SUPPORTING INFORMATION

Design Aspects of Doped-CeO$_2$ for Low-Temperature Catalytic CO Oxidation: Transient Kinetics and DFT Approach

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S1. MATERIALS AND METHODS

S1.1. TM doped-CeO$_2$ preparation

*Synthesis example*

ZrOCl$_2$.8H$_2$O precursor salt was used to finally obtain Zr-Ce-O (Zr-doped CeO$_2$, solid solution). A citric acid solution was used as a complexing agent, and an aqueous solution was prepared in molar excess, maintaining the total metal loading to citric acid at 0.75 (M$_{tot}$/citric acid=0.75 mol/mol). The metal and citric acid solutions were then mixed and then heated in a microwave reactor (duration < 15 min) at mild conditions, ca. 130 °C and 800 W. Mixed metal oxides of previously mentioned materials were obtained through calcination in static air, ca. 500 °C for 6 h under atmospheric pressure. An analogous procedure was followed for all the other binary mixed metal oxides (TM-doped ceria).

S1.2. TM-doped CeO$_2$ materials characterization

To study the crystal structure of the calcined TM-doped CeO$_2$ solids, powder X-ray diffraction (XRD) was employed using a D2-Phaser® apparatus (Bruker, MA, USA) operated at the excitation wavelength of Cu $K\alpha$ (1.5418 Å), and a generator power at 30 kV and 20 mA. A scan range within 10 - 100° 2theta was applied with 0.02° step size. Scherrer equation was employed to estimate the average crystallite size using the (111) peak broadening line of ceria. Williamson-Hall plots ($\beta \cos \theta/\lambda$ vs. $\sin \theta/\lambda$) were constructed and used to estimate the lattice strain.
High-resolution 3Flex Micromeritics (Atlanta, USA) adsorption apparatus with high-vacuum system and three 0.1 Torr pressure transducers was employed for textural measurements through the N$_2$ physisorption method at 77 K. A degassing process was carried out prior to the measurements to remove any residual moisture (degassing at 150 °C for 12 h) and weakly bound carbon dioxide. The BET surface area was calculated from the adsorption isotherm data in the relative pressure range of P/P$_0$=0.04-0.25. Information regarding the pore size distribution and specific pore volume (cm$^3$/g) were obtained after applying the Barrett-Joyner-Halenda (BJH) method$^1$.

The surface morphology of solid TM-doped CeO$_2$ catalysts was examined using the JSM 7610F-Field Emission Scanning Electron Microscope (JEOL Ltd., Tokyo, JPN), in both secondary (SE) and low-angle-backscattered imaging (BSE). H$_2$ temperature-programmed reduction (H$_2$-TPR) experiments were carried out in a conventional quartz reactor connected to a Thermal Conductivity Detector (TCD). The material was mounted on a U-shaped quartz tubular reactor (Autochem 2920, Micromeritics, Atlanta, USA). A gas stream of 10 vol% H$_2$/Ar was passed over 0.2 g of the pre-calcined sample (20 vol.% O$_2$/He, 500 °C, 2 h) at the flow rate of 30 NmL/min. The temperature was raised at 30 °C/min from room T to 500 °C and kept at this temperature for 2 h, while the TCD signal was recorded continuously.

CO$_2$-TPD experiments were conducted using Autochem 2920 (Micromeritics, Atlanta, USA). The materials were mounted on a U-shaped quartz sample tube and placed in a flow-through reactor. A gas flow of 5 vol% CO$_2$/Ar (30 NmL/min) was passed over 0.2 g of the pre-calcined (20 vol%O$_2$/He, 500 °C, 2 h) sample for 30 min. The temperature of the sample was then increased at the heating rate of 30 °C/min to 500 °C and kept there for 2 h, while the TCD signal was recorded continuously.

Information regarding surface elemental composition and chemical states were obtained using X-ray Photoelectron Spectroscopy (XPS, Thermo-Fisher Scientific East Grinstead, UK, Theta Probe spectrometer). A monochromatic Al Kα X-ray source (hν = 1486.6 eV) and an X-ray spot of radius ~ 400 μm were employed to record XPS spectra for the calcined materials. Survey and high-resolution spectra were acquired using pass energies of 300 eV and 50 eV, respectively. C 1s peak (285.0 eV) was taken into consideration in all spectra to account for charging effects during
acquisition, and correct binding energies, accordingly. The non-linear (Shirley) background was eliminated from all spectra for the purpose of obtaining high resolution core level spectra for quantitative surface chemical analyses. The experiment was coupled with the manufacturer’s Avantage software that acquires the appropriate sensitivity correction factors for the electron energy analyzer transmission function.

HR-TEM studies were performed over the solids with the use of an electron microscope (model Titan 80-300 ST, operated at 300 kV). The microscope was equipped with a spherical aberration (Cs) corrector for the image (CEOS CETCOR), and an energy filter (model GIF Quantum 963, Gatan, Inc.). Selected powdered specimens were dispersed in ethanol and drop casted onto carbon-coated copper grid (200 mesh) to perform imaging, structure, composition, and elemental mapping analyses. The high-resolution imaging was performed in aberration corrected TEM mode, while the structure analysis was carried out using the selected area electron diffraction (SAED) technique of TEM. The composition of samples was determined using X-ray energy dispersive spectroscopy (EDX). However, nanoscale elemental quantification was carried out using scanning TEM (STEM) mode. For the elemental quantification, STEM-EDX experiments were performed by setting the same electron beam conditions for the specimens of each sample. The entire TEM data acquisition and post processing was done by utilizing Gatan Microscopy Suite (GMS, version 3.2).

