

Supplementary Information

B-sites Modification of $\text{LaMn}_{0.9}\text{Co}_{0.1}\text{O}_3$ Perovskite Using Selective Dissolution Method in C_3H_6 Oxidation

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1. Experimental

The sol-gel method was used to prepare LaMnO₃ perovskite for comparison. La(NO₃)₃·6H₂O, Mn(NO₃)₃·4H₂O, Co(NO₃)₂·6H₂O and anhydrous citric acid were weighted at mass ratio of 1.0:0.9:0.1 and dissolved in deionized water. Then the solution was kept at 90 °C for 2 h with stirring until the formation of gel, afterwards the formed gel was dried and foamed at 110 °C overnight. Subsequently, the obtained sample was ground and transferred into a crucible and placed in a muffle furnace at 1 °C/min from room temperature to 200 °C for 1 h. Then, the temperature was continuously increased to 750 °C for 2 h at a heating rate of 5 °C/min. At last, a black powdery LaMnCoO₃ perovskite material was obtained. After that, the sample was immersed in 10% HNO₃ for 12 h for etching. After acid treatment, the pH value was neutralized by centrifugation and dried. The samples were named LaMnCoO₃ and LaMnCoO₃-H, respectively.

2. Catalytic activity test and characterization

In the C₃H₆ oxidation experiment, 50 mg catalyst (40-60 mesh) was used. The typical reaction feed gas contained 1000 ppm C₃H₆, 10% O₂ and N₂ as the balance gas (200 mL min⁻¹). The gas hourly space velocity (GHSV) was approximately 240,000 cm³ g⁻¹ h⁻¹. The reaction temperature was increased from 20 °C to 270 °C. The concentrations of CO and CO₂ in the inlet and outlet streams was continually monitored by a FTIR spectrometer (MKS6030HS).

Where [C₃H₆]_{in} and [C₃H₆]_{out} were the concentration of Propylene in and out gas, respectively.

$$X_{C_3H_6}(\%) = 100 \times \frac{[C_3H_6]_{in} - [C_3H_6]_{out}}{[C_3H_6]_{in}} \quad \text{Equation S1}$$

S1

In order to determine the activation energy of the catalyst, this study controlled the conversion rate of C₃H₆ to be less than 20% by reducing the amount of catalyst during the measurement. The reaction rate constant was calculated by Equation S1:

$$k = -\frac{F}{m} \times \ln(1 - x) \quad \text{Equation S2}$$

In the formula, k represents the reaction rate constant ($\mu\text{mol g}^{-1}\text{s}^{-1}$), F represents the gas flow rate ($\mu\text{mol/s}$), m represents the amount of catalyst used in the test (g), and x represents the conversion rate of C_3H_6 . Calculate the reaction rate constant k according to the above formula, and then use the Arrhenius formula (see Equation S1-2) to perform scatter fitting to obtain the Arrhenius line graph,

$$\ln k = -\frac{E_a}{RT} + \ln A \quad \text{Equation S3}$$

With $1000/T$ as the horizontal coordinate and $\ln k$ as the vertical coordinate, the slope is expressed as the E_a of apparent activation energy.

XRD was performed on a powder X-ray diffractometer (Rigaku, SmartLab 9 kW, Japan) with Cu K α radiation. The scanning angles are fixed at 10 to 80 ° and the scan speed is 8 °/min.

Analyses of the element content were performed by inductively coupled plasma spectroscopy (ICP) on a Thermo Fisher Scientific iCAP-7000 spectrometer.

The N_2 adsorption-desorption isotherms were measured at a liquid nitrogen temperature by a micromeritics ASAP 2460 instrument in the static mode. Before the measurement, the catalysts were degassed at 350 °C for 4 h. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) equation. The pore volumes and average pore diameters were determined using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the N_2 adsorption isotherm.

Morphology of the as-prepared samples was observed by scanning electron microscopy (SEM) using a JSM7900F microscope at an accelerating voltage of 5 kV.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Fisher Scientific EscaLab 250Xi instrument. Catalyst charging during the measurements was compensated by an electron flood gun.

