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Supporting Information

Sustainable production of bio-propionic acid: synergy between vacancy and thermoelectron in MoS_2/MoO_3 composite enhanced hydrodeoxygenation of lactic acid

Ruixue Liu[a], Xinli Li[a], Kai Ma[b], Zhi Chen[a*], and Congming Tang[a*]

([a]School of Chemistry and Chemical Engineering, Chongqing University of Technology, Chongqing 400054, PR China; [b]Synthetic Lubricants Research Institute of Sinopec Lubricant Co.,Ltd., Chongqing 400039, PR China)

1. Experimental section

1.1 Catalyst characterization

Powder X-ray diffraction (XRD). XRD analysis was performed using a Dmax/Ultima IV diffractometer operated at 40 kV and 20 mA with Cu-Ka radiation.

X-ray fluorescence (XRF). XRF analysis was performed using ARL Perform'X instrument, operating in Moseley's law and using Cu-K_β radiation from a generator operating at 50 kV and 50 mA. The dried sample is crushed and mixed in a mound, spread and compacted, then the boric acid is placed on top of the sample and pressed into tablets.

X-ray photoelectron spectroscopy (XPS). XPS analysis was conducted on a Thermo Scientific TM K-Alpha^{TM} X-ray Photoelectron Spectrometer equipped with a monochromatic Al Kα X-ray source (1486.6 eV) operating at 100 W. Samples were analyzed under vacuum ($P < 10^{-8}$ mbar) with a pass energy of 150 eV (survey scans) or 25 eV (high-resolution scans). All peaks would be calibrated with C *1s* peak binding energy at 284.8 eV for adventitious carbon. The experimental peaks were fitted with Advantage software.

Scanning electron microscope (SEM) and transmission electron microscopy (TEM). The morphologies of as-synthesized materials were characterized by a Hitachi S4800 field-emission scanning electron microscope (SEM) and high-resolution transmission electron microscopy (HR-TEM). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) characterization and

EDS were acquired using a FEI Talos F200S Super-X microscope operated at 200 kV. The samples were sonicated for 30 min in ethanol and dropped onto a lacey carbon coated copper grid, then dried in air at room temperature.

Electron paramagnetic resonance (EPR). EPR was measured using Bruker EMX X-band continuous wave EPR spectrometer. The paramagnetic sample was placed in a rectangular resonate at 9.750302 GHz. The resonator was positioned between two electromagnets where varying magnetic field (0-0.6 T) was induced by the changing current through the electromagnets. Reflected microwaves were directed into the detector by the circulator and the resonance was calculated from the amount of microwave radiation absorbed.

UV-Visible diffuse reflectance spectroscopy (UV-Vis DRS). UV-Vis DRS measurements were performed on a Shimadzu UV-2401 PC spectrometer in a diffuse-reflectance mode by using an integrating sphere (internal diameter 60 mm) and $BaSO_4$ was used as the reference.

Electrochemical measurements. Electrochemical measurements were performed with an electrochemical workstation (CS310M, Wuhan CorrTest Inc.) in a 1 M KOH aqueous solution. Ag/AgCl electrode (saturated KCl) and platinum plate electrode were used as the reference and counter electrodes, respectively. 4 mg of the catalyst powders was dispersed in 1 mL of 4:1 (v/v) water-ethanol mixed solvents along with 80 μL of Nafion solution, and the mixture was sonicated for 30 min. Then, 5 μL of the above solution was drop-cast onto the surface of a glassy carbon (GC) disk electrode at a catalyst loading of 0.285 $mg \cdot cm^{-2}$. EIS measurements were carried out at a potential of −0.2 V (vs RHE) over a frequency range from 0.01 Hz to 100 kHz at an AC amplitude of 10 mV.