S1.3. Catalytic CO oxidation performance studies

The catalytic oxidation of carbon monoxide over the various TM-doped CeO$_2$ materials was carried out in a differential packed-bed quartz U-tube flow reactor (i.d. = 9 mm) mounted in the middle of a programmable split tube furnace (Lindberg/Blue M Mini-Mite Tube Furnace - Thermo). A catalyst sample of 50 mg was packed between two thin layers of glass wool. Thermocouples (K-type) were located at the inlet and outlet of the catalyst bed for gas-phase temperature monitoring, very close to that at the external surface of catalyst grains (powder form). The signal from the thermocouple was acquired using USB-6008 Multifunction I/O and NI-DAQmx (National Instruments) data acquisition system. The composition of the exit gas stream from the micro-reactor was analyzed using an infrared gas analyzer (IR200, Yokogawa). The feed gas mixture consisted of 4 vol% CO, 20 vol% O$_2$ and He as balance gas. Unless otherwise
mentioned, regulated gas mixture total flow – (use of digital thermal mass flow controllers (HI-TEC Model F-201CV-10K-AGD-22-V Multi-Bus DMFC; Bronkhorst) was set at 50 mL/min (STP) corresponding to a space velocity (SV) of ~ 60,000 cm³ g_cat⁻¹ h⁻¹. After stabilization, the temperature of the catalyst bed was raised at 5 °C min⁻¹ in the flow of CO/O₂/He gas mixture. Labview-configured data acquisition software was used to record and store the vol% composition in CO, CO₂ and O₂ alongside the temperature throughout the CO activity vs T procedure. Further catalytic stability experiments were conducted on selected catalysts under continuous feed gas stream, ca. 20 h at 530 °C.

S1.4. DFT Calculations
The all-electron wave functions and the pseudo-potentials for the electron-ion interactions are described within the projector-augmented wave (PAW)² method. The exchange and correlation (XC) potentials were generated within the generalized gradient approximation (GGA) scheme according to Perdew, Burke and Ernzerhof (PBE)³. The Kohn-Sham wave functions were expanded in plane waves up to an energy cut-off of 50 Ryd, while the cut-off for the electron density representation was set to 300 Ry. This ensures the energy convergence within 1 mRy per atom. For a proper description of the atomic and electronic structures of chemisorbed CO on the TMs doped-CeO₂ surface, it is necessary to account for the strong electron-electron correlation of the highly localized f states. We applied a DFT+U scheme⁴ with an additional interatomic Coulomb repulsion term, U= 5 eV. This value usually provides a good description of the electronic structure of CeO₂ surface and its oxidation states⁴. A 6x6x1 Monkhorst-Pack mesh⁵ was used to sample the corresponding Brillouin zone (BZ). In order to simulate the doped-CeO₂ surfaces with two-dimensional translational symmetry, the repeated slab method was used. For a low heteroatom coverage of TMs atoms, we used slabs of nine CeO₂ layers with a lateral p(2×2) surface unit cell. A vacuum thickness corresponding to nine layers (15 Å) was chosen to separate the two surface slabs and to avoid artificial interactions between them. The atoms in the top six layers were allowed to fully relax until the forces become smaller than 1 meV/Å, while the remaining layers at the bottom of the slab were kept fixed. The optimized lattice parameter of bulk CeO₂, based on the above computational settings, was a=5.431 Å. This is in good agreement with measurements and previous calculations reported⁶.
S2. RESULTS AND DISCUSSION

S2.1. Structural, textural and morphological studies on TM-doped CeO$_2$ materials

S2.1.1. Textural properties

The N$_2$ adsorption/desorption isotherms recorded at 77 K for the Mn-Ce-O catalyst are presented in Fig. S1C, whereas specific surface area values are listed in Table 1. All catalysts demonstrated type-IV adsorption isotherm according to IUPAC classification, which is associated to capillary condensation occurring due to the mesoporous (pore width ~ 2-50 nm) nature of the solid catalysts. A hysteresis type-H3 is identified in all materials at ~ P/Po > 0.45 through the steep trend of the desorption curve towards the closure point, as well as the infinite vertical behavior of the adsorption curve towards high P/Po values (~ 0.99), which is indicative of the macropores nature (pore width > 50 nm) of the materials. This is in agreement with SEM images (Fig. S1B). Usually, adsorption hysteresis is related to specific shaped pores, and H3-type indicates that the synthesized catalysts acquire a slit-shaped pores. The low N$_2$ uptake at a low relative pressure is observed in all the mixed metal-oxides due to the lack of micropores (pore width < 2 nm). The surface area and cumulative specific pore volume were obtained through the BET and Barret-Joyner-Halenda (BJH) methods, respectively.
Figure S1: (A) Powder XRD patterns of the various TM-doped ceria catalysts in the 23-39 2theta range. (B) SEM photos of the Cu-Ce-O catalyst along with the elemental mapping (B1, B2). (C) N\textsubscript{2} adsorption-desorption isotherms obtained at 77 K over the Cu-Ce-O catalyst.

Variations in the BET area as well as pore volume are observed due to dopant-type effect (Table 1). BET area values for the mixed metal oxides varied in the 12 - 63 m\textsuperscript{2}/g range. The BET area of ceria (14.8 m\textsuperscript{2}/g) is enhanced after doping with particular transition metals (i.e. Mn, Fe and Cu), whereas for the other TM-dopants, no improvement is observed. Mn-Ce-O solid exhibited the highest BET area (63 m\textsuperscript{2}/g) as well as specific total pore volume (0.130 cm\textsuperscript{3}/g). A reason for this might be its small crystallite size as confirmed by the powder XRD results (Fig. S1A), where it is expected that smaller particles exhibit higher specific surface area. On the other hand, Ce\textsubscript{0.8}M\textsubscript{0.2}O\textsubscript{2-δ} (i.e. Zn, Ni, Co) possessed lower BET area and cumulative pore volume. This explanation, however, does not apply for Cu and Fe mixed metal oxide systems. Cu-Ce-O had a BET area \(\sim 16.2\) m\textsuperscript{2}/g – among the lowest- but acquired the second highest total pore volume, ca. \(\sim 0.085\) cm\textsuperscript{3}/g. This could be attributed to the highly dense macro/mesoporous particles.
Zr⁴⁺-doping of ceria improved significantly the surface area of pristine ceria from 14.8 to 61.2 m²/g (Zr-Ce-O). This result agrees with previous findings and indicates that Zr⁴⁺ incorporation in ceria enhances the resistance of ceria against surface area drop under thermal treatment in high temperatures (627-827 °C). All mixed metal oxides demonstrated wide distribution of macro/mesopores induced by microwave synthesis.

