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Elucidating the Nature of the Active Phase in Copper/Ceria Catalysts for CO Oxidation

Joseph S. Elias,‡ Nongnuch Artrith,§ Matthieu Bugnet,‡ Livia Giordano,§§ Gianluigi A. Botton,‡ Alexie M. Kolpak,§ and Yang Shao-Horn*§

1Department of Chemistry, ‡Department of Mechanical Engineering, §Research Laboratory of Electronics and §Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
3Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada
4Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, 20125 Milan, Italy

ABSTRACT: The active phase responsible for low-temperature CO oxidation in nanoparticulate CuO/CeO₂ catalysts was identified as surface-substituted CuₓCe₂₋ₓOₓ. Contrary to previous studies, our measurements on a library of well-defined CuO/CeO₂ catalysts have proven that the CuO phase is a spectator species while the surface-substituted CuₓCe₂₋ₓ phase is active for CO oxidation. Using in-situ X-ray absorption spectroscopy, we found that the copper ions in CuₓCe₂₋ₓ remain at high oxidation states (Cu²⁺ and Cu⁴⁺) under oxygen-rich catalytic conditions without any evidence for Cu⁺. Artificial neural network potential Monte-Carlo simulations suggest that Cu²⁺ and Cu⁴⁺ preferentially segregate to the [100] surface of the CuₓCe₂₋ₓ nanoparticle, which is supported by aberration-corrected electron microscopy measurements. These results pave the way for understanding, at the atomic level, the mechanisms and descriptors pertinent for CO oxidation on these materials and hence the rational design of next generation catalysts.

KEYWORDS: Surface science, computational chemistry, electron microscopy, carbon monoxide, copper, ceria.

The efficient removal of poisonous carbon monoxide (CO) gas at ambient pressures and temperatures for applications in fuel-cell technology, respirators and catalytic converters is an area of active research in heterogeneous catalysis. Metal-oxide-based catalysts such as gold on titanium(IV) oxide (Au/TiO₂),¹ copper(II) oxide on cerium(IV) oxide (CuO/CeO₂),² and hopcalite (CuMn₂O₄)³ are among the most active for low-temperature CO oxidation. CuO/CeO₂ₙ, first reported by the group of Flytzani-Stephanopoulos,⁴ is more cost effective than state-of-the-art gold-based catalysts and is particularly promising for large-scale CO oxidation applications under ambient conditions. Despite extensive studies in the past 20 years, the nature of the active site(s) for CO oxidation on the surface of CuO/CeO₂ is not fully understood.⁵⁶ Initially, these studies suggested that CO oxidation catalysis turns over at dispersed Cu⁺ sites. Subsequent studies suggested that bulk-phase CuO sites at the perimeter of the CuO/CeO₂ interface are responsible for the rate enhancement and that the CuₓCe₂₋ₓ solid solution phase is inactive.⁵⁷ On the other hand, our single-phase CuₓCe₂₋ₓOₓ has shown activities comparable to those reported for CuO/CeO₂ in the absence of any detectable CuO or Cu⁺. XAS analysis of CuₓCe₂₋ₓOₓ has shown that the copper ions exist as an admixture of Cu²⁺ and Cu⁴⁺, and it is hypothesized that the catalytically-active copper ions segregate to the surface of CuₓCe₂₋ₓOₓ.⁶ In this study, we test these hypotheses by synthesizing single-phase CuₓCe₂₋ₓOₓ with different copper substitution and mixed-phase samples with CuₓCe₂₋ₓOₓ and CuO and comparing their intrinsic activity for CO oxidation. We demonstrate that the CuₓCe₂₋ₓ phase is the only contributor to catalysis of CO oxidation, while computational methods paired with aberration-corrected STEM-EELS support our claim that the copper ions segregate to the surface of the nanoparticles, forming copper-segregated regions distinct in nature from bulk CuO.

Solid-solution CuₓCe₂₋ₓOₓ and mixed-phase CuO/CuₓCe₂₋ₓOₓ catalysts were prepared according to our previous report.¹² Powder X-ray diffraction (PXRD, Figure 1A) confirms that the synthesis afforded single-phase CuₓCe₂₋ₓOₓ (space group #225, Fm-3m) with Cu substitution up to y = 0.08. Attempts to prepare samples with substitution beyond y = 0.09 resulted in the precipitation of bulk-phase CuO (space group #15, C2/c) as confirmed by PXRD (Figure 1A). Copper substitution in individual CuₓCe₂₋ₓOₓ nanoparticles in both types of catalysts was determined by HAADF-EDS (Figure S3, Supporting Information).
CO oxidation catalysis was performed in excess oxygen (9% CO, 2.5% O2). Increasing Cu substitution in Cu,CeyO2-x led to significant catalytic rate enhancement for the mass-normalized activity for CO oxidation, with the mixed-phase CuO/Cu,CeyO2-x catalysts having the highest activities in this study (Figure 2A). Notably, the most active CuO/Cu,CeyO2-x catalyst turns over CO oxidation at a rate of 0.2 μmol s⁻¹ g⁻¹ at 45 °C, which is comparable to CuO/CeO2 catalysts reported previously (0.02 – 0.5 μmol s⁻¹ g⁻¹ at 45 °C). These rates were then normalized to the concentration of copper on the surface of solid-solution Cu,CeyO2-x (neglecting contributions from the bulk CuO phase) assuming a homogeneous copper substitution (as determined by BET and HAADF-EDS, see the Experimental Section of the Supporting Information). Remarkably, the turnover frequencies (TOFs) for all catalysts are comparable within experimental uncertainty, as shown in Figure 2B. This observation strongly suggests that Cu,CeyO2-x is the active phase for CO oxidation, not the CuO/CeO2 interface as proposed previously. It should be noted that these turnover frequencies assume homogeneous substitution of copper within the entire lattice of Cu,CeyO2-x, which is, as we’ll see below, unrealistic. Assuming that all copper ions segregate to the surface, these TOFs will be scaled by a factor that is proportional to 1/d, where d is the average crystallite diameter (see the Experimental Section of the Supporting Information). Since the magnitude of d changes very little between the catalysts studied here (Table S3), TOFs for the different catalysts calculated assuming copper surface segregation do not vary within the experimental uncertainty of the measurement (Figure S6), consistent with our claim. Compared to other model systems, the measured TOFs for CO oxidation are reasonable. For example, the TOF (0.07 s⁻¹) measured here at 120 °C for Cu0.08Ce0.92O2-x is comparable to that found for CuO/CeO2 (0.09 s⁻¹). The CuO phase seems to improve catalysis by enhancing the surface area of the catalyst (Table S3, Supporting Information) while providing a source for copper dispersion. The mixed-phase CuO/Cu,CeyO2-x catalysts all have significantly higher surface areas than phase-pure Cu,CeyO2-x. We believe this is due to the presence of higher concentrations of oleylamine (or polymers thereof) in the as-synthesized samples. This higher organic content would act as a soft template during the subsequent annealing step, thereby increasing the surface areas of these samples. Moreover, the apparent activation energies found for mass-normalized activities in Figure 2A for all the catalysts are comparable (Table S3), which suggests that CO oxidation follows the same reaction mechanism on Cu,CeyO2-x independent of copper content.