1.2 Catalyst evaluation

Synthesis of propionic acid (PA) from lactic acid (LA) via hydrodeoxygenation reaction was carried out in a 100 mL parallel-autoclave reactor made of stainless steel – 316L having facilities for gas inlet, outlet, temperature-controlled heating and controllable agitation (see in Fig. S1). In a typical reaction, 0.5 g of catalyst, 20 g lactic acid aqueous solution (10 wt%) and a stir bar were placed in reactors. The reactors were firstly purged several times with hydrogen and subsequently pressurized 3.0 MPa at room temperature. The reactants were heated up to 215 °C within 60 min. When the temperature reaches 215 °C, magnetic stirring is turned on and the reaction process at this temperature for 12 h. Then the magnetic stirring was stopped and reaction system was cooled to room temperature. The catalyst was filtered for recovery, and the liquid sample was immediately analyzed by SP-6890 gas chromatograph with FFAP capillary column connected to FID (for propionic acid, acetaldehyde and n-propanol) and LC-20AD liquid chromatograph with a reverse C18 column connected to UV detector (for lactic acid). The samples were also analyzed by GC-MS using Agilent 5973N Mass Selective Detector. The LA conversion and product selectivity were calculated according to equations (1) and (2).

$$Conversion/\% = \frac{n_0 - n_1}{n_0} \times 100 \quad \text{------(1)} \qquad Selectivity/\% = \frac{n_p}{n_0 - n_1} \times 100 \quad \text{------(2)}$$

where n_0 is the molar quantity of LA fed into reactor, n_1 is the molar quantity of LA for residue after reaction, and n_p is the molar quantity of lactic acid converted to PA or other byproducts such as acetaldehyde and n-propanol.

The rate of hydrodeoxygenation of lactic acid was calculated assuming a pseudo-first-order reaction as below,

$$\ln(1-x) = -k\, C_{cat}\, t$$

where k is the pseudo-first-order rate constant (h^{-1}), x is the conversion of lactic acid, C_{cat} is the concentration of catalyst under reaction system and t is the reaction time (h).

To ensure the reliability of the experimental data, activity test was repeated at least three times. The error of all repeated experiments was controlled within 3%.

1.3 Computational Details

The DFT simulations via CASTEP code were performed to comprehend the adsorption of lactic acid molecule and H_2 molecule on the surface of MoS_2/ MoO_3. The Perdew−Burke−Ernzerhof (PBE) function within the generalized gradient approximation (GGA) and work function was used to implement DFT calculations. The reasonable vacuum layers were set around 15 Å in the z-direction for avoiding interaction between planes. A cutoff energy of 400 eV was provided and a 3 × 3 × 1 Monk horst Pack k-point sampling was chosen for the well-converged energy values. Geometry optimizations were pursued until the force on each atom falls below the convergence criterion of 0.02 eV/Å and energies were converged within 10^{-5} eV. The adsorption energy E_{ads} could be obtained as follows:

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

where E_{total} is the total energy of lactic acid adsorbate covered on a surface, E_{surf} is the energy of a surface and $E_{adsorbate}$ presents the energy of free lactic acid molecule in vacuum. A negative E_{ads} indicates the stability of lactic acid absorbed on the surface thermodynamically.

