Preferential CO Oxidation on a Highly Active Cu Single Atom Catalyst Supported by Ce-TiO₂₆

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A heterogeneous single-atom catalyst (SAC) based on a tiny Cu loading (0.05 wt.%) supported on CeO₂-TiO₂ (Ce/Ti=0.18) shows very high Cu mass-normalized CO oxidation activity, 100% selectivity for CO₂, between 60 and 100 °C and essentially no deactivation during 17 h on stream in the preferential oxidation of CO (PROX) at 120 °C. Based on state of the art, this catalyst is among the most active and PROX-selective catalysts. Employing a combination of ex-situ and operando methods, we infer that the isolated Cu single sites are incorporated with redox-active Cu²⁺−O−Ce⁴⁺ ⇌ Cu⁺−Ce³⁺ moieties connected by labile oxygen and are exposed on the surface of highly dispersed ceria. This high dispersion is promoted by TiO₂ which itself does not participate in redox steps during PROX, as Ti ions remain essentially tetravalent while Cu and Ce undergo reversible redox shuttles.

Introduction

In view of the global climate change, replacing fossil fuels with renewable energy sources is the greatest current challenge. Fuel cells, in particular polymer exchange membrane fuel cells (PEMFCs), have become one of the most important power generation systems in the new energy scenario.[1] They are powered with hydrogen, which should ideally come from renewable sources, but is currently still mainly produced by steam reforming of hydrocarbons and subsequent water gas shift reaction.[2] This hydrogen usually contains approximately 0.5 to 1 vol.% of unconverted CO, which is a poison for the Pt anode of the PEMFCs. Therefore, the CO concentration in reformate gases must be reduced to a few ppm which is usually done by preferential oxidation of CO (CO-PROX). This is a challenging catalytic process since, for being efficient, catalysts must be able to oxidize CO completely to CO₂ at high rates and temperatures within the operation window of the PMFC (80–130 °C) while suppressing undesired oxidation of H₂ to H₂O to avoid the loss of H₂ fuel.[3] Supported noble metals such as Pt or Au have been commonly used as commercial PROX catalysts, however, those metals are rare, expensive and show frequently low CO₂ selectivity (due to H₂ activation on the noble metals already at low temperature) as well as low resistance to CO₂ formed as product.[4]

In recent years copper-ceria materials emerged as outstanding catalysts for a number of heterogeneous catalytic reactions involving redox steps, such as CO oxidation,[5] water-gas shift,[6] selective catalytic reduction of NO,[7] and also CO-PROX.[8] Comprehensive discussions of catalyst properties and structure-reactivity relationships are provided in several excellent reviews.[9] There is agreement that the peculiar performance of CuOₓ−CeO₂ catalysts in these reactions arises from the unique ability of CeO₂ to store and release oxygen (driven by oxygen vacancies) and by the interplay between Cu²⁺/Cu⁺ and Ce⁴⁺/Ce³⁺ redox pairs at the interface between CuOₓ and CeO₂.[10]

In most previous papers on CO oxidation and CO-PROX, Cu contents of at least 5 wt.% or more have been used, leading to the formation of separate but loosely attached CuOₓ and CeO₂ nanoparticles.[11] In contrast, we have recently presented highly active Cu/CoOₓ−TiO₂ (Ce/Ti=0.3) catalysts for CO oxidation with Cu contents well below 1 wt.%. Their Cu-mass normalized rates scaled with the amount of single Cu atoms exposed on the surface and were much higher than those of Cu/CoOₓ catalysts with higher Cu content.[12] We have shown that active sites in these materials are single Cu ions exposed on the surface of CeO₂ particles that undergo reversible Cu²⁺−O−Ce⁴⁺ ⇌ Cu⁺−Ce³⁺ redox shuttles, thus providing active oxygen. By lowering the Ce/Ti ratio to 0.18 (compared to Ce/Ti=0.3) we could even achieve a more than 20-fold increase of the Cu-mass normalized CO₂ formation rate with a Cu content of only 0.05 wt.%, which again indicates clearly that CO oxidation activity is driven by Cu single sites.[13]

Inspired by these very promising results, we present now a Cu/CoOₓ−TiO₂ (Ce/Ti=0.18) catalyst for CO-PROX at low tem-
perature (60 to 150 °C) which contains only 0.05 wt.% of Cu, exclusively as single atoms. To derive structure-reactivity relationships under most relevant reaction conditions, in situ and operando spectroscopic studies using Electron Paramagnetic Resonance (EPR), FTIR spectroscopy in diffuse reflectance mode (DRIFTS) and near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) have been performed in addition to standard characterization techniques.

