
Supplementary Information

Sustainable production of pyruvic acid: Oxidative dehydrogenation of lactic acid over the FeMoO/P catalyst

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Supplementary Materials & Methods

Materials

L-(+)-Lactic acid (80 wt% and 98.5 wt%, fermentation type with maize) was obtained from Henan Jindan Lactic Acid Technology Co., Ltd, and the former (80 wt%) was directly used for oxidative dehydrogenation of LA to pyruvic acid without further purification, and the later (98.5 wt%) was used as a standard reference sample. Pyruvic acid, acetaldehyde, acetone, acrylic acid, and isopropanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Acetaldehyde, acetone, and acrylic acid were used for gas chromatograph reference samples, and isobutyl alcohol was used as an internal standard sample. Pyruvic acid was used for standard reference sample in analysis with liquid chromatograph. Ferric nitrate, ammonium phosphomolybdate and urean were purchased from Energy Chemical Company, being used for preparation of catalysts.

Preparation of catalysts

Fe-Mo bimetallic oxide catalysts decorated by P element (denoted as FeMoO/P) as well as corresponding single metallic oxides (FeO/MoO) were synthesized with hydrothermal method under alkaline condition, followed by calcination in air. In a typical experiment to prepare FeMoO/P, 8 mmol of Fe(NO₃)₃·9H₂O, 1.33 mmol of ammonium phosphomolybdate ((NH₄)₃PMo₁₂O₄₀·H₂O) and 36 mmol of CO(NH₂)₂ were dissolved in 60 mL of distilled water and stirred at room temperature for 20 min. Next, the resultant solution was transferred to 100 mL of PTFE-lined stainless steel hydrothermal reactor, placed in an oven, and kept at 120 °C for 8 h.

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Then the precipitate was formed, and washed several times with distilled water and absolute ethanol, and dried at 50°C for 3 h. Besides corresponding single metallic oxides such as FeO and MoO were prepared in a similar manner. Prior to use for catalyzing oxidative dehydrogenation of LA and catalyst characterization, all catalysts were calcined at 500 °C for 3 hours in air. In addition, the mixed catalyst (denoted as FeMoO/P*) was prepared by direct mixture using two corresponding single metallic oxides (FeO and MoO).

Catalyst characterization

The specific surface areas of catalysts were measured through nitrogen adsorption at 77 K using JW-BK100C instrument. Prior to adsorption, the samples were treated at 250 °C under vacuum for 6 h and the specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) method. Pore size of catalysts is calculated from desorption branch data on the Barrett-Joyner-Halenda (BJH) model. Powder X-ray diffraction measurement was conducted on a Dmax/Ultima IV diffractometer operated at 40 kV and 20 mA with Cu-K α radiation. The FTIR spectra of the catalysts were recorded in the range of 500~4000 cm⁻¹ on a FTIR-8400S spectrometer. Diffuse reflectance UV-Vis spectra were recorded on a Shimadzu UV-2401 PC spectrometer in a diffuse-reflectance mode using an integrating sphere (internal diameter 60 mm) and BaSO₄ was used as the reference. Redox properties of the samples were estimated by H₂-TPR on a Finesorb-3010 Instrument. The sample (ca. 50~60 mg) was purged with dry Ar (50 mL/min, purity > 99.999 v_i%) at 300 °C for 1.0 h, followed by reducing the furnace temperature to 50 °C, and switching to a flow of 10.0 v_i% H₂/Ar to execute H₂-TPR in the range of 50~800°C at a rate of 10 °C/min. 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. Spectra were obtained using an aluminum anode (Al K α = 1486.6 eV) operating at 72 W and a spot size of 400 μ m. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The background pressure was 2 \times 10⁻⁹ mbar and during measurement 3 \times 10⁻⁷ mbar Argon because of the charge compensation dual beam source. Data analysis was performed using CasaXPS software. The binding energy was corrected for surface charging by taking the C 1s peak of contaminant carbon as a reference at 284.6 eV. Surface acid and base properties of the samples were estimated by NH₃-TPD and CO₂-TPD, respectively, on a Finesorb-3010 Instrument. The