S2.1.2. Structural properties

The X-ray diffraction pattern of Zr-Ce-O at a first glance confirmed the formation of a fluorite structured solid solution, with a lattice parameter of 5.69 Å compared to 5.82 Å of pure ceria. The ionic radius of Zr⁴⁺ (0.80 Å) is smaller than that of Ce⁴⁺ (0.97 Å), which causes shrinkage of the unit cell after Zr⁴⁺ incorporation (decrease in the lattice parameter). This finding is in agreement with a previous study conducted on CeO₂-ZrO₂ with similar composition⁹. The crystallite size obtained for Zr-Ce-O prepared by the microwave synthesis is smaller than that of similar composition obtained by the coprecipitation method (10 and 13 nm, respectively)¹⁰.
**Figure S2:** Powder XRD patterns of (A) Zr-Ce-O, (B) Zoom-in of (A) in the 55-60 2theta range, (C) Mn-Ce-O, and (D) the (C) in the 50-60 2theta range.

**Figure S3:** Powder XRD pattern of (E) Cu-Ce-O, (F) Ni-Ce-O, (G) Zn-Ce-O, (H) Fe-Ce-O, (I) Fe-Ce-O, and (J) Co-Ce-O doped-ceria materials.
Figure S4: Williamson-Hall plots related to (A) Co-Ce-O, (B) Mn-Ce-O, (C) Fe-Ce-O, (D) Cu-Ce-O, (E) Co-Ce-O, (F) Ni-Ce-O, (G) Zn-Ce-O, and (H) Zr-Ce-O solids.
Figure S5: Raman spectra of (A) Zr-Ce-O, (B) Zn-Ce-O, (C) Fe-Ce-O, (D) Mn-Ce-O, (E) Ni-Ce-O, (F) Co-Ce-O, and (G) Cu-Ce-O solids.

Table S1. Literature overview about the formation of solid solution for the doped-ceria solids.

| Dopant          | Content (at.%) | Formula                  | Synthesis Method            | Calcination conditions (°C/h) | Dopant oxide | Reference |
|-----------------|----------------|--------------------------|-----------------------------|-------------------------------|--------------|-----------|
| Cu, Cr, Co, Zn, Ni, Mn, Fe, Zr | 10            | Ce_{0.9}M_{0.1}O_{2-δ}   |                             | 800°C/ 4 h                    | No           | (11)      |
| Mn, Fe, Zr and Pr, La, or Sm | 20-30         | Ce_{1-x}TM_{x}O_{2-δ} and Ce_{1-x}RE_{x}O_{2-δ} | Co-precipitation         | 773 and 1073 K/ 5 h               | Only in the case of Mn-dopant (Mn_3O_4) | (12)      |
| Mn              | (5-30)         | Ce_{1-x}Mn_{x}O_{2-δ}    | Reverse homogeneous precipitation | 1300°C                        | Mn_3O_4      | (13)      |
| Dopant Oxide | Raman Bands (cm\(^{-1}\)) | References |
|--------------|-----------------------------|------------|
| ZnO          | 275, 437, 580               | (22-26)    |
| Fe\(_2\)O\(_3\) | 200, 300, 613              | (22-26)    |
| Co\(_3\)O\(_4\) | 282, 330, 616              | (22-26)    |
| Mn\(_3\)O\(_4\) | 308, 353, 647              | (22-26)    |
| NiO          | 500                         | (22-26)    |

### S2.1.3. Elastic energy upon doping of ceria:

The elastic energy is given by the following formula:

\[
W = 6Gd_o\Delta d^2
\]  

(1)
where $G$ is the shear Modulus, and $d_0$ is the lattice parameter for the host oxide ($\text{CeO}_2$). $G$ value of 92.5 GPa was used for $\text{CeO}_2$ $^{21}$. The elastic energy values for the Cu, Co, Ni, Zn, Fe, Mn were found to be 8.4, 5.2, 4.9, 6.5, 7.1 and 5.2 ($\times 10^{-9}$) N-Å.

### S2.2. Oxidation states of TM-dopants in doped-$\text{CeO}_2$ catalytic materials

The oxidation states of transition metals on the surface of TM-doped $\text{CeO}_2$ were identified based on the core level binding energy signal and the presence or absence of shake-up satellites in the XPS spectra. The Cu 2p$^{3/2}$ peak is observed at $\sim$ 933.4 eV, and there is a broad shake-up satellite at a binding energy of 941-944 eV (Fig. S6E). The satellite peak is observed only for Cu$^{2+}$ and a binding energy of 933.7 ± 0.1 eV is expected for CuO, and 932.3 ± 0.1 eV for Cu$_2$O. Hence, Cu atoms predominantly exist within the mixed metal oxide (solid solution formation) in the 2+ oxidation state$^{27}$.

The Co 2p$^{3/2}$ peak (Fig. S6F), occurs at a binding energy of 780.2 eV and there is a satellite peak at $\sim$785 eV. These peak positions and the spectral shape recorded are in very good agreement with that of CoO reference material than the mixed oxidation states of Co$_3$O$_4$$^{28}$, demonstrating the predominance of Co$^{2+}$ oxidation state in the present mixed metal oxide Co-Ce-O solid composition. This finding also indicates that Co$^{2+}$ species are more populated than the other possible oxidation states, Co$^0$ or Co$^{3+}$ $^5$. However, an overlap between CoO, Co$_3$O$_4$, Co$_2$O$_3$ and CoOOH exists at the same binding energy. Interestingly, it has been reported that Cu$^+$ and Co$^{2+}$ species are preferred over Cu$^{2+}$ and Co$^{3+}$, respectively, during CO oxidation reaction$^{29, 30}$. This finding was correlated with the CO conversion performance of Cu-Ce-O and Co-Ce-O catalysts.