H_2 -TPR and O_2 -TPD experiments were performed on a chemisorption analyzer (Micromeritics, AutoChem 2920 ThermoStar). During H_2 -TPR, the catalyst in the quartz

reactor was pretreated at 350 °C in He for 1 h and cooled to 50 °C. Then, the temperature was increased to 900 °C with a feeding mixture of 10% H₂/He (50 mL min⁻¹) at a rate of 10 °C/min. The consumption of H₂ was continuously recorded. For the O₂-TPD analysis, 20 mg of freshly prepared sample was loaded into a quartz U-shaped reactor. The sample was initially treated with He at a flow rate of 30 mL/min to 150 °C (10 °C/min) for 30 min to remove moisture. And then cooled to 50 °C and pure O₂ was introduced to the sample, following by 30 mL/min He flushing. After 30 min equilibrium, the temperature ramped at ramp rate of 10 °C/min from room temperature to 900 °C. The variation in O₂ concentration from the cell effluent was monitored on-line by the TCD detector.

C₃H₆-TPD experiment was performed using a FTIR spectrometer (MKS, MultiGas 6030HS). First, the sample were pretreated at 300 °C in a N₂ flow (50 ml/min) for 1 h. Then, C₃H₆ (50 ml/min) was absorbed to sample for 1 h after cooling down to room temperature, followed by N₂ purging for 30 min. Finally, the temperature was increased to 800 °C (10 °C /min) under a N₂ flow.

3. Results and discussion

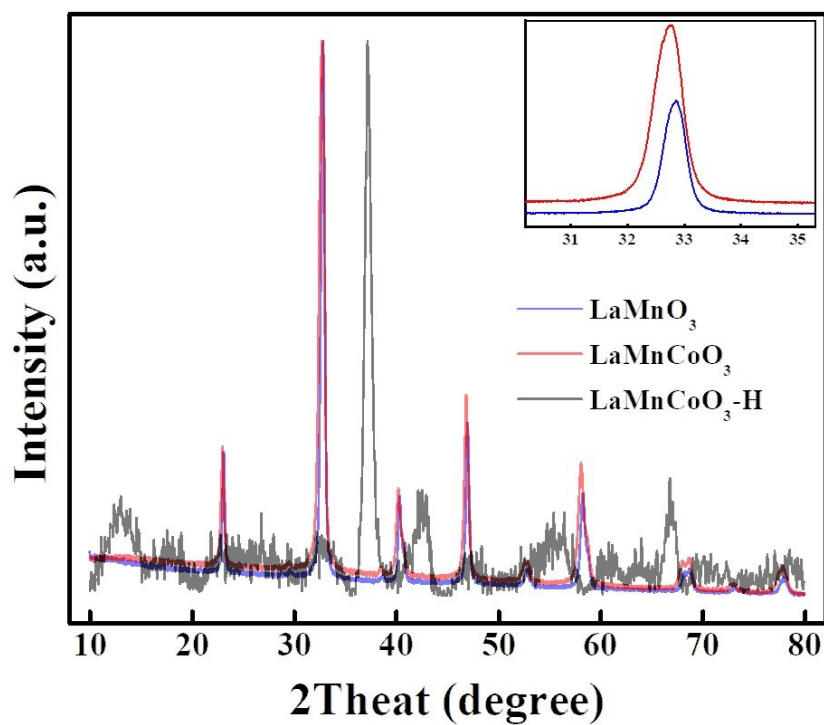


Fig. S1 X-ray diffraction pattern of LaMnO_3 , LaMnCoO_3 , and $\text{LaMnCoO}_3\text{-H}$ catalysts.