We propose that the active sites for CO oxidation on the surfaces of Cu,CeyO2-x nanoparticles are associated with surface oxygen vacancies induced by copper substitution at the surface. In our previous DFT study, we hypothesized that Cu segregation on the nanoparticle surface promotes the formation of oxygen vacancies, which is considered central to the catalytic activity of these compounds. Using aberration-corrected STEM-EELS, we show...
direct evidence of the enrichment of Ce$^{3+}$ on the surface of Ce$_{0.08}$Cu$_{0.92}$O$_{2-x}$ nanoparticles, indicative of the presence of oxygen vacancies on the surface. We carefully analyzed the Ce M$_{4,5}$-edge across individual Ce$_{0.08}$Cu$_{0.92}$O$_{2-x}$ crystallites, where we found a high concentration of Ce$^{3+}$ at the nanoparticle surface (Figure 3) as evidenced by the appearance of a sharp low-energy feature (Figure 3A, 882 eV at the M$_{4,5}$-edge).

![Figure 3](image)

Figure 3. STEM-EELS analysis of a cluster of three Ce$_{0.08}$Cu$_{0.92}$O$_{2-x}$ nanoparticles. (A) Ce M$_{4,5}$-EELS spectra corresponding to surface and core areas highlighted in (B), (B) Dark field image acquired simultaneously with the spectrum image, (C) map corresponding to the signal in the ranges 880.4–882.4 eV and 898.4–900.4 eV (red windows in (A)), (D) map corresponding to the signal in the ranges 882.4–884.4 eV and 900.4–902.4 eV (green windows in (A)), and (E) sum of (C) and (D); scale bars: 5 nm.

The enrichment of Ce$^{3+}$ on the surface of Ce$_{0.08}$Cu$_{0.92}$O$_{2-x}$ particles is correlated to the presence of surface oxygen vacancies. While reduction at surfaces of ceria can occur under the electron beam, and given that unsubstituted, nanoparticulate ceria can have Ce$^{3+}$-rich surfaces, our observation is in principle consistent with surface copper segregation. The copper ions exist as an admixture of Cu$^{2+}$ and Cu$^{3+}$ from previous XAS studies, and may form oxygen vacancies more easily on the surface, which in turn can increase the concentration of Ce$^{3+}$ measured at the surface. This argument is supported by previous work that shows Sm-rich surfaces in Sm-doped CeO$_2$ nanoparticles having highly reduced Ce$^{3+}$ ions on the surface. Unfortunately the Cu L$_{2,3}$-edge, which has a weak cross-section and falls in the tail of the Ce M$_{4,5}$-edge white lines, could not be used for the quantitative analysis of Cu compositions across individual nanoparticles from the center to surface.

Surface copper segregation is further supported by DFT+$U$ and Artificial Neural Network Potential Monte-Carlo calculations. We investigated the thermodynamic driving force for copper segregation in CeO$_2$ by performing DFT+$U$ calculations using three [111]-terminated, 3x3x4 slabs having the stoichiometry Cu$_x$Ce$_{34}$O$_{72-x}$, with copper substitution at cerium sites (Figure 4A). Three modes of copper substitution were studied to examine different degrees of dispersion of copper in ceria. The solid-solution (ss-) model simulates a homogeneous dispersion throughout the lattice of CeO$_2$, while the nearest-neighbor (nn-) and next-nearest-neighbor (nnn-) models simulate surface segregation of copper (Figure 4A inset).

![Figure 4](image)

Figure 4. Computational modeling of Cu$_x$Ce$_{34}$O$_{72-x}$ catalysts by DFT and artificial neural network potential Monte-Carlo simulations. (A) Relative Gibbs free energy of formation for three [111]-terminated Cu$_x$Ce$_{34}$O$_{72-x}$ models at various oxidation states, (B) radial probability of Cu substitution and (C) pair distribution function for Cu-Cu distances in 3.6 nm Cu$_{54}$Ce$_{30}$O$_{74}$ nanoparticles. Relative values for ∆G$_f$ were calculated at 700 K using the oxygen chemical potential associated with 0.21 atm O$_2$. Monte Carlo calculations were carried out simulating annealing from 5000 to 300 K.

Consistent with our previous studies on Ce$_{0.08}$Cu$_{0.92}$O$_{2-x}$, we found Cu$^{3+}$ and Cu$^{2+}$ to be the most thermodynamically stable forms of copper, independent of the mode of substitution (Figure 5, Supporting Information) under oxygen-rich conditions. Corroborating this, we found no experimental evidence, by means of in-situ XAS, for the presence of Cu$^{+}$ in Ce$_{0.08}$Cu$_{0.92}$O$_{2-x}$ in air or under our experimental, oxygen-rich conditions even at 300 °C (Figure 5). While we cannot rule out the presence of Cu$^{+}$ under oxygen-lean conditions (< 10$^{-6}$ atm O$_2$ according to Figure 5), these data suggest that copper exists as an admixture of Cu$^{2+}$ and Cu$^{3+}$ under the catalytic conditions of Figure 1. We should also note that these studies do not necessarily negate the existence of a very small number (< 5% of all copper sites) of Cu$^{+}$ or Cu$^{0}$ species, below the detection limit of XAFS that might be responsible for CO oxidation catalysis.
Cu K-edge XAS measurements of Cu$_{x}$Ce$_{y}$O$_{2.9}$ performed under reaction conditions: (A) near-edge spectra and (B) the Fourier transform of the EXAFS in air at 25 °C (blue traces), in 1% CO + 2.5% O$_2$ at 25 °C (green traces) and in 1% CO + 2.5% O$_2$ at 300 °C (orange traces). Measurements were performed in the Cu K-edge spectra.

Regardless of copper oxidation state, copper segregation in the nn-Cu$_{x}$Ce$_{y}$O$_{2.9}$ structure is consistently 1 eV more stable than ss-Cu$_{x}$Ce$_{y}$O$_{2.9}$, as shown in Figure 4A and Figure S7 (Supporting Information). Interestingly, the Gibbs free energy of formation for nn-Cu$_{x}$Ce$_{y}$O$_{2.9}$, which we found to be the most stable structure of all investigated, is 1 eV more stable than the related nnn-Cu$_{x}$Ce$_{y}$O$_{2.9}$ structure. These calculations suggest that upon segregation to the surface, it is energetically favorable for copper to aggregate to form copper-segregated regions of the Cu$_{x}$Ce$_{y}$O$_{2.9}$ surface that are distinct from CuO. In each case, copper ions relax towards the (100) plane of oxygen atoms to accommodate a square-planar coordination environment with the oxygen ligands; this manifests as a reconstruction of the [111] surface to include (100) terraces with these square-planar copper motifs (Figure 4A inset).

We further examined how the copper ions are distributed within an entire nanoparticle by employing Monte-Carlo simulations of entire 3.6 nm Cu$_{x}$Ce$_{y}$O$_{2.9}$ nanoparticles using artificial neural network (ANN) potentials trained to DFT reference energies (see Figures S2 and Table S2 in the Supplementary Information for further details).9,20 Consistent with our slab studies, copper prefers to sit at the surface of the nanoparticle (at distances 1.6 to 1.8 nm from the center), and very little is found in the subsurface or deeper layers (1.0 to 1.6 nm from center, Figure 4B). In addition, these simulations confirm that copper ions associate to form O$^{2-}$-bridged clusters (Figure 4C), which manifest as nearest neighbor interactions on [111] and next nearest neighbor interactions on [100], accounting for over 70% of the pair distribution function. It is noteworthy that the copper prefers to associate on the higher-energy [100] and [100]/[111] edge sites (Figure 4C inset), which requires further examination, but is generally consistent with single-crystal X-ray crystallography studies of copper adsorption on CeO$_2$ (111).21 These studies found that copper preferentially adsorbs to step edges rather than (111) terraces. This preference might be attributed to a lower penalty for the formation of oxygen vacancies on the [100] surfaces, which is supported by the fact that such preferential reduction of Ce$^{3+}$ to Ce$^{2+}$ on [100] vs [111] facets has been observed on ceria nanocrystals.20,24 This preferential reduction on [100] facets was also observed experimentally in our STEM-EELS measurements of Mn$_{x}$Ce$_{y}$O$_{2.9}$ nanoparticles (Figure S8, Supporting Information).

