Supporting Information

Synergetic effects of hydrogenation and acidic sites in phosphorus modified nickel catalyst for selective conversion of furfural to cyclopentanone

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Table S1 Deconvoluted peaks of Ni 2p over different samples.

Sample	Peak	Position (eV)	Area	(%)
0%P	$Ni^{\delta+}$ been reduced by H_2	855.6	1889	78.8
	Ni^{2+} not been reduced by H_2	862.0	507	21.2
10%P	$Ni^{\delta+}$ been reduced by H_2	855.6	455	5.7
	$Ni^{\delta+}$ in nickel phosphide phase	856.2	3879	48.4
	Ni^{2+} ions with phosphate ions	862.1	3680	45.9
25%P	$Ni^{\delta+}$ been reduced by H_2	855.6	270	1.8
	$Ni^{\delta+}$ in nickel phosphide phase	856.8	8563	55.7
	Ni^{2+} ions with phosphate ions	861.8	6538	42.5

Table S2 Deconvoluted peaks of Ni 2p over different samples.

Sample	Peak	Position (eV)	Area	Total	(%)
0%P	*	*	*		*
10%P	reduced $P\delta^{1-}$	133.2	867	3659	23.7
	reduced $P\delta^{2-}$ ($\delta^{2-} > \delta^{1-}$)	133.9	1155		31.6
	$H_2PO_3^-$ (passivated layer of Ni-P catalyst)	134.6	1637		44.7
25%P	reduced $P\delta^{1-}$	133.6	3964	8737	45.5
	reduced $P\delta^{2-}$ ($\delta^{2-} > \delta^{1-}$)	134.4	2759		31.7
	$H_2PO_3^-$ (passivated layer of Ni-P catalyst)	135.0	1984		22.8

Table S3 Distribution of acidic sites over the nickel catalysts obtained by NH_3-TPD (NH_3 uptake)

Entry	Catalyst	Weak acidity (μmol/g)	Medium strong acidity (μmol/g)	Strong acidity (μmol/g)	Total acidity (μmol/g)
1[a]	15%P -5%Ni	2.24	3.62	0	5.86
2[a]	15%P -10%Ni	2.24	3.66	0	5.90
3[a]	15%P -15%Ni	3.60	3.81	0	7.41
4[a]	15%P -20%Ni	2.82	3.69	0.45	6.97
5[a]	15%P -25%Ni	6.95	3.37	0.54	10.86
6[a]	15%P -30%Ni	7.00	2.87	0.68	10.54

[a]P-Ni/Al_2O_3 catalyst with loading P species first.

Table S4 Distribution of the products during hydrogenation of furfural over the P-Ni/Al_2O_3 catalyst with loading P species first at 110°C[a]

Entry	Catalyst[b]	Con. (%)	Yield (mol%)				Total (%)	FA Selectivity (%)
			CPO	FA	TFA	CPL		
1	15%P-0%Ni	1.1	0	0.3	0.0	0.0	0.3	27.3
2	15%P-5%Ni	2.5	0.2	1.0	0.0	0.0	1.2	40.0
3	15%P-10%Ni	41.0	6.4	28.5	0.0	0.0	34.9	69.5
4	15%P-15%Ni	62.1	11.0	39.9	0.0	0.0	50.9	64.3
5	15%P-20%Ni	59.0	12.5	32.7	0.0	0.0	45.2	55.4
6	15%P-25%Ni	19.3	8.6	5.0	0.0	2.2	15.8	25.9
7	15%P-30%Ni	16.3	7.6	3.5	0.0	2.0	13.1	21.5
8	0%P-30%Ni	70.9	0	0	56.8	0.0	56.8	0.0

[a]Reaction conditions: furfural loaded: 0.42 mmol, deionized water loaded: 3.96 g, catalyst loaded: 0.04g, P_0 (H_2) = 3 MPa (at room temperature), T = 110°C, reaction time: 2 h.

[b]P-Ni/Al_2O_3 catalyst with loading P species first.

