

Electronic Supplementary Material (ESI)

Revealing the intrinsic nature of Ni-, Mn-, and Y-doped CeO₂ catalysts with positive, additive, and negative effects for CO oxidation using *operando* DRIFTS-MS

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S1.1 Catalyst preparation

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S1. Supplementary information

SI.1 Catalyst preparation

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were purchased from Shanghai Macklin (China). $\text{Mn}(\text{NO}_3)_2$ was obtained from Aladdin (China). Those nitrates were used as the precursors of Ni, Y, Ce, and Mn, respectively.

The atomic ratio of dopants (Ni, Mn, or Y) to Ce (host) was 1:1 by controlling the amounts of cerium nitrate and dopant metal nitrate precursors. The obtained catalysts were named Ni-CeO₂, Mn-CeO₂, Y-CeO₂ respectively. NiO, Mn₂O₃, Y₂O₃, CeO₂, Ni-doped, Mn-doped, and Y-doped CeO₂ catalysts were prepared at decomposition temperature of 600 °C using the aerosol pyrolysis method.¹

SI.2 Catalyst characterization

The crystal form and crystallinity of the catalyst were determined by XRD (Rigaku Ultimate IV type, Rigaku, Japan) operated at 40 mA, 40 kV, 10~80°, and 5 °/min.

X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Thermo Fisher Scientific, USA) was used to measure element distribution and oxidation states on the catalyst surfaces under conditions: Al K α ray: $h\nu=1486.6$ eV, beam spot: 400 μm , chamber vacuum: better than 5.0E-7 mBar, working voltage: 12 kV, filament current: 6 mA.

A fully automatic specific surface and porosity analyzer (Micromeritics ASAP2460, Micromeritics, USA) was used to measure the specific surface areas, pore diameters, and pore volumes. All catalyst samples were dried at 150°C for 6 h, degassed at 300°C for 8 h. Brunauer-Emmett-Teller (BET) was used to calculate specific surface areas of the catalysts. The pore diameter and pore volume of the samples were determined using Barrett-Joyner-Halenda (BJH) calculation.

The surface morphologies of the catalysts were observed using a scanning electron microscope (SEM, Hitachi Regulus 8100, Hitachi, Japan) with a SE2 secondary electron detector. The lattice stripes and elements distribution on the catalyst surfaces were detected with a high-resolution electric field emission transmission electron microscope (HRTEM, FEITecnaif20, USA).

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS, Nicolet IS50, Thermo Scientific, USA) equipped with a temperature-programmed reaction (TPR) cell (HVC-DRP-5, Harrick, USA), narrow-band mercury cadmium telluride (MCT-A) detector with liquid nitrogen cooling in collecting DRIFTS spectra between 4000 and 650 cm^{-1} , and mass spectrometer (MS, Tilon LC-D200M, Ametek, USA) was used to monitor surface species on each catalyst and gas signals during CO oxidation.¹ The Kubelka-Munk function was used to convert the obtained spectra into absorption spectra.

S2. Figures

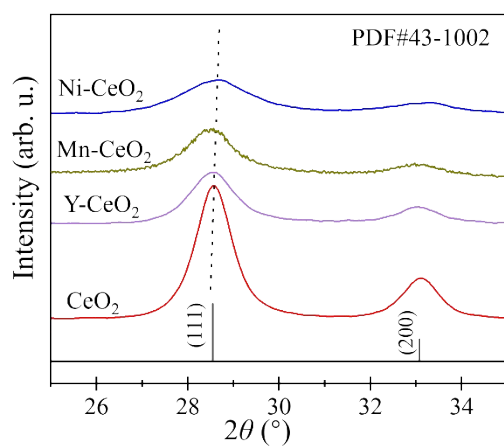


Fig. S1 XRD patterns.

