Supplementary Information (SI) for Green Chemistry.
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Supporting Information

Hydrogen bonds regulation to enhance catalytic C-C bonds cleavage of polylactic acid wastes in H_2O to produce H_2

This file includes:

Supplementary Methods

Chemicals and materials

Polylactic acid (PLA) plastic particles, lactic acid, 3-hydroxypropanoic acid, glyceric acid and propanoic acid were purchased from Aladdin Chemistry CO., Ltd. PLA powder, fork, spoon, straw and cup were obtained from Liaoning Jinliang Biotechnology Co., Ltd. NaOH was acquired from Tianjin Kemiou Chemical Reagent Co., Ltd. DMSO-d_6 was purchased from Sigma-Aldrich. The different nickel-based catalyst precursors powders were obtained from Dalian Tongyong Chemical Co., Ltd. Carbon dioxide (>99%), methane (>99%), ethane (>99%), propane (>99%), butane (>99%), hydrogen (>99%) and the mixed standard gas were obtained from Zhengzhou Gas Products Co., Ltd. Milli-Q water was used in all experiments.

Characterization

Scanning electron microscopy (SEM) characterization: SEM was conducted on a JEM-7800F (JEOL) microscope, and it was operated at 1.0 kV.

Transmission electron microscopy (TEM) characterization: TEM and EDS elemental maps were performed with JEM-2100 (JEOL) microscope, the operated voltage was 200 kV.

Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis: ICP-OES was conducted by ICPS-8100 (Shimadzu), which was operated with the radio-frequency power of 1.0 kW. The catalyst was dissolved in aqua regia and then diluted to a certain volume in the volumetric flask.

X-ray diffraction (XRD) analysis: XRD was carried out with the Rigaku D/Max 2500/PC

diffractometer, Cu Kα radiation (λ = 0.15418 nm) was operated at 40 kV/200 mA. And the wide-angle patterns were scanned from 10° to 90° (2θ) at a scan rate of 2.5° min^{-1}.

^{1}H nuclear magnetic resonance (NMR) spectra: NMR analysis was conducted on a Bruker ADVANCE III 400 MHz spectrometer. Lactic acid, lactic acid and H_2O mixture were operated from 25 to 50 °C in DMSO-d_6.

Density functional theory (DFT) calculations: The first-principles[1,2] was employed to perform DFT calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) formulation.[3] We have chosen the projected augmented wave (PAW) potentials[4,5] to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 520 eV. Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method with a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-6} eV. A geometry optimization was considered convergent when the energy change was smaller than 0.03 eV $Å^{-1}$. In this structure, the U correction was used for Ni (4.96 eV) and Fe (4.66 eV) atoms. The vacuum spacing in a direction perpendicular to the plane of the structure is 20 Å for the surfaces. The Brillouin zone integration is performed using 2×2×1 Monkhorst-Pack k-point sampling for a structure. The free energy was calculated using the equation:

$$G = E_{ads} + ZPE - TS \quad (1)$$

where G, E_{ads}, ZPE and TS were the free energy, total energy from DFT calculations, zero-point energy and entropic contributions, respectively. Finally, transition states for elementary reaction steps were determined by a combination of the nudged elastic band (NEB) method[6]

and the dimer method.[7-9] In the NEB method, the path between the reactant and product was discretized into a series of structural images. The image that was closest to a likely transition state structure, which was then employed as an initial guess structure for the dimer method.

Supplementary Figure

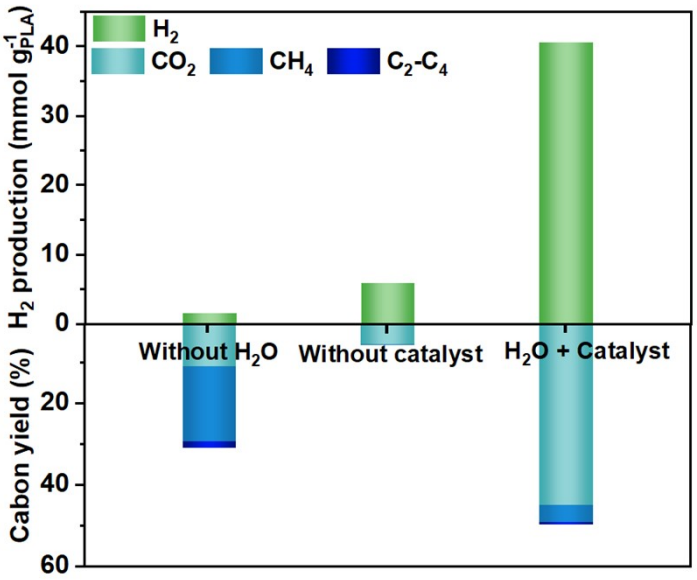

Fig. S1 Influence of catalyst and H_2O on the conversion of PLA to H_2. Reaction condition: 0.2 g PLA, 1.5 mmol Ni-Fe catalyst, 15 mL H_2O, 10 bar N_2, 300 °C, 5 h.