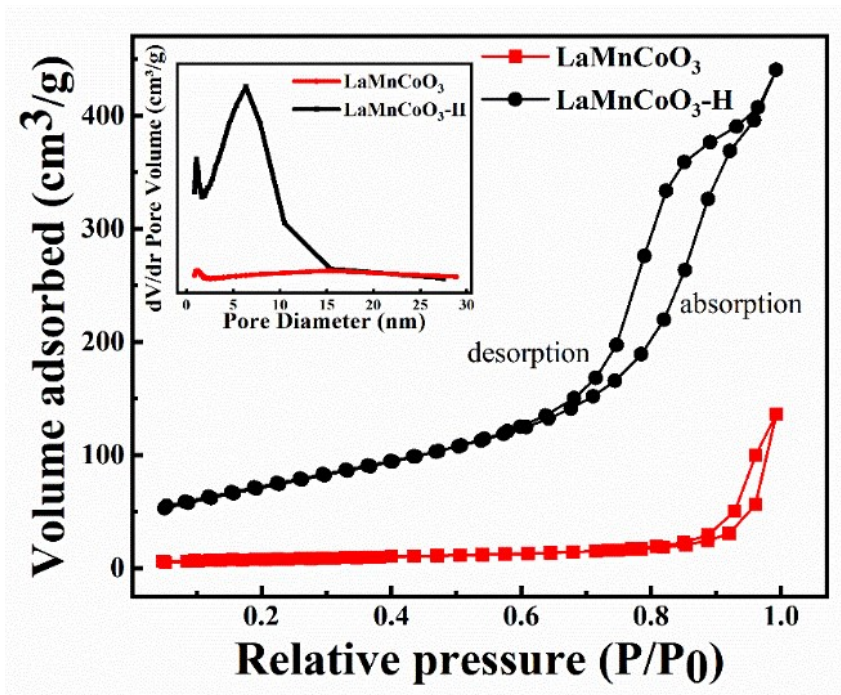


Fig. S2 N_2 adsorption-desorption isotherm and pore size distribution of $LaMnCoO_3$ and $LaMnCoO_3-H$ catalysts.

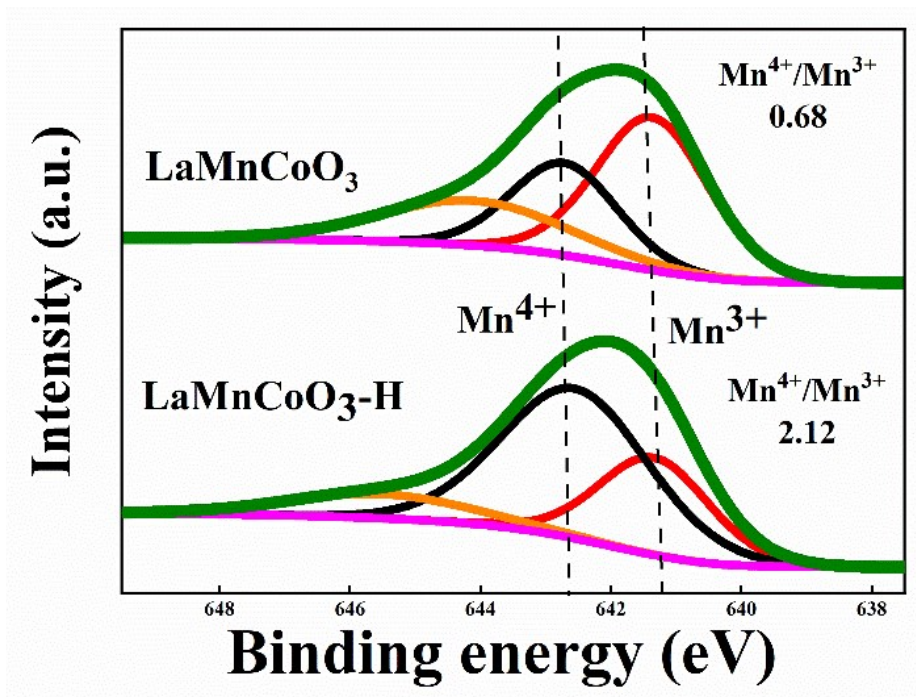


Fig. S3 Mn 2p XPS spectrum of LaMnCoO_3 and $\text{LaMnCoO}_3\text{-H}$ catalysts.