

Supplementary Material for

Investigating the differences of active oxygen species and carbonate species on the surface of $\text{Ce}_{0.95}\text{M}(\text{M}=\text{Mn and Zr})_{0.05}\text{O}_{2-\delta}$ catalysts prepared by aerosol method during CO oxidation using *operando* TPR-DRIFTS-MS

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1. Experimental Section

1.1 Catalyst preparation

50 mL aqueous solution of cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$) and manganese nitrate ($\text{Mn}(\text{NO}_3)_2$) or zirconium nitrate pentahydrate ($\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$) were in a glass bottle (500 mL) equipped with an ultrasonic atomizer (ZP-01, Chenyang Electric, China). All nitrate were purchased from Shanghai Maclin Bio-Chemical Co., LTD., China. The mists mixed with N_2 gas (0.8 L/min) passed a heated tube (60 °C) and nitrate mists become nitrate aerosols, then entered the quartz tube ($12 \times 10 \times 320 \text{ mm}^3$) for high-temperature pyrolysis. An electric furnace (KSL-6D-11, Shandong Longkouxian) was used to control the pyrolysis temperature of the quartz tube (600 °C). The nitrate aerosols decomposed to solid oxide particles were collected using two-stage water adsorption. High speed centrifuge (10000 rpm, TG16-WS, China Liangyou Instrument Company) was used to separate solid oxide particles from water. The precipitate of solid oxide particles were washed three times with pure water and ethanol, and dried at 80 °C for 12 h.

1.2 Catalyst characterization

The X-ray diffraction (XRD) measurements are conducted using an AXS D8 instrument (Bruker, Japan) with the following parameters: 40 mA, 40 kV, test angle range of 5-120°, and a step length of 0.02° (with a minimum step length of 0.0001°).

The specific surface area and porosity of the catalysts are analyzed utilizing a specific surface and porosity analyzer (Autosorb-iQ2, Conta, USA). The specific surface area (S_{BET}) is determined through N_2 adsorption and calculated using the Brunauer-Emmett-Teller (BET) multipoint method. The pore diameter and pore volume are determined using Barrett-Joyner-Halenda (BJH) analysis to observe the morphology, mixing, and doping properties of the catalysts.

The catalyst structures are examined and characterized using high-resolution transmission electron microscopy (HRTEM) conducted with a Talos F200S instrument (Thermo Scientific, USA) operating at high vacuum and 200 kV.

The catalyst powder is gold-coated using the Oxford Ultim Max 65 (45 s, 10 mA), and subsequently analyzed with the SEM-EDS (Regulus 8100, Hitachi, Japan) at an acceleration voltage of 3 kV to obtain morphology photographs and 20 kV for EDS mapping photographs. The detector used is an SE2 secondary electron detector.

The X-ray photoelectron spectroscopy (XPS) analysis is conducted on the composition and valence states of surface elements (Ce and O) using the K-Alpha instrument (Thermo Scientific, USA). The excitation source used is Al $K\alpha$ at 12 kV ($h\nu=1486.6 \text{ eV}$). The observed elemental spectra are calibrated using the C 1s binding energy of 284.8 eV.

Raman spectroscopy is utilized to examine the reaction characteristics of the catalyst surface using the LabRAM HR Evolution instrument (Horiba Scientific, Japan). A laser with a wavelength of 532 nm and 100 mW is employed, and the scanning range used is 200-900 cm^{-1} .

EPR spectrum of 9.4 GHz is recorded using the Bruker Elexsys-II spectrometer. The experimental conditions are as follows: microwave power 3.17 mW, modulation amplitude 5 G, modulation frequency 100 kHz, conversion time 60 ms. Spectral simulation and spectral analysis using EasySpin software package.