2. Fig. S1-S6

Fig. S1. Parallel-autoclave reactor

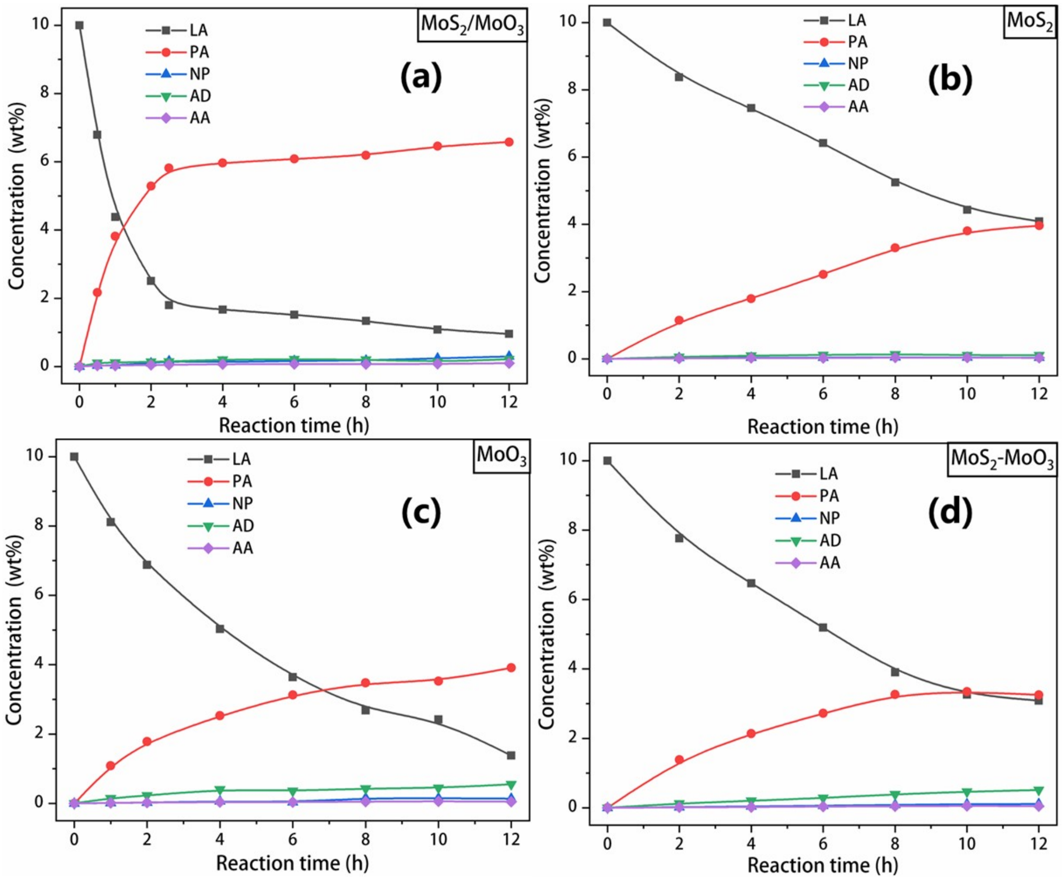


Fig. S2. Concentration-time profile during LA conversion course over each catalyst. Reaction conditions: catalyst, 0.5 g; H_2 initial pressure, 3 MPa; LA feedstock, 20 g (10% wt); reaction temperature, 215 °C. LA, lactic acid; PA, propionic acid; NP, n-propanol; AD, acetaldehyde; AA, acrylic acid.

