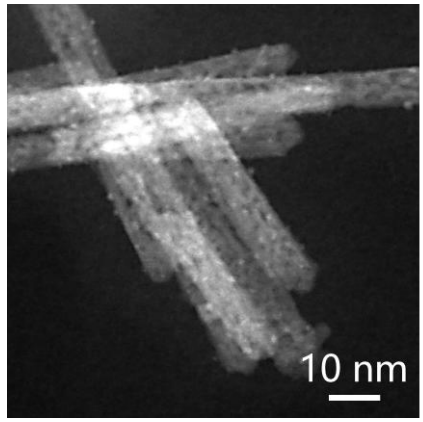
Supplementary Figure 1. XRD patterns of the PN-CeO_2, NR-CeO_2, Pt/PN-CeO_2 and Pt/NR-CeO_2 catalysts.



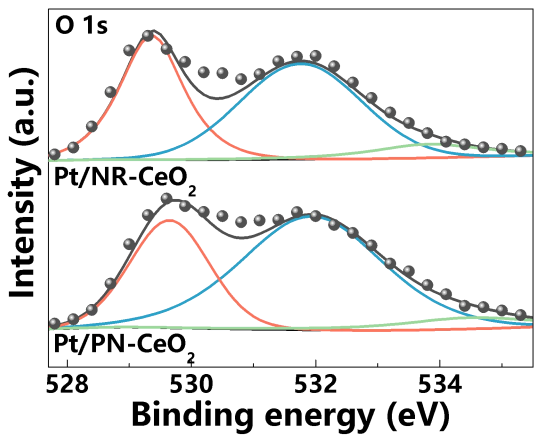
Supplementary Figure 2. Dark-field TEM images of (A) NR-CeO_2 and (B) PN-CeO_2; High-resolution dark-field TEM images of (C) NR-CeO_2 and (D) PN-CeO_2.



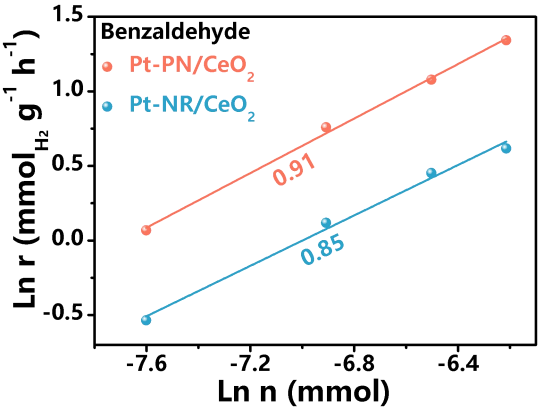
Supplementary Figure 3. XPS analysis of (A) Ce 3d and (B) O 1s of NR-CeO_2 and PN-CeO_2.



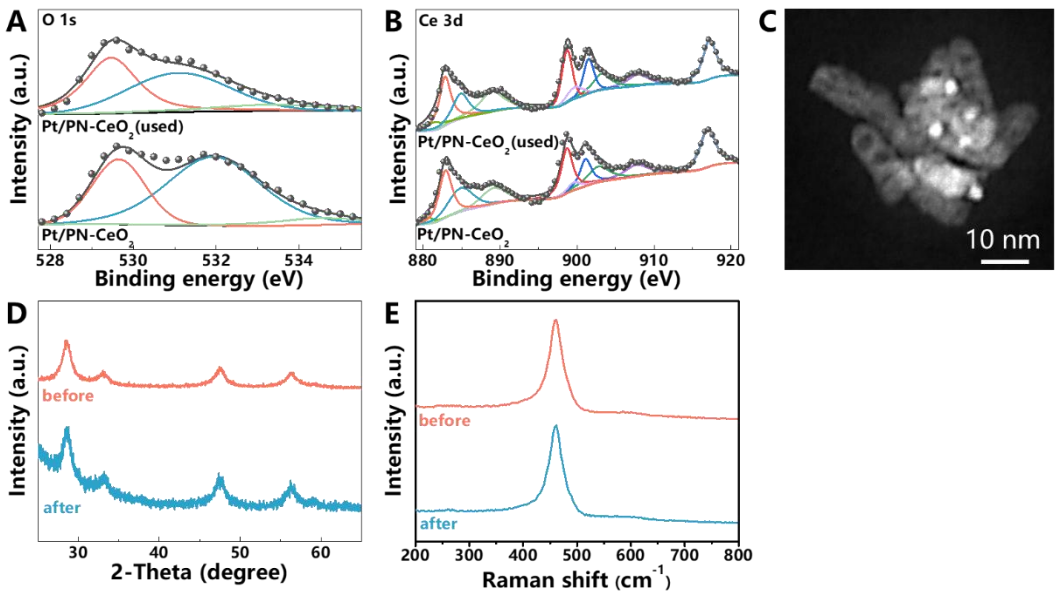
Supplementary Figure 4. Dark-field TEM of Pt/NR-CeO_2.



