Boosted oxidative dehydrogenation of lactic acid into pyruvic acid on polyvinylpyrrolidone modified Fe$_2$O$_3$:

Synergistic effect of facet and oxygen vacancy

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1 Experimental

1.1 Materials

All chemicals and solvents were purchased from Micxy Chemical Reagent Co., Ltd and used as received unless otherwise noted. Deionized water (18.2 MΩ cm) was prepared by Pure Water System (GWA-UN) and used throughout experiment.

1.2 Preparation of catalysts

RC: α-Fe$_2$O$_3$ nano-sphere (RC) was prepared by hydrothermal synthesis according to previous work[1]. Typically, 10 mmol of Fe(NO$_3$)$_3$·9H$_2$O and 36 mmol of CO(NH$_2$)$_2$ were dissolved in 60 mL of deionized water, and stirred until complete dissolution. Subsequently, the resultant solution was transferred to a hydrothermal kettle (80 mL) lined with polytetrafluoroethylene (PTFE), and reacted at 120°C for 8 h. The precipitate was washed with anhydrous ethanol, and dried at 50 °C for 3 h. Finally, the sample was calcined under air atmosphere in a muffle furnace at 500 °C for 3 h.

PVP modified RC: The uncalcined α-Fe$_2$O$_3$ (RC) and polyvinylpyrrolidone (PVP) were mixed together and dispersed in 60 mL of deionized water, stirred for 30 min at room temperature and then transferred to an 80 mL of hydrothermal kettle lined with PTFE, and reacted at 120°C for 8 h. The precipitate was washed with anhydrous ethanol and dried at 50 °C for 3 h. Then, the sample was calcined under air atmosphere in a muffle furnace at 500 °C for 3 h.

RC-H: The uncalcined α-Fe$_2$O$_3$ (RC) was etched in a tube furnace at 400°C for 3 h under 5 vol.%H$_2$/Ar atmosphere.

1.3 Catalyst characterization

Powder X-ray diffraction measurement was conducted on a Dmax/Ultima IV diffractometer operated at 40 kV and 20 mA with Cu-Ka radiation. The morphologies of the catalysts were determined by a Hitachi S4800 field-emission scanning electron microscope (SEM). TEM and HRTEM images were obtained using a Tecnai G2F20 U-TWIN microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific K-Alpha spectrometer, equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. The binding energy was corrected for surface charging by taking the C 1s peak of contaminant carbon as a reference at 284.6 eV.

1.4 Computational details

In order to fully understand the mechanism of the oxidative dehydrogenation of LA to PA, DFT calculation was performed using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) and the work function in Material studio's CASTEP module using calculations[1]. In order to avoid interactions between different atoms and

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charges, it is necessary to first optimize the geometry of the Fe_2O_3 cell, a step that is intended to optimize the structure of the cell. After that, the (110) and (012) planes are truncated separately[2]; finally, the truncated planes are geometrically optimized again, and this step is mainly to optimize the atomic distances between the layers. The truncation energy is set to 570 eV in order to ensure the convergence and accuracy of the calculation results, and the vacuum layer is set to about 15 Å in order to exclude the influence of the upper crystal layer on the established crystal structure, and avoid the interaction between the planes. The k-point convergence test method is chosen for the (110) and (012) crystal planes and the k-point is set to 3×3×1. The crystal relaxation convergence value is set to 10^{-6} eV, because CASTEP can only perform periodic calculations. The established LA molecules have to be optimized in a periodic cell, and it is necessary to ensure that the cell size of the LA and the cell size of the adsorption plane to be calculated. A layer of the catalyst surface is used in the calculation to simulate the process of surface lactate adsorption, and two relaxation layers are fixed at the bottom. The adsorption energy E_{ads} is calculated as follows:

$$E_{ads}=E_{total} - E_{surf} - E_{adsorbate}$$

where E_{total} is the total energy of lactic acid adsorption on a particular crystal surface of the catalyst, E_{surf} is the energy of a particular crystal surface, and $E_{adsorbate}$ is the energy of lactic acid in the periodic structure. The calculated E_{ads} are generally negative, and the smaller the value is, the easier the adsorption is.

1.5 Catalyst evaluation

The oxidative dehydrogenation of LA to PA was carried out in a fixed bed reactor consisting of a quartz tubular reactor, a gas flow controller, a liquid flow controller and a sample collector. The catalyst was pressed, crushed and sieved, and 20-40 mesh of catalyst particles were selected. The quartz tubular reactor was placed in a furnace, heated from room temperature to the given reaction temperature at a rate of 10 °C min^{-1} and maintained for 30 min. Then, the LA aqueous solution (10 wt% LA) was pumped into the reactor with 2.0 mL/h by a peristaltic pump, and air flow rate was controlled in 2.5 mL/min. Samples were condensed in ice-water bath, and collected at an hour interval. The samples were analyzed by LC-20AD liquid chromatograph with C18 column for PA and LA and SP-6890 gas chromatograph with FFAP capillary column for acetaldehyde, acetic acid and acrylic acid, respectively.