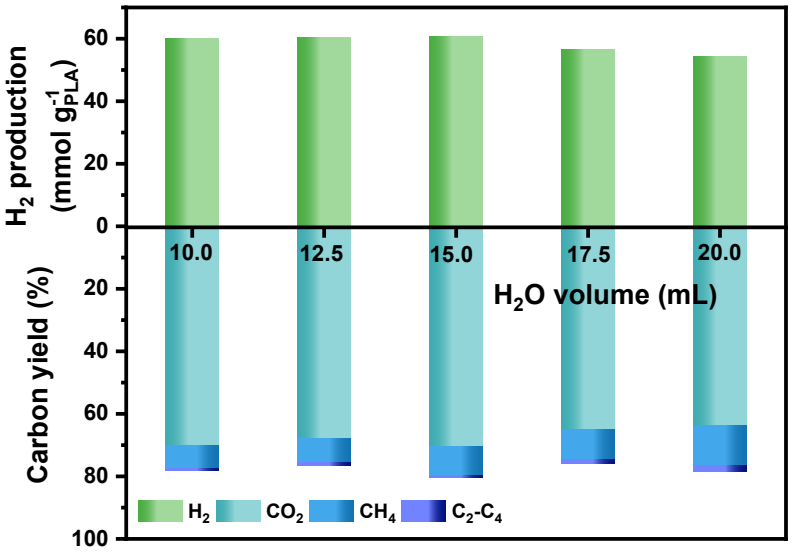

Fig. S2 Effect of H_2O volume on the catalytic conversion of PLA to H_2. Reaction condition: 0.2 g PLA, 1.5 mmol Ni-Fe catalyst, H_2O, 10 bar N_2, 310 °C, 5 h.

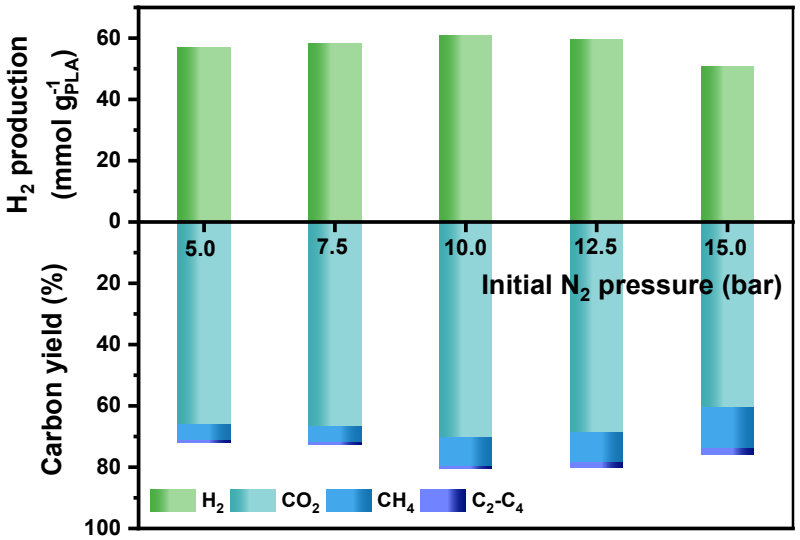

Fig. S3 Effect of initial N_2 pressure on the catalytic conversion of PLA to H_2. Reaction condition: 0.2 g PLA, 1.5 mmol Ni-Fe catalyst, 15 mL H_2O, 310 °C, 5 h.