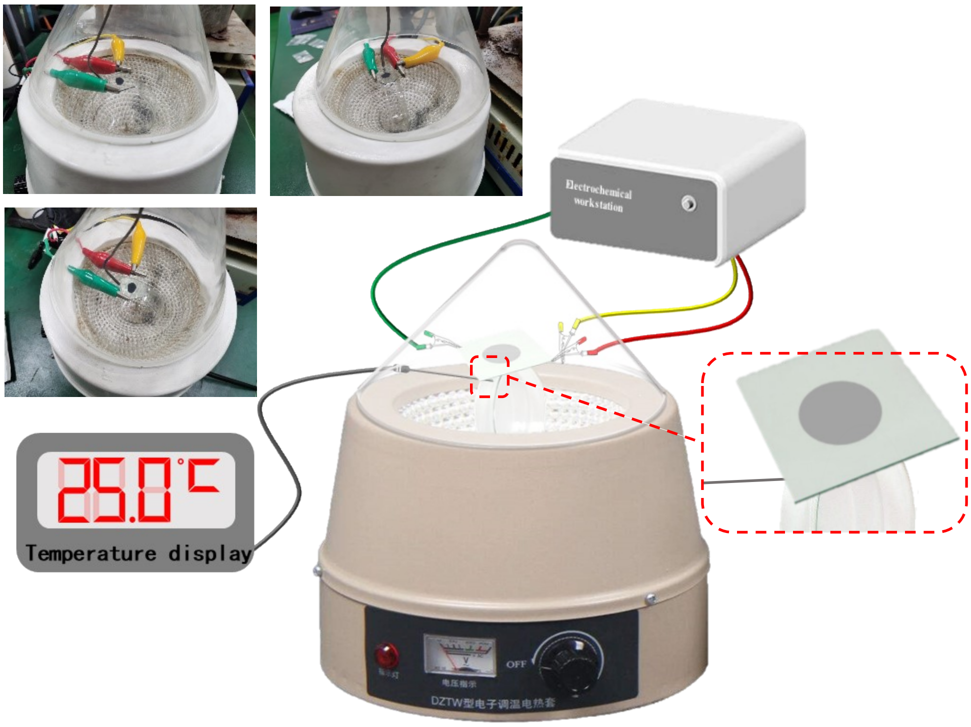
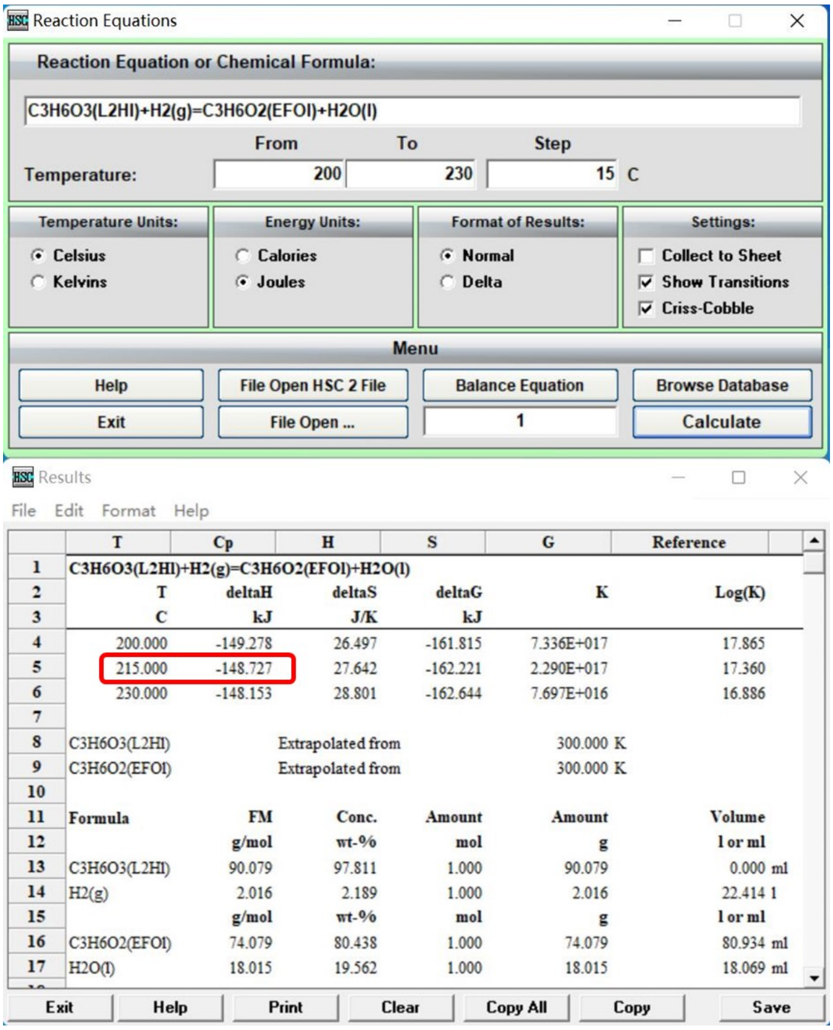


Fig. S3. The experimental setup for detecting the thermoelectric flow

The thermoelectric flow experimental setup is shown in Fig. S3, where the catalyst is uniformly coated on high temperature resistant Fluorine Doped Tin Oxide glass (FTO) (10*10 mm) with a load of about 0.1 mg/cm^2. The FTO (with/without catalyst) is placed on the insulating support, and then placed a furnace with a controllable temperature. In order to avoid heat dissipation and errors caused by the environment, the additional layer of insulation glass is placed outside the FTO. The thermocouple is close to the insulation support, not touching the FTO, to avoid its impact. The current response (short-circuit current-time) was monitored at 25°C, 50°C and 80°C, respectively. In order to exclude current change caused by external energy, the voltage value is set to 0 mV during the whole process of measuring short-circuit current-time. The current response under this condition is the hot electron flow generated by the material itself. The experimental temperature error was less than 1°C within a measurement time of 180 seconds.