These calculations verify our chemical intuition that we expect copper substitution to be inhomogeneous in Cu$_{x}$Ce$_{y}$O$_{2.9}$. Since Figure 2B assumes that copper substitution is homogeneous throughout the ceria lattice, this plot likely overestimates the TOF since copper segregates to the surface. Nevertheless, our conclusions from Figure 2B are still valid since this overestimation does not depend on copper content (y) (see Experimental Section of the Supporting Information). These calculations shed light on what structural features might be present for the catalytically-active copper sites. They suggest that site-isolated, square-planar copper sites, stabilized in the Cu$^{3+}$ oxidation state on (100) terraces, are responsible for the catalytic rate enhancement for CO oxidation we see in Figure 2, which can be used for the design of highly active catalysts for CO oxidation.

In this work, we show that the mass activity of CO oxidation increases with copper content in both single-phase Cu$_{x}$Ce$_{y}$O$_{2.9}$ and two-phase-mixtures CuO/Cu$_{x}$Ce$_{y}$O$_{2.9}$, while the TOFs are comparable, independent of copper content. This observation indicates that CO oxidation is catalyzed directly by dispersed copper ions in the Cu$_{x}$Ce$_{y}$O$_{2.9}$ phase, not by bulk CuO or its interface with Cu$_{x}$Ce$_{y}$O$_{2.9}$, as reported previously.5,10,11 Supported by DFT calculations, in-situ XAS reveals that the surface-substituted copper ions remain as Cu$^{3+}$ and Cu$^{2+}$ under oxygen-rich conditions, even at elevated temperatures. While these observations suggest that Cu$^{3+}$ and Cu$^{2+}$ in Cu$_{x}$Ce$_{y}$O$_{2.9}$ are the active sites, we cannot rule out the possibility of the existence of a very small number (<5%) of undetectable Cu$^{4+}$ species that could be responsible for all CO oxidation catalysis.15,16 We propose that the active sites for CO oxidation are associated with surface oxygen vacancies induced by copper segregation. Aberration-corrected STEM-EELS shows direct evidence of an enrichment of Ce$^{3+}$ sites on the surface of Cu$_{x}$Ce$_{y}$O$_{2.9}$ nanoparticles, which is consistent with surface segregation. A thorough computational treatment of the local structure and distribution of copper in Cu$_{x}$Ce$_{y}$O$_{2.9}$ nanoparticles supports copper segregation on the [100] and, to a lesser extent, on the [111] surfaces. These results have important consequences for practical and fundamental aspects of CO oxidation catalysis. Moving forward, further mechanistic studies are needed to provide an atomic-level description of the active site during CO oxidation, and establish reliable descriptors for the rational design of the next generation of catalysts.

ASSOCIATED CONTENT

Supporting Information. Experimental and computational details, additional HRTEM, HAADF, and STEM images, Raman spectra, Arrhenius plots, computational phase diagrams,
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AUTHOR INFORMATION

Corresponding Author
E-mail: shaohorn@mit.edu
Notes
The authors declare no competing financial interest.
Supporting Information

Elucidating the Nature of the Active Phase in Copper/Ceria Catalysts for CO Oxidation

Joseph S. Elias,† Nongnuch Artrith,§ Matthieu Bugnet,‡ Livia Giordano,§§ Gianluigi A. Botton,‡ Alexie M. Kolpak,§ and Yang Shao-Horn*§

†Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
§Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
§§Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada
#Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Via R. Cozzi 53, 20125 Milan, Italy

* Corresponding Author e-mail: shaohorn@mit.edu
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General experimental considerations

All reagents were obtained from commercial vendors and were used without further purification. All reactions were performed under ambient conditions unless otherwise noted. The precursor compounds \( \text{Cu}^{II}-3\text{-MeO-salpn} \), \( \text{Ce}^{	ext{III}}-3\text{-MeO-salpn} \) and \( \text{Cu}^{II}\text{-Ce}^{	ext{III}}-3\text{-MeO-salpn} \) were prepared according to our previous report.\(^1\)

General procedure for the preparation of single-phase \( \text{Cu}_{y}\text{Ce}_{1-y}O_{2-x} \) nanoparticles

Single-phase nanoparticles with the stoichiometry \( \text{Cu}_{y}\text{Ce}_{1-y}O_{2-x} \) for \( y = 1, 3, 8\% \) were prepared according to our previous report.\(^1\) Appropriate amounts, not exceeding 1.0 mmol total, of the parent \( \text{Ce}^{	ext{III}}-3\text{-MeO-salpn} \) and \( \text{Cu}^{II}\text{-Ce}^{	ext{III}}-3\text{-MeO-salpn} \) complexes were heated with magnetic stirring in 40 mL oleylamine at 180 °C under an Ar flow for 4 hours in a three-neck flask equipped with a reflux condenser and bump trap. The resulting dark brown solutions were divided into eight 5 mL fractions, flocculated with ethanol (40 mL each) and the flocculant was isolated by centrifugation (7100 rpm for 15 min). The flocculant was then redissolved in hexanes (5 mL each) and bulk precipitates were removed by centrifugation (5000 rpm for 1 min) and decanting of the dark brown hexanes solutions. This process was repeated once to give dark-brown hexanes solutions of phase-pure \( \text{Cu}_{y}\text{Ce}_{1-y}O_{2-x} \).

To remove the organic capping layer for catalysis and further characterization, as-prepared solutions of \( \text{Cu}_{y}\text{Ce}_{1-y}O_{2-x} \) were dropcast into alumina crucibles and annealed at 400 °C in synthetic air for 4 hrs to give phase-pure, free-flowing powders of \( \text{Cu}_{y}\text{Ce}_{1-y}O_{2-x} \).

Synthesis of \( \text{Cu}_{0.01}\text{Ce}_{0.99}O_{2-x} \) nanoparticles

\( \text{Cu}_{0.01}\text{Ce}_{0.99}O_{2-x} \) was prepared from the pyrolysis of \( \text{Ce}^{	ext{III}}-3\text{-MeO-salpn} \) (0.633 g, 0.947 mmol) and \( \text{Cu}^{II}\text{-Ce}^{	ext{III}}-3\text{-MeO-salpn} \) (0.038 g, 0.052 mmol) in 40 mL oleylamine (vide supra) to give \( \text{Cu}_{0.01}\text{Ce}_{0.99}O_{2-x} \) as a pale khaki powder after annealing (0.091 g, 0.53 mmol, 53%).

Synthesis of \( \text{Cu}_{0.03}\text{Ce}_{0.97}O_{2-x} \) nanoparticles

\( \text{Cu}_{0.03}\text{Ce}_{0.97}O_{2-x} \) was prepared from the pyrolysis of \( \text{Ce}^{	ext{III}}-3\text{-MeO-salpn} \) (0.501 g, 0.749 mmol) and \( \text{Cu}^{II}\text{-Ce}^{	ext{III}}-3\text{-MeO-salpn} \) (0.183 g, 0.250 mmol) in 40 mL oleylamine (vide supra) to give \( \text{Cu}_{0.03}\text{Ce}_{0.97}O_{2-x} \) as a khaki powder after annealing (0.040 g, 0.24 mmol, 24%).