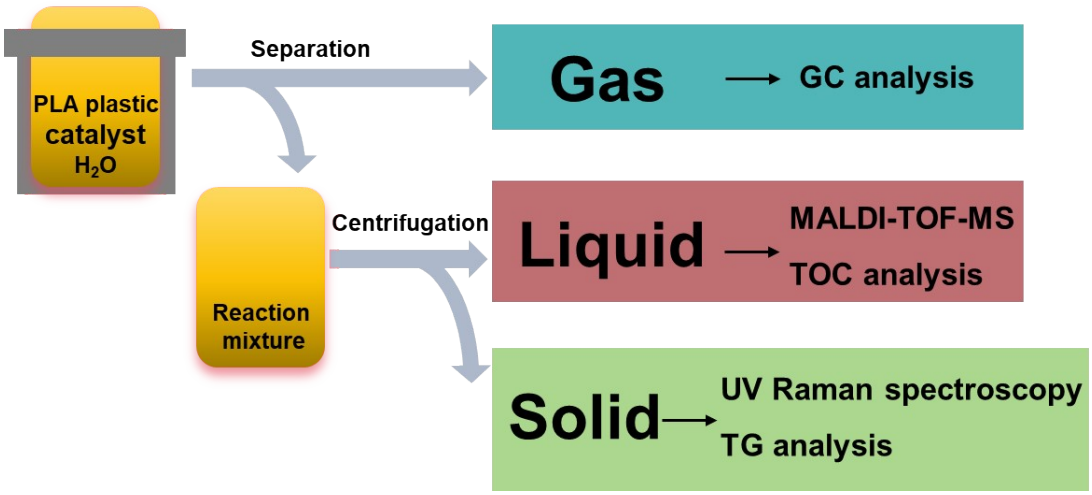

Fig. S4 The products analysis for the catalytic transformation of PLA. The gas, liquid and solid products were collected and analyzed after reaction.

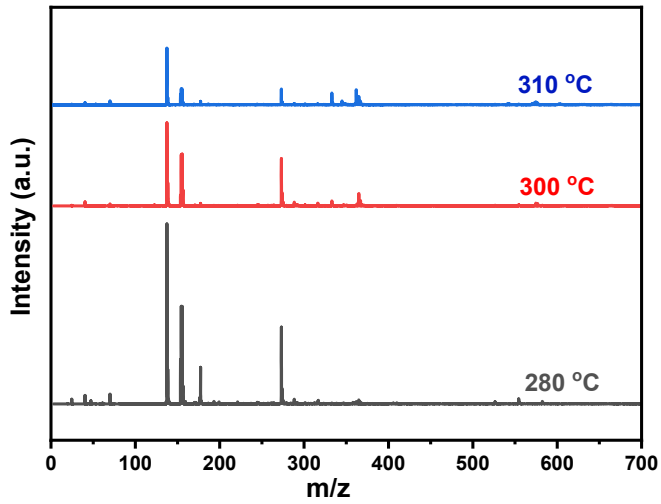

Fig. S5 MALDI-TOF-MS spectra of liquid products with different reaction temperatures. Reaction condition: 0.2 g PLA, 1.5 mmol Ni-Fe catalyst, 15 mL H_2O, 10 bar N_2, 5 h.

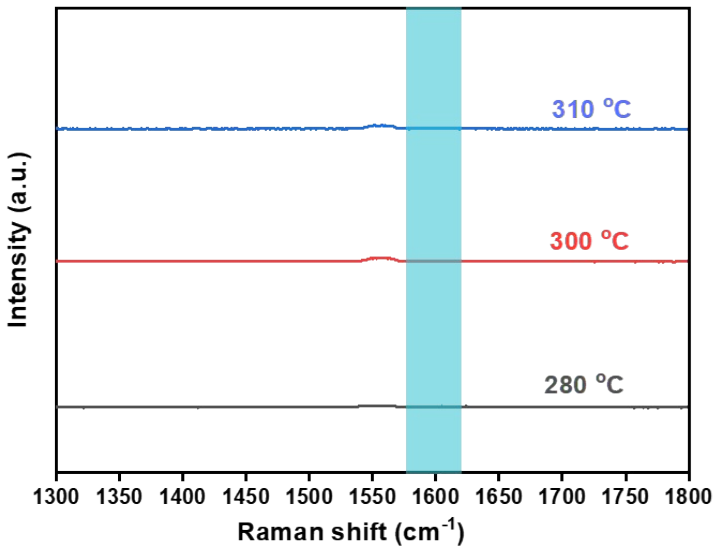

Fig. S6 UV Raman spectra of solid residue with different reaction temperatures. Reaction condition: 0.2 g PLA, 1.5 mmol Ni-Fe catalyst, 15 mL H_2O, 10 bar N_2, 5 h.