Reaction Equation or Chemical Formula:
C3H6O3(L2HI)+H2(g)=C3H6O2(EFOI)+H2O(l)

Temperature: From 200 To 230 Step 15 C

Temperature Units: ● Celsius ○ Kelvins

Energy Units: ○ Calories ● Joules

Format of Results: ● Normal ○ Delta

Settings: ☐ Collect to Sheet ☑ Show Transitions ☑ Criss-Cobble

1

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        T           Cp          H           S           G               Reference
1   C3H6O3(L2HI)+H2(g)=C3H6O2(EFOI)+H2O(l)
2             T      deltaH      deltaS      deltaG            K              Log(K)
3             C          kJ         J/K          kJ
4       200.000    -149.278      26.497    -161.815    7.336E+017             17.865
5       215.000    -148.727      27.642    -162.221    2.290E+017             17.360
6       230.000    -148.153      28.801    -162.644    7.697E+016             16.886
7
8   C3H6O3(L2HI)            Extrapolated from          300.000 K
9   C3H6O2(EFOI)            Extrapolated from          300.000 K
10
11  Formula             FM       Conc.      Amount      Amount              Volume
12                   g/mol        wt-%         mol           g              l or ml
13  C3H6O3(L2HI)    90.079      97.811       1.000      90.079            0.000 ml
14  H2(g)            2.016       2.189       1.000       2.016            22.414 l
15                   g/mol        wt-%         mol           g              l or ml
16  C3H6O2(EFOI)    74.079      80.438       1.000      74.079           80.934 ml
17  H2O(l)          18.015      19.562       1.000      18.015           18.069 ml
```

Fig. S4. HDO reaction enthalpy of HSC calculation