1.3 Definition of normalized peak intensity

The collected DRIFTS spectra were normalized for relatively quantitative analysis. The normalization is based on the ratio of positive peak intensity to the strongest intensity ($P_{i\max}$) or the negative peak intensity to the weakest peak intensity ($P_{i\min}$), using Eqs. S1 and S2, respectively.

$$N_i = \frac{P_i}{P_{i\max}} \quad (\text{S1})$$

$$N_i = \frac{P_i}{|P_{i\min}|} \quad (\text{S2})$$

N_i represents the normalized intensity of peak i ; P_i represents the peak intensity of peak i from collected DRIFTS spectra.

Reference:

- [1] M.-C. Biesinger, B.-P. Payne, A.-P. Grosvenor, L.-W.-M. Laua, A.-R. Gerson, R.-S.-C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni, *Appl. Surf. Sci.*, 2024, **257**, 2717-2730.
- [2] A. Jia, G. Hu, L. Meng, et al. CO oxidation over CuO/Ce_{1-x}Cu_xO_{2-δ} and Ce_{1-x}Cu_xO_{2-δ} catalysts: Synergetic effects and kinetic study, *J. Catal.* 2012, **289**, 199-209.
- [3] J. Qing, C. Sun, N. Li, et al. Kinetic study of CO oxidation over CuO/MO₂ (M = Si, Ti and Ce) catalysts, *Appl. Surf. Sci.* 2023, **287**, 124-134.

2. Figures

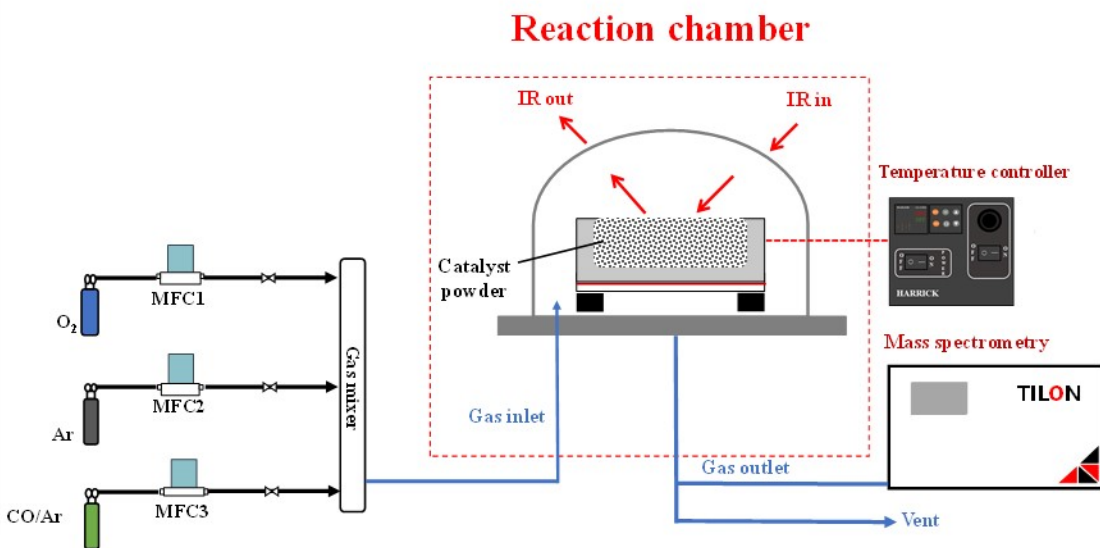


Fig. S1. Experimental setup of the *operando* TPR-DRIFTS-MS system.

Fig. S2 shows the decomposition profiles of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2$, and $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ using TG analysis. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is completely dehydrated at 225 °C and completely decomposed into CeO_2 at 500 °C. $\text{Mn}(\text{NO}_3)_2$ is decomposed into MnO_x at about 200 °C. $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ is completely dehydrated at a temperature around 190 °C and then decomposed to $\text{ZrO}_x(\text{NO}_3)_y$ and finally to ZrO_2 at 600 °C. Although the temperature of the quartz tube for nitrate decomposition was controlled at 600 °C, the different decomposition temperatures of nitrate precursor led to the decomposition of different nitrates successively, which became the core and shell of catalyst particles, resulting in the actual surface ratio of $\text{M}/(\text{M}+\text{Ce})$ ($\text{M}=\text{Mn}$ or Zr) on the catalyst surface measured using EDS mapping being lower than the atomic ratio calculated from the amount of nitrate precursors.