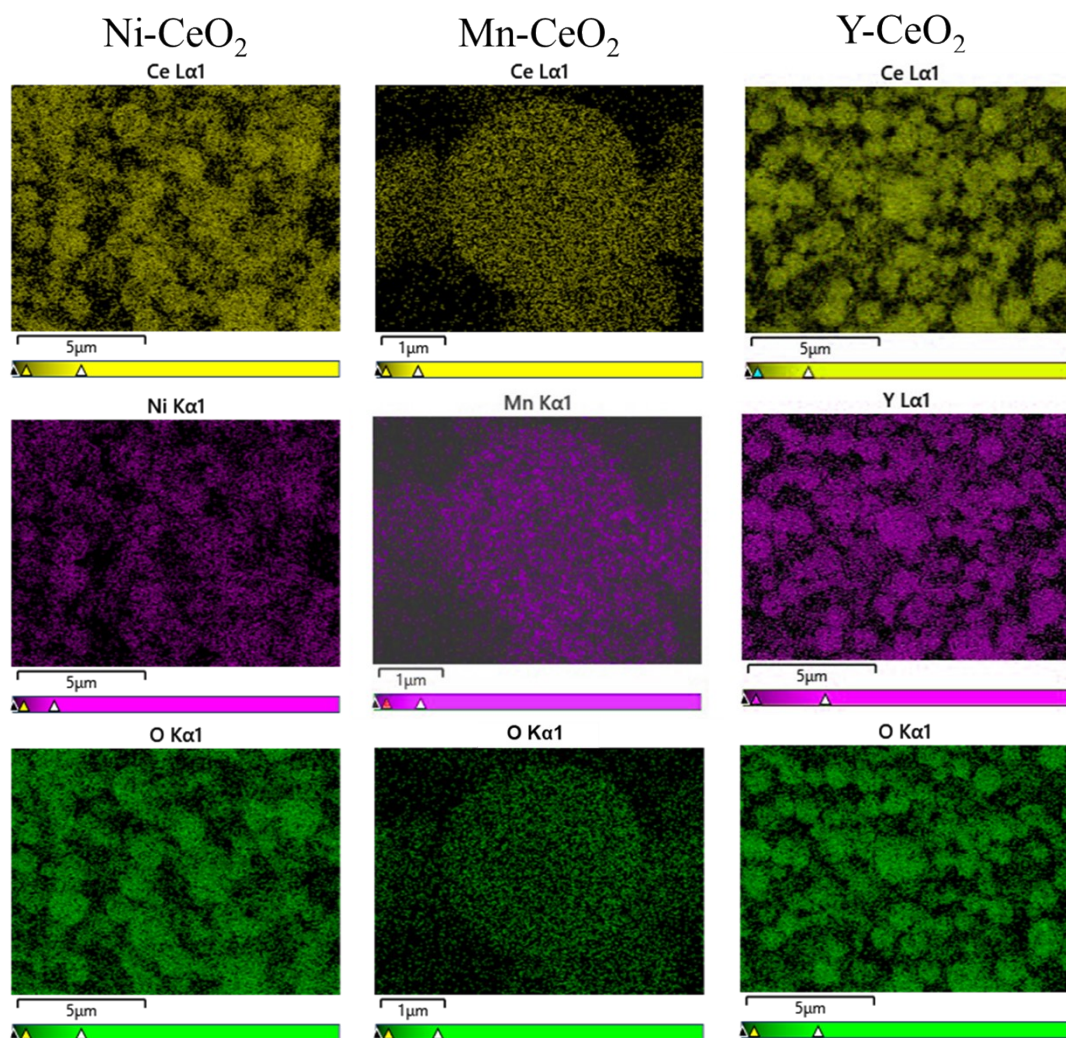


Fig. S2 EDS mapping images of Ni, Mn, and Y doped CeO₂ catalysts.

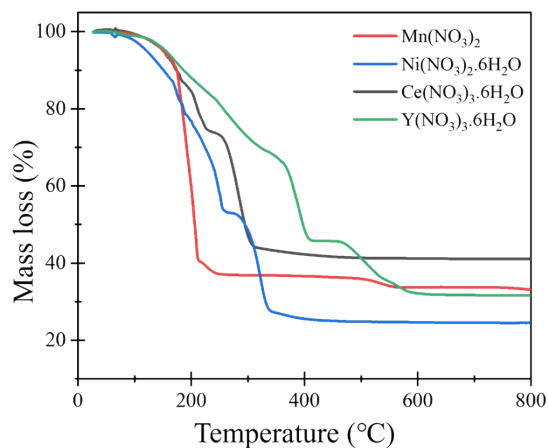


Fig. S3 TG profiles of different nitrate precursors.