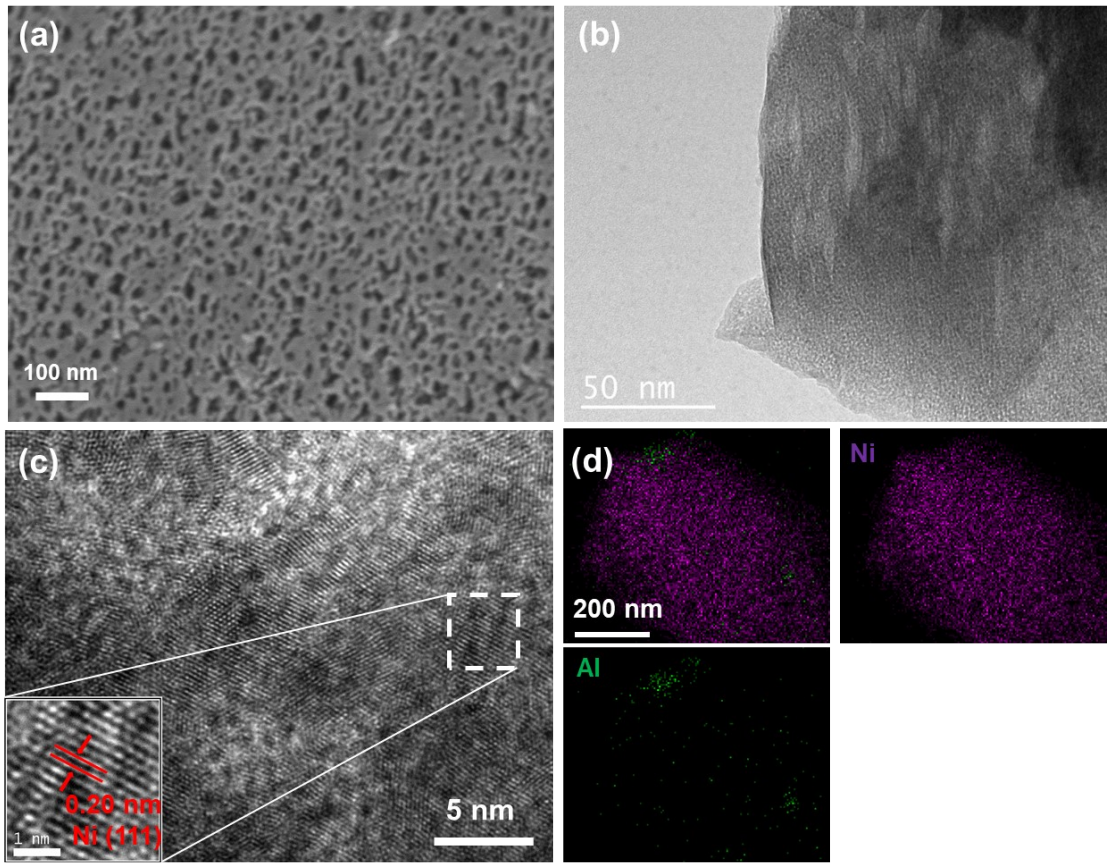

Fig. S7 SEM and TEM images of Ni catalyst. (a) SEM image of Ni catalyst. (b-d) TEM images with EDS elemental mapping of Ni catalyst.