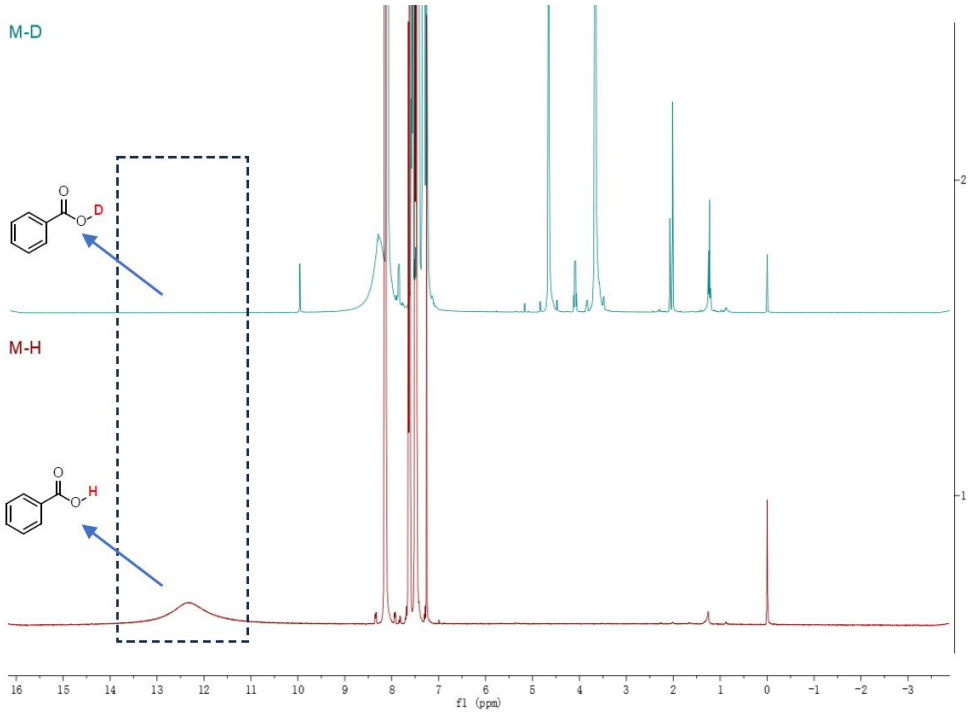
Supplementary Figure 5. XPS analysis of O 1s of the Pt/PN-CeO_2 and Pt/NR-CeO_2 catalysts.