Results and Discussion

Catalytic Performance

Figure 1a illustrates the performance of the catalyst in the CO-PROX reaction. An almost linear increase of the CO oxidation rate (based on the Cu mass) was observed with rising temperature and the CO₂ selectivity was 100% up to 100 °C. Only at higher temperatures undesired oxidation of H₂ was observed. This led to formation of H₂O at the expense of CO₂. López et al. have used Eq. 3 to rank the intrinsic catalytic activity of more than 40 CuOₓ·CeO₂ catalysts from literature.[11] For comparison, the k₇ values of their best catalyst A (prepared by a citrate method with 10 wt.% Cu[12]) and the sample of this work are plotted in Figure 1b. It is evident that our catalyst clearly outperforms catalyst A of ref. [11] and, consequently, all other CuOₓ·CeO₂ based CO-PROX catalysts in this ranking of 2008 (not reproduced in Figure 1b), since it shows higher intrinsic activity at much lower Cu contents. Note that our sample contains only 0.05 wt.% Cu compared to 10 wt.% of catalyst A. Also, in the last decade we could hardly find CuOₓ·CeO₂ based catalysts with higher intrinsic CO-PROX activity than the catalyst of this work (Table S1). Moreover, it is very stable and showed almost no deactivation within 17 h time on stream at 120 °C (Figure S1), though at this temperature minor H₂ oxidation gave rise to some water formation, the competitive adsorption of which is known to cause deactivation of CuOₓ·CeO₂ catalysts.[13]

To find out reasons for the observed high activity and selectivity, we have to consider the results of structural characterization presented in the next sections.

Catalyst characterization

Elemental analysis by ICP-OES confirmed a Ce/Ti ratio of about 0.2 for both the bare support and the Cu-containing catalyst as well as a Cu content of 0.05 wt.% for the latter, which are close to the values established in the synthesis solution. Both samples show type IV N₂ adsorption/desorption isotherms with hysteresis loops typical for mesopores (Figure S3).[14] The BET surface area decreased slightly on adding Cu while the average pore diameters increased, and the total pore volume did not change much (Table 1).

![Figure 2. Powder XRD patterns of the fresh CeO₂–TiO₂ support and the Cu catalyst.](image)

![Figure 1. (a) Cu mass normalized rate of CO conversion and H₂O formation rates (left axis) and CO₂ selectivity (right axis), b) intrinsic catalytic activity constants k₇ (Eq. 2) for the Cu catalyst of this work in comparison to the best catalyst (A) of ref. [11] The bare support was inactive (Figure S2).](image)

Table 1. Elemental composition, surface, and pore properties.

| Sample   | elemental composition | Molar ratio Ce/Ti | S_BET [m²·g⁻¹] | Pore Volume [cm³·g⁻¹] | average pore diameter [nm] |
|----------|-----------------------|-------------------|----------------|------------------------|--------------------------|
| Support  | –                     | 0.19              | 143            | 0.32                   | 6.4                      |
| Cu Cat   | 0.05                  | 0.18              | 111            | 0.27                   | 7.3                      |

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Raman spectra of both the support and the Cu catalyst are also nearly identical. In agreement with the XRD patterns, they show the typical bands of anatase at 148, 403, 517, and 640 cm$^{-1}$ (Figure 3) and a weak band at 463 cm$^{-1}$ corresponding to the F$_{2g}$ vibration mode of the CeO$_2$ cubic fluorite structure.\textsuperscript{[15–16]} No Raman bands related to Cu–O vibrations could be observed in good agreement with XRD results, as expected for the very low Cu content of 0.05 wt.%. 