Table S5 Distribution of the products during hydrogenation of furfural over the P-Ni/Al_2O_3 catalyst with loading P species first at 130°C[a]

Entry	Catalyst[b]	Con. (%)	Yield (mol%)				Total (%)	CPO Selectivity (%)
			CPO	FA	TFA	CPL		
1	15%P-0%Ni	0	0.0	0.0	0.0	0.0	0.0	0
2	15%P-5%Ni	13	5.97	0.0	0.0	2.6	8.6	45.9
3	15%P-10%Ni	75.2	53.1	5.9	0.0	0.0	59.0	70.6
4	15%P-15%Ni	68.6	38.7	4.2	0.0	6.6	49.4	56.4
5	15%P-20%Ni	45.0	15.1	0.3	0.0	15.6	31.0	33.6
6	15%P-25%Ni	43.3	16.7	0.3	0.0	19.2	36.2	38.6
7	15%P-30%Ni	44.2	18.2	1.0	0.0	24.2	43.4	41.2
8	0%P-30%Ni	100.0	0.0	0.0	73.2	0.0	73.2	0.0

[a]Reaction conditions: furfural loaded: 0.42 mmol, deionized water loaded: 3.96 g, catalyst loaded: 0.04g, P_0 (H_2) = 3 MPa (at room temperature), T = 130°C, reaction time: 2 h.

[b]P-Ni/Al_2O_3 catalyst with loading P species first.

Table S6 Distribution of the products during hydrogenation of furfural over the P-Ni/Al_2O_3 catalyst with loading P species first at 150°C[a]

Entry[a]	Catalyst[b]	Con. (%)	Yield (mol%)				Total, % (CPO+CPL)	Selectivity of CPL (%)
			CPO	FA	TFA	CPL		
1	15%P-0%Ni	6.2	0	0	0	0	0	0
2	15%P-5%Ni	19.3	15.7	0.8	0	0	15.7	0
3	15%P-10%Ni	83.5	69.6	3.4	0	4.1	70.1	4.9
4	15%P-15%Ni	88.1	72.8	1.1	0	1.7	74.5	1.9
5	15%P-20%Ni	79.5	3.2	0.2	0	58.5	61.7	73.6
6	15%P-25%Ni	70.1	2.0	0.7	0	50.2	52.2	71.6
7	15%P-30%Ni	69.0	16.8	0.6	0	39.3	56.14	57.0
8	0%P-30%Ni	100.0	0	0	71.4	0	0	0
9	γ–Al_2O_3	3.2	0	0	0	0	0	0

[a]Reaction conditions: furfural loaded: 0.42 mmol, deionized water loaded: 3.96 g, catalyst loaded: 0.04g, P_0 (H_2) = 3 MPa (at room temperature), T = 150°C, reaction time: 2 h.

[b]P-Ni/Al_2O_3 catalyst with loading P species first.

Table S7 Product distribution in the furfural hydrogenation catalyzed by different Ni-P/γ–Al_2O_3 catalysts at 190°C[a]

Entry	Catalyst[b]	Con. (%)	Yield (mol%)				Total (%)	CPL Selectivity (%)
			CPO	FA	TFA	CPL		
1	15%Ni-0%P	100.0	0.0	0.0	73.6	0.0	73.6	0.0%
2	15%Ni-1%P	100.0	0.2	0.0	65.3	0.0	65.5	0.0
3	15%Ni-3%P	100.0	1.4	0.0	62.4	0.0	63.8	0.0
4	15%Ni-5%P	97.2	24.0	1.2	0.0	59.0	84.2	60.7
5	15%Ni-10%P	100.0	1.8	5.7	0.0	22.1	29.6	22.1
6	15%Ni-15%P	99.8	3.4	0.4	0.0	58.6	62.4	58.7
7	15%Ni-20%P	97.2	7.6	1.0	0.0	49.0	57.6	50.4
8	15%Ni-25%P	97.6	72.4	0.3	0.0	21.1	93.8	21.6
9	15%Ni-30%P	98.0	54.3	0.7	0.0	9.4	64.4	0.0

[a]Reaction conditions: furfural loaded: 0.42 mmol, deionized water loaded: 3.96 g, catalyst loaded: 0.04g, P_0 (H_2) = 3 MPa (at room temperature), T = 190°C, reaction time: 2 h.

[b]Ni-P/Al_2O_3 catalyst with loading nickel first.