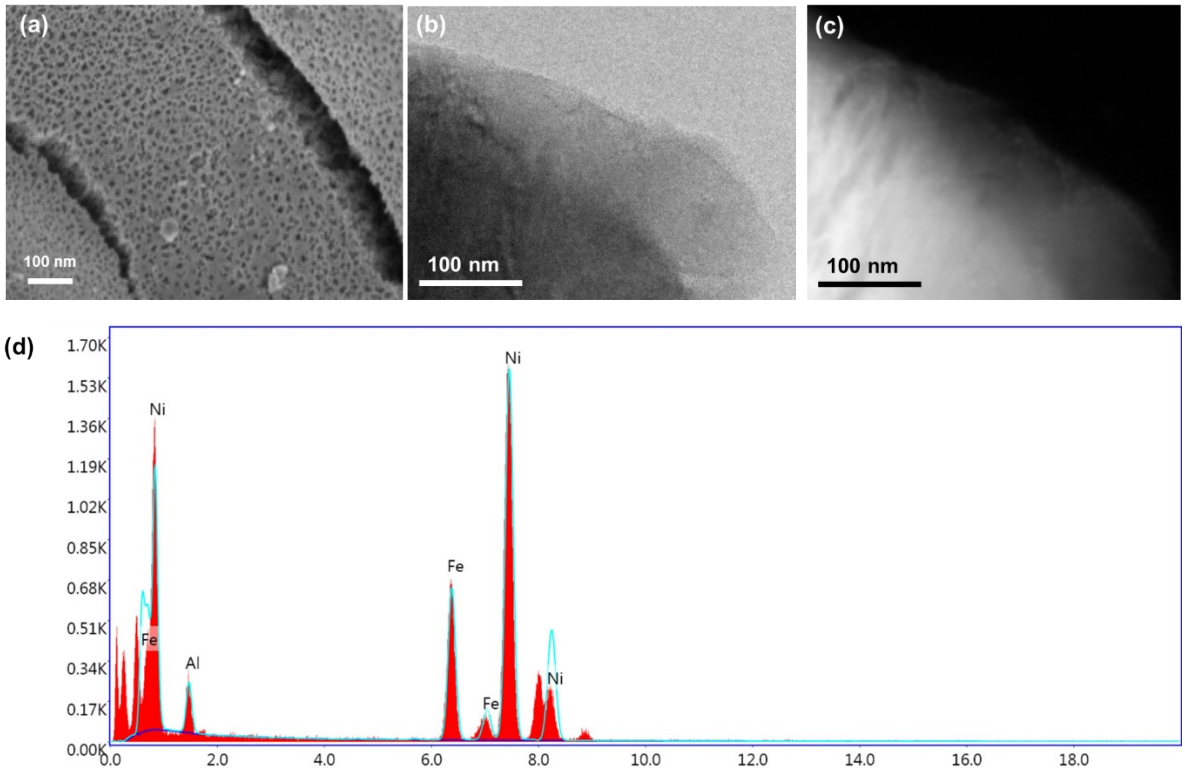

Fig. S8 SEM and TEM images of Ni-Fe catalyst. (a) SEM image of Ni-Fe catalyst. (b-d) STEM images with elemental analysis of Ni-Fe catalyst.

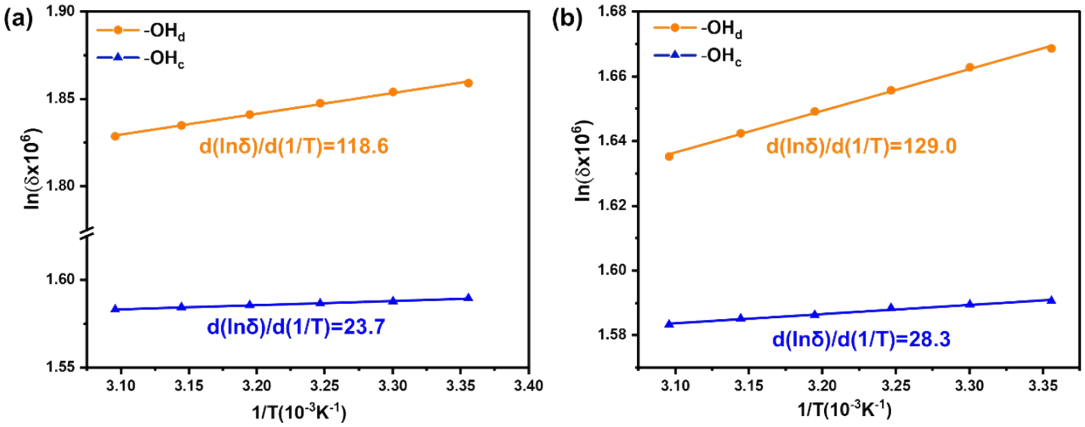

Fig. S9 Linear fits of lnδ versus 1/T. (a) Linear fits of lnδ versus 1/T for -OH_d and -OH_c in lactic acid. (b) Linear fits of lnδ versus 1/T for -OH_d and -OH_c in lactic acid and H_2O with the mole ratio of 1:1.