The conversion of LA and the selectivity toward pyruvic acid or other by-products were calculated on equations (1) and (2).

$$\text{Conversion/\%}=\frac{n_0-n_1}{n_0}\times100 \text{-----(1)}, \quad \text{Selectivity/\%}=\frac{n_p}{n_0-n_1}\times100 \text{------(2)}$$

Where n_0 is the molar quantity of LA fed into reactor, n_1 is the molar quantity of LA in the effluent, and n_p is the molar quantity of lactic acid converted to pyruvic acid or other byproducts.
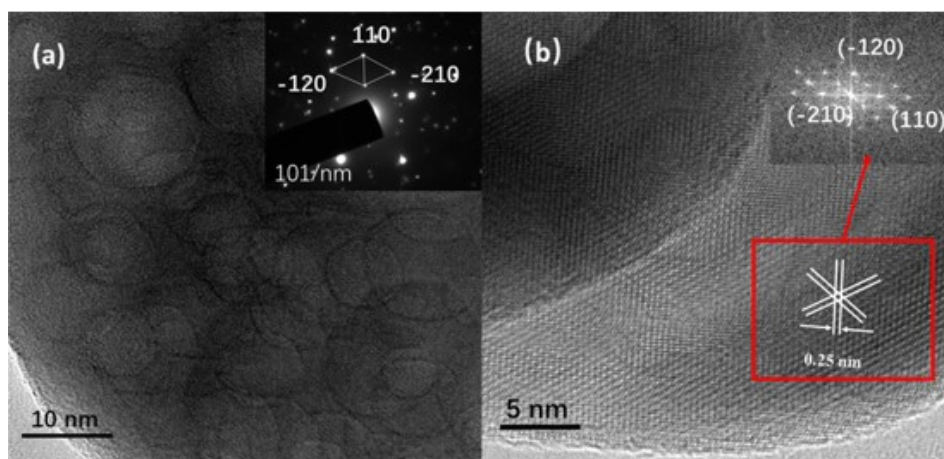
Contact time was defined as equation (3).

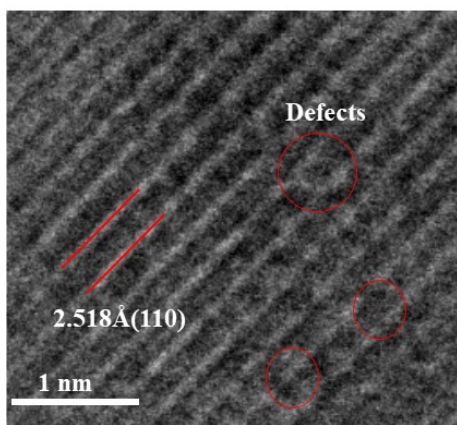$$\text{Contact time /h}=\frac{V_{Cat.}}{V_{LA}} \text{------(3)}$$

Where V_{Cat} is the volume loaded catalyst into reactor (mL), and V_{LA} is the volume flow rate of LA (mL h^{-1}).
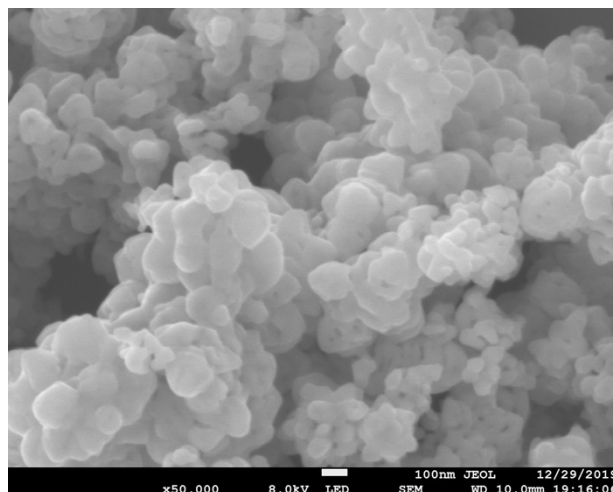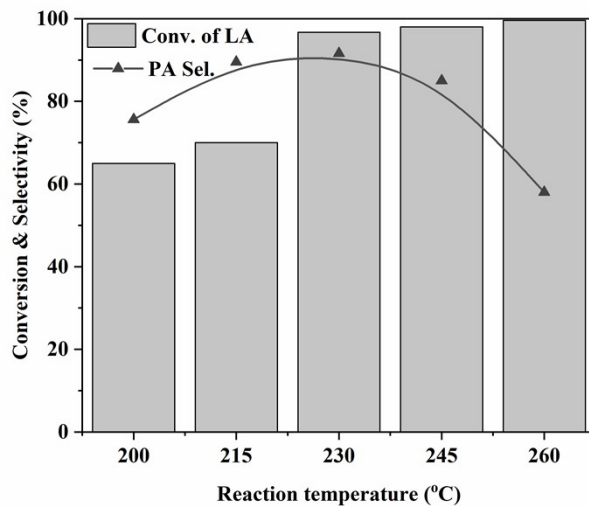
Fig. S1 SEM image of RC