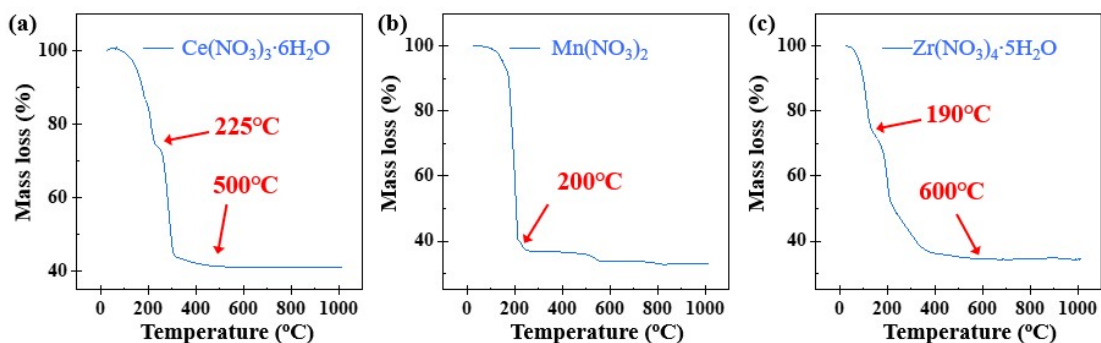


Fig. S2. Profiles of different nitrate decomposition: (a) $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. (b) $\text{Mn}(\text{NO}_3)_2$. (c) $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$.

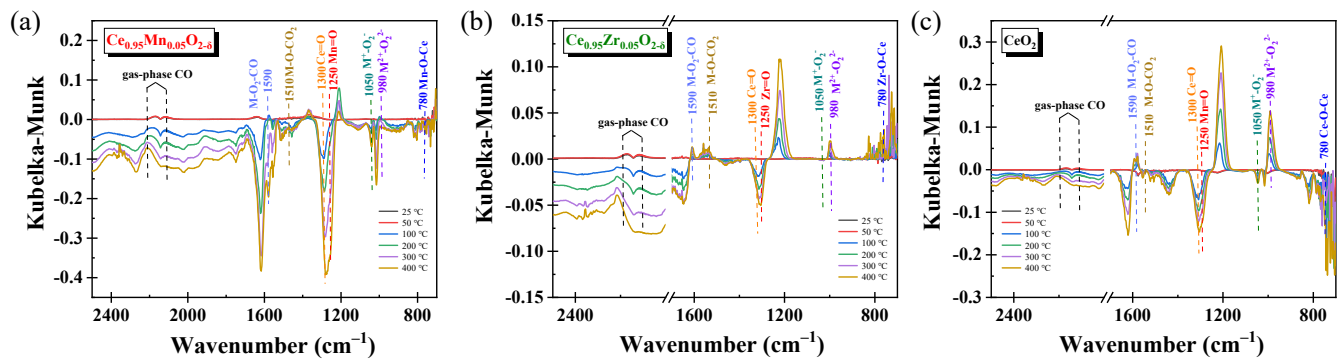


Fig. S3. DRIFTS spectra of Ce_{0.95}M(M=Mn and Zr)_{0.05}O_{2-δ} catalysts under CO+O₂/Ar oxidation.

Table S1 Composition of the gases fed to the reaction chamber.

Gas atmosphere	Composition (%)	Total gas flow rate (mL/min)
CO/Ar	CO: 2.37%, Ar: balance	38
CO+O ₂ /Ar	CO: 2.37%, O ₂ :10%, Ar: balance	38
O ₂ /Ar	O ₂ : 5.26%, Ar: balance	38
CO ₂ /Ar	CO ₂ : 2.37%, Ar: balance	38