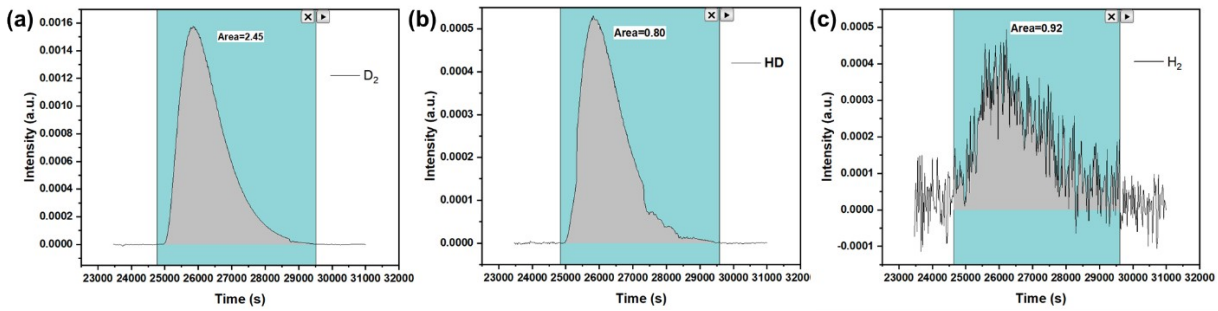

Fig. S10 Mass spectrometry analysis of hydrogen production from the catalytic conversion of PLA in qualitative and semi-quantitative. Reaction condition: 0.2 g PLA-based cup, 1.5 mmol Ni-Fe catalyst, 15 mL D_2O, 10 bar N_2, 310 °C, 5 h.

Supplementary Table

Table S1 H_2 production, H_2 selectivity, carbon yield of gas products and the detailed distribution of CO_2, CH_4 and C_2-C_4 hydrocarbons over the different catalysts.

Entry[a]	Catalyst	H_2 production (mmol g_{PLA}^{-1})	H_2 selectivity (%)	Gas carbon yield (%)	Gas carbon products distribution (mol%)		
					CO_2	CH_4	C_2-C_4
1[b]	Fe	$10.3_{\pm0}$	$63.0_{\pm2.3}$	$19.8_{\pm0.8}$	$77.0_{\pm0.8}$	$20.2_{\pm0.7}$	$2.8_{\pm0}$
2[c]	Ni	$22.4_{\pm0.4}$	$79.2_{\pm2.0}$	$34.0_{\pm0.2}$	$85.8_{\pm0.8}$	$13.0_{\pm0.8}$	$1.2_{\pm0}$
3	Ni-Fe	$40.6_{\pm0.4}$	$98.4_{\pm0.4}$	$49.7_{\pm0.2}$	$90.5_{\pm2.3}$	$8.4_{\pm2.2}$	$1.1_{\pm0.1}$
4[d]	Ni-Sn	$20.9_{\pm0.3}$	$57.7_{\pm0.8}$	$43.0_{\pm0.2}$	$74.1_{\pm0.5}$	$21.8_{\pm0.4}$	$4.2_{\pm0.1}$
5[e]	Ni-Mo	$19.0_{\pm0.3}$	$89.2_{\pm0}$	$25.5_{\pm0.5}$	$91.6_{\pm1.2}$	$7.5_{\pm1.0}$	$0.9_{\pm0}$

[a]The hydrogen and carbon yield of gas products were quantified by GC analysis, reaction condition: 0.2 g PLA, 1.5 mmol Ni-Fe catalyst, 15 mL H_2O, 10 bar N_2, 300 °C, 5 h.

[b]2.0 mmol Fe catalyst.

[c]2.0 mmol Ni catalyst.

[d]1.6 mmol Ni-Sn catalyst.

[e]1.9 mmol Ni-Mo catalyst.

Table S2 H_2 production, H_2 selectivity, carbon yield of gas products and the detailed distribution of CO_2, CH_4 and C_2-C_4 hydrocarbons without H_2O or catalyst.

Entry[a]	Reaction condition	H_2 production (mmol g_{PLA}^{-1})	Gas carbon yield (%)	Gas carbon products distribution (mol%)		
				CO_2	CH_4	C_2-C_4
1	Without H_2O	1.5	30.9	35.7	59.3	5.0
2	Without catalyst	5.9	5.8	95.3	3.2	1.5
3	H_2O + Catalyst	40.6	49.7	90.5	8.4	1.1

[a]Reaction condition: 0.2 g PLA, 1.5 mmol Ni-Fe catalyst, 15 mL H_2O, 10 bar N_2, 300 °C, 5 h.

Table S3 H_2 production, H_2 selectivity, carbon yield of gas products and the detailed distribution of CO_2, CH_4 and C_2-C_4 hydrocarbons with the different reaction temperature.