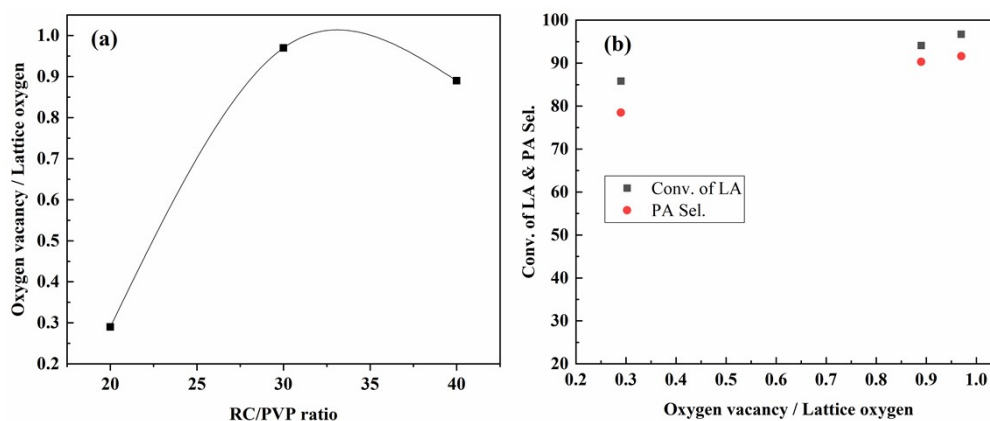**Fig. S2** (a) Transmission electron microscopy image of RC; inset: SAED image. (b) HRTEM image of RC

**Fig. S3** HRTEM image of the PVP modified RC

Fig. S4 Effect of reaction temperature on catalytic performance

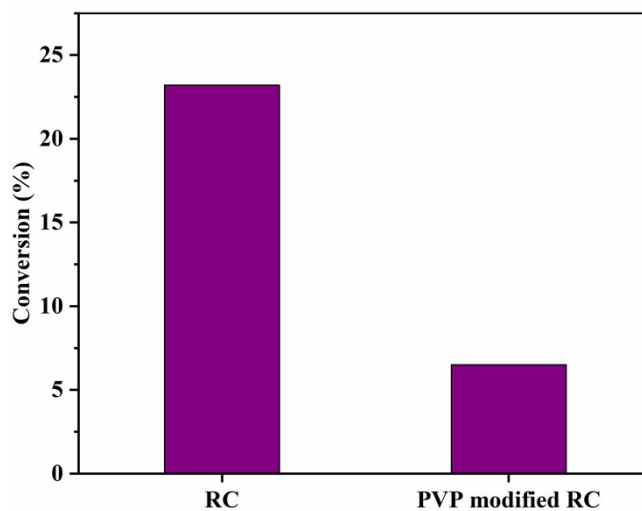Conditions: PA, 10 wt%, feed flow rate, 2.0 mL/h; air, 2.5 mL/min.

Fig. S5 (a) Effect of PVP amount on oxygen vacancy concentration, and (b) effect of the corresponding oxygen vacancy concentration on catalytic performance