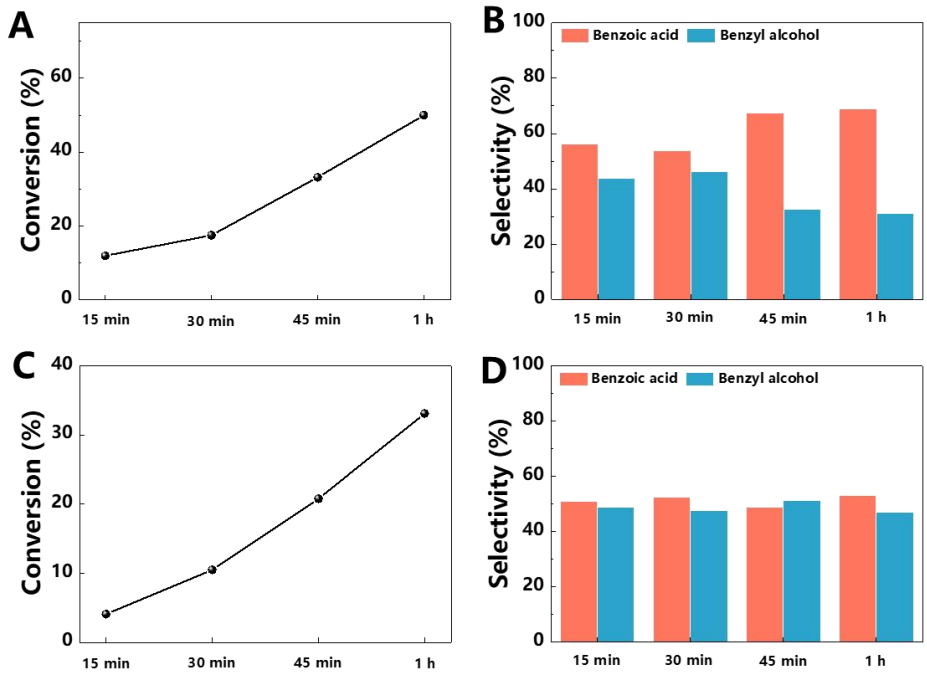
Supplementary Figure 6. *Ln r*, derived from the hydrogen generation rate (mol H_2 g_{cat}^{-1} h^{-1}), as a function of *Ln* n_{PhCHO} over various catalysts. Reaction conditions: Different concentration of PhCHO and H_2O, 1, 4-dioxane (1 mL), NaOH (2.5 mmol), 0.5 MPa N_2, 180°C and 10 h.



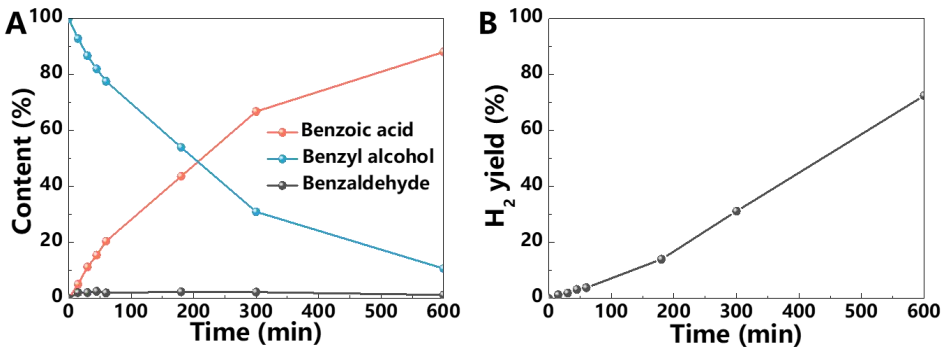
Supplementary Figure 7. XPS analysis of (A) O 1s and (B) Ce 3d peaks for the used Pt/PN-CeO_2 catalysts. (C) TEM image and (D) XRD patterns of the used Pt/PN-CeO_2 catalysts; (E) Raman spectra of Pt/PN-CeO_2 before and after catalytic reactions.



Supplementary Figure 8. ^{1}H NMR of liquid product in the $H(D)_2O$/benzaldehyde systems with Pt/PN-CeO_2 as catalysts. Reaction conditions: PhCHO (1 mmol), H_2O/D_2O (0.5 mL), 1, 4-dioxane (1 mL), NaOH (2.5 mmol), catalysts (30 mg), 0.5 MPa N_2, 180℃ and 10 h.



Supplementary Figure 9. (A and B) Catalytic performance of Pt/PN-CeO_2 for the AWS of benzaldehyde. Reaction conditions: PhCHO (1 mmol), H_2O (0.5 mL), 1, 4-dioxane (1 mL), NaOH (2.5 mmol), catalysts (30 mg), 0.5 MPa N_2, 180℃ and 10 h. (C and D) The disproportionation of benzaldehyde. Reaction conditions: PhCHO (1 mmol), H_2O (0.5 mL), 1, 4-dioxane (1 mL), NaOH (2.5 mmol), 0.5 MPa N_2, 180℃ and 10 h.