Entry[a]	Reaction temperature (°C)	H_2 production (mmol g_{PLA}^{-1})	Gas carbon yield (%)	Gas carbon products distribution (mol%)		
				CO_2	CH_4	C_2-C_4
1	280	$16.3_{\pm0.4}$	$21.2_{\pm0.1}$	$80.7_{\pm1.3}$	$17.1_{\pm1.4}$	$2.2_{\pm0}$
2	290	$26.0_{\pm0.3}$	$31.2_{\pm0.3}$	$87.9_{\pm0.2}$	$10.2_{\pm0.1}$	$1.9_{\pm0.1}$
3	300	$40.6_{\pm0.4}$	$49.7_{\pm0.2}$	$90.5_{\pm2.3}$	$8.4_{\pm2.2}$	$1.1_{\pm0.1}$
4	310	$60.8_{\pm0.2}$	$80.4_{\pm0.5}$	$87.0_{\pm0.1}$	$11.8_{\pm0.2}$	$1.2_{\pm0}$
5	320	$62.0_{\pm0.3}$	$82.1_{\pm0.2}$	$87.1_{\pm0.5}$	$11.4_{\pm0.4}$	$1.5_{\pm0.1}$

[a]Reaction condition: 0.2 g PLA, 1.5 mmol Ni-Fe catalyst, 15 mL H_2O, 10 bar N_2, 5 h.

Table S4 H_2 production, H_2 selectivity, carbon yield of gas products and the detailed distribution of CO_2, CH_4 and C_2-C_4 hydrocarbons with the different H_2O volume.

Entry[a]	H_2O volume (mL)	H_2 production (mmol g_{PLA}^{-1})	H_2 selectivity (%)	Gas carbon yield (%)	Gas carbon products distribution (mol%)		
					CO_2	CH_4	C_2-C_4
1	10.0	60.2	92.4	78.2	89.6	9.3	1.1
2	12.5	60.3	94.7	76.4	89.0	9.8	1.2
3	15.0	60.8	90.7	80.4	87.0	11.8	1.2
4	17.5	56.6	89.3	76.0	85.7	12.6	1.7
5	20.0	54.2	83.1	78.4	81.2	16.4	2.4

[a]Reaction condition: 0.2 g PLA, 1.5 mmol Ni-Fe catalyst, H_2O, 10 bar N_2, 310 °C, 5 h.

Table S5 H_2 production, H_2 selectivity, carbon yield of gas products and the detailed distribution of CO_2, CH_4 and C_2-C_4 hydrocarbons with the different initial N_2 pressure.

Entry[a]	Initial N_2 pressure (bar)	H_2 production (mmol g_{PLA}^{-1})	H_2 selectivity (%)	Gas carbon yield (%)	Gas carbon products distribution (mol%)		
					CO_2	CH_4	C_2-C_4
1	5.0	57.0	95.1	72.0	91.6	7.3	1.1
2	7.5	58.3	96.4	72.6	91.7	7.2	1.1
3	10.0	60.8	90.7	80.4	87.0	11.8	1.2
4	12.5	59.6	89.2	80.1	85.7	12.3	2.0
5	15.0	50.7	80.2	76.0	79.8	17.5	2.7

[a]Reaction condition: 0.2 g PLA, 1.5 mmol Ni-Fe catalyst, 15 mL H_2O, N_2, 310 °C, 5 h.

Table S6 H_2 production, carbon yield of gas products and the detailed distribution of CO_2, CH_4 and C_2-C_4 hydrocarbons with the different reaction time.

Entry[a]	Reaction time (min)	H_2 production (mmol g_{PLA}^{-1})	Gas carbon yield (%)	Gas carbon products distribution (mol%)		
				CO_2	CH_4	C_2-C_4
1	10	16.7	21.5	91.3	8.0	0.7
2	30	23.6	29.5	86.5	12.6	0.9
3	60	32.4	37.8	90.0	9.3	0.7
4	120	54.5	70.9	87.3	11.3	1.4
5	180	56.9	72.2	87.7	10.9	1.4
6	300	60.8	80.4	87.0	11.8	1.2
7	420	60.8	78.7	86.6	11.8	1.6

[a]Reaction condition: 0.2 g PLA, 1.5 mmol Ni-Fe catalyst, 15 mL H_2O, 10 bar N_2, 310 °C.

Table S7 H_2 yield, carbon yield of gas products and the detailed distribution of CO_2, CH_4 and C_2-C_4 hydrocarbons from the model compounds conversion over Ni catalyst.