Synthesis of \( \text{Cu}_{0.08}\text{Ce}_{0.92}O_{2-x} \) nanoparticles

\( \text{Cu}_{0.08}\text{Ce}_{0.92}O_{2-x} \) was prepared from the pyrolysis of \( \text{Ce}^{	ext{III}}-3\text{-MeO-salpn} \) (0.223 g, 0.333 mmol) and \( \text{Cu}^{II}\text{-Ce}^{	ext{III}}-3\text{-MeO-salpn} \) (0.487 g, 0.667 mmol) in 40 mL oleylamine (vide supra) to give \( \text{Cu}_{0.08}\text{Ce}_{0.92}O_{2-x} \) as a dark khaki powder after annealing (0.127 g, 0.675 mmol, 76.5%).

General procedure for the preparation of \( \text{CuO/\text{Cu}_{y}\text{Ce}_{1-y}O_{2-x}} \)
Mixed-phase CuO/Cu$_y$Ce$_{1-y}$O$_{2-x}$ materials were prepared under conditions similar to the preparation of single-phase Cu$_y$Ce$_{1-y}$O$_{2-x}$ described above with notable differences; the reaction was carried out in air and with excess Cu$^{II}$-3-MeO-salpn precursor. Appropriate amounts of Cu$^{II}$-Ce$^{III}$-3-MeO-salpn and Cu$^{II}$-3-MeO-salpn were heated with magnetic stirring in 40 mL oleylamine at 180 °C in air for 4 hours in a three-neck flask equipped with a reflux condenser and bump trap. The resulting dark-brown solutions were worked up with ethanol and hexanes as described above for Cu$_y$Ce$_{1-y}$O$_{2-x}$, dropcast into alumina crucibles, and annealed in air at 400 °C for 4 hours to give free-flowing powders of CuO/Cu$_y$Ce$_{1-y}$O$_{2-x}$.

**Synthesis of CuO/Cu$_{0.05}$Ce$_{0.95}$O$_{2-x}$ nanoparticles**

CuO/Cu$_{0.05}$Ce$_{0.95}$O$_{2-x}$ was prepared from the pyrolysis of Cu$^{II}$-3-MeO-salpn (0.807 g, 2.00 mmol) and Cu$^{II}$-Ce$^{III}$-3-MeO-salpn (0.730 g, 1.00 mmol) in 40 mL oleylamine (vide supra) to give CuO/Cu$_{0.05}$Ce$_{0.95}$O$_{2-x}$ as an olive powder after annealing (0.119 g).

**Synthesis of CuO/Cu$_{0.08}$Ce$_{0.92}$O$_{2-x}$ nanoparticles**

CuO/Cu$_{0.08}$Ce$_{0.92}$O$_{2-x}$ was prepared from the pyrolysis of Cu$^{II}$-3-MeO-salpn (0.332 g, 0.822 mmol) and Cu$^{II}$-Ce$^{III}$-3-MeO-salpn (0.730 g, 1.00 mmol) in 40 mL oleylamine (vide supra) to give CuO/Cu$_{0.08}$Ce$_{0.92}$O$_{2-x}$ as an olive powder after annealing (0.050 g).

**Synthesis of CuO/Cu$_{0.09}$Ce$_{0.91}$O$_{2-x}$ nanoparticles**

CuO/Cu$_{0.09}$Ce$_{0.91}$O$_{2-x}$ was prepared from the pyrolysis of Cu$^{II}$-3-MeO-salpn (0.167 g, 0.413 mmol) and Cu$^{II}$-Ce$^{III}$-3-MeO-salpn (0.730 g, 1.00 mmol) in 40 mL oleylamine (vide supra) to give CuO/Cu$_{0.09}$Ce$_{0.91}$O$_{2-x}$ as an olive powder after annealing (0.078 g).

**Powder X-ray diffraction (PXRD)**

Powder X-ray diffraction patterns were collected on a PANalytical X’Pert PRO diffractometer using Bragg-Brentano geometry and nickel-filtered Cu-K$_\alpha$ radiation ($\lambda$ = 1.54056 Å). Samples were prepared using 0.2 mm deep zero-background sample wells composed of boron-doped, p-type silicon from MTI Corporation. Powder profiles were fit with pseudo-Voigt functions using the FullProf suite. In each case, the crystallite sizes ($d$) of the Cu$_y$Ce$_{1-y}$O$_{2-x}$ phase were estimated using the Scherrer equation to the fitted (220) peak assuming a shape factor $K$ of 0.94 for spherical crystallites of cubic symmetry, after accounting for instrumental line broadening. The crystallite sizes thus obtained were used to estimate the turnover frequencies assuming surface segregation of copper sites (vide infra).

**Transmission electron microscopy (TEM)**

Samples studied by transmission electron microscopy were prepared by dropcasting dilute ethanol suspensions of annealed (CuO)/Cu$_y$Ce$_{1-y}$O$_{2-x}$ onto lacey carbon gold TEM grids. Bright field images were acquired at 200 keV using a low-background beryllium sample holder on a JEOL 2010-FEG transmission electron microscope at MIT, which is equipped with a field-emission electron gun and an ultra-high resolution pole piece, resulting in a point-to-point
resolution of 1.9 Å. Fast Fourier transforms (FFTs) were implemented using the ImageJ software. For the acquisition of bright-field images, care was taken to prevent beam-induced reconstruction of individual nanocrystals by minimizing the duration of beam exposure. Energy dispersive X-ray spectroscopy (EDS) was performed in scanning transmission mode using a 1 nm diameter electron beam. Quantification was carried out by using a simple ratio technique in INCA (Oxford Instruments), which accounts for X-ray absorption and thickness effects. Nevertheless, the thickness parameter used in quantification was varied to determine if the inconsistent apparent thicknesses of the samples shown in Figure S3 contribute to the inconsistencies in the copper quantification. For all samples measured, we saw no significant change in copper content, suggesting that X-ray absorption is minimal in these samples. Copper substitution was quantified for the Cu$_x$Ce$_{1-y}$O$_{2-x}$ phase only by judicious choice of probe position; CuO phases were avoided by differentiating them by image contrast.

Electron Energy Loss Spectroscopy

Cu$_{0.1}$Ce$_{0.9}$O$_{2-x}$ and Mn$_{0.1}$Ce$_{0.9}$O$_{2-x}$ samples were prepared by diluting annealed nanoparticle powders in HPLC grade methanol, ultrasonicating, and dropcasting onto Si$_3$N$_4$ window grids (Norcada Inc.). Experiments were carried out on a FEI Titan cubed (80-300) (S)TEM at McMaster University, equipped with aberration correctors of the probe and image forming lenses and a high resolution GIF Quantum spectrometer. The microscope was operated at 80 kV in STEM mode, and the spectrum images were recorded with a collection angle of ~55 mrad, and a current below 40 pA to minimize beam damage.

Raman Spectroscopy

Raman spectra were acquired at room temperature on a LabRAM HR800 microscope (Horiba Jobin Yvon) using an external 17 mW HeNe 632.8 nm laser (Melles Griot) focused with a 50× objective lens and a 25% filter. A silicon substrate was used to calibrate the Raman shift. The sampling time and range were identical for all spectra (100-1000 cm$^{-1}$, 5 × 10 s) using a 600 mm$^{-1}$ grating.

