

■ Catalysis

Role of Interfacial Cu-Ions in Polycrystalline Cu-CeO₂: In-Situ Raman, In-situ DRIFT and DFT Studies for Preferential Oxidation of CO in Presence of Excess H₂**

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In this work, we designed a polycrystalline Cu-CeO₂ catalyst with defect sites, and it has superior CO oxidation activity in presence of excess H₂. The oxygen defects of Cu-CeO₂ influence the adsorption of unlike surface di-oxygen types, and the catalyst was characterized through XRD (X-Ray Diffraction) analysis, TEM (Transmission electron microscopy), *in-situ* Raman spectroscopy, *in-situ* DRIFT (Diffuse reflectance infrared fourier transform) spectroscopy. TEM showed that CeO₂(111) plane are

the exposed plane for this reaction. Raman spectroscopy showed nature of the defects of the prepared catalyst and how it works in the reaction environment. In-situ DRIFT spectroscopy showed that the Cu⁺ ↔ Cu²⁺ system is working in this reaction environment. Role of interfacial Cu ions was confirmed by in-situ DRIFT spectroscopy and DFT (Density functional theory) study.

Introduction

Defect sites of cerium oxide (CeO₂) play a crucial role in catalytic reactions to give very high conversion of products at minimal activation energy.^[1–3] The preferential oxidation (PROX) reaction of CO (CO + 1/2 O₂ + H₂ = CO₂ + H₂) is usually applied as a part of a purification process and the reformat gas that facilitates the production of pure hydrogen (H₂) through the oxidation of harmful carbon monoxide content in the feed into CO₂.^[4] This purification of H₂ is needed for PEM-Fuel cell or ammonia synthesis. Otherwise, the catalysts will easily be poisoned by CO.^[5] Due to the redox properties, ceria (CeO₂) is categorized as rapid oxygen (O₂) storage and its delivery material under dynamic reaction atmosphere.^[6] While the oxidation rate in ceria is substantially faster, the rate of ceria reduction is often slow. As a result, much effort has gone into promoting its reducibility. Because the oxygen diffusion is dependent on the dimension, and intensity of oxygen

vacancies, the cerium oxide reduction is considered to be regulated by the oxygen vacancies' nature, as explained in the reported literature.^[7,8] Esch et al. found that at normal temperature, tiny oxygen vacancies of the ceria surface (CeO₂,111) were stationary, but clusters of these vacancies were linearly formed at higher temperatures. As a result, operating parameters that favour the production of more oxygen vacancies will improve the reducible property of ceria.^[8] The population of Ce³⁺-O-Ce⁴⁺ defect sites also promote the catalytic action of CeO₂, and there are several literature reports on the defective sites of Ce (e.g., oxygen vacancy and Ce³⁺) exploiting several spectroscopic methods. The crystal planes are related to other surface planes, when handling the polycrystalline cerium oxide powder (CeO₂) to interpret experimental data, every probable surface plane must be evaluated. However, we concentrated on the CeO₂(111) plane as it is energetically most stable among the CeO₂(100), (110), and (111) surfaces.^[9,10] The theoretical simulations have revealed that various crystallographic planes of ceria such as (111), (110), and (100) reveal other properties such as interaction with surface molecules and O₂ vacancies formation energy.^[11] Qiang Wan et al. investigated the dissociation of a single Cu atom from CeO₂(111) supported Cu clusters with and without CO adsorption. They also showed that the CO adsorption on Cu lowers its dissociation energy, facilitating the creation of single atom entities on CeO₂(111).^[12] From theoretical simulations, T. X. T. Sayle et al. showed that there was an optimal amount of O-vacancies for the CO oxidation reaction. They demonstrated how the activity of the catalyst might be adjustable by designing the oxygen vacancy concentration and hence the oxygen content of the catalyst.^[13] Due to outstanding sensitivity towards microstructural development, Raman spectroscopy has become prevalent in diverse research fields, including materials science and catalysis. This technique

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[**] DRIFT- Diffuse Reflectance Infrared Fourier Transform

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has been exploited to explore the molecules with defect sites present in the ceria lattice.