The Ce3d region (Fig. S6A) is a typical Ce 3d spectrum, as it is discussed in the main manuscript, where the 4+ valence state is predominant, with little evidence for 3+ cerium oxidation state, indicative of almost a fully oxidized $\text{CeO}_2$. The Fe 2p region (not shown) is rather complicated by the presence of two Ce Auger peaks (M$_4$N$_{4.5}$N$_{6.7}$ at $\sim$716 eV and M$_5$N$_{4.5}$N$_{6.7}$ at $\sim$732 eV). The Fe 2p$^{3/2}$ and Fe 2p$^{1/2}$ peaks occur at the binding energies of 710.9 and 724.2 eV. These binding energies agree very well with Fe in the Fe$^{3+}$ oxidation state$^{31}$.

The Mn 2p spectra show the Mn 2p$^{3/2}$ peak at a binding energy of 641.7 eV, and a broad shake-up satellite peak at $\sim$ 645 eV (Fig. S6D). The peak/satellite binding energies and shape are in best
agreement with MnO (in comparison to other manganese oxides). Hence, Mn$^{2+}$ is the predominant oxidation state for this dopant in the Mn-doped CeO$_2$ structure.

In Fig. S6C, the Ni 2p$_{3/2}$ peak occurs at a binding energy of 855.0 eV. This binding energy is typical of Ni$^{2+}$ but the observed peak shape does not agree very well with either NiO or Ni(OH)$_2$ and the binding energy lies mid-way between that of NiO (854.7 eV) and Ni(OH)$_2$ (855.3 eV). Thus, in the Ni-Ce-O mixed metal oxide, the Ni is predominantly present as Ni$^{2+}$, but the XPS Ni 2p peak shape observed does not clearly correspond with that of NiO due to the presence of Ni(OH)$_2$ at the surface which can be due to the atmosphere exposure of the Ni containing catalyst.

Finally, Zn exists only in its 2+ state when oxidized. The Zn 2p$_{3/2}$ peak (Fig. S6B) shows a sharp peak at a binding energy of 1021.9 eV, which is in excellent agreement with ZnO recorded by Klein and Hercules.

**Figure S6:** XPS high resolution spectra of Ce3d (A), Zn 2p (B), Ni 2p (C), Mn 2p (D), Cu 2p (E), and Co 2p (F).
**Figure S7:** Overlaid Ce3d5/2 for doped samples and CeO2 reference

**Table S3:** Binding energies (eV) and corresponding oxidation states of TM - dopants in the doped-CeO2 catalytic materials after calcination at 500 °C.

| Material (Ce0.8M0.2O2) | Binding Energy (eV) | Oxidation States |
|-------------------------|---------------------|-----------------|
| Ce-Cu-O                 | 933                 | Cu^{2+}         |
| Ce-Co-O                 | 780                 | Co^{2+}         |
| Ce-Fe-O                 | 709, 711            | Fe^{2+}, Fe^{3+}|
| Ce-Mn-O                 | 641                 | Mn^{4+}         |
| Ce-Ni-O                 | 853.8, 858.8        | Ni^{2+}/Ni^{3+} |
| Ce-Zn-O                 | 495                 | Zn^{2+}         |
S2.3. Redox properties

H$_2$-TPR was employed to investigate the effect of the nature of dopant (size, oxidation state) on the reducibility of M-Ce-O catalysts. H$_2$-TPR profiles shown in Fig. 4C and Fig. S8A, B suggest that the variations in the reduction behavior of the binary metal oxide systems are due to dopant-type as well as to the different dopant cation oxidation state (i.e. divalent, trivalent, and quadrivalent). According to the literature, pure ceria experiences two reduction peaks both appearing at temperatures higher than 350 °C$^{35,36}$. In pure ceria, an initial reduction peak at ~ 485 °C is attributed to surface shell reduction, and a high temperature reduction peak at ~ 765 °C is attributed to bulk material reduction$^{37,38}$. In microwave-assisted prepared ceria, the reduction peaks are observed at ~ 247 °C (sub-surface), 467 °C and 1000 °C (bulk)$^{39}$. The preparation route has been known to affect the reduction properties of ceria-based catalysts$^{40,41}$.

Divalent cations: Fig. 4C shows the effect of divalent cations, Co$^{2+}$, Cu$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ on the doped-ceria reducibility. The Cu-Ce-O reduction profile presents an intense peak at very low temperatures, at ~ 200 °C, with a shoulder peak at around 100 °C that extends up to 150 °C. These peaks correspond to the stepwise reduction of CuO, for example, Cu$^{2+}$ to Cu$^+$, and Cu$^+$ to Cu$^{042}$. The broader narrow peak above 400 °C is attributed to the reduction of the remaining Ce$^{4+}$ $^{42}$. CuO has been reported to have one reduction peak at ~ 300°C$^{43}$, where Cu-Ce-O Ce$_{0.8}$Cu$_{0.2}$O$_{2-δ}$ is reduced at lower temperatures than both single oxides of CeO$_2$ and CuO, demonstrating the successful synergy achieved by introducing Cu$^{2+}$ into the CeO$_2$ lattice. From the synthesis perspective, it can be stated that microwave synthesis enhanced the homogeneous dispersion of Cu in the ceria lattice, since the low reduction temperature peak ~ 100°C is absent for the same composition prepared via the co-precipitation method due to agglomeration. One main reduction peak also appears at ~ 250 °C$^{44}$. Another study on 10 wt% Cu-doped ceria$^{35}$ reported the first (lowest temperature) reduction peak to occur at 245, 230 and 190 °C, respectively, for the same solid composition prepared via three different routes, namely, deposition-precipitation, co-precipitation, and complexation-combustion. The reduction of ceria surface is promoted with copper addition$^{35}$, and with the combined effect of microwave-assisted synthesis, the reduction occurs at clearly lower temperatures. The high reducibility shown by Cu-Ce-O can be correlated to the powder XRD results, which confirmed the formation of solid solution, thus, improved interaction between Cu and Ce cations in the crystal lattice structure.
**Figure S8:** H$_2$-TPR profiles (A-B) of ceria doped with trivalent (A) and quadrivalent (B) TM dopants. CO$_2$-TPD profiles of ceria doped with divalent (C), trivalent (D) and quadrivalent (E) TM dopants.