Table S8 Distribution of the products during hydrogenation of furfural over the P-Ni/Al_2O_3 catalyst with loading P species first at 190°C[a]

Entry	Catalyst[b]	Con. (%)	Yield (mol%)				Total (%)	FA Selectivity (%)
			CPO	FA	TFA	CPL		
1	15%P-0%Ni	29.4	1.3	0.0	0.0	0.9	2.2	3.1
2	15%P-5%Ni	95.9	64.7	0.3	0.0	6.4	71.4	6.7
3	15%P-10%Ni	100.0	8.4	0.2	0.0	40.9	49.5	40.9
4	15%P-15%Ni	99.8	3.4	0.4	0.0	49.0	52.8	49.1
5	15%P-20%Ni	99.9	0.5	0.2	0.0	44.1	44.8	44.1
6	15%P-25%Ni	99.8	0.5	1.2	0.0	16.6	18.3	16.6
7	15%P-30%Ni	99.3	0.5	0.5	0.0	22.6	23.6	22.8
8	0%P-30%Ni	99.9	0.0	0.0	58.3	0.0	58.3	0.0

[a]Reaction conditions: furfural loaded: 0.42 mmol, deionized water loaded: 3.96 g, catalyst loaded: 0.04g, P_0 (H_2) = 3 MPa (at room temperature), T = 190°C, reaction time: 2 h.

[b]P-Ni/Al_2O_3 catalyst with loading P species first.

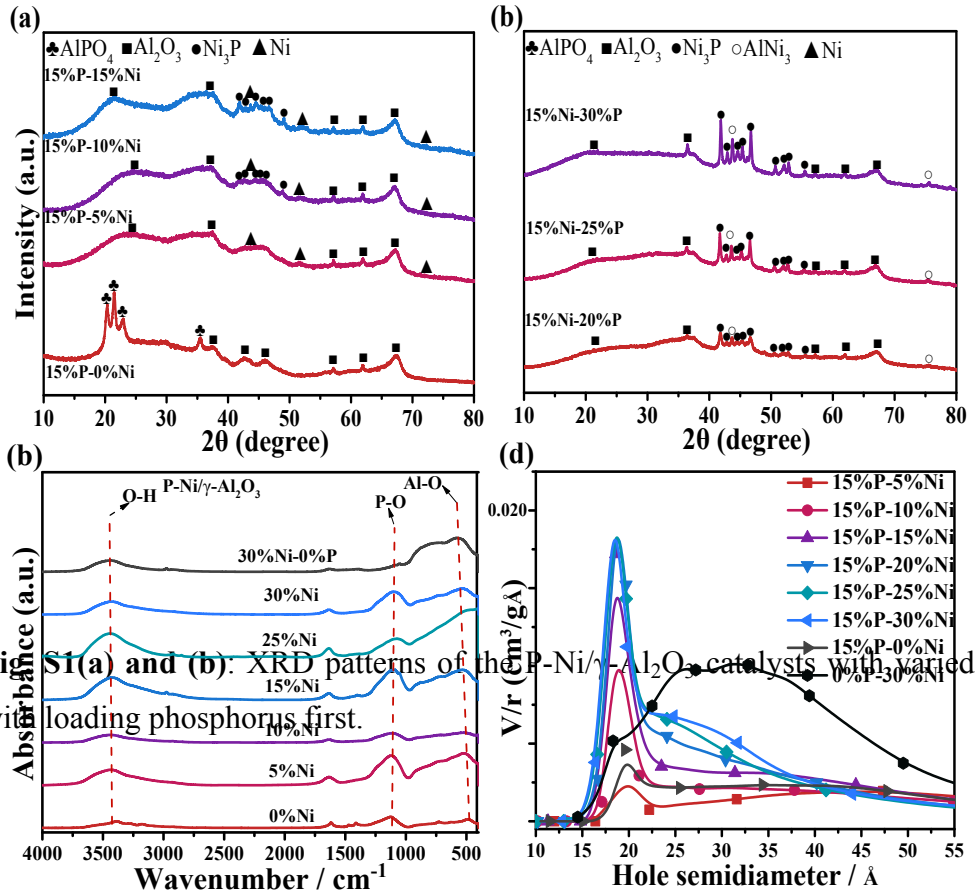

Fig. S1(a) and (b): XRD patterns of the CP-Ni/γ-Al_2O_3 catalysts with varied nickel loading and with loading phosphorus first.