Results and Discussion

Catalytic activity: The activities of hydrothermally prepared catalyst (2.8% Cu-CeO₂^{HT}) and catalyst prepared by conventional impregnation method (2.8% Cu-CeO₂^{comm}) are shown in Figure 1. Without H₂ in the gas feed, the 2.8% Cu-CeO₂^{HT} catalyst exhibits superior activity (10% CO conversion, 25 °C and 100% CO conversion, 55 °C) in comparison to the 2.8% Cu-CeO₂^{comm}. In presence of excess H₂, 2.8% Cu-CeO₂^{HT} catalyst shows the CO conversion 100% and O₂ selectivity 100% (O₂ will only oxidize CO, not H₂) at 75 °C, whereas 2.8% Cu-CeO₂^{comm} catalyst showed 100% CO conversion at 200 °C and O₂ selectivity was only 52%. 2.8% Cu-CeO₂^{HT} catalyst did not show any deactivation even after 100 h, whereas the 2.8% Cu-CeO₂^{comm} catalyst showed significant deactivation during 100 h of time on stream (Figure S4, supporting information). For practical PEM fuel cell application, the operating temperature should be below 120 °C, and the CO concentration level must be below 10 ppm, and O₂ selectivity should be 100%.

In the case of PROX, apparent activation energies were evaluated from the Arrhenius plots. R² (the coefficient of determination) of linear regressions were found above 0.98 (Figure 2A and B). 2.8% Cu-CeO₂^{HT} and 2.8% Cu-CeO₂^{comm} catalysts show apparent activation energy values of 59.27 and 85.95 KJ/mol, respectively. Since Cu-CeO₂^{HT} has less apparent activation energy than Cu-CeO₂^{comm} (E_{a,comm} > E_{a,HT}), oxidation of CO facilitates easily over the Cu-CeO₂^{HT} catalyst compare to Cu-CeO₂^{comm}.

Catalyst characterization: TEM images of fresh 2.8% Cu-CeO₂^{HT} catalyst exhibits particles in the range of 3–18 nm.

The SAED (selected area electron diffraction) pattern of Cu-CeO₂ showed in Figure 3(d), and it reveals as prepared catalyst is in polycrystalline nature.

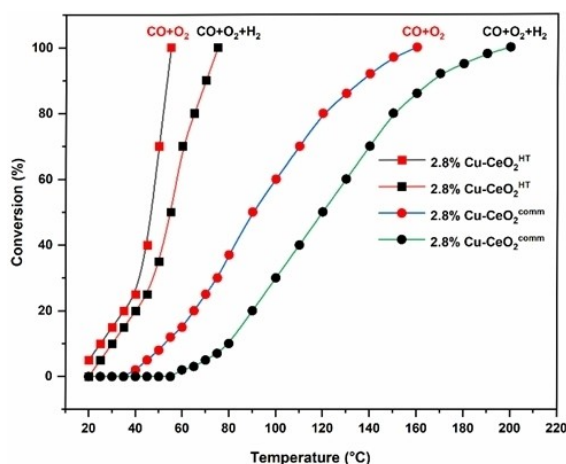


Figure 1. Light off curve for 2.8% Cu-CeO₂^{HT} and 2.8% Cu-CeO₂^{comm} with the molar ratio of the gas mixture CO:O₂:H₂:He = 1:2:60:37, where CO conversions with no H₂ (GHSV:7000 h⁻¹) and with H₂ (GHSV:15000 h⁻¹).

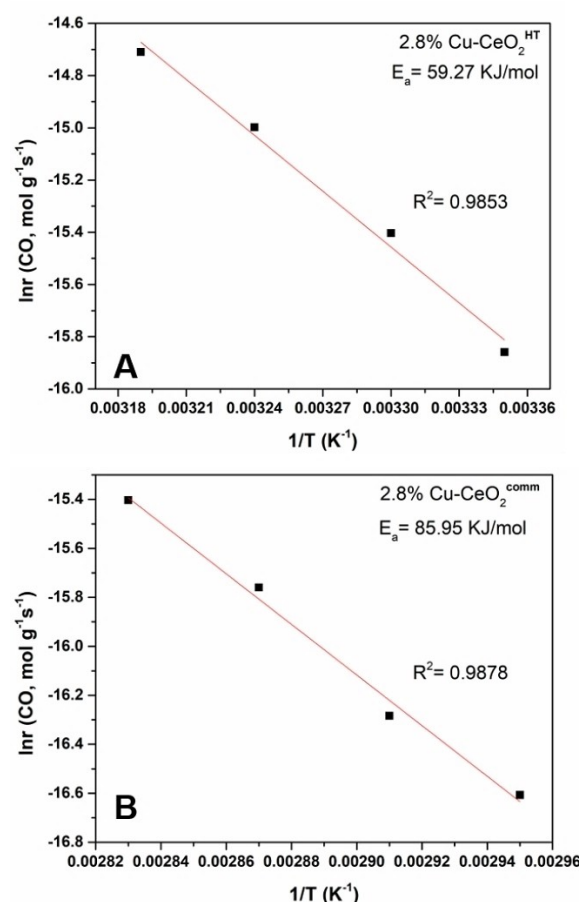


Figure 2. Arrhenius plots for A) 2.8% Cu-CeO₂^{HT}, B) 2.8% Cu-CeO₂^{comm} respectively.