On the contrary, Zn-Ce-O reduction profile (Fig. S9) is appeared rather suppressed (in terms of intensity), with Zn$^{2+}$ species being relative inactive, even though they are highly populated on the surface (as confirmed by XPS). Therefore, it can be concluded that the hydrogen reduction peaks are mainly due to the reduction of Ce$^{4+}$ species, where ZnO presence confirmed by XRD, contributes to the enhancement of the synergy with the mixed metal oxide which shifts the reduction peaks towards lower temperatures compared to those of pure ceria, in agreement with the literature$^{45,46}$. It was reported that ZnO is not easily reducible, though Zn$^{2+}$ reduction can be facilitated when it is adjacent to a metal cation by a synergistic effect between the mixed metal cations$^{46}$.

Co-Ce-O TPR profile demonstrates the stepwise reduction processes involved due to the highly dispersed cobalt species in ceria (Fig. 4C & Fig. S9). The addition of Co greatly boosts the surface reduction of Ce$^{4+}$ as indicated by the peak at 300 °C, whereas the formation of Ce$_{0.8}$Co$_{0.2}$O$_{2.5}$ solid...
solution implies that Co\(^{3+}/\)Co\(^{2+}/\)Co and Ce\(^{4+}/\)Ce\(^{3+}/\) reduction processes can also take place. Namely, (a) reduction of surface oxygen and Ce\(^{4+}/\), (b) Co\(^{3+}/\) to Co\(^{2+}/\), (c) Co\(^{2+}/\) to Co and (d) reduction of surface ceria species (~ 545°C). This observation is in agreement with previous reported literature on cobalt-doped ceria\(^{37}/\).

Figure S9: Deconvoluted H\(_2\)-TPR profiles of the Zn-Ce-O, Ni-Ce-O and Co-Ce-O solids.

H\(_2\)-TPR reduction profile of Ce\(_{0.8}\)Ni\(_{0.2}\)O\(_{2-\delta}\) shown in Fig. 4C and Fig. S9 exhibits peaks that can be assigned according to the following. Pure NiO only shows one reduction peak at ~ 400°C, which corresponds to reduction of NiO to metallic Ni\(^0/\). Upon introduction in the ceria lattice, lower temperature peaks arise due to strong interactions between ceria and NiO. The low reduction peaks at ~ 155 and 235°C are attributed to reduction of ceria surface oxygen species. The presence of surface-active oxygen vacancies in the Ni-Ce-O solid solution (as confirmed by XRD, Raman) can be explained by Ni\(^{2+}/\) having lower cation charge than Ce\(^{4+}/\) which causes lattice distortion\(^{47,48}/\). The high temperature peak observed at 380-500 °C corresponds to the simultaneous reduction of NiO to Ni\(^0/\) and remaining Ce\(^{4+}/\). Microwave-assisted synthesized Ni-Ce-O presented more mobile oxygen species than other similar in composition NiO-CeO\(_2\) catalysts prepared by co-precipitation or sol-gel methods. In fact, the conventional methods reported reduction peaks for NiO-CeO\(_2\)
similar to that of pure NiO. Thus, it can be concluded that Microwave synthesis strengthens the interaction between NiO and CeO₂ that allows reduction to commence at lower temperatures.

**Trivalent Cations:** Fig. S8A presents the H₂-TPR profiles of the rest of the catalysts. According to previous studies, bare Fe₂O₃ experiences three reduction peaks at 373, 590 and 724 °C. The first hydrogen consumption peak is attributed to the reduction of Fe₂O₃ to Fe₃O₄. The other two peaks correspond to the stepwise reduction of Fe₃O₄ to intermediate FeO and metallic iron (i.e. Fe⁰). In the case of Fe-Ce-O, an overlap between the reduction peaks of pure ceria as well as those of Fe₂O₃ is expected. The H₂-TPR trace (Fig. S8A) shows the first low temperature peak at 265 °C. This peak is attributed to the reduction of surface Fe³⁺ and Ce⁴⁺ species. This behavior is reported also on previous studies on Fe-doped ceria. The peak is shifted towards lower temperatures due to the synergy between the cation and pure ceria through solid solution formation (confimed by XRD and Raman), which facilitates the reducibility of the mixed oxide as explained above. The high temperature peak is observed in the 450-600 °C range, which corresponds to reduction of Ce⁴⁺ as well as of Fe₃O₄ to FeO. The H₂-TPR trace obtained for the microwave-assisted synthesized Fe-Ce-O shows resemblance to other studies on Fe-doped ceria. However, a shift in the low-temperature peak is favored in microwave synthesized Fe-doped ceria compared to other traditional methods. The first reduction peak is observed at 384 °C for a sol-gel prepared 10 mol% Fe (~ 20 wt%) in ceria, whereas microwave-assisted prepared Ce₀.8Fe₀.2O₂-δ provides the same peak at 265 °C. This behavior can be explained by taking into account that microwave synthesis enhances the dispersion of dopant cation on the surface, or/and promotes the formation of oxygen vacancies (confirmed by Raman) by allowing Fe³⁺ to substitute for Ce⁴⁺, which introduces charge compensation.

**Quadrivalent Cations:** Zr-Ce-O TPR profile features two main asymmetric reduction peaks in the 100-400 °C range and at ~ 580 °C (Fig. S8B). The peak asymmetry indicates the overlap between surface and bulk reduction of Ce⁴⁺ species. The reduction peaks of microwave prepared Ce₀.8Zr₀.2O₂-δ are shifted towards lower temperatures compared to those prepared via the coprecipitation method, according to Lan Li et al., who reported asymmetric TPR consumption peak at ~ 650°C. Zr-Ce-O TPR profile maintains the feature of CeO₂ with slight variation in peaks.
intensity and position. The first peak corresponds to reduction of the accessible Ce\textsuperscript{4+} species, whereas the second peak corresponds to oxygen removal from the bulk\textsuperscript{54}.