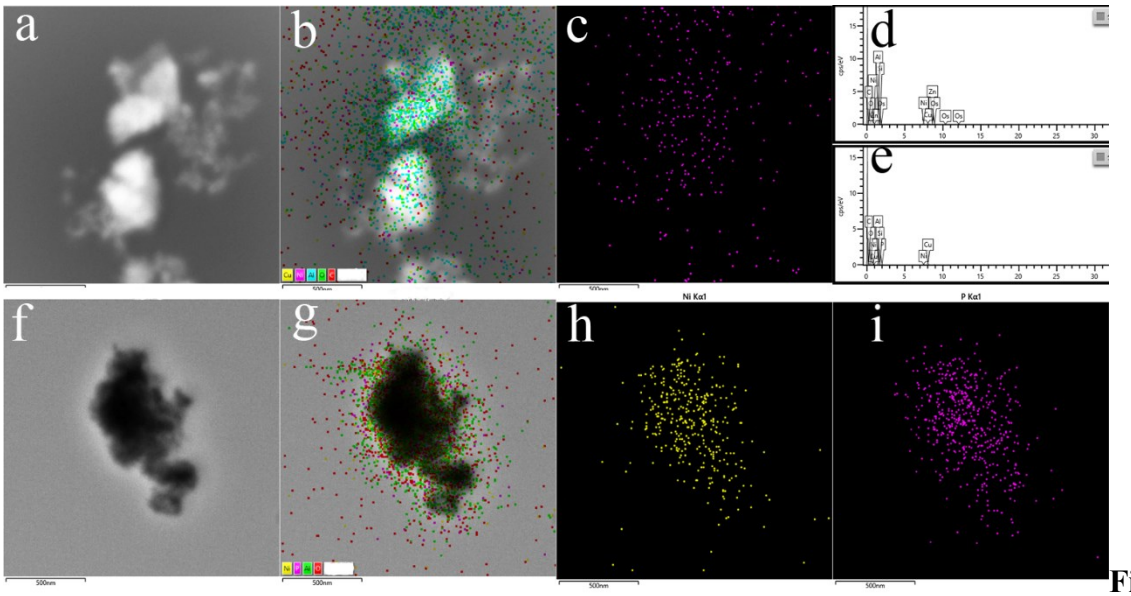

Fig. S2(a) and (b): XRD patterns of the P-Ni/γ-Al_2O_3 catalysts with varied nickel loading and with loading phosphorus first.

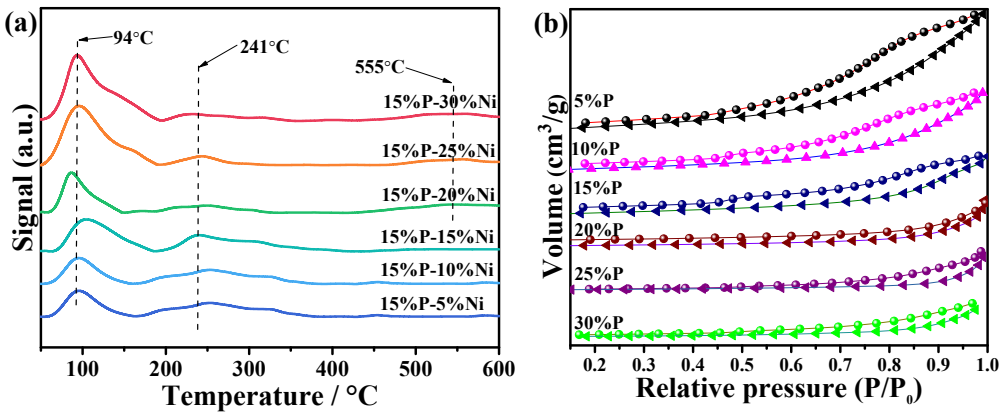

Fig. S3 (a): NH_3−TPD spectra for the P-Ni/γ-Al_2O_3 (loading P first) catalyst. **(b):** Isothermal adsorption curve (BET) of Ni-P/γ-Al_2O_3 (loading Ni first) .

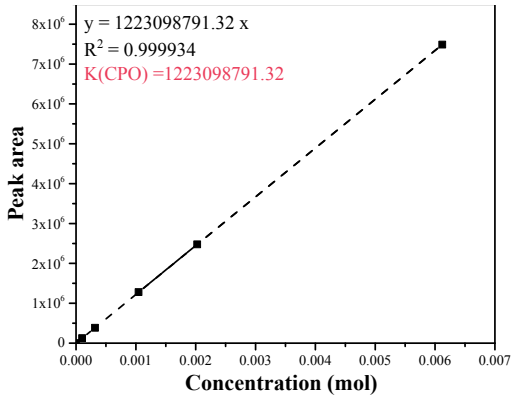

Fig. S4 The external standard curve of CPO.