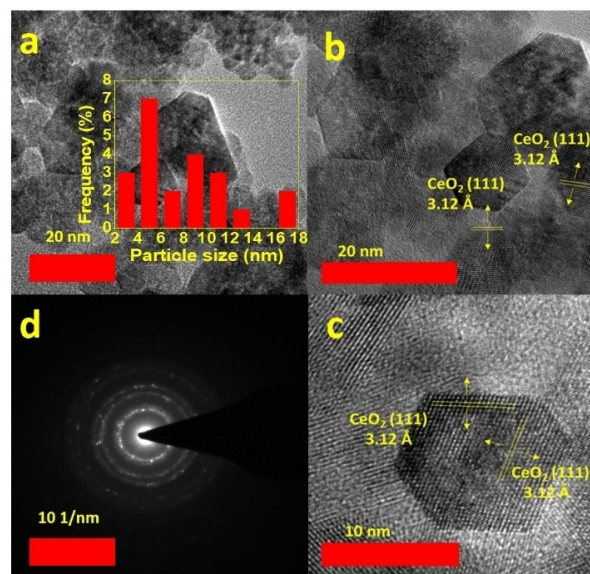


Figure 3. (a–d) shows the TEM image of the fresh 2.8% Cu-CeO₂^{HT} catalyst.

Figure 3(c) shows the HRTEM (high resolution transmission electron microscopy) image of the Cu-CeO₂ catalyst, and the inter-planar d-spacings is 0.31 nm only, and it corresponds to the CeO₂(111) facets. The XRD (X-ray diffraction) analysis detects no Cu species (Figure 4). TEM images of fresh 2.8% Cu-CeO₂^{comm} catalyst exhibits large sized and agglomerated particles. Due to this, the measurement of particle size is impossible (Figure S5). The SAED (selected area electron diffraction) pattern of 2.8% Cu-CeO₂^{comm} showed in Figure S5(d), and it reveals as prepared catalyst is in polycrystalline nature. The XRD peaks of CeO₂^{syn}, 2.8% Cu-CeO₂^{HT} and 2.8% Cu-CeO₂^{comm} are shown in Fig. 4 A and it was found that the 2θ value shifted for 2.8% Cu-CeO₂^{HT} and 2.8% Cu-CeO₂^{comm} (Fig 4 A inset). The lattice parameter was calculated taking the highest intense peaks ~28° and found that the value is 5.4201, 5.4059 and 5.4367 Å, respectively for CeO₂^{syn}, 2.8% Cu-CeO₂^{HT} and 2.8% Cu-CeO₂^{comm}. It is known that, when smaller ions (Cu²⁺, ionic radius 0.87 Å) replace larger size ions (Ce⁴⁺, ionic radius 1.01 Å) within the lattice, lattice contraction occurred (Vegard's law). In case of Cu-CeO₂^{HT}, it was observed that the contraction of the lattice parameter occurred from 5.4201 to 5.4059 Å, and this is confirmed from XRD pattern as the 2θ