HAADF-STEM images together with corresponding Energy-dispersive X-ray spectroscopy (EDS) maps of the CeO$_2$–TiO$_2$ support and the Cu catalyst for visualizing the distribution of Ti (red) and Ce (green) are shown in (Figure 4). ED spectra from selected catalyst areas are plotted in Figure S9. A quite homogeneous distribution of Ti and Ce throughout the whole sample is evident in the Cu-free support (Figure 4b), suggesting a rather uniform distribution of CeO$_2$ on TiO$_2$. In contrast, the Cu catalyst (Figure 4d) shows regions of enriched TiO$_2$ and almost pure CeO$_2$ (marked with a circle in Figure 4d) in addition to areas with uniform distribution of Ce and Ti. Cu species could not be observed in the HAADF STEM images of (Figure 4c and e), which might be due to the very low Cu content. Additionally, the HAADF STEM images are dominated by contrast from heavy, strongly scattering Ce atoms which hinders to discern tiny Cu species in their vicinity. Likewise, Ti and Cu are not easy to distinguish since they have similar atomic numbers (i.e., low Z-contrast). Cu could also not be detected by EDS mapping (Figure 4d), which suggests that it is present either in very few large separate entities not comprised by mapping or as highly dispersed single atoms. Interestingly, EPR and DRIFT spectroscopy results presented below provide evidence for the presence of isolated Cu single sites.

By recording electron energy loss spectra (EELS) at the Ce M-edge from different positions marked as 1 and 2 in the ADF image of (Figure 4e), it was possible to obtain information on the Ce valence state. Area 1 is located on a big particle consisting of pure CeO$_2$ (like the green entity in (Figure 4d)) while in region 2 Ti and Ce are quite homogeneously distributed (similar as in the Cu-free support of (Figure 4d)).\textsuperscript{[17]} In the EEL spectrum of area 1 (black trace in (Figure 4f), the Ce white lines appear at energy losses characteristic for Ce$^{4+}$ while the corresponding signals of area 2 are slightly shifted to lower loss energies. This indicates that the large separate CeO$_2$ particles in the Cu catalyst contain Ce essentially in its highest valence state $+4$ while Ce is markedly reduced to +3 when it is highly dispersed on TiO$_2$.\textsuperscript{[17]}

**Operando and in situ spectroscopic studies**

As we will show in this section, the combined evaluation of results from different in situ and operando studies was very helpful to learn more about reaction induced metal valence changes. We start the discussion with NAP-XPS to deepen the results of EELS concerning the valence state of cerium.

**NAP-XPS.** In the Ce 3d region, all spectra of the bare support and the Cu catalyst show the characteristic doublets of Ce$^{3+}$ at 916.86/898.59 eV (u/v), 901.09/882.7 eV (u/v) and...
907.67/887.29 eV (u/ν) as well as those of Ce\(^{4+}\) at 903.65/885.05 eV (u/ν) and 899.75/880.87 eV (u/ν) (Figure 5).\(^{[18]}\) The surface percentage of Ce\(^{4+}\) has been determined from the area ratio of the signal sub-components defined by Eq. 1 and is listed on the left side of the spectra.

\[
\text{Ce}^{4+} (\%) = \frac{u_0 + 2u^0 + u^0' + v'}{\sum u' + v'}
\] (1)

The surface of the bare support is already partially reduced at 127 °C in N\(_2\) and exposes 34 % Ce\(^{4+}\) (Table 2, Figure 5a), in accordance with previously reported studies.\(^{[19]}\) This is also supported by EPR spectroscopy discussed below. Pretreatment of the bare support at 250 °C in 10 % H\(_2\)/N\(_2\) led to a slight increase of surface Ce\(^{4+}\) to 39 %. Surprisingly, no reoxidation of Ce\(^{4+}\) was observed upon subsequent switching to the complete CO-PROX feed at 120 °C and no CO\(_2\) formation could be detected by online mass spectrometry (MS6). This is much different for the Cu catalyst (Table 2, Figure 5b). The surface of the fresh material in N\(_2\), at 127 °C contained only 21 % of Ce\(^{4+}\), but this percentage increased markedly to 32 % after reductive pretreatment at 250 °C. Upon switching to the CO-PROX feed at 120 °C, the whole Ce\(^{4+}\) formed during pretreatment in H\(_2\)/N\(_2\) was reoxidized to Ce\(^{3+}\) and the formation of CO\(_2\) and H\(_2\)O was detected by online MS (Figure 5f). Interestingly, no change of the Ti valence state was observed, which remained essentially at +4 on both the support and the catalyst surface under all conditions (Figure 5g). This suggests that the extraordinary Ce\(^{3+}\)/Ce\(^{4+}\) redox activity on the catalyst surface might be created by the presence of copper which, however, could not be detected by NAP-XPS due to its very low content of only 0.05 wt.%. Therefore, to gain more information about the impact of Cu on the redox behavior of the catalyst, we used operando EPR spectroscopy which is a very sensitive and specific method to detect Cu\(^{2+}\) species.