X-ray absorption spectroscopy (XAS)

X-ray absorption measurements at the copper K-edge were performed at the bending magnet station X11A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The electron storage ring operated at 2.8 GeV with a stored current in the range of 200 – 300 mA. The excitation energies were selected with a double crystal monochromator (Si-(111)), which was detuned by 40% to suppress higher harmonics. The incident and transmitted beams were monitored using ionization chambers equilibrated with appropriate mixtures of nitrogen and argon gas. The energy calibration of the monochromator was set by calibrating the inflection point of the absorption spectrum of transition-metal foils to their literature values. Copper K-edge spectra were acquired in fluorescence yield (FY) mode using a resistively-heated in-situ catalyst furnace equipped with a 5-grid Lytle fluorescence detector (both from the EXAFS Company). For FY measurements, the signal passed through a silver Soller slit assembly prior to detection by the ionization chamber, which had a continuous flow of Ar. The pellet for in-situ studies was prepared by first sieving Cu$_{0.08}$Ce$_{0.92}$O$_{2-x}$ (10.5 wt%), boron...
nitride (75.5 wt%) and high-surface area Vulcan XC-72 carbon (14 wt%, Cabot) to 400 mesh followed by thorough mixing and grinding with an agate mortar and pestle. A 50 mg pellet (5 mm x 12 mm) was pressed and introduced into the catalyst furnace, the window of which was sealed with Kapton tape. Gas mixtures (CO and O₂ balanced in He) were flowed through the catalyst pellet by means of mass-flow controllers at flow-rates of 50 mL min⁻¹. The pellet was slowly heated to 300 °C under lean conditions (0.01 atm CO and 0.025 atm O₂ at a flow rate of 50 mL min⁻¹) and gases were allowed to equilibrate for 15 minutes before the acquisition of XAFS spectra.

Absorption spectra were normalized using the Autobk algorithm found in the IFEFFIT program⁷ of the Horae XAFS analysis suite.⁸ First, a linear fit of the pre-edge line was subtracted from the spectrum. A fourth-order knot-spline polynomial was used to fit the post-edge line and the edge step was normalized to unity. Prior to Fourier transforms, the EXAFS was multiplied by a Hanning window covering the first and last ~10% of the data range.

**Single-point BET surface area determination**

Values for the surface areas of annealed (CuO)/CuₓCe₁₋ₓO₂₋ₓ powders were estimated from single-point BET measurements from desorption of N₂ at room temperature (after adsorption at 77 K in 30% N₂/He) using a ChemBET Pulsar apparatus (Quantachrome). For the calculation of the turnover frequency (TOF) in mixed phase CuO/CuₓCe₁₋ₓO₂₋ₓ powders, it was assumed in that the measured BET surface area was attributed to the CuₓCe₁₋ₓO₂₋ₓ phase since the crystallite size is significantly smaller than CuO by TEM and PXRD.

**CO oxidation catalysis**

CO oxidation kinetic measurements were acquired in a home-made 3.81 mm i.d. quartz plug-flow reactor. For each measurement, the annealed catalyst powder (20 mg) was mixed with 1.705 g oven-dried sand (V_bed = 1.086 cm³) and was then loaded into center of the reactor, filling the remaining volume with sand. The temperature of the catalyst was recorded using a K-type thermocouple inserted into the catalyst bed. The compositions of the feed and down-stream gases were recorded by on-line gas chromatography (Agilent 490 supplied with a molecular sieve COX column and a thermal conductivity reactor), recording every 5 °C. The percent conversion was calculated according to

\[
\% \text{ Conversion} = \frac{p_{\text{CO}_2}}{p_{\text{CO}} + p_{\text{CO}_2}} \cdot 100\%
\]

where \( p_{\text{CO}_2} \) and \( p_{\text{CO}} \), the partial pressures of CO₂ and CO, respectively, are determined directly from the relative peak area of the CO₂ and CO peaks normalized to the internal He standard. Prior to and following each catalytic test, the flow rate of the gas upstream was measured directly with a bubble flowmeter, and the percent conversion below 12.5% was converted to mass-normalized rates of CO oxidation (in units of µmol CO s⁻¹ g⁻¹cat) for the Arrhenius plots according to

\[
r_{\text{mass}} = \frac{\% \text{ Conversion} \cdot r_{\text{CO}} \cdot 1000}{V_m \cdot 60 \cdot m_{\text{cat}}}
\]
\[
\% \text{Conversion} \cdot r_{\text{CO}} = \frac{6 \cdot V_m \cdot m_{\text{cat}}}{r_{\text{CO}} \cdot \frac{V_m}{RT/p} \cdot V_m \cdot m_{\text{cat}}}
\]

where \( r_{\text{CO}} \) is the volumetric flow rate of CO of the feed stream (in mL min\(^{-1}\)), \( V_m \) is the molar volume of a gas (from the ideal gas law, \( V_m = RT/p \), in mol/L) and \( m_{\text{cat}} \) is the mass of the loaded catalyst in grams. The specific (area-normalized) rates for CO oxidation (in units of mol CO s\(^{-1}\) m\(^{-2}\)) were thus calculated according to

\[ r_{\text{area}} = \frac{r_{\text{mass}}}{A_S} \cdot 10^{-6} \]

where \( A_S \) is the surface area of the catalyst (in m\(^2\) g\(^{-1}\)) as measured by BET (\textit{vide supra}). Finally, the turnover frequency (TOF) as reported in Figure 2B was estimated according to the formula

\[ TOF \approx \frac{r_{\text{area}} \cdot N_A}{PD_{111} \cdot y} \]

where \( N_A \) is Avogadro’s number, \( PD_{111} \) is the planar density of cerium atoms in the \{111\} plane of CeO\(_2\) (in units of atoms m\(^{-2}\)) and \( y \) is the amount of copper ions substituted into the Cu\(_y\)Ce\(_{1-y}\)O\(_{2-x}\) phase as determined by STEM-EDS. The planar density of the \{111\} facet was used in the calculation of the TOF because (a) it was found by HRTEM to be the most predominant crystallographic termination in individual Cu\(_y\)Ce\(_{1-y}\)O\(_{2-x}\) nanoparticles (the other being \{100\}),\(^1\) and (b) \( PD_{111} \) is only 15.5\% larger than \( PD_{100} \) (7.89*10\(^{18}\) Ce m\(^{-2}\) and 6.83*10\(^{18}\) Ce m\(^{-2}\), respectively), and hence likely underestimates the actual TOF.

This calculation assumes homogeneous copper substitution into the CeO\(_2\) lattice and, according to the discussion in the main text, is thus likely overestimating the actual TOF because copper segregates to the surface. To take surface segregation into account, we can estimate a correction factor to the TOF reported above based on the geometry and crystal structure of a representative nanoparticle

\[
\frac{n_{\text{Cu, homogeneous}}}{n_{\text{Cu, surface segregation}}} = \frac{A_{S,\text{np}} \cdot PD_{111} \cdot y}{V_{\text{np}} \cdot \left(\frac{Z}{V_{\text{cell}}}\right) \cdot y}
\]

where \( n_{\text{Cu, surface segregation}} \) is the number of copper sites that segregate to the surface, which, for our purposes, we assume to be all of the copper sites in the nanoparticle. \( n_{\text{Cu, homogeneous}} \) is the total number of copper sites at the surface of an individual nanoparticle assuming that copper is distributed evenly within the ceria lattice. Here, \( V_{\text{np}} \) and \( A_{S,\text{np}} \) are the volume and surface area of the nanoparticle, respectively, and \( Z \) is the number of cerium atoms in the unit cell of CeO\(_2\) (which has a volume of \( V_{\text{cell}} \)). In the case of Cu\(_y\)Ce\(_{1-y}\)O\(_{2-x}\), we have established that the crystal habit is a truncated octahedron, which has a known volume and surface area:
\[
\frac{n_{Cu, \text{homogeneous}}}{n_{Cu, \text{surface segregation}}} = \frac{(6 + 12\sqrt{3})e^2 \cdot PD_{111}}{8\sqrt{2}a^2 \cdot \left(\frac{Z}{V_{\text{cell}}}\right)}
\]