value increased from 28.50° to 28.58°.^[14] On the other hand, in case of Cu-CeO₂^{comm}, it was found that expansion of the lattice parameter occurred from 5.4201 to 5.4367 Å and this is confirmed from XRD pattern as the 2θ value decreased 28.50° to 28.42°. This is because Ce⁴⁺ (ionic radius 1.01 Å) is reduced to Ce³⁺ (ionic radius 1.15 Å).^[15] Evaluation of lattice constants of 2.8% Cu-CeO₂^{HT}, synthesized CeO₂, and 2.8% Cu-CeO₂^{comm} were accomplished by the program PROZSKI. In fact, a drop in the lattice constant from 5.4059 due to CeO₂ (pure) to 5.4005 due to 2.8% Cu-CeO₂^{HT} confirms Cu²⁺ insertion in the CeO₂ lattice.^[16,17] According to XRD studies, Cu²⁺ ions are integrated into the matrix of cerium oxide, indicating the feasibility of Cu–O–Ce solid-solution formation. (Figure 4B).^[14] This finding was consistent with what has been reported in the previously published journals.^[16,17,18] In case of 2.8% Cu-CeO₂^{comm}, Ce⁴⁺ becomes reduced to Ce³⁺ by the adjacent ions, and the lattice parameter becomes the highest (5.4367 Å).^[14] The smaller nanocrystallite formation occurred during the hydrothermal method than the impregnated one. The decrease of crystallite sizes is confirmed from the XRD peak broadening (Figure 4). The CeO₂ crystallite size for the 2.8% Cu-CeO₂^{HT} catalyst is 9.51 nm, whereas the CeO₂ crystallite size for the 2.8% Cu-CeO₂^{comm} catalyst is 36.19 nm. So, it is very clear that the catalyst prepared by the hydrothermal method produces very small CeO₂ crystallites compare to the catalyst prepared by the conventional impregnation method. The CeO₂ crystallite size of the 2.8% Cu-CeO₂^{HT} was almost four times lower than the CeO₂ crystallite prepared by the conventional impregnation method (2.8% Cu-CeO₂^{comm}). It was also found that the smaller the CeO₂ crystallite size, the higher is the activity in the CO conversion. It was found that, at 75 °C and keeping all the reaction parameters constant, 2.8% Cu-CeO₂^{HT} catalyst showed ~100% CO conversion, whereas 2.8% Cu-CeO₂^{comm} catalyst is showing very negligible CO conversion (~8%). Comparing the activity of both catalysts, we can say that the activity of the 2.8% Cu-CeO₂^{HT} catalyst is almost 12 times higher than the 2.8% Cu-CeO₂^{comm} catalyst, as shown in Table 1. From the Rietveld refined XRD analysis, we can conclude that with solid-solution formation, oxygen vacancy in the crystal lattice increases, favouring the catalytic reactivity in the case of hydrothermally prepared catalysts, 2.8% Cu-CeO₂^{HT} (Table 2, Figure 4B and S1).

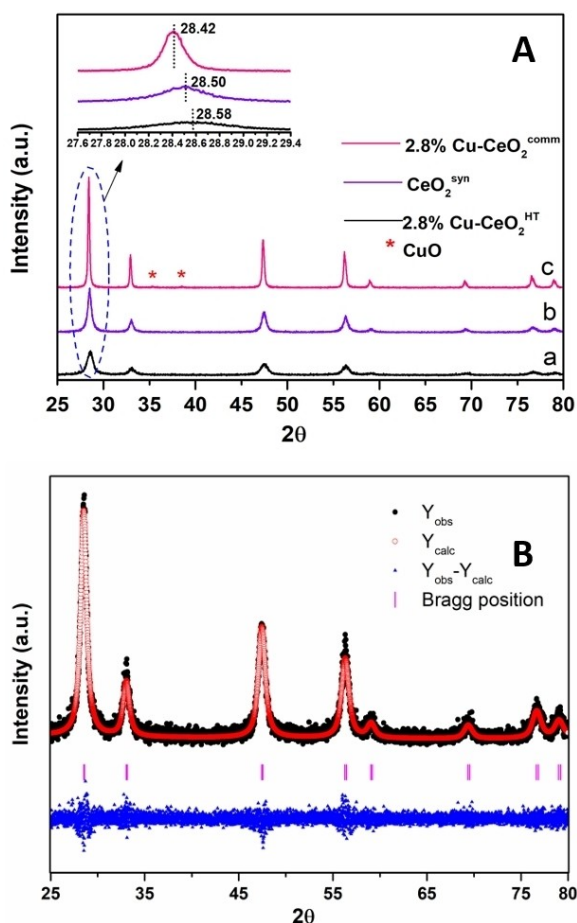


Figure 4. A) X-ray pattern of a) 2.8% Cu-CeO₂^{HT}; b) CeO₂^{syn}; c) 2.8% Cu-CeO₂^{comm}; B) Rietveld refined XRD arrangement of 2.8% Cu-CeO₂^{HT}. R_{Bragg} 7.65, R_F 6.01, χ² 1.21.

Table 1. Comparison of CO-conversion (at 75 °C) with the catalyst's crystallite sizes.

Material	Crystallite sizes (nm)	Conversion (%)
2.8% Cu-CeO ₂ ^{HT}	9.51	100
2.8% Cu-CeO ₂ ^{comm}	36.19	8

Table 2. Comparison of Rietveld refined XRD analysis of the catalysts.