**In situ and Operando EPR.** The EPR spectrum of the Cu-free support shows a weak isotropic signal at g\(=2.004\) from electrons trapped in oxygen vacancies,\(^{[20]}\) and another weak axial signal with g\(_x\)=1.967 and g\(_y\)=1.943 (poorly resolved) which was also observed previously in pure ceria as well as in CeO\(_2\)-TiO\(_2\) materials and attributed to electrons trapped in vacancies next to cerium ions, to Ce\(^{3+}\) or to some kind of Ce\(^{3+}\)–O–Ce\(^{4+}\) defect sites (Figure 6a).\(^{[21]}\) Though this assignment is somewhat controversial, it suggests at least the presence of Ce\(^{3+}\) in the sample which is also evident from the XPS and EELS data discussed above. Besides these signals, the bare support (as well as the Cu/CeO\(_2\)-TiO\(_2\)) shows a strong roughly isotropic line at g\(=2.020\) from O\(^{2-}\) species formed by transfer of electrons trapped in anionic vacancies to adsorbed O\(_2\) molecules.\(^{[21c]}\)

The EPR spectrum of the Cu-containing catalyst contains two signals of isolated Cu\(^{2+}\) single sites that show hyperfine structure (hfs) due to the coupling of the single electron spin (d\(^2\), S=1/2) with the nuclear spin of Cu (I=3/2) in different local environment. The g and A tensor parameters were derived by spectra simulation (Figure 5f). Signal I with g\(_x\)=2.425, g\(_y\)=2.075, A\(_x\)=266 MHz and A\(_y\)=80 MHz reflects tetragonally distorted octahedral Cu\(^{2+}\) species in the bulk of the CeO\(_2\)-TiO\(_2\) support.\(^{[22]}\) Signal II is characterized by a lower g\(_x\) and a higher A\(_x\) value (g\(_x\)=2.300, g\(_y\)=2.058, A\(_x\)=290 MHz, A\(_y\)=65 MHz). Both values point to a higher tetragonal distortion of the Cu\(^{2+}\) environment and may be consistent with a Cu\(^{2+}\) site in square-pyramidal geometry exposed on the catalyst surface.\(^{[23]}\)

When the catalyst was heated in argon flow to 250 °C, both Cu\(^{2+}\) signals turned into a broad asymmetric line with g\(_x\)=2.327 and g\(_y\)=2.063 in which only A\(_x\) is poorly resolved (Figure 6b). This loss of resolution is due to the increase in

Table 2. Metal surface percentages obtained from NAP-XPS measurements ion.

|            | Ti [at.%] | Cu catalyst | Bare support | Cu catalyst |
|------------|-----------|-------------|--------------|-------------|
| N\(_2\), 127 °C | 22.9      | 19.32       | 3.81, 1.3 (34) | 5.34, 1.1 (21) |
| H\(_2\)/N\(_2\), 250 °C | 20.03     | 17.01       | 3.78, 1.5 (39) | 4.07, 1.3 (32) |
| H\(_2\)/CO/O\(_2\), 120 °C | 19.25     | 15.92       | 4.14, 1.6 (39) | 4.93, 1.1 (22) |

Figure 5. NAP-XPS spectra in the Ce 3d region of the support (a) and (b) the Cu catalyst measured under different conditions at a total pressure of 2 mbar.