The enthalpy of reaction for the preparation of propionic acid by hydrodeoxygenation of LA at 215°C can be calculated by HSC software as ΔH=-148.727 kJ/mol. According to the conversion formula between electron volts (eV) and joule heat (kJ/mol):

$$1\ \text{eV}=W\times N_A=1.6\times10^{-19}\times6.02\times10^{23}\times10^{-3}=96.32\ \text{kJ/mol}$$

The formula W is an electron through the unit volt electric field after the acceleration of the kinetic energy obtained, its value is about 1.6×10^{-19} J. N_A is the number of basic units (such as molecules or atoms) contained in 1 mol of a substance and has a value of about 6.02×10^{23}. The conversion gives the reaction enthalpy of LA hydrodeoxygenation to prepare propionic acid as ΔH = -148.727 kJ/mol = -1.55 eV.

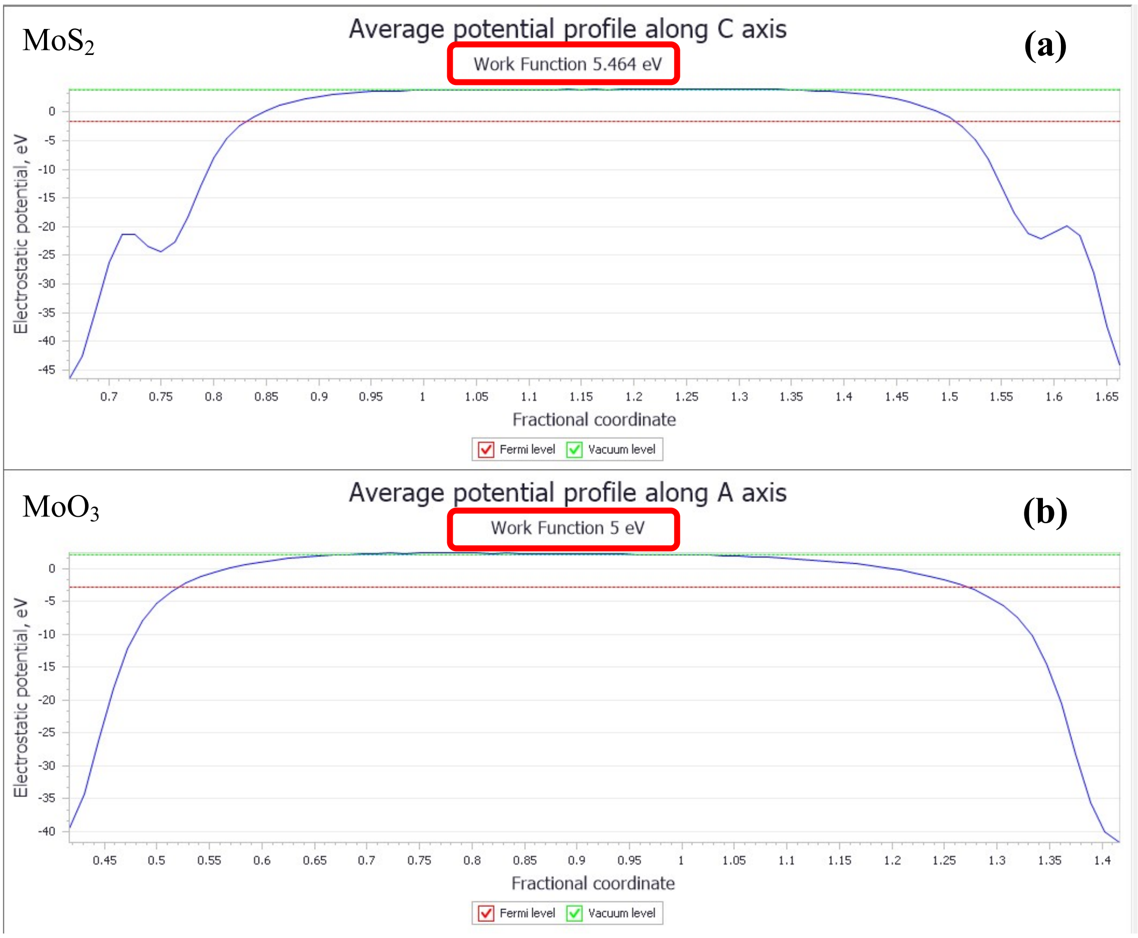


Fig. S5. Calculations of the work function for (a) MoS$_2$ and (b) MoO$_3$.

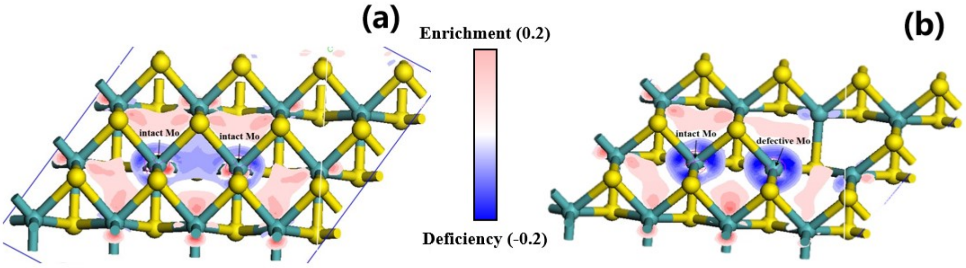


Fig. S6. (a) Charge density of Mo on intact MoS$_2$ and (b) defective MoS$_2$ (S Vacancy). Electron deficiency is shown in blue and electron enrichment is shown in red.

3. Table S1-S4

Table S1. Conversion and selectivity over each catalyst at different reaction times.

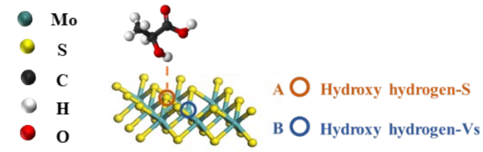
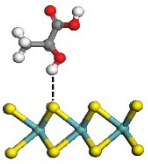
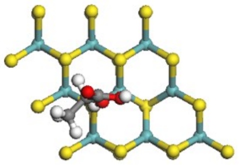
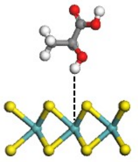
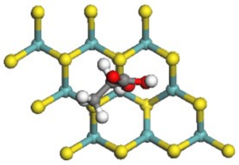
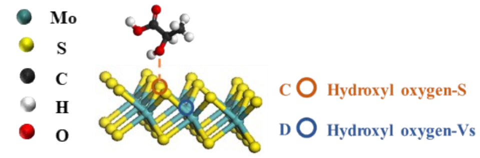
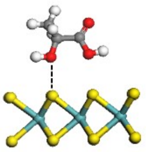
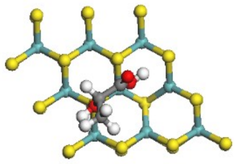
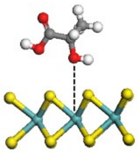
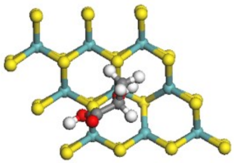
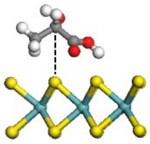
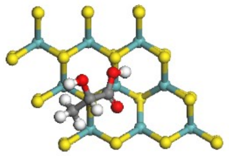
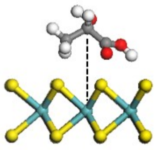