Catalyst	R _{Bragg}	R _F	χ ²
2.8% Cu-CeO ₂ ^{HT}	7.65	6.01	1.21
2.8% Cu-CeO ₂ ^{comm}	4.16	4.23	1.89

The BET surface area of 2.8% Cu-CeO₂^{HT} (fresh) and 2.8% Cu-CeO₂^{comm} (fresh) catalysts are 55 m²/g and 10 m²/g, respectively.

Raman spectroscopy: For this catalyst, we employed the *in-situ* Raman spectroscopy to analyze the properties of lattice-O defects and the nature of oxygen vacancies. Figure 5 demonstrates the Raman spectra of 2.8% Cu-CeO₂^{HT} catalyst in the course of PROX reaction.

An intense peak at about 459 cm⁻¹, which agrees with F_{2g} vibration mode of cubic fluorite assembly of CeO₂.^[19,20,21] The F_{2g} band shows the shifts from 459 to 457 cm⁻¹ (459→440→449→456→457). This red-shift is mostly owing to thermal strain; spectrum broadening and intensity quenching, on the other hand, are attributable to anharmonicity effects.^[22]

For the 2.8% Cu-CeO₂^{comm} catalyst, we employed the *in-situ* Raman spectroscopy to analyze the properties of lattice-O defects and the nature of oxygen vacancies. Figure 6 demonstrates the Raman spectra of 2.8% Cu-CeO₂^{comm} catalyst in the course of PROX reaction. The F_{2g} band shows the shifts from 459.4 to 459.8 cm⁻¹ (459.4→450.1→459.7→459.8). This blue-

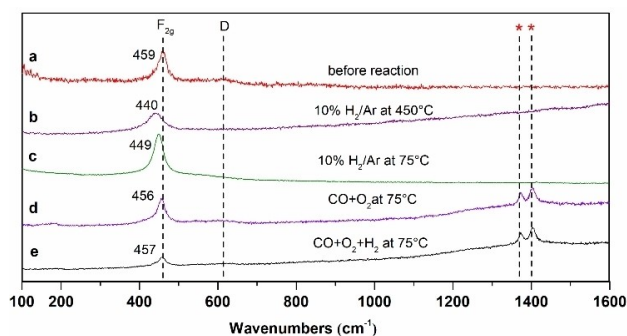


Figure 5. *In-situ* Raman spectra of 2.8% Cu-CeO₂^{HT} catalyst in PROX reaction condition. Asterisk (*) indicates carbonate species. The spectra are normalized by intensity at 459 cm⁻¹, F_{2g} mode at 633 nm laser power with 50% filter.

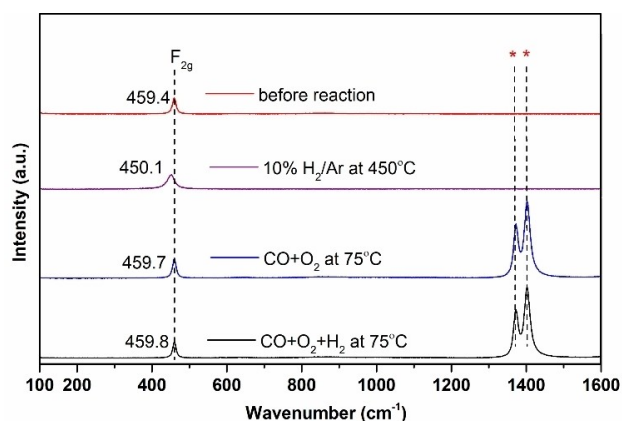


Figure 6. *In-situ* Raman spectra of 2.8% Cu-CeO₂^{comm} catalyst in PROX reaction condition. Asterisk (*) indicates carbonate species. The spectra are normalized by intensity at 459 cm⁻¹, F_{2g} mode at 633 nm laser power with 50% filter.

shift advocates the formation of larger CuO and CeO₂ particle during reaction.^[23]

The band at ~ 460 cm⁻¹ (F_{2g}) suggests (Figure 7) the insertion of copper into the lattice of cerium oxide to form a solid solution in 2.8% Cu-CeO₂^{HT} as the peak at ~ 460 cm⁻¹ (F_{2g}) becomes broad, and intensity becomes lower than the synthesized CeO₂.^[23] The relative concentration of oxygen vacancies was calculated by analyzing the ratio of the intensities of D and F_{2g} cm⁻¹ (Table 3, I_D/I_{F2g}).^[23] The ratios of I_D/I_{F2g} at room temperature follows the order: 2.8%Cu-CeO₂ (0.0413) > CeO₂^{syn} (0.0235), suggesting that the introduction of copper ions in CeO₂ lattice enhances the concentration of oxygen vacancies in the CeO₂ lattice.