where \(a\) is the edge length of the truncated octahedron. In our previous study, we found the diameter of annealed \(\text{Cu}_{0.08}\text{Ce}_{0.92}\text{O}_{2-\text{x}}\) to be 36 Å from Scherrer analysis of the X-ray powder diffraction patterns,\(^1\) which is consistent with our HRTEM results here. If we define the diameter of a truncated octahedron as \(3a\), and use crystallographic parameters for \(\text{CeO}_2\) (\(Z = 4, V_{\text{cell}} = 158.46\ \text{Å}^3\)), this correction is \(\sim 0.62\), which is within the scatter of the kinetic measurements summarized in Figure 2B. Nevertheless, these corrections are tabulated in Table S3 and are used as the basis for the estimation of the turnover frequencies (assuming \textit{surface segregation} of copper sites) summarized in Figure S5. Although the turnover frequencies for the catalysts studied here do decrease assuming surface segregation of copper sites, this decrease is systematic. The turnover frequencies for the different catalysts are identical within the scatter of the measurement, consistent with Figure 2 and the conclusion of the main text.

**Computational Methods**

**DFT+U slab studies of \{111\}-terminated \(\text{Cu}_2\text{Ce}_{34}\text{O}_{72-\text{x}}\)**

Plane-wave basis set spin-polarized DFT+\(U\) calculations were executed employing the exchange and correlation energy functional expressed in the Perdew-Burk-Ernzerhof (PBE) generalized gradient approximation (GGA)\(^9\)-\(^12\) using projector-augmented wave (PAW) pseudopotentials.\(^{13,14}\) All calculations were performed within the Vienna Ab Initio Simulation Package (VASP) suite\(^{15-18,14}\) using either the Cray XE6 (“Hopper”) or Cray XC30 (“Edison”) supercomputers at the National Energy Research Scientific Computing Center (NERSC).

A 3x3x4 hexagonal slab model of the \(\text{CeO}_2\) (111) surface (\(\text{Ce}_{36}\text{O}_{72}\)) was used as the starting point for models of the \(\text{Cu}_x\text{Ce}_{1-y}\text{O}_{2-\text{x}}\) catalyst, separated by 15 Å of vacuum to prevent interactions between slabs. To simulate copper substitution, two copper atoms were placed in cerium vacancies (\(\text{Cu}^\times_{\text{Ce}}\) in Kröger-Vink notation) in the parent \(\text{Ce}_{36}\text{O}_{72}\) slab to give the aliovalent, copper-substituted models of stoichiometry \(\text{Cu}_2\text{Ce}_{34}\text{O}_{72}\). As described in the text, three configurations were considered to study the relative thermodynamic stability of copper segregation and agglomeration (Figure 4A inset). In the solid solution (ss-) models, copper atoms replace cerium atoms in the first and third \(\text{CeO}_2\) layers (Ce-Ce interatomic distance = 12.859 Å). In the nearest-neighbor (nn-) models, copper atoms replace nearest-neighbor cerium atoms on the first \(\text{CeO}_2\) layer of the slab (Ce-Ce interatomic distance = 3.877 Å), and in the next-nearest-neighbor (nnn-) model, copper atoms replace next-nearest-neighbor cerium atoms on the first \(\text{CeO}_2\) layer (Ce-Ce interatomic distance = 6.715 Å). To simulate aliovalent substitution of the copper ions (\(\text{Cu}^{3+}, \text{Cu}^{2+}, \text{and} \text{Cu}^+\), or \(\text{Cu}^\times_{\text{Ce}}, \text{Cu}^\times_{\text{Ce}}, \text{and} \text{Cu}^\times_{\text{Ce}}\) in Kröger-Vink notation), an appropriate number of oxygen atoms were removed in the vicinity of the transition-metal centers for charge compensation; the removal of a single oxygen atom corresponds to the reduction of
each copper atom by 1 electron. For example, removal of a single oxygen atom from Cu$_2$Ce$_{34}$O$_{72}$ to give Cu$_2$Ce$_{34}$O$_{71}$ suggests that each of the copper atoms in the slab has been reduced by one electron from Cu$^{4+}$ to Cu$^{3+}$. Hence, these models are denoted as Cu$^{(4-x)+}$$_2$Ce$_{34}$O$_{72-x}$, where $x$ refers to the number of charge-compensating oxygen atoms removed (the oxygen non-stoichiometry). For all nn-Cu$_2$Ce$_{34}$O$_{72-x}$ structures, as well as ss-Cu$^{5+}$$_2$Ce$_{34}$O$_{72}$, ss-Cu$^{3+}$$_2$Ce$_{34}$O$_{72}$, nnn-Cu$^{4+}$$_2$Ce$_{34}$O$_{72}$ and nnn-Cu$^{3+}$$_2$Ce$_{34}$O$_{71}$ surfaces, reduction at the copper (as opposed to surrounding cerium atoms) was confirmed by inspecting the net magnetization for each atom of the slab and examination of the partial density of states. Interestingly, for the ss-Cu$^{2+}$$_2$Ce$_{34}$O$_{70}$ slab, copper reduction was accompanied by reduction of the cerium atoms surrounding the oxygen vacancy.

The (111) surface of CeO$_2$ was chosen on the basis of HRTEM analysis both here and in earlier studies, which indicate that the (111) is the predominant surface exposed in truncated octahedral Cu$_3$Ce$_{11}$O$_{21}$ crystallites. The choice of a 3x3x4 slab with substitution of two copper atoms was also rationalized in terms of experimental data; these models give 5.6% Cu substitution in CeO$_2$ while we have found here that $y$ in Cu$_y$Ce$_{11}$O$_{21-x}$ can vary between 1 and 9% Cu *(vide supra)*. A 3x3x4 slab was also chosen in order to simulate varying degrees of substitutional homogeneity *(i.e. the ss-, nn-, and nnn- models mentioned above).*

A Hubbard $U_{\text{eff}}$ ($U_{\text{eff}} = U - J$) correction term of 4.0 eV acting on the 4$f$ orbitals of cerium was included in all calculations to allow for a more accurate description of the electronic structure of both oxidized and reduced ceria, which has been discussed previously. The inclusion of a Hubbard $U_{\text{eff}}$ term acting on the copper 3$d$ orbitals may perturb the energies of oxygen formation in the model slabs and hence the thermodynamic preference of one oxidation state over the other. We found that the introduction of a Hubbard $U_{\text{eff}}$ term on the copper 3$d$ states did not perturb the relative values of $\Delta G_F$ for the slabs studied here. Only after applying values for $U_{\text{eff}}$ in excess of 4.0 eV did we see any changes in the ordering of $\Delta G_F$ vs. $\mu_O$ plots, hence we set $U_{\text{eff}}$ to 0.0 eV for copper 3$d$ states for all studies on Cu$^{(4-x)+}$$_2$Ce$_{34}$O$_{72-x}$.