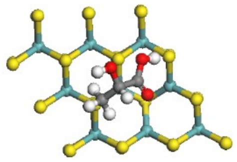
Catalyst	Reaction time/h	Conv. of LA/%	Sel. /%				
			PA	NP	AD	AA	Others
MoS_2/MoO_3	0.5	32.1	82.1	1.4	7.0	1.2	8.3
MoO_3	1	18.9	70.0	1.1	16.3	1.1	11.4
MoS_2/MoO_3		56.2	82.6	1.1	4.4	0.7	11.3
blank	2	3.84	69.6	4.7	21.3	2.6	1.8
MoS_2/MoO_3		74.9	85.8	2.0	3.8	0.8	7.5
MoS_2		16.3	85.7	2.6	8.0	1.0	2.6
MoO_3		31.2	69.4	1.2	15.0	1.0	13.4
MoS_2-MoO_3		22.4	75.2	1.3	11.4	1.0	11.1
MoS_2/MoO_3	2.5	82.0	86.2	2.9	3.7	0.8	6.3
blank	4	6.8	72	4.3	20.6	2.3	0.8
MoS_2/MoO_3		83.3	87.0	2.3	5.0	1.1	4.6
MoS_2		25.4	85.7	2.3	7.8	1.2	3
MoO_3		49.7	61.9	1.8	16.6	1.0	18.7
MoS_2-MoO_3		35.3	73.7	1.8	11.9	0.8	11.8
blank	6	11.04	75.1	4	17.4	2.1	1.4
MoS_2/MoO_3		84.4	87.2	3.0	5.3	1.1	3.4
MoS_2		35.8	85.3	1.6	6.7	0.9	5.5
MoO_3		63.6	59.8	0.9	11.5	0.8	27.0
MoS_2-MoO_3		48.1	68.8	1.8	12.1	1.0	16.3
blank	8	15.3	77.5	3.9	16.2	1.9	0.5
MoS_2/MoO_3		86.3	87.1	3.1	4.8	1.0	4.0
MoS_2		47.5	84.4	1.5	6.0	1.0	7.1
MoO_3		73.2	57.7	3.1	12.0	0.8	26.3
MoS_2-MoO_3		61.0	65.0	2.1	13.1	0.9	18.9

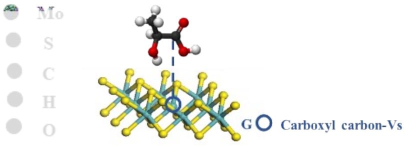
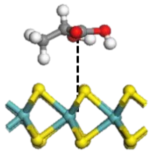
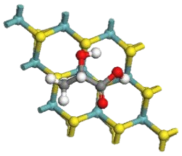
blank	10	18.26	80.1	3.6	14.5	1.3	0.5
MoS_2/MoO_3		89.2	88.0	4.1	3.2	1.1	3.6
MoS_2		55.7	83.0	1.2	4.1	0.8	10.9
MoO_3		75.8	56.5	2.9	12.0	1.0	27.4
MoS_2-MoO_3		67.4	60.3	2.3	14.1	1.1	22.2
blank	12	20.71	81.8	3.1	13.9	1.1	0.1
MoS_2/MoO_3		90.4	88.4	4.9	4.9	1.4	0.4
MoS_2		59.1	81.4	0.9	3.8	0.7	13.3
MoO_3		86.2	55.1	2.4	13.1	0.7	28.7
MoS_2-MoO_3		69.1	57.2	2.4	15.2	0.8	24.3

Reaction conditions: catalyst, 0.5 g; H_2 initial pressure, 3 MPa; LA feedstock, 20 g (10% wt); reaction temperature, 215 °C. PA, propionic acid; NP, n-propanol; AD, acetaldehyde; AA, acrylic acid.