Figure 6. (a) EPR spectra of the fresh calcined support (black) and the Cu-containing catalyst (red) recorded at −180 °C; (b) of the Cu catalyst during 1 h pretreatment in 10 % H\(_2\)/Ar flow at 250 °C.
mobility of the Cu\(^{2+}\) sites and the loss of coordinated water which changes their local environment and, thus, also the spin Hamiltonian parameters\(^{26}\). Upon switching to H\(_2\), the Cu\(^{2+}\) single sites were reduced to EPR silent Cu\(^{+}\). This lowered the intensity of the Cu\(^{2+}\) EPR signal while that of oxygen vacancies at g = 2.004 slightly increased (Figure 6b). After 1 h reductive pretreatment, about 53% of the Cu\(^{2+}\) single sites were reduced while the rest remained divalent (calculated from the double integrals of the EPR signals before and after exposure to H\(_2\)/Ar flow). The Cu\(^{2+}\) sites persisting reduction are probably incorporated in the bulk of the catalyst and, thus, shielded from contact with reactants. A similar Cu\(^{2+}\) reduction behavior was also observed in our previous Cu/CeO\(_2\)–TiO\(_2\) material\(^{24}\) and other Cu/CeO\(_2\) catalysts.

When the pre-reduced Cu catalyst was exposed to the CO-PROX feed flow of 1\% CO, 1\% O\(_2\), 80\% H\(_2\)/Ar, reoxidation of reduced Cu species led to an increase of the EPR signal intensity of isolated Cu\(^{2+}\) species (g\(_1\) = 2.329, g\(_2\) = 2.065) with time (Figure 7a). The slight changes in the spin Hamiltonian parameters of Cu\(^{2+}\) sites are attributed to the slight changes in the their local environment upon interaction with CO/O\(_2\).\(^{26}\) This reoxidation was very fast and comprised the vast majority of the Cu sites already during the first 10 min (Figure 7b). However, only about 90\% of the initial Cu\(^{2+}\) intensity was reached at steady state under PROX conditions. This may suggest that reduction of Cu\(^{2+}\) to Cu\(^{+}\) by CO is slightly faster than reoxidation of the latter by O\(_2\), rendering the total EPR-active Cu\(^{2+}\) amount in time average under steady state conditions slightly lower than in the freshly calcined catalyst. It should be noted that the EPR signal of oxygen vacancies and superoxide species are only detectable at low temperature (Figure 6a). Remarkably, the percentage of single Cu sites participating in reversible redox cycles in this Cu catalyst is much higher than in our previous catalyst with a similar low Cu content of 0.06\% but a higher Ce/Ti ratio of 0.32 and much larger separated CeO\(_2\) particles in the micrometer range, for which we found that only about 3\% of the Cu sites participate in CO oxidation.\(^{26}\) Note that the ionic radius of Cu\(^{2+}\) is only slightly lower than that of Ce\(^{4+}\) (0.77 pm and 0.87 pm in 6-fold coordination, respectively) but significantly higher than that of Ti\(^{4+}\) (0.61 pm).\(^{25}\) This could favor the incorporation of Cu\(^{2+}\) in Ce\(^{4+}\) rather than in Ti\(^{4+}\) lattice positions, and the much lower particle size of CeO\(_2\) in the present catalyst might lead to a higher percentage of accessible Cu single sites exposed on the surface of CeO\(_2\). The online mass spectrometry data in Figure 5a also showed the formation of CO\(_2\) during the PROX conditions at the outlet of the EPR flow reactor.

**Operando DRIFTS.** DRIFT spectra of the bare support and the Cu catalyst (both pre-reduced for 1 h at 250\°C in H\(_2\)) recorded at 80\°C under CO-PROX feed are shown in (Figure 8a). The bare support shows a broad weak band at 2127 cm\(^{-1}\) which is superimposed on the typical modes of gaseous CO(g) and decreased quickly within the first 10 min (Figure 8b). For CO adsorbed on bare CeO\(_2\), a band at a similar frequency was previously attributed to a CO–Ce\(^{3+}\) species.\(^{26}\) Since Ce\(^{3+}\) is also evident in the NAP-XP spectra of the bare support, this DRIFT band is not surprising.