To correct for any systematic errors arising from the periodic boundary conditions with the asymmetric slabs studied here, a linear electrostatic potential *(i.e. a dipole correction)* was applied to the local potential. Electronic and ionic optimization of the slabs was carried out using the conjugate gradient algorithm employing a plane-wave cutoff of 400 eV. All atomic layers were allowed to relax until all the forces acting on the atoms reached a value below 0.01 eV Å$^{-1}$. Owing to the large size of the slabs studied here, all data were reported from the integration of the Brillouin zone at the $\Gamma$ point only. We found that the slab energies calculated at the $\Gamma$ point varied by less than 35 meV from those calculated using a 2x2x1 Monkhorst-Pack mesh, which justifies our choice of integration at the $\Gamma$ point only.

Estimates for the Gibbs energy of formation ($\Delta G_F$) of the different slabs of Cu$^{(4-x)+}$$_2$Ce$_{34}$O$_{72-x}$ as a function of oxygen partial pressure were determined according to a strategy previously reported by Reuter, *et al.* $\Delta G_F$ was determined relative to a reference structure (ss-Cu$_2$Ce$_{34}$O$_{72}$) by taking into account the formation of oxygen vacancies:

$$\Delta G_{F,x} = G(\text{Cu}_2\text{Ce}_{34}\text{O}_{72-x}) - G(\text{ss-Cu}_2\text{Ce}_{34}\text{O}_{72}) + x\mu_0(p,T)$$

If changes in entropy of the solid phases are neglected, we can express $\Delta G_F$ in terms of energy ($E$) calculated by DFT:

$$\Delta G_{F,x} = E(\text{Cu}_2\text{Ce}_{34}\text{O}_{72-x}) - E(\text{ss-Cu}_2\text{Ce}_{34}\text{O}_{72}) + x\mu_0(p,T)$$
where the chemical potential for oxygen ($\mu_O$) is

$$\mu_O(p,T) = \mu_O(p_0,T) + \frac{1}{2} k_B T \ln \frac{p}{p_0}$$

The standard chemical potential for oxygen at $p_0 = 1$ atm ($\mu_O(p_0,T)$) is found from thermodynamic tables. The value for $\mu_O(p,T)$ is referenced with respect to the total energy of an oxygen atom in a molecule of O$_2$ as calculated by DFT. The temperature used in these calculations (700 K where $\mu_O(p_0,T) = -0.73$ eV) was chosen to roughly correspond to the temperature at which Cu$_{y}$Ce$_{1-y}$O$_{2-x}$ samples were annealed.

**Nanoparticle model for Monte-Carlo simulations**

To allow a direct comparison with experiment, we devised an atomistic nanoparticle model based on the experimentally observed Wulff shape with a {111} to {100} surface ratio of 3:1. The relative areas of the two crystal faces as function of their relative distance from the particle center, $h_{\{111\}}/h_{\{100\}}$, are

$$A_{\{100\}} = 12 \left( \sqrt{3} \frac{h_{\{111\}}}{h_{\{100\}}} - 1 \right)^2$$

and

$$A_{\{111\}} = 6\sqrt{3} - 8\sqrt{3} \left( \frac{\sqrt{3} h_{\{111\}}}{h_{\{100\}}} - \frac{3}{2} \right)^2$$

for $\frac{1}{\sqrt{3}} \leq \frac{h_{\{111\}}}{h_{\{100\}}} \leq \frac{2}{\sqrt{3}}$, so that $A_{\{111\}}/A_{\{100\}} = 3$ corresponds to $h_{\{111\}}/h_{\{100\}} \approx 0.887$ (see graphical solution in Fig. S1). We used this relationship to build the nanoparticle structure with approximately 3.5 nm diameter and the desired relative surface areas shown in Figs. 3b and 3c.

![Graphical solution of the surface area ratio as function of the surface distance from the particle center.](image)

**Figure S1.** Graphical solution of the surface area ratio as function of the surface distance from the particle center. The solid black and red lines indicate the {111} and {100} surface areas, respectively. The dotted black line corresponds to 1/3 of the {111} surface area, and the blue circle points out the {111}:{100} ratio of 3:1.

**Artificial neural network potential for Cu$_y$Ce$_{1-y}$O$_{2-x}$ nanoparticles**

The size of the nanoparticle model and the extensive sampling required to determine the copper distribution throughout the particle prevent the direct application of density functional
theory (DFT). We therefore follow the approach by Behler and Parrinello and employ artificial neural networks (ANNs) for the accurate interpolation of DFT reference calculations. An invariant representation of the local atomic environment is achieved by using a basis set of radial and angular functions (Behler symmetry functions). The basis parameters employed in this work are given in Tables S1 and S2; see previous work for the analytical function definitions. The atomic energy network (ænet) package was used for all simulations with ANN potentials.

**Table S1.** Parameters of the radial basis function (Behler symmetry function) \( G^2 \) of reference used for the description of the local atomic structure within a cutoff radius of \( R_c = 6.5 \) Å.

| No. | Species | \( \eta (\text{Å}^{-2}) \) |
|-----|---------|-----------------|
| 1   | Ce      | 0.003214        |
| 2   | O       | 0.003214        |
| 3   | Cu      | 0.003214        |
| 4   | Ce      | 0.035711        |
| 5   | O       | 0.035711        |
| 6   | Cu      | 0.035711        |
| 7   | Ce      | 0.071421        |
| 8   | O       | 0.071421        |
| 9   | Cu      | 0.071421        |
| 10  | Ce      | 0.124987        |
| 11  | O       | 0.124987        |
| 12  | Cu      | 0.124987        |
| 13  | Ce      | 0.214264        |
| 14  | O       | 0.214264        |
| 15  | Cu      | 0.214264        |
| 16  | Ce      | 0.357106        |
| 17  | O       | 0.357106        |
| 18  | Cu      | 0.357106        |
| 19  | Ce      | 0.714213        |
| 20  | O       | 0.714213        |
| 21  | Cu      | 0.714213        |

In total, around 1100 \( \text{Cu}_y\text{Ce}_{1-x}\text{O}_{2-x} \) periodic bulk, surface (\{111\} and \{100\}), and isolated cluster structures were used for the construction of the ANN potential. The DFT calculations of these reference structures were carried out using the FHI-aims package using tight settings (6th order expansion of the Hartree potential, radial integration grids with 434 points in the outer shell, and a tier 2 basis set). Relativistic effects were included with atomic ZORA. Structural energies were generally converged to 1 meV/atom, and atomic forces to 10 meV/Å. For all calculations the exchange-correlation functional by Perdew, Burke, and Ernzerhof was used.

Around 1000 reference structures were used for the training of the ANN potential, and the accuracy of the interpolation was verified against an independent testing set of around 100 structures that were not used for training. The root mean squared error (RMSE) of the final ANN potential is 6.8 meV/atom for the training set and 8.7 meV/atom for the testing set. The mean absolute errors are 5.4 and 7.1 meV/atom for the training and the testing set, respectively. The ANN potential energies of all structures in the reference set are compared to their DFT references in Fig. S2. We stress that the excellent accuracy of the ANN potential could only be achieved because all reference structures are closely related to the nanoparticle model of the previous section. The ANN potential of this work would not be suitable for the investigation of structurally very different Cu/ Ce/O systems.