Supplementary Figure 10. (A) Distributions of reactants and products of the benzyl alcohol dehydrogenation catalyzed by Pt/PN-CeO_2 at intervals during a period of 10 h; (B) H_2 evolution profile as a function of reaction time. Reaction conditions: $PhCH_2OH$ (1 mmol), H_2O (0.5 mL), 1, 4-dioxane (1 mL), NaOH (2.5 mmol), catalysts (30 mg), 0.5 MPa N_2, 180℃ and 10 h.

Supplementary Table 1. Optimization of amount of H_2O for AWS of benzaldehyde[a]

Entry	Cat. (2% loading)	H_2O (eq.)	Conv. (%)	Sel. (%) Benzoic acid	Yield (%) H_2
1	Pt-PN/CeO_2	5	80.32	66.68	17.42
2	Pt-PN/CeO_2	10	78.25	86.44	42.65
3	Pt-PN/CeO_2	28	99.81	99.56	85.89
4	Pt-PN/CeO_2	56	78.49	86.38	58.27

[a] Reaction conditions: 1 mmol of benzaldehyde, 30 mg of catalyst, 1 mL of 1, 4-dioxane, 2.5 mmol of NaOH, 180 °C, 10 h, 0.5 MPa N_2.

Supplementary Table 2. Optimization of bases for AWS of benzaldehyde[a]

Entry	Cat. (2% loading)	Base (2.5 eq.)	Conv. (%)	Sel. (%) Benzoic acid	Yield (%) H_2
1	Pt-PN/CeO_2	NaOH	99.81	99.56	85.89
2	Pt-PN/CeO_2	KOH	87.34	86.50	35.91
3	Pt-PN/CeO_2	Na_3PO_4	26.83	87.92	10.85
4	Pt-PN/CeO_2	Na_2CO_3	77.19	86.29	40.67
5	Pt-PN/CeO_2	DBU	2.67	24.91	0
6	Pt-PN/CeO_2	DMAP	58.02	99.82	0

[a] Reaction conditions: 1 mmol of benzaldehyde, 30 mg of catalyst, 1 mL of 1, 4-dioxane, 0.5 mL of H_2O, 2.5 mmol of base, 180 °C, 10 h, 0.5 MPa N_2.

Supplementary Table 3. Optimization of amount of NaOH for AWS of benzaldehyde[a]

Entry	Cat. (2% loading)	NaOH (eq.)	Conv. (%)	Sel. (%) Benzoic acid	Yield (%) H_2
1	Pt-PN/CeO_2	1	46.64	83.27	37.46
2	Pt-PN/CeO_2	2.5	99.81	99.56	85.89
3	Pt-PN/CeO_2	5	81.10	86.19	41.73

[a] Reaction conditions: 1 mmol of benzaldehyde, 30 mg of catalyst, 1 mL of 1, 4-dioxane, 0.5 mL of H_2O, 180 °C, 10 h, 0.5 MPa N_2.

Supplementary Table 4. Screen of the deposited metals for AWS of benzaldehyde[a]

Entry	Cat. (2% loading)	NaOH (eq.)	Conv. (%)	Sel. (%) Benzoic acid	Yield (%) H_2
1	Ir-PN/CeO_2	2.5	80.84	95.36	78.65
2	Rh-PN/CeO_2	2.5	86.30	88.97	70.28
3	Au-PN/CeO_2	2.5	76.94	66.32	41.73
4	Pd-PN/CeO_2	2.5	78.10	56.53	27.58
5	Ru-PN/CeO_2	2.5	72.59	76.95	58.12
6	Pt-PN/CeO_2	2.5	99.81	99.56	85.89
7	Pt-NR/CeO_2	2.5	79.04	76.31	39.12

[a] Reaction conditions: 1 mmol of benzaldehyde, 30 mg of catalyst, 1 mL of 1, 4-dioxane, 0.5 mL of H_2O, 2.5 mmol of NaOH, 180 °C, 10 h, 0.5 MPa N_2.