It is clearly seen that oxygen vacancy concentration represented by oxygen vacancy / lattice oxygen area ratio value is manipulated by PVP amount, which can well regulate the catalytic performance.
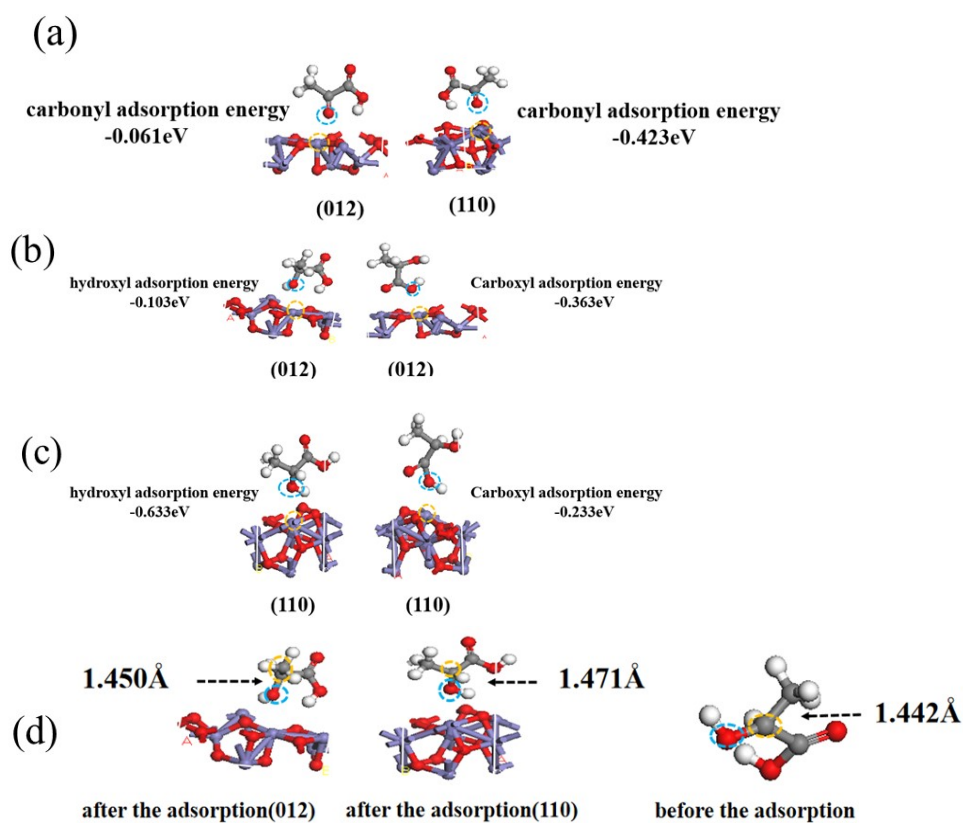
Fig. S6 Adsorption energies of lactic acid and pyruvic acid molecules on (110) and (012) facets. (a) adsorption energies of pyruvic acid on (012) and (110) facets; (b) hydroxyl and carboxyl sites of lactic acid adsorbed on (012) facet, and (c) hydroxyl and carboxyl sites of lactic acid adsorbed on (110) facet; (d) C-OH bond length change

Fig. S7 Conversion of PA over the PVP modified RC, and RC at 230 °C

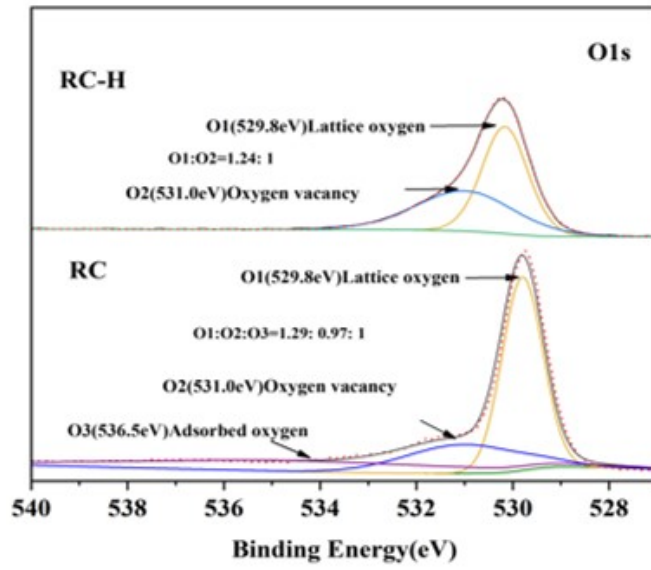Conditions: PA, 10 wt%, feed flow rate, 2.0 mL/h; air, 2.5 mL/min.

Fig. S8 XPS of O1s for RC-H and RC

Table S1 Comparison of reactivity in the conversion of Lactic acid to pyruvic acid over the α-Fe$_2$O$_3$ modified with PVP, along with other catalysts from the literatures.

Entry	Catalyst	Reaction temp. [°C]	Conv. [%]	PA Sel. [%]	References
1	PVP modified RC	230	96.7	91.6	This work
2	3Pb-1Pt/CB	90	70.7	80.6	3
3	Fe(PO$_4$)$_3$	230	60.2	62.3	4, 5
4	Mo/Fe(PO$_4$)$_3$	205	70.1	63.2	6, 7
5	Nb-Ni-O	250	30.5	50.3	8
6	MoO$_3$-TiO$_2$	200	60.6	80.2	9
7	FeMoO/P	230	88.7	75.3	10
8	HS	230	94.0	55.3	1
9	RC	230	94.6	81.7	1
10	MoS$_2$	300	80	42	11

Table S2 Oxidative dehydrogenation of LA to PA over the RC-H

Catalyst	Reaction temp./°C	Conv. of LA/%	PA Sel./%
RC-H	230	95.3	85.2

Conditions: catalyst, 0.3g, carrier gas Air, 2.5 mL/min, LA feedstock 10 wt%, feed flow rate 2.0 mL/h.

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