sample (ca. 50-60 mg) was purged with dry He (50 mL/min, purity > 99.999 v/v%) at 300 °C for 1.0 h, followed by reducing the furnace temperature to room temperature, and switching to a flow of 8 v/v% NH₃/He or 10 v/v% CO₂/He for 1 h to execute NH₃ or CO₂ adsorption. Next, the samples were swept by dry He (50 mL/min, purity > 99.999 v/v%) at 80 °C for 1.0 h to remove the dissociative NH₃ or CO₂ on the surface of samples. Then, NH₃ or CO₂ chemically adsorbed on the sample was desorbed in the range of 80-650°C at a rate of 10 °C/min. Besides, isopropanol dehydration/dehydrogenation on catalyst to form corresponding propylene /acetone at reaction temperature of 240°C was used to characterize acidic-basic properties of catalyst.

Catalyst evaluation

The vapor phase oxidative dehydrogenation of LA to pyruvic acid was performed with a continuous up-down fixed-bed quartz tubular reactor (4 mm inner diameter) under atmospheric pressure. The catalyst (ca. 0.35 g, 20-40 meshes) was placed between two layers of quartz wools inside reactor. Firstly, the catalyst was heated from room temperature to 230 °C at a rate of 3°C/min, and kept at the temperature for 1.0 h by following air (3.0 mL/min). Then the feedstock (10 wt% aqueous solution of LA, 2.0 mL/h) was pumped into the reactor and driven through the catalyst bed by air (0.1 MPa, 3.0 mL/min). The contact time of reactant over the catalyst was around 0.30 s, and the contact time was estimated according to equation (1) reported by previous references^{1,2}. The liquid products were condensed using ice-water bath and analyzed off-line using a SP-6890 gas chromatograph with a FFAP capillary column connected to a FID for acrylic acid and acetaldehyde, and LC-20AD liquid chromatograph with a reversed-phase C18 column connected to a UV detector for lactic acid and PA. GC-MS analyses of the samples were performed using Agilent 5973N Mass Selective Detector attachment. The reaction tail gas was analyzed using GC with a packed column of 5A connected to TCD detector. The conversion of LA and the product selectivity were calculated according to equations (2) and (3).

$$t_c = \frac{3600 \times 273.15 \times V_{\text{cat}}}{22400 \times (n_{\text{LA}} + n_{\text{H}_2\text{O}} + n_{\text{C}}) \times T} \text{-----(1)}$$

Where t_c is contact time (s), V_{cat} is catalyst volume (mL), n_{LA} is the moles of lactic acid passed per hour, $n_{\text{H}_2\text{O}}$ is the moles of water in lactic acid aqueous solution feed passed per hour, n_{C} is the moles of carrier gas (air) passed per hour and T is reaction temperature (K).

$$\text{Conversion (\%)} = \frac{n_0 - n_1}{n_0} \times 100 \text{ -----(2)}, \text{ Selectivity (\%)} = \frac{n_p}{n_0 - n_1} \times 100 \text{ -----(3)}$$

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 PA or other byproducts such as acetaldehyde and acrylic acid.

Area-specific catalytic rate was defined as previous references reported^{3, 4}, and was determined with equations (4) and (5).

$$\text{LA consumption rate} = \frac{\text{amount of LA consumed per hour in the reactor (mmol/h)}}{\text{surface area of catalyst in the reactor (m}^2\text{)}} \text{ -----(4)}$$

$$\text{PA formation rate} = \frac{\text{amount of PA formed per hour in the reactor (mmol/h)}}{\text{surface area of catalyst in the reactor (m}^2\text{)}} \text{ -----(5)}$$