Entry[a]	Substrate	H_2 yield (%)	Gas carbon yield (%)	Gas carbon products distribution (mol%)		
				CO_2	CH_4	C_2-C_4
1	PLA	18.7	24.9	88.0	10.4	1.6
2	Lactic acid	20.8	21.6	87.6	10.6	1.8
3	Glyceric acid	47.5	62.1	86.4	13.1	0.5
4	Propionic acid	9.1	4.5	86.7	6.7	6.6
5	3-Hydroxypropionic acid	32.1	50.9	67.2	27.5	5.3

[a]Reaction condition: 0.2 g substrate, 2.0 mmol Ni catalyst, 15 mL H_2O, 10 bar N_2, 290 °C, 5 h.

Table S8 H_2 yield, carbon yield of gas products and the detailed distribution of CO_2, CH_4 and C_2-C_4 hydrocarbons from the model compounds conversion over Ni-Fe catalyst.

Entry[a]	Substrate	H_2 yield (%)	Gas carbon yield (%)	Gas carbon products distribution (mol%)		
				CO_2	CH_4	C_2-C_4
1	PLA	31.2	31.2	87.9	10.2	1.9
2	Lactic acid	39.7	41.6	92.7	6.1	1.2
3	Glyceric acid	70.8	82.0	82.5	16.2	1.3
4	Propionic acid	55.1	59.5	82.7	11.0	6.3
5	3-Hydroxypropionic acid	71.7	81.2	80.9	14.4	4.7

[a]Reaction condition: 0.2 g substrate, 1.5 mmol Ni-Fe catalyst, 15 mL H_2O, 10 bar N_2, 290 °C, 5 h.

Table S9 The content of C, H and O in PLA plastic wastes.

Entry[a]	Substrate	C (%)	H (%)	O (%)	Others (%)
1	Powder	50.3	5.4	43.6	0.7
2	Fork-spoon	37.5	4.2	32.6	25.7
3	Straw	42.7	4.4	35.7	17.2
4	Cup	49.9	5.3	43.2	1.6

[a]According to the content of C, H and O in PLA plastic wastes, the mole numbers of C, H and O in a certain amount of PLA plastic wastes could be calculated. Others contained N, S and ash.

In our work, the content of C, H and O in PLA-based cup was measured, which could be denoted as a chemical formula of $C_3H_4O_2$. For the catalytic conversion of PLA-based cup to CO_2 and H_2, the theoretical chemical equation was shown as follows:

$$C_3H_4O_2 + 4\,H_2O \rightarrow 3\,CO_2 + 6\,H_2$$

However, in our experiment, some other gas products, such as CH_4 and C2-C4 hydrocarbons, also generated. And the coefficient of gas products was determined on the basis of the mole percentage of gas products after the reaction at 310 °C. Furthermore, the coefficient of $C_3H_4O_2$ and H_2O was calculated according to the gas carbon yield and hydrogen yield. Ultimately, the chemical equation based on our experiment results was shown below:

$$14.6\,C_3H_4O_2 + 57.3\,H_2O \rightarrow 65.3\,H_2 + 31.5\,CO_2 + \underset{\text{Others}}{}$$

Hereinto, others included the deposited carbon species and small amount of organic molecules, etc.

Table S10 H_2 production, H_2 selectivity, carbon yield of gas products and the detailed distribution of CO_2, CH_4 and C_2-C_4 hydrocarbons with different PC plastic wastes.

Entry[a]	Substrate	H_2 production (mmol $g_{plastic}^{-1}$)	H_2 selectivity (%)	Gas carbon yield (%)	Gas carbon products distribution (mol%)		
					CO_2	CH_4	C_2-C_4
1	Powder	$53.8_{\pm0.5}$	$97.4_{\pm0.2}$	$66.3_{\pm0.7}$	$90.1_{\pm0.3}$	$8.8_{\pm0.3}$	$1.1_{\pm0}$
2	Fork-spoon	$49.3_{\pm0.3}$	$98.9_{\pm0.7}$	$59.8_{\pm0.7}$	$91.0_{\pm0.4}$	$7.7_{\pm0.4}$	$1.3_{\pm0}$
3	Straw	$52.0_{\pm0.1}$	99.8±0	$62.6_{\pm0.1}$	$90.9_{\pm0.5}$	$8.0_{\pm0.4}$	$1.1_{\pm0}$
4	Cup	$62.6_{\pm0.2}$	$93.5_{\pm0.2}$	$80.5_{\pm0.1}$	$90.1_{\pm0.2}$	$8.6_{\pm0.2}$	$1.3_{\pm0}$

[a]Reaction condition: 0.2 g PLA-based substrates, 1.5 mmol Ni-Fe catalyst, 15 mL H_2O, 10 bar N_2, 310 °C, 5 h.

Reference

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