In the spectra of the Cu catalyst, characteristic bands of gaseous CO\(_2\) at 2362 and 2339 cm\(^{-1}\) can be seen right after introducing the CO-PROX feed, indicating that the catalyst was working (Figure 8). These bands are not present in the spectra of the bare support, since no catalytic activity was observed in the range between 60 and 150\°C (Figure S2). A strong band of adsorbed CO appeared at 2125 cm\(^{-1}\) right after switching to the CO-PROX feed. The fact that it is much more intense than on the bare support indicates that CO is much stronger adsorbed on Cu than on Ce\(^{3+}\) sites (Figure 8a). Since the catalyst was pre-reduced at 250\°C before exposure to the CO-PROX feed, the surface Cu species should have an oxidation state lower than +2. This agrees with the NAP-XP results in Figure 5b and also with TPR results of our previous 0.06 wt.% Cu/CeO\(_2\)–TiO\(_2\) catalyst.\(^{24}\) Since an assignment to a distinct reduced Cu valence state is difficult under reaction conditions, we ascribe the band at 2125 cm\(^{-1}\) to CO adsorbed on interfacial Cu\(^{+}\) atoms.\(^{27}\) The continuous decrease of the band intensity suggests reoxidation of the reduced Cu species to Cu\(^{2+}\) with time on the CO/O\(_2\)/H\(_2\)/He stream. This agrees well with the results of operando EPR (Figure 7a).

**Figure 7.** (a) Operando EPR spectra at 120\°C of the Cu catalyst (prereduced for 1 h in H\(_2\) at 250\°C) during exposure to PROX feed flow of 1\% CO + 1\% O\(_2\) + 80\% H\(_2\) (spectrum after 1 h pretreatment in H\(_2\) at 250\°C and cooling to 120\°C subtracted), (b) intensity ratio of the Cu\(^{2+}\) EPR signal in plot (a) to the one in the in the initial calcined catalyst (based on double integrals).

**Figure 8.** DRIFT spectra recorded as a function of time at 80\°C in a flow of 1\% O\(_2\), 1\% CO, 80\% H\(_2\)/He of (a) the Cu catalyst and (b) the bare support (both prereduced for 1 h at 250\°C in H\(_2\)). From top to bottom: 30 s to 120 min.
Conclusion

Comparison with the state of the art revealed that our 0.05 wt.% Cu/\(\text{CeO}_2-\text{TiO}_2\) (Ce/Ti = 0.18) catalyst prepared by a sol-gel method outperforms the best known CeO\(_2\)-based PROX catalysts significantly. The Cu-free support consists of separate \(\text{TiO}_2\) anatase and CeO\(_2\) cubic fluorite phases that are finely mixed and quite homogeneously distributed throughout the Cu-free support. In this support, Ce\(^{4+}\) coexists with Ce\(^{3+}\) and Ti\(^{4+}\) on the surface (confirmed by NAP-XPS), whereby neither Ti nor Ce showed any significant redox activity under PROX conditions. This might be the reason why the Cu-free support is catalytically inactive. Incorporation of Cu in the catalyst led to segregation of small monophasic CeO\(_2\) particles (<20 nm). In contrast to the bare support, a significant and reversible Ce\(^{4+}/\text{Ce}^{3+}\) redox shuttle occurs under PROX conditions while Ti remains essentially tetravalent.

Due to its very small amount, copper was only detected as Cu\(^{2+}\) by EPR which confirmed its prevailing single-site nature. About 50% of these Cu single sites undergo reversible redox cycles under CO-PROX conditions. This quantity is much larger than what had been detected in our previous study of the 0.06% Cu/\(\text{CeO}_2-\text{TiO}_2\) (Ce/Ti = 0.32) catalyst which showed only 3% redox-reversible Cu sites during CO oxidation and contained very large CeO\(_2\) particles in the micrometer range.\(^{[24]}\) Obviously the higher percentage of TiO\(_2\) (Ce/Ti = 0.18) in the present catalyst is helpful in promoting the dispersion of CeO\(_2\) particles.\(^{[28]}\) Apparently, the extent of redox reversibility of Ce and Cu under CO-PROX conditions is similar, suggesting that Cu might be located in close vicinity to Ce, probably on the surface of the small CeO\(_2\) particles. Thus, we propose that active sites for CO-PROX on the 0.05 wt.% Cu/\(\text{CeO}_2-\text{TiO}_2\) (Ce/Ti = 0.18) catalyst in this work are the same as for CO oxidation on our previous 0.06% Cu/\(\text{CeO}_2-\text{TiO}_2\) (Ce/Ti = 0.32) catalyst, namely single Cu ions within redox-active Cu\(^{2+}\)–\(\text{O}^2-\text{Ce}^{4+}\) ⇌Cu\(^{3+}\)–\(\text{O}^2-\text{Ce}^{3+}\) moieties connected by labile oxygen on the surface of CeO\(_2\) particles, yet their concentration is markedly higher due to the lower Ce/Ti ratio and much smaller CeO\(_2\) particles. The extraordinarily high selectivity of CO\(_2\) up to 100°C is presumably attributed to low tendency of Cu single sites for hydrogen activation at such low temperatures (also confirmed by H\(_2\)-TPR results\(^{[26]}\)).