Supplementary Results and discussion

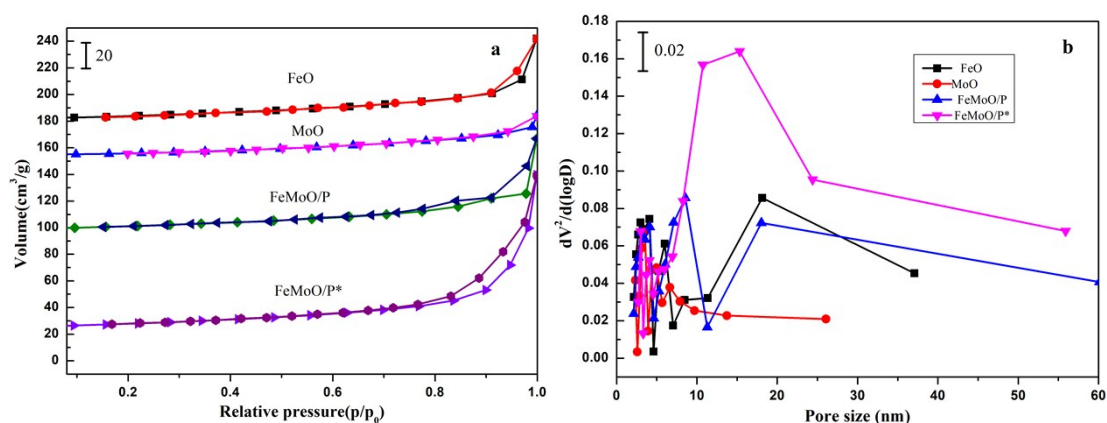


Fig.S1 Nitrogen adsorption and desorption isotherms of different catalysts (a) and their corresponding pore size distributions (b)

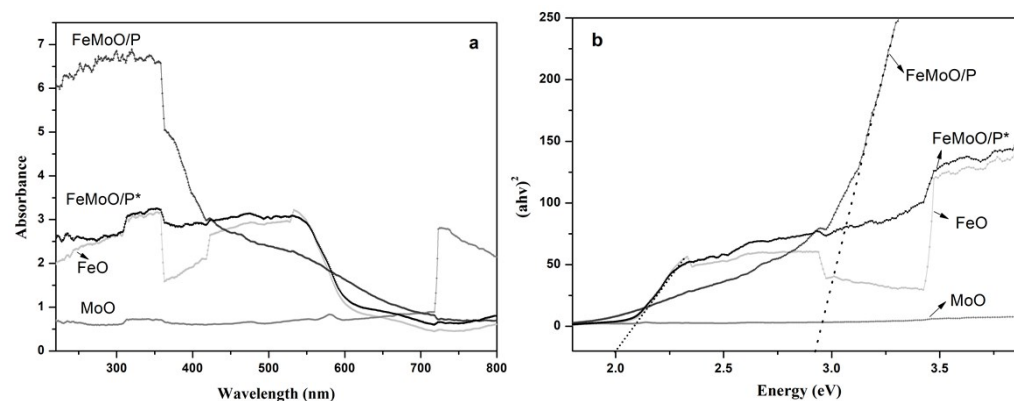


Fig. S2 UV-Vis absorption spectra (a) and corresponding Tauc plots for fresh samples before

reaction

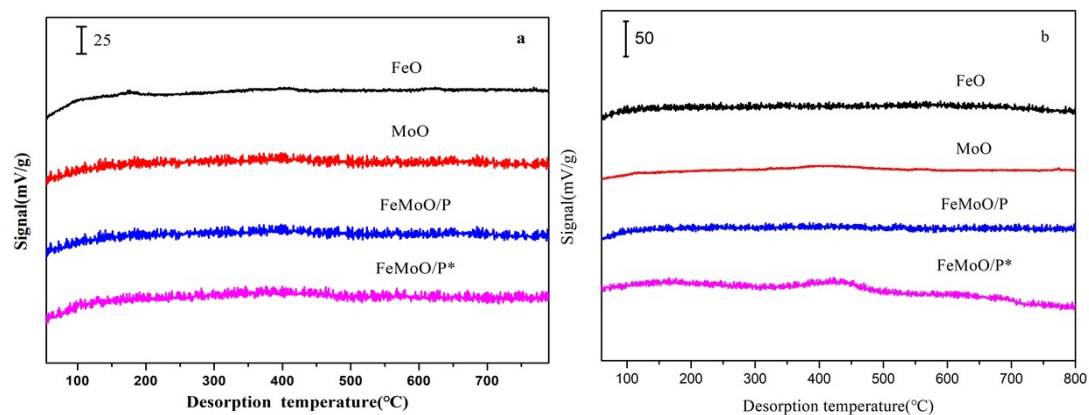


Fig. S3 NH_3 -TPD profiles of fresh samples before reaction (a) and their corresponding CO_2 -TPD profiles (b)