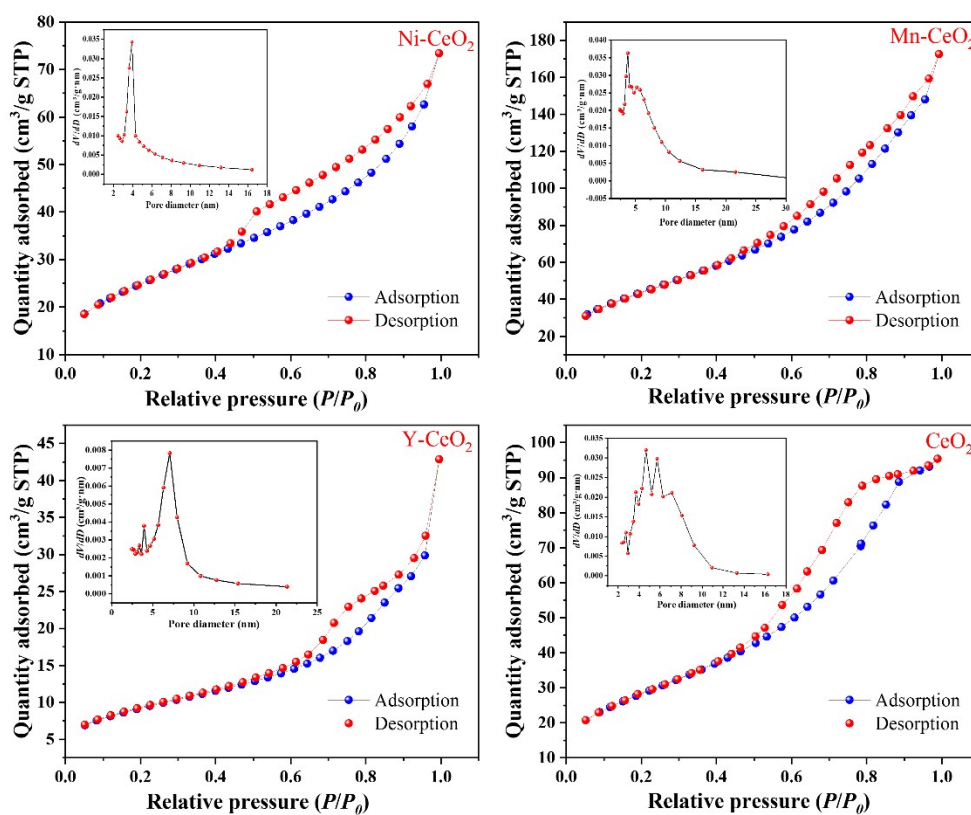


Fig. S4 N_2 adsorption/desorption isotherms of the catalysts (insert: BJH pore diameter distribution).

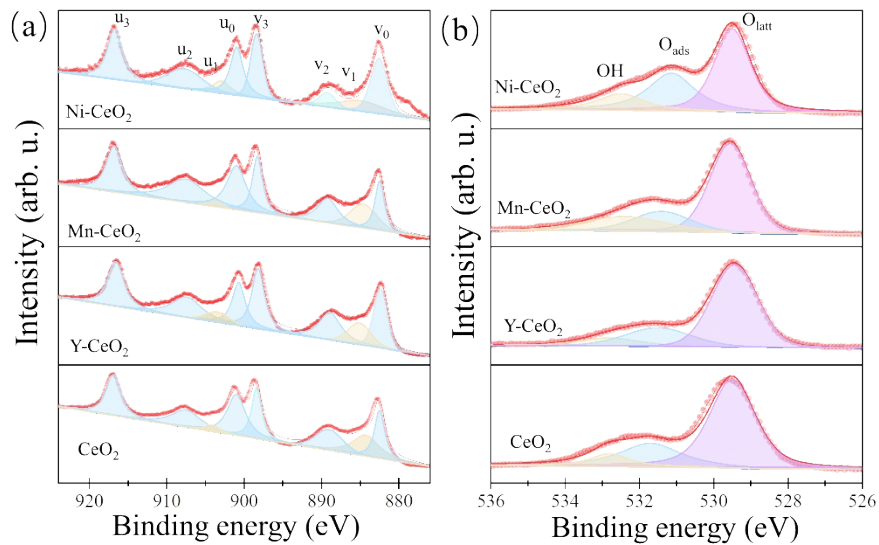


Fig. S5 XPS spectra of as-prepared catalysts: (a) Ce 3d and (b) O 1s.