Experimental Section

Catalyst synthesis and standard characterization

Catalyst synthesis and standard characterization methods are the same like in our recent paper.\(^{[20]}\) Therefore, this information is summarized here only briefly.

Catalyst synthesis: The bare CeO\(_2\)-TiO\(_2\) support and the Cu-containing catalyst have been prepared by the same sol-gel method described previously. Briefly, 1.37 g (2.58 mmol) of (NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) was dissolved in 8.75 ml anhydrous ethanol at 60 °C and 3.75 ml Ti(B) isopropoxide and 1.62 ml of ethyl acetate were added, followed by stirring for 1 h at room temperature. Dropwise addition of 2.25 ml HNO\(_3\) (0.1 M) under stirring formed a spongy gel which was extracted by supercritical ethanol at 245 °C and 60 bar to create an aerogel that was calcined at 500 °C (Nabertherm GmbH) for 3 h in static air. In case of the Cu-containing catalyst, the required amount of CuCl\(_2\) \(_2\) H\(_2\)O was also added to the ethanolic solution. This resulted in a catalyst with a Ce/Ti ratio of about 0.2 and a Cu content of 0.05 wt.% as confirmed by elemental analysis.

Standard characterization: The elemental composition was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a 715-ES ICP emission spectrometer (Varian, Palo Alto, CA, USA) after dissolution in HF/aqua regia at 200 °C and 60 bar. Specific surface area, pore volume and average pore diameters were derived from N\(_2\) adsorption on a Micromeritics ASAP 2010 device using the BET and BJH methods. XRD powder patterns were recorded on an X’Pert diffractometer (Panalytical) with Cu K\(_\alpha\) radiation in 0.0167° steps with 25 s per step. Phases were identified using the PDF-2 database of the International Center of Diffraction Data (ICDD). Raman spectra were acquired with a Horiba Jobin Yvon LabRam micro-spectrometer IHR 550 using a 660 nm laser (laser power 0.1–10.0 mW), a diffraction grating of 1800 mm\(^{-1}\), and an entrance slit in the spectrometer of 200 μm. The LabSpec 6, Jobin Yvon Horiba, built-in software package was used to analyze the data. Scanning transmission electron microscopy (STEM) images were recorded at 200 kV with an aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS), equipped with High-Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF) detectors, a JED-2300 energy dispersive X-ray spectrometer (JEOL) having a silicon drift detector (dry SD60G) and an Enfimun ER (GATAN) electron energy-loss spectrometer with Dual EELS for chemical analysis. For position control during EELS acquisition, the annular dark field (ADF) detector was used. The dry catalyst was deposited on a holey carbon supported Cu grid (mesh 300).