We prepared catalyst with higher loading and performed Raman analysis. A blue-shift from 459 to 462 cm⁻¹ of the F_{2g} peak was observed when loading was increased from 2.8% (2.8%Cu-CeO₂^{HT}) to 7% (7%Cu-CeO₂^{HT}) as shown in Figure 8. Earlier report says that the peak position shift and broadening

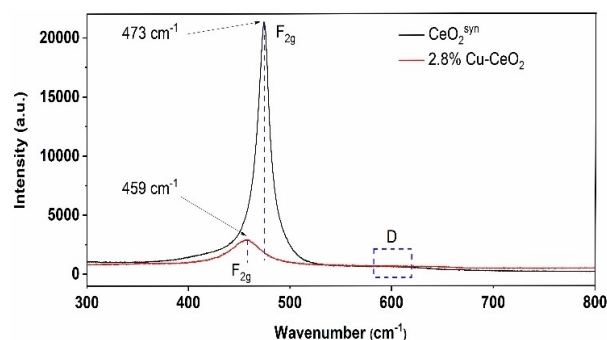


Figure 7. *Ex-situ* Raman spectra of 2.8% Cu-CeO₂^{HT} catalyst and CeO₂^{syn} recorded at 633 nm laser power with 50% filter at 25 °C.

Table 3. *Ex-situ* Raman spectroscopy showing the intensity of the defects (I_D/I_{F2g} ratio) during incorporation of copper ions in CeO₂ lattice, recorded at 633 nm laser power with 50% filter at 25 °C.

Material	I _D (a.u.)	I _{F2g} (a.u.)	I _D /I _{F2g}
CeO ₂ ^{syn}	462	19626	0.0235
2.8% Cu-CeO ₂ ^{HT}	82	1983	0.0413

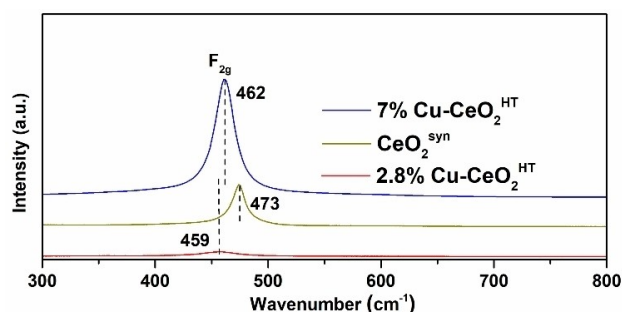


Figure 8. *Ex-situ* Raman spectroscopy showing the nature of the defects (I_D/I_{F2g}) during incorporation of copper ions in CeO₂ lattice, recorded at 633 nm laser power with 50% filter at 25 °C.

of the F_{2g} peak are influenced not only by the particle sizes but also by the incorporation of copper in the cerium oxide lattice.^[24] This blue shift suggests forming larger-sized Cu-CeO₂ particles.^[24] In general, the higher red-shift is correlated with more copper incorporation into the ceria to form a solid solution, creating more lattice vacancies.^[24]

To understand the profound nature of reactive oxygen and the mechanism of reaction, we performed reactions at different feeds (reaction with CO only, with CO + O₂ and with CO + O₂ + H₂) over the 2.8% Cu-CeO₂^{HT} catalyst. Here, we showed the *in-situ* Raman spectra where only CO feed was used (Figure 9), and the characteristic F_{2g} mode of vibration of the cubic fluorite assembly of CeO₂ at 460 cm⁻¹ is shown, while the band 617 cm⁻¹ (D1) corresponds to the presence of MO₈ sites (O in CeO₂ lattice) as shown in Figure 9.^[25] The band component between 500–600 cm⁻¹ (D2, asymmetric per-oxo species) have been ascribed to defect spaces involving an oxygen vacancy.^[25,26] No Raman lines of any copper species were observed due to the high dispersion of Cu species.^[27] The broadband ~1150 cm⁻¹ is attributed to superoxide species.^[26] To explore the nature of active oxygen species, we introduced