Table S2. Adsorption energy of LA on MoS_2

Interactions of LA with MoS_2 surface

Binding Configuration	**Side View**	**Top View**
 		
A		
B		
 		
C		
D		
 		
E		
F		

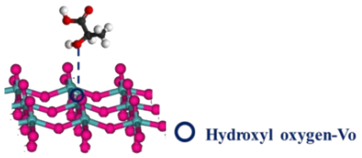
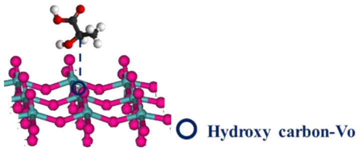
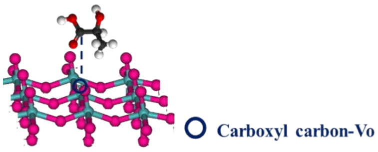
		
G		

LA binding configuration	Energy (eV)	Adsorption Energy (eV) *
A	-256.43	-0.58
B	-238.35	17.49
C	-251.10	4.74
D	-249.44	6.40
E	-251.10	4.74
F	-256.68	-0.84
G	-253.41	2.44

* Adsorption energy calculation formula, $E_{ads}=E_{total} - E_{surf} - E_{adsorbate}$, the energy of lactic acid adsorbed on MoS_2; Exothermic binding is indicated by a negative value for the adsorption energy.

Table S3. Adsorption energy of LA on MoO_3

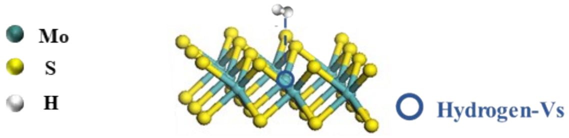
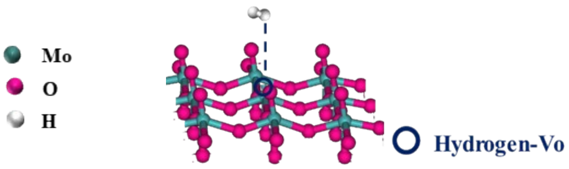
Interactions of LA with MoO_3 surface

LA binding configuration	**Energy (eV)**	**Adsorption Energy (eV) ***
	-309.06	0.19
● **Mo** ● **O** $_{MoO_3}$ ● **C** ● **H** ● **O LA** 	-309.58	-0.33
	-309.85	-0.60

* Adsorption energy calculation formula, $E_{ads}=E_{total} - E_{surf} - E_{adsorbate}$, the energy of lactic acid adsorbed on MoO_3; Exothermic binding is indicated by a negative value for the adsorption energy.

Table S4. Adsorption energy of H_2 on MoS_2 or MoO_3

Interactions of H_2 with MoS_2 or MoO_3 surface

H_2 binding configuration	**Energy (eV)**	**Adsorption Energy (eV) ***
	-30.40	-0.10
	-37.23	-0.12

* Adsorption energy calculation formula, $E_{ads}=E_{total} - E_{surf} - E_{adsorbate}$, the energy of H_2 adsorbed on MoS_2 or MoO_3; Exothermic binding is indicated by a negative value for the adsorption energy.