The H\textsubscript{2}-TPR profile of Mn-doped CeO\textsubscript{2} (Fig. S8B) shows reduction peaks at ~ 100, 180, 390 and 500 °C. The first peak could be referred to the reduction of highly dispersed MnO\textsubscript{2}/Mn\textsubscript{2}O\textsubscript{3} to Mn\textsubscript{3}O\textsubscript{4}, and the second peak can be assigned to the reduction of Mn\textsubscript{3}O\textsubscript{4} to MnO and surface Ce\textsuperscript{4+} species. The third peak is associated with the reduction of remaining ceria and manganese oxides\textsuperscript{55}. The observed peaks are shifted towards lower temperatures compared to CeO\textsubscript{2}, which implies a synergistic interaction between ceria and manganese through the solid solution formation (confirmed by XRD). The latter promotes surface reduction of Mn-Ce-O. This result is in agreement with previous findings on Mn-doped ceria\textsuperscript{55-57}. Moreover, the reduction peaks are shifted towards lower temperatures due to the catalyst preparation method effect (microwave-assisted synthesis). The first and second reduction peaks for 30 wt% Mn in ceria, prepared by the co-precipitation method, were found to be located at 315 and 410 °C\textsuperscript{58}. This observation emphasizes the role of microwave-assisted synthesis in enhancing the reduction properties of ceria-based mixed metal oxides system.

S2.4. CO\textsubscript{2}-Temperature Programmed Desorption (CO\textsubscript{2}-TPD) on TM-doped CeO\textsubscript{2}

CO\textsubscript{2}-TPD traces were obtained over the mixed metal oxides in order to study the surface-CO\textsubscript{2} interaction characterizing their surface basicity (Fig. S8C). As CO\textsubscript{2} is an acid molecule, it is expected to interact with basic surface sites\textsuperscript{59}.

*Divalent ions*: Fig. S8C shows that all the mixed metal oxides demonstrate an initial CO\textsubscript{2} desorption peak at ~ 100°C with a higher intensity than that of pure ceria. This observation indicates that transition metal doping of ceria strengthens the Lewis-type surface basic cites of ceria at the low-temperature region (50-150°C). The initial desorption peak intensity of all divalent TM doped ceria was independent of dopant chemical nature. The desorption peaks at intermediate desorption temperatures varied in terms of intensity. This finding indicates that dopant chemical nature has an influence on the surface basic nature of the catalyst altering the intermediate and strong basic sites. Zn-Ce-O tends to have strong basic surface character as the CO\textsubscript{2} desorption peak is in the 200-450 °C range. On the other hand, Cu-Ce-O tends to have higher surface basicity at
temperatures higher than 400 °C. The tendency of the surface basicity of mixed metal oxides throughout the temperature range is highly correlated with their CO conversion activity behavior.

CO$_2$-TPD trace of Ni-Ce-O (Fig. S8C) shows the highest surface basicity compared to the other TM-doped ceria solids. CO$_2$ desorption starts at temperatures slightly below 100°C, which indicates basic centers enrichment of Ni-doped ceria. Similar CO$_2$-TPD trace at low temperatures was obtained for the NiO-CeO$_2$ system prepared by the wet impregnation method$^{60}$. However, with the present microwave-assisted synthesis, the basic centers are extended up to higher temperatures (400-600 °C), indicating a continuous desorption of CO$_2$. Previous work conducted on NiO-CeO$_2$ prepared by molten-salt method showed the same CO$_2$-TPD behavior as the one presented here. Mn$^{2+}$-doping showed great modification of the basic centers of pure ceria at high temperatures. CO$_2$-TPD trace of Mn-Ce-O (Fig. S8E) shows four desorption peaks with overlapping at 140, 250, 400 and 500 °C, which is in agreement with data reported in the literature$^{61}$.

Trivalent ions: Pure iron (III) oxide is considered basic due to its metal ion electronegativity (El(Fe$^{3+}$)= 12.6)$^{62}$ and according to the acid - base classification reported by Tanabe et al.. Doping of ceria has higher basic nature (e.g., El(Ce$^{4+}$)=9.9)$^{62}$ and it is expected to increase the basicity of the mixed metal oxide system. According to the literature$^{62}$, Fe$_2$O$_3$ displays complex CO$_2$-TPD trace with multiple desorption peaks (Fig. S8D). The most intense desorption peak is observed at low temperatures, ~ 70°C, whereas additional weak desorption peaks are observed at 250, 490 and 650 °C. Fig. S8D shows that doping of ceria with Fe$^{3+}$ causes the CO$_2$-TPD trace to broaden over a wider temperature range compared to pure CeO$_2$ (Fig. S8C). It is noticed that the low desorption peak is maintained at similar intensity, however, the intensity of the high-temperature peaks is increased (350-450 °C). This finding reflects the wide heterogeneity of basic centers developed for Fe-Ce-O catalyst.

Quadrivalent ions: Modification of the basic sites of ceria was also observed with quadrivalent cation doping (e.g., Zr$^{4+}$) as shown in Fig. S8E. The CO$_2$-TPD trace recorded on Zr-Ce-O shows characteristic desorption peaks of ZrO$_2$, which indicates alteration in the basicity of ceria with Zr$^{4+}$ incorporation. Based on the literature$^{63,64}$, bare ZrO$_2$ exhibits two CO$_2$ desorption peaks at ~ 120
and 300 °C, which also appear in the CO₂-TPD profile of the present microwave-assisted prepared Zr-Ce-O with slight shift towards lower temperatures. However, additional peaks are observed starting at 400 °C and extending to temperatures higher than 600 °C. Addition of ZrO₂ induces basicity alteration on the Zr-Ce-O surface within 100-400 °C. On the other hand, MW synthesis modifies the basic sites at temperatures higher than 500 °C. The higher temperature peak was not observed in commercially prepared CeO₂-ZrO₂. This can be justified by the well-established fact that synthesis process strongly affects the acid-base properties of mixed metal oxides.