only CO to the fresh 2.8% Cu-CeO₂^{HT} catalyst. We found a gradual increase in the D2 intensity (shown in Figure 9). After 50 min decrease of D1 was observed, and it was confirmed that CO was oxidized initially with surface oxygen (superoxide species) as long as it is available.^[26] After that, it reacts with oxygen from Cu²⁺-O-Ce⁴⁺ moiety (D1), which creates more oxygen vacancies and the intensity of D1 decreases (Figure 9). But the band intensity around ~1150 cm⁻¹ completely disappeared after 120 minutes. From this observation, we can say that surface superoxide species are most easily accessible than other species, and it is used as long it is available. When surface oxygen is not available, then lattice O₂ is involved in CO oxidation and that the resulting formation of oxygen vacancies is observed (increasing intensity of D2, asymmetric peroxo species). Comparing the reaction data between CO + O₂ and CO + O₂ + H₂ (Figures 10 and 11), we can see that both the series of spectra are identical in PROX reaction condition with 2.8% Cu-CeO₂^{HT}.

in-situ DRIFT spectroscopy: Figure 12 demonstrates the *in-situ* DRIFT spectra, recorded in CO + O₂ condition for the 2.8% Cu-CeO₂^{HT}.

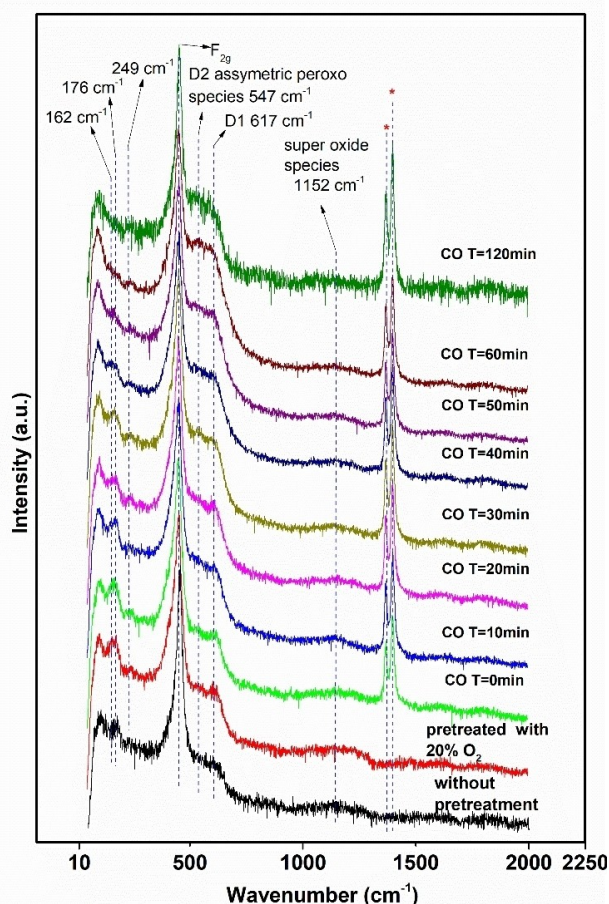


Figure 9. *In-situ* Raman study of 2.8% Cu-CeO₂^{HT} at 75 °C under CO flow after pre-treatment in O₂ at 450 °C. Asterisk (*) indicates carbonate species. The spectra are normalized by intensity at 460 cm⁻¹, F_{2g} mode at 633 nm laser power with 50% filter.