Instructions on the external standard method:

1.Preparation of standard samples: CPO was diluted with acetone to a specified concentration (0.2%, 0.1%, 0.06%, 0.03%, 0.01%). Then, K (CPO) was calculated based on the concentration and peak area of CPO.

2. The liquid products were diluted with acetone until the concentration met the requirements in external standard curve.

3. Calculate the yield and selectivity of CPO in the liquid products. CPL and other liquid products were tested and calculated in the same way.

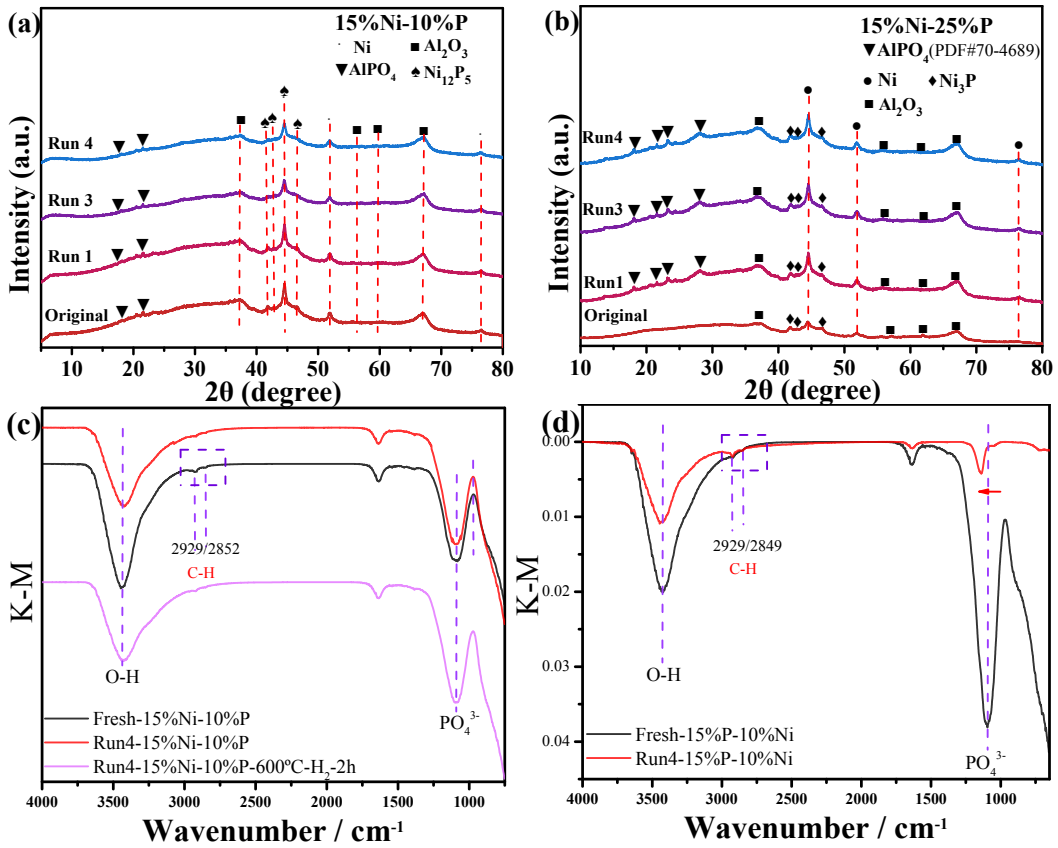

Fig. S5 Recyclability test in the furfural hydrogenation catalyzed by 15Ni-10%P/γ–Al_2O_3 and 15Ni-25%P/γ–Al_2O_3 catalysts. Reaction conditions: furfural loaded: 0.42 mmol, deionized water loaded: 3.96 g, catalyst loaded: 0.04 g, H_2: 3MPa, T = 150°C, reaction time: 2 h.

(a): XRD patterns of the 15Ni-10%P/γ–Al_2O_3 catalyst after the recyclability test at 150°C.

(b): XRD patterns of the 15Ni-25%P/γ–Al_2O_3 catalyst after the recyclability test at 190°C.

(c)-(d): FT-IR spectra of 15%Ni-10%P and 15%P-10%Ni catalysts in cyclic stability experiments.