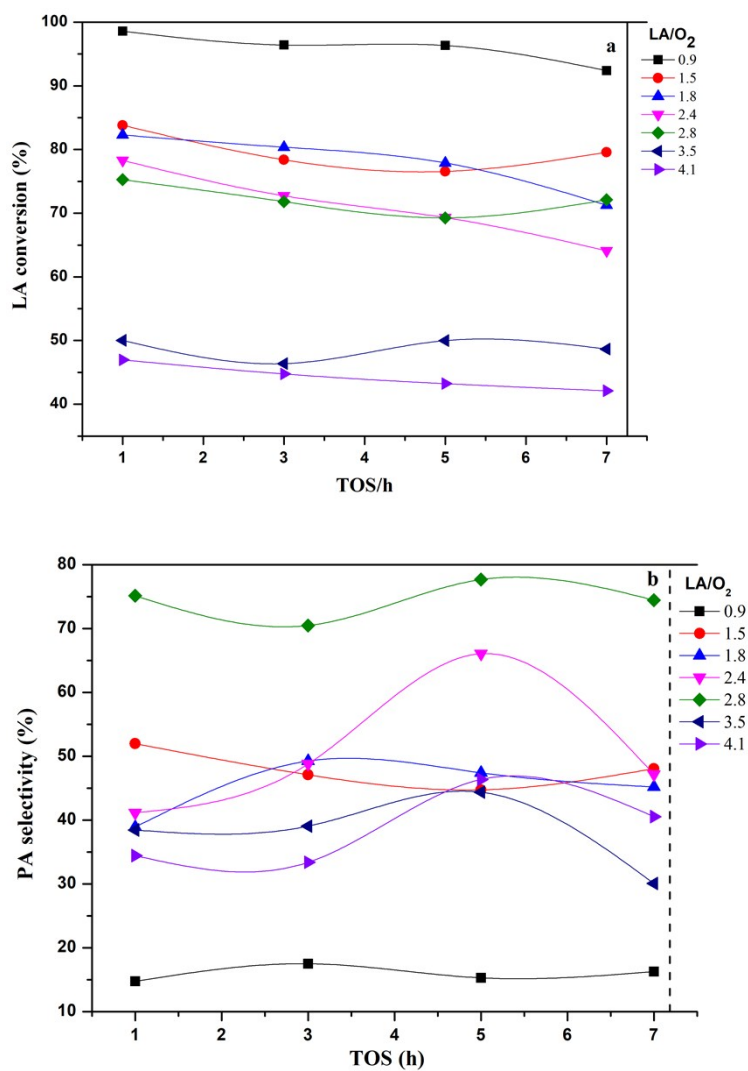


Fig. S4 Effect of LA/ O_2 molar ratios on LA conversion and PA selectivity

Conditions: Catalyst, FeMoO/P, 0.38mL, 0.37g; reaction temperature, 230°C; particle size, 20-40meshes; carrier gas air, 3.0 mL/min; LA feedstock, LA 10wt% in water; LA, lactic acid; PA, pyruvic acid.

Table S1 Oxygen content of catalyst obtained from XPS characterizations

catalyst	Oxygen content (atomic %)
FeO	46.51
MoO	48.21
FeMoO/P	50.47

Table S2 Blank experiment

Catalyst	LA Conv.(%)	Sel.(%)			
		PA	AD	AA	others
Blank	28.9	1.2	5.1	3.9	89.8

Reaction temperature, 230°C; particle size, 20-40 meshes; air, 3.0mL/min; feed flow rate, 2.0 mL/h; LA feedstock, LA 10wt% in water; TOS, 1-7 h. LA, lactic acid; PA, pyruvic acid; AD, acetaldehyde; AA, acrylic acid.

References

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