S2.5. ¹⁶O/¹⁸O Isotopic exchange followed by CO/Ar reaction

Fig. S10 presents the transient response curves of the rate of formation of the C¹⁸O₂ obtained over selected TM-doped ceria catalysts according to the experiment described in Section 2.4 and presented in Section 3.4.

![Graph showing transient rates of C¹⁸O₂ production](image)

**Figure S10:** Transient rates (μmol g⁻¹ s⁻¹) of C¹⁸O₂ production during the step-gas switch Ar → 4 vol% CO/2 vol% Kr/Ar (20 min) performed at 250 °C on (a) Cu-Ce-O, (b) Co-Ce-O, (c) Mn-Ce-O and (d) Zn-Ce-O doped-ceria solids following ¹⁶O/¹⁸O oxygen exchange.

S2.6. SSITKA-DRIFTS studies
**Figure S11:** (A) DRIFTS spectra recorded in the 1700-900 cm⁻¹ IR region after 30 min in $^{12}$CO/$O_2$ over the Cu-Ce-O solid at 125 or 250 °C. Feed gas composition: $^{12}$CO = 4 vol%, $O_2$ = 20 vol%, balance Ar; $F_T = 50$ NmL min⁻¹. (B) DRIFTS spectra recorded in the 1700–900 cm⁻¹ IR region after 30 min in $^{12}$CO/$O_2$ over CeO$_2$, Zn-Ce-O and Cu-Ce-O solids. Feed gas composition: $^{12}$CO = 4 vol%, $O_2$ = 20 vol%, balance Ar; $F_T = 50$ NmL min⁻¹.

**Figure S12:** SSITKA-DRIFTS spectra recorded in the 1700-900 cm⁻¹ region after 30 min in $^{12}$CO/$O_2$ at 250 °C followed by the step-gas switch $^{12}$CO/$O_2$ → $^{13}$CO/$O_2$ (5 min) for the CeO$_2$ (A) and Zn-Ce-O (B) solids. Feed gas composition of non-isotopic and isotopic gas: $^{12}$CO or $^{13}$CO = 4 vol%, $O_2$ = 20 vol%, balance Ar; $F_T = 50$ NmL min⁻¹.
Figure S13: DRIFTS spectra recorded in the 1700-900 cm\(^{-1}\) IR region after 30 min in \(^{12}\)CO\(_2\)/O\(_2\)/Ar gas mixture followed by the step-gas switch \(^{12}\)CO\(_2\)/O\(_2\)/Ar \(\rightarrow\) \(^{13}\)CO\(_2\)/O\(_2\)/Ar (5 min) for the CeO\(_2\) and Zn-Ce-O solids. Feed gas composition of non-isotopic and isotopic gas: \(^{12}\)CO\(_2\) or \(^{13}\)CO\(_2\) = 2 vol\%, O\(_2\) = 20 vol\%, balance Ar; \(F_T = 50\) NmL min\(^{-1}\).

S2.7. Kinetic studies

S2.7.1. Estimation of Apparent Activation Energy, \(E_a\) (kJ/mol)

Table S4. Kinetic analysis of CO oxidation rate data over CeO\(_2\) catalyst.

| Temperature (°C) | 1/T (K\(^{-1}\)) | Catalyst mass (mg) | Total Flow (ml min\(^{-1}\)) | \(R_{CO}\) (mol g\(^{-1}\) s\(^{-1}\)) | Ln (\(R_{CO}\)) |
|-----------------|------------------|--------------------|-----------------------------|-----------------|------------------|
| 150             | 0.00236          | 50                 | 50                          | 2.72E-07        | -15.115          |
| 180             | 0.00221          | 50                 | 100                         | 6.81E-07        | -14.199          |
| 210             | 0.00207          | 50                 | 100                         | 1.91E-06        | -13.169          |
| 240             | 0.00195          | 50                 | 100                         | 4.36E-06        | -12.342          |
| 270             | 0.00184          | 50                 | 100                         | 8.83E-06        | -11.637          |

Table S5. Kinetic analysis of CO oxidation rate data over Zn-Ce-O catalyst.

| Temperature (°C) | 1/T (K\(^{-1}\)) | Catalyst mass (mg) | Total Flow (ml min\(^{-1}\)) | \(R_{CO}\) (mol g\(^{-1}\) s\(^{-1}\)) | Ln (\(R_{CO}\)) |
|-----------------|------------------|--------------------|-----------------------------|-----------------|------------------|
| 150             | 0.002363         | 50                 | 50                          | 3.408E-07       | -14.892          |
Table S6. Kinetic analysis of CO oxidation rate data over Mn-Ce-O catalyst.

| Temperature (°C) | 1/T (K⁻¹) | Catalyst mass (mg) | Total Flow (ml min⁻¹) | R_CO (mol g⁻¹ s⁻¹) | Ln (R_CO) |
|------------------|------------|--------------------|-----------------------|-------------------|-----------|
| 150              | 0.002363   | 10                 | 200                   | 1.090E-05         | -11.426   |
| 180              | 0.002207   | 10                 | 200                   | 2.726E-05         | -10.51    |
| 210              | 0.002070   | 10                 | 200                   | 5.316E-05         | -9.842    |
| 240              | 0.001949   | 5                  | 200                   | 10.36E-05         | -9.175    |
| 270              | 0.001841   | 5                  | 210                   | 17.176E-05        | -8.669    |

Table S7. Kinetic analysis of CO oxidation rate data over Cu-Ce-O catalyst.