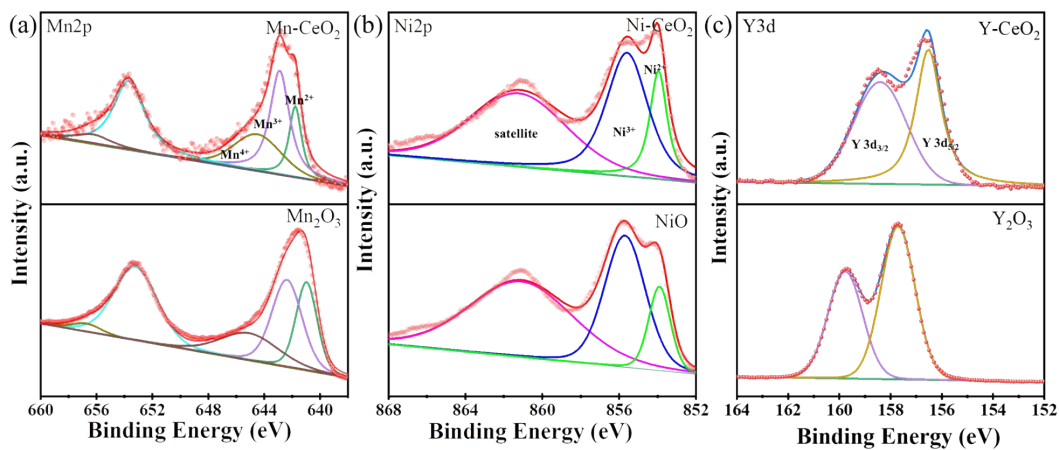


Fig. S6 XPS spectra of Mn2p, Ni2p, and Y3d.

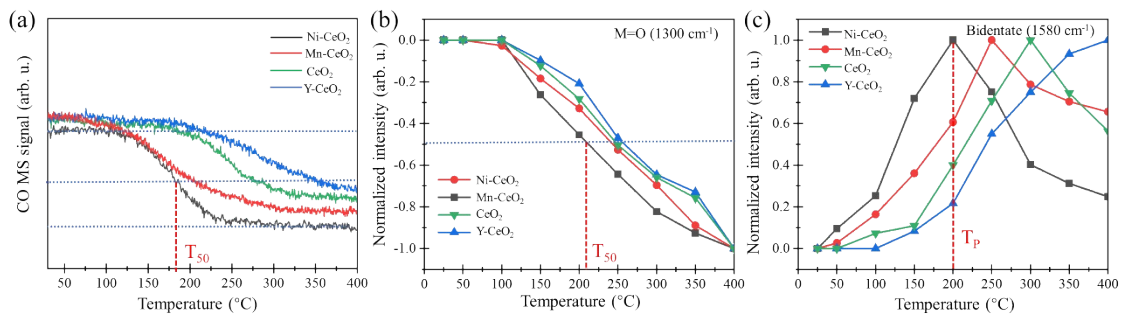


Fig. S7 (a) MS-CO intake T_{50} , (b) M=O consumption T_{50} , and (c) top temperature for bidentate carbonate accumulation (T_p).