**Table S2.** Parameters of the angular basis function (Behler symmetry function) \( G^4 \) of reference used for the description of the local atomic structure within a cutoff radius of \( R_c = 6.5 \) Å. Each set of parameters listed in the table corresponds to 6 equivalent functions for the 6 possible combinations of atomic species (Ce-Ce, Ce-O, Ce-Cu, O-O, O-Cu, Cu-Cu) among neighboring atom pairs in the local structural environment of an atom (Ce, O, Cu).
| No.  | $\eta$ (Å$^2$) | $\lambda$ | $\zeta$ |
|------|---------------|-----------|---------|
| 22-27 | 0.000357      | 1.0       | 1.0     |
| 28-33 | 0.000357      | -1.0      | 1.0     |
| 34-39 | 0.000357      | 1.0       | 4.0     |
| 40-45 | 0.000357      | -1.0      | 4.0     |
| 46-51 | 0.010713      | 1.0       | 1.0     |
| 52-57 | 0.010713      | -1.0      | 1.0     |
| 58-63 | 0.010713      | 1.0       | 4.0     |
| 64-69 | 0.010713      | -1.0      | 4.0     |
| 70-75 | 0.028569      | 1.0       | 1.0     |
| 76-81 | 0.028569      | -1.0      | 1.0     |
| 82-87 | 0.028569      | 1.0       | 4.0     |
| 88-93 | 0.028569      | -1.0      | 4.0     |

**Figure S2.** Comparison of the cohesive energies predicted by the ANN potential and their DFT reference values. The diagonal (blue line) corresponds to perfect correlation. The energies of structures from the training and test sets are shown as black and red points, respectively.

**Monte-Carlo simulations**

The Monte-Carlo (MC) simulations were carried out in the grand canonical ensemble, i.e., the copper grand potential

$$
\Phi_{\text{Cu}} = E^{\text{ANN}} - TS - \mu_{\text{Cu}} N_{\text{Cu}}
$$

was minimized in the simulated annealing runs for a given oxygen vacancy concentration and copper chemical potential, $\mu_{\text{Cu}}$. In the above equation, $E^{\text{ANN}}$ is the configurational energy
predicted by the ANN potential, $T$ is the temperature, $S$ is the configurational entropy, and $N_{Cu}$ is the number of copper atoms in the nanoparticle.

All MC simulations were repeated at least three times to guarantee reproducibility. The nanoparticle that was analyzed for the article is representative and has a copper concentration closest to the experimentally observed 10%.
Figure S3. High angle annular dark-field (HAADF) images acquired in STEM mode coupled with X-ray energy dispersive spectroscopy (EDS) of CuO/Cu$_{y}$Ce$_{1-y}$O$_{2-x}$ catalysts. Mean copper substitution is 5.4(6)%, 8(3)%, 9(1)%, 8(1)%, 3.4(7)% and 1.0(2)%, respectively.
Figure S4. HRTEM of annealed CuO/Cu$_{y}$Ce$_{1-y}$O$_{2-x}$ catalysts. Included are low-magnification images (left), high-resolution images of the Cu$_{y}$Ce$_{1-y}$O$_{2-x}$ phase (center) and their fast Fourier transforms (right).
Figure S5. Raman spectra of $\text{Cu}_y\text{Ce}_{1-y}\text{O}_{2-x}$ and CuO/$\text{Cu}_y\text{Ce}_{1-y}\text{O}_{2-x}$ acquired at room temperature. (A) Raw spectra and (B) measured frequency of the $F_{2g}$ mode as a function of copper substitution in $\text{Cu}_y\text{Ce}_{1-y}\text{O}_{2-x}$ ($y$).
Figure S6. Arrhenius plots for CO oxidation over CuO/Cu$_{y}$Ce$_{1-y}$O$_{2-x}$ normalized by surface copper site in Cu$_{y}$Ce$_{1-y}$O$_{2-x}$ assuming surface segregation of copper. Rates were measured in 1% CO, 2.5% O$_2$ balanced in He at a flow rate of 1300 mL min$^{-1}$ g$^{-1}$.
Figure S7. DFT+U-calculated phase diagrams for ss-, nnn- and nn-Cu2Ce34O72-x slab models computed at 700 K. The dashed grey lines correspond to 0.21 atm O2 (i.e. air). The lowest-energy slabs for each of the three models, corresponding to the stoichiometry Cu3+2Ce34O71, are also shown for comparison.
Figure S8. STEM-EELS analysis of an individual Mn$_{0.1}$Ce$_{0.9}$O$_{2-x}$ nanoparticle. (A) Dark field image acquired simultaneously with the spectrum images (scale bar: 2 nm), (B) Ce M$_{4,5}$-edge spectra corresponding to the boxed regions in A. The dotted line in B refers to the peak at 882 eV ascribed to Ce$^{3+}$. 
**Table S3.** Apparent activation energies ($E_A$) for CO oxidation on CuO/Cu$_y$Ce$_{1-y}$O$_{2-x}$ powders, their BET surface areas, ($A_S$) and crystallographic parameters for the Cu$_y$Ce$_{1-y}$O$_{2-x}$ phase. Standard uncertainties in the last digits are included in parentheses.

| Compound                   | $E_A$ (kJ mol$^{-1}$) | $A_S$ (m$^2$ g$^{-1}$) | $a$ (Å)       | $d_{\text{Scherrer}}$ (220) (Å) | $R$ factors (%) | $\chi^2$ | $n_{\text{homog.}}$/$n_{\text{surf. seg.}}$ | $y$ (EDS) |
|---------------------------|-----------------------|------------------------|---------------|----------------------------------|-----------------|----------|---------------------------------------------|----------|
| CuO/Cu$_{0.05}$Ce$_{0.95}$O$_{2-x}$ | 31                    | 114                    | 5.4143(2)     | 59.0                             | 1.55, 1.97      | 1.16     | 0.38                                        | 0.054(6) |
| CuO/Cu$_{0.08}$Ce$_{0.92}$O$_{2-x}$ | 44                    | 119                    | 5.4159(6)     | 52.0                             | 1.94, 2.66      | 2.01     | 0.43                                        | 0.08(3)  |
| CuO/Cu$_{0.09}$Ce$_{0.91}$O$_{2-x}$ | 33                    | 78                     | 5.4145(1)     | 54.7                             | 2.45, 3.19      | 2.24     | 0.41                                        | 0.09(1)  |
| Cu$_{0.08}$Ce$_{0.92}$O$_{2-x}$     | 40                    | 52                     | 5.420(3)      | 33.8                             | 2.15, 2.80      | 1.23     | 0.66                                        | 0.08(1)  |
| Cu$_{0.03}$Ce$_{0.97}$O$_{2-x}$     | 50                    | 17                     | 5.426(4)      | 36.6                             | 2.25, 2.84      | 1.28     | 0.61                                        | 0.034(7) |
| Cu$_{0.01}$Ce$_{0.99}$O$_{2-x}$     | 42                    | 29                     | 5.4156(6)     | 52.8                             | 2.16, 2.79      | 1.17     | 0.42                                        | 0.010(2) |

**Table S4.** Crystallographic parameters for the CuO phase in CuO/Cu$_y$Ce$_{1-y}$O$_{2-x}$ powders. Standard uncertainties in the last digits are included in parentheses.

| Compound                   | $a$ (Å)       | $b$ (Å)       | $c$ (Å)       | $\beta$ (°) | $d_{\text{Scherrer}}$ (111) (Å) |
|---------------------------|---------------|---------------|---------------|-------------|----------------------------------|
| CuO/Cu$_{0.05}$Ce$_{0.95}$O$_{2-x}$ | 4.6836(3)     | 3.4341(3)     | 5.1338(4)     | 99.360(4)   | 274.5                            |
| CuO/Cu$_{0.08}$Ce$_{0.92}$O$_{2-x}$ | 4.693(1)      | 3.435(1)      | 5.129(2)      | 99.34(2)    | 152.1                            |
| CuO/Cu$_{0.09}$Ce$_{0.91}$O$_{2-x}$ | 4.646(4)      | 3.439(2)      | 5.146(4)      | 99.31(3)    | 115.5                            |
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