Catalytic tests

Catalytic tests were performed in a fixed bed tubular microreactor (i.d. 4 mm) under differential conditions (conversion below ≤ 20%) by diluting catalyst particles of 150–250 μm with different amounts of inert α-Al\(_2\)O\(_3\) (calcined at 900 °C before use). A catalyst bed of 0.24 cm\(^3\) and a total gas flow of 30 ml·min\(^{-1}\) were used to establish a gas hourly space velocity (GHSV) of 7500 h\(^{-1}\). After pretreatment for 1 h at 250 °C in a flow of 10% H\(_2\)\(\text{O}_2\) the catalyst was exposed to the feed mixture of 1% CO, 1% \(\text{O}_2\), 80% H\(_2\)\(\text{N}_2\) at different temperatures between 60 and 150 °C. The Cu mass-normalized rates of CO conversion and H\(_2\)O formation were calculated by Eq. 2, 3 in which \(R_{\text{CO},\text{in}}\) and \(D_{\text{CO},\text{out}}\) are the molar flows of CO at the inlet and H\(_2\)O vapor at the outlet of the reactor and \(m_{\text{Cu}}\) is the mass of Cu in the sample. From these values, intrinsic catalytic activity constants \(k\) have been derived by Eq. \([29]\) in which \(P_{\text{CO},\text{in}}\) and \(P_{\text{CO},\text{out}}\) are the partial pressures of CO and \(\text{O}_2\) and \(K\) is the CO adsorption equilibrium constant (Eq. 5). Lopez et al. used \(k\) in an attempt to rank copper-based CO-PROX catalysts from literature\(^{[11]}\) and in this work we use the same approach to compare the intrinsic activity of our catalyst with the state of the art. The selectivity for CO\(_2\) (S\(_{\text{CO}_2}\)) was derived by Eq. 6 in which \(C_{\text{CO}_2}\) and \(C_{\text{H}_2\text{O}}\) are the concentrations of CO\(_2\) and H\(_2\)O at the reactor outlet.

In situ and operando spectroscopic investigations

Electron Paramagnetic Resonance (EPR) Spectroscopy: EPR measurements were performed on an X-band cw-spectrometer ELEXSYS 500-10/12 (Bruker). A microwave power of 6.3 mW, a modulation frequency of 100 kHz, and amplitude up to 5 G were used. Operando EPR experiments were carried out in a home-made quartz...
plug-flow reactor (3.0 mm inner diameter, 0.5 mm wall thickness), equipped with a gas dosing device with mass flow controllers (Bronkhorst) and a quadrupole mass spectrometer (Omnistar, Pfeiffer Vacuum GmbH) for online product analysis at the outlet. Measurements were done using 50 mg of catalyst particles (size 250–350 μm) and a total gas flow of 50 ml·min⁻¹. After reductive pre-treatment in 10% H₂/Ar for 1 h, the reaction was performed at 120 °C followed by a second reaction stage at 80 °C under flowing 1% O₂, 1% CO, 80% H₂/He gas. For each temperature, the reaction time was 60 min. After the PROX reaction, the samples were flushed with Ar (50 ml·min⁻¹) and cooled down to room temperature and to −173 °C for recording EPR spectra. The software package Easyspin was used spectra simulation.¹⁰

Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS): NAP-XPS measurements were performed with monochromatic Al Kα radiation on a laboratory NAP-XPS (SPES Surface Nano Analysis GmbH, Germany), equipped with a differentially pumped Phoibos 150 electron energy analyzer with a 500 μm nozzle and a laser for sample heating. Gases were fed to the analysis chamber by mass flow controllers (Brooks, GF40) at a total pressure of 2 mbar. Reactants and products were monitored by a quadrupole mass spectrometer (QMS, MKS e-vision 2) attached to the lens system of the spectrometer (Figure S6 and S7). The sample powder was pressed on a stainless-steel holder. Temperature was controlled by a thermocouple attached to the sample surface. Electron binding energies are referenced to the C 1s core level (284.8 eV). Peaks were deconvoluted with Gaussian-Lorentzian curves using the software Unifit 2021.

Operando Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS): DRIFT spectra were recorded on a Nicolet 6700 FTIR spectrometer using a high temperature Praying Mantis reaction cell (Harrick) equipped with CaF₂ windows and a temperature control unit (Eurotherm). The cell was connected to a gas dosing system with mass flow controllers (Bronkhorst). After pretreatment in a flow of 10% H₂/He (30 ml/min) at 250 °C for 1 h, the catalyst was exposed to the reactant feed of 1% O₂, 1% CO, 80% H₂/Ar for 120 min and subsequently at 120 °C for another 120 min. The spectra were collected with a resolution of 4 cm⁻¹ and an accumulation of 50 scans per spectrum. The intensity of the signals is given in log(1/R) scale. The gas outlet was connected to a quadrupole mass spectrometer (Omnistar, Pfeiffer Vacuum GmbH) for online product analysis (Figure S8).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Preferential CO oxidation · Operando spectroscopy · Cu/Co₃O₄ · single site catalyst

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