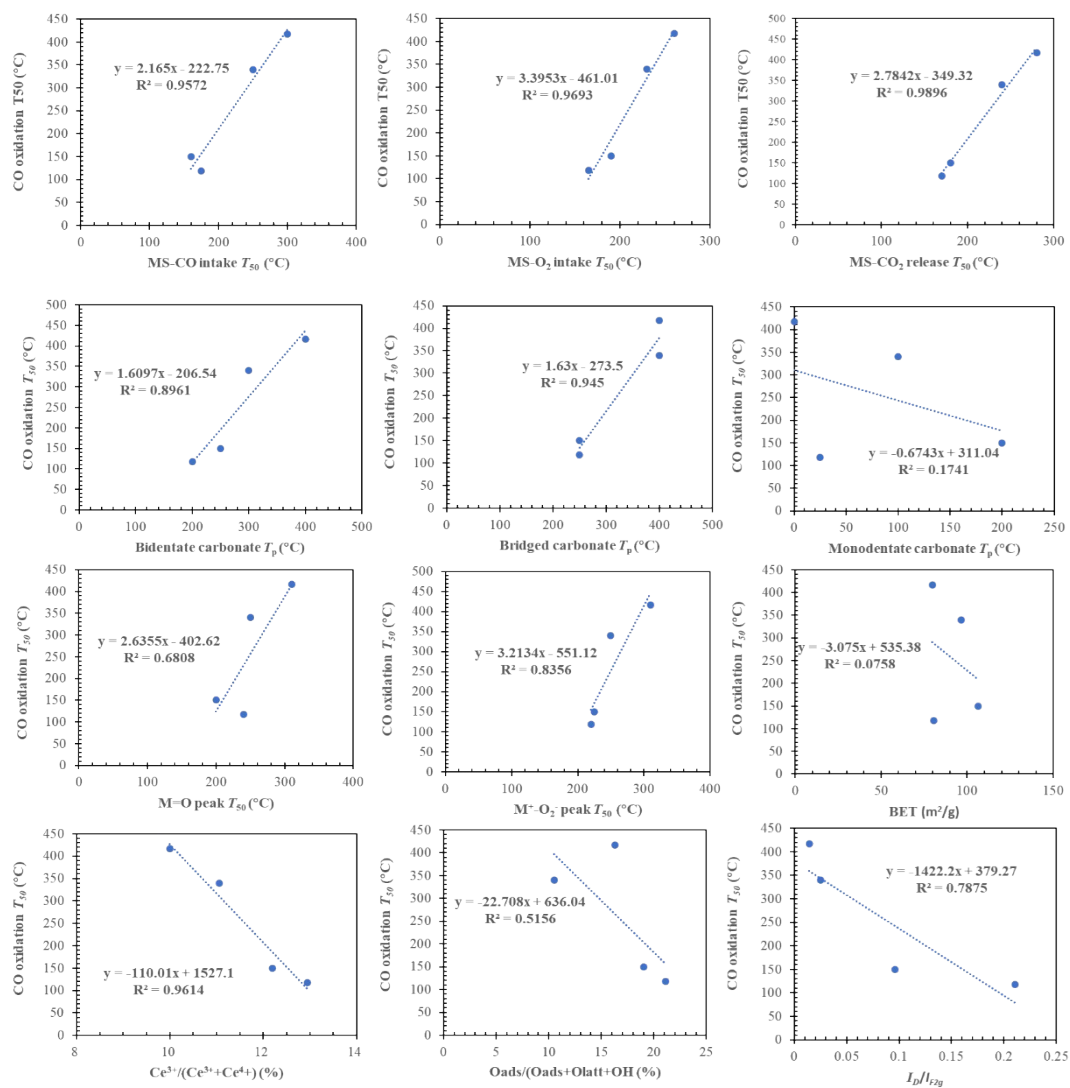


Fig. S8 Correlations of CO oxidation activity T_{50} and intrinsic, surface, structure factors of the catalysts.

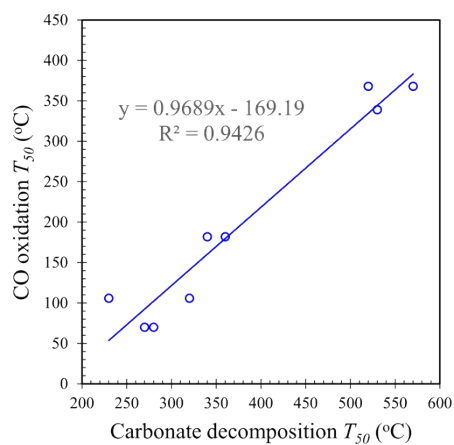


Fig. S9. Correlations of CO oxidation activity T_{50} and carbonate decomposition T_{50} (°C), data from Table S2.

S3. Tables

Table S1 Mn³⁺, Mn⁴⁺, and Ni³⁺ ratios

Catalyst	Mn ³⁺ /(Mn ²⁺ +Mn ³⁺ +Mn ⁴⁺) (%)	Mn ⁴⁺ /(Mn ²⁺ +Mn ³⁺ +Mn ⁴⁺) (%)	Ni ³⁺ /(Ni ²⁺ +Ni ³⁺) (%)
Mn-CeO ₂	47.3	32	
Mn ₂ O ₃	43.5	26.2	
Ni-CeO ₂			72
NiO			69.4

Table S2. Decomposition temperatures of different carbonates

Carbonate*	Carbonate decomposition T ₅₀ (°C)**	Catalyst	CO oxidation T ₅₀ (°C)***	Reference
NiC ₂ O ₄ ·2H ₂ O	340	NiO	182	2
CuCO ₃ ·H ₂ O	280	CuO	70	3
CuCO ₃	270	CuO	70	4
Ce(CO ₃)(OH)	530	CeO ₂	339	5
MnCO ₃	230	Mn ₂ O ₃	106	6
FeCO ₃	360	Fe ₂ O ₃	182	7
YOHCO ₃	570			
Y ₂ (CO ₃) ₃ ·2.5H ₂ O	520	Y ₂ O ₃	368	8

* Raw materials used to measure the decomposition features.

** The reported temperature at which 50% carbonate decomposed during thermogravimetry analysis.

*** Data obtained in this study.

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