| Temperature (°C) | 1/T (K⁻¹) | Catalyst mass (mg) | Total Flow (ml min⁻¹) | R_CO (mol g⁻¹ s⁻¹) | Ln (R_CO) |
|------------------|------------|--------------------|-----------------------|-------------------|-----------|
| 120              | 0.00254    | 1                  | 200                   | 2.88E-04          | -8.154    |
| 135              | 0.00245    | 1                  | 200                   | 4.77E-04          | -7.647    |
| 150              | 0.00236    | 1                  | 200                   | 7.49E-04          | -7.197    |
| 165              | 0.00228    | 1                  | 200                   | 1.09E-03          | -6.826    |

2.7.2. Estimation of Reaction Orders in the CO Oxidation

2.7.2.1. Reaction Order in CO (x)

Table S8. Reaction order analysis with regards to CO over the CeO₂ catalyst.

| P_CO | 1/T (K⁻¹) | Catalyst mass (mg) | Total Flow (ml min⁻¹) | R_CO (mol g⁻¹ s⁻¹) | Ln (R_CO) |
|------|------------|--------------------|-----------------------|-------------------|-----------|
|      | (T=)       |                    |                       |                   |           |
### Table S9. Reaction order analysis with regards to CO over the Zn-Ce-O catalyst.

|       | 1/T (K⁻¹) (T=210°C) | Catalyst mass (mg) | Total Flow (ml min⁻¹) | R_CO (mol g⁻¹ s⁻¹) | Ln (R_CO ) |
|-------|----------------------|---------------------|------------------------|---------------------|------------|
| 0.06  | 0.002207             | 50                  | 100                    | 2.356E-06           | -12.958    |
| 0.04  | 0.002207             | 50                  | 100                    | 1.908E-06           | -13.169    |
| 0.03  | 0.002207             | 50                  | 100                    | 1.630E-06           | -13.326    |
| 0.02  | 0.002207             | 50                  | 100                    | 1.363E-06           | -13.505    |
| 0.01  | 0.002207             | 50                  | 100                    | 9.542E-07           | -13.862    |

### Table S10. Reaction order analysis with regards to CO over the Mn-Ce-O catalyst.

|       | 1/T (K⁻¹) (T=210°C) | Catalyst mass (mg) | Total Flow (ml min⁻¹) | R_CO (mol g⁻¹ s⁻¹) | Ln (R_CO ) |
|-------|----------------------|---------------------|------------------------|---------------------|------------|
| 0.06  | 0.002207             | 10                  | 200                    | 7.034E-03           | -6.703     |
| 0.04  | 0.002207             | 10                  | 200                    | 5.316E-05           | -9.562     |
| 0.03  | 0.002207             | 10                  | 200                    | 4.457E-05           | -9.842     |
| 0.02  | 0.002207             | 10                  | 200                    | 3.762E-05           | -10.018    |
| 0.01  | 0.002207             | 10                  | 200                    | 2.426E-05           | -10.626    |

### Table S11. Reaction order analysis with regards to CO over the Cu-Ce-O catalyst.

|       | 1/T (K⁻¹) (T=2150°C) | Catalyst mass (mg) | Total Flow (ml min⁻¹) | R_CO (mol g⁻¹ s⁻¹) | Ln (R_CO ) |
|-------|----------------------|---------------------|------------------------|---------------------|------------|
| 0.06  | 0.002363             | 1                   | 200                    | 1.226E-03           | -6.703     |
Figure S14: Determination of the reaction order $n_{O_2}$ (or y) with respect to the O$_2$ partial pressure in the CO oxidation reaction at T=210°C for Mn-Ce-O and CeO$_2$ solids, and at T=150°C for the Cu-Ce-O solid. The partial pressure of O$_2$ was varied in the 0.15 t- 0.2 bar range.

Table S12. Reaction order analysis with regards to O$_2$ over the CeO$_2$ catalyst.

| $P_{O_2}$ (bar) | 1/T (K$^{-1}$) | Catalyst mass (mg) | Total Flow (ml min$^{-1}$) | $R_{CO}$ (mol g$^{-1}$ s$^{-1}$) | Ln ($R_{CO}$) |
|-----------------|----------------|-------------------|-----------------------------|-------------------------------|----------------|
| 0.200           | 0.002207       | 50                | 100                         | 1.908E-06                     | -13.169        |
| 0.185           | 0.002207       | 50                | 100                         | 1.908E-06                     | -13.169        |
| 0.170           | 0.002207       | 50                | 100                         | 1.908E-06                     | -13.169        |
| 0.150           | 0.002207       | 50                | 100                         | 1.908E-06                     | -13.169        |

Table S13. Reaction order analysis with regards to O$_2$ over the Mn-Ce-O catalyst.
Table S14. Reaction order analysis with regards to O₂ over the Cu-Ce-O catalyst.

| P_O₂ (bar) | 1/T (K⁻¹) T= 210°C | Catalyst mass (mg) | Total Flow (ml min⁻¹) | R_CO (mol g⁻¹ s⁻¹) | Ln (R_CO ) |
|------------|---------------------|--------------------|-----------------------|---------------------|------------|
| 0.200      | 0.002207            | 10                 | 200                   | 5.31E-05            | -9.842     |
| 0.185      | 0.002207            | 10                 | 200                   | 5.31E-05            | -9.842     |
| 0.170      | 0.002207            | 10                 | 200                   | 5.31E-05            | -9.842     |
| 0.150      | 0.002207            | 10                 | 200                   | 5.31E-05            | -9.842     |

Table S14. Reaction order analysis with regards to O₂ over the Cu-Ce-O catalyst.

| P_O₂ (bar) | 1/T (K⁻¹) T= 210°C | Catalyst mass (mg) | Total Flow (ml min⁻¹) | R_CO (mol g⁻¹ s⁻¹) | Ln (R_CO ) |
|------------|---------------------|--------------------|-----------------------|---------------------|------------|
| 0.200      | 0.002363            | 1                  | 200                   | 7.52E-4             | -7.192     |
| 0.185      | 0.002363            | 1                  | 200                   | 7.52E-4             | -7.192     |
| 0.170      | 0.002363            | 1                  | 200                   | 7.52E-4             | -7.192     |
| 0.150      | 0.002363            | 1                  | 200                   | 7.52E-4             | -7.192     |

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