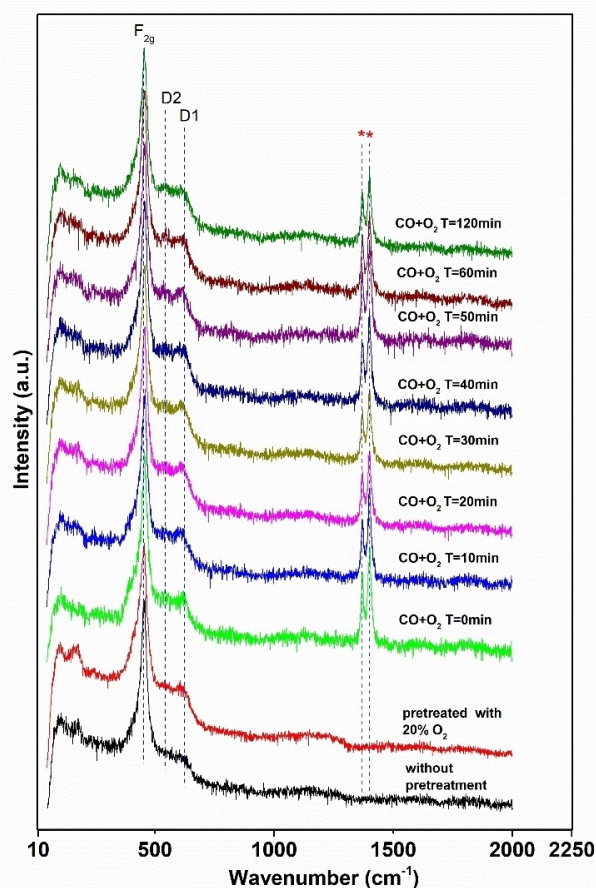


Figure 10. *In-situ* Raman study of 2.8% Cu-CeO₂^{HT} at 75 °C under CO + O₂ flow after pre-treatment in O₂ at 450 °C. Asterisk (*) indicates carbonate species. The spectra are normalized by intensity at 460 cm⁻¹, F_{2g} mode at 633 nm laser power with 50% filter.

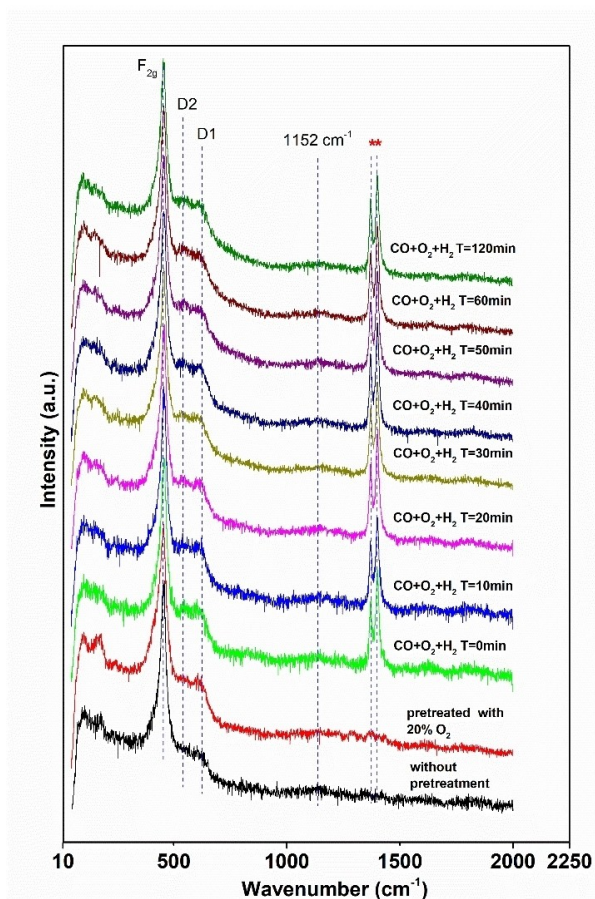


Figure 11. In-situ Raman study of 2.8% Cu-CeO₂^{HT} at 75 °C under CO + O₂ + H₂ flow after pre-treatment in O₂ at 450 °C. Asterisk (*) indicates carbonate species.

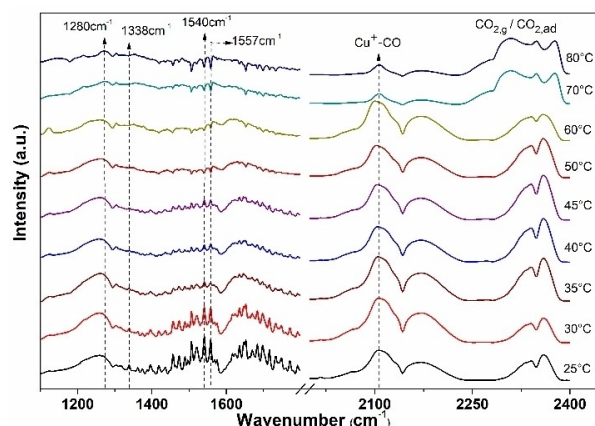


Figure 12. In-situ DRIFT study of 2.8% Cu-CeO₂^{HT} at 25–80 °C under CO + O₂ flow after pre-treatment in O₂ at 450 °C.

The most noticeable changes noticed in the DRIFT spectra (accompanied by reaction feed) are in the regions attributed to carbonyl and carbonate species (Figure 12). Small deviations are too noticed to be generated in the region attributed to hydroxyl species (not shown). Bands at 1469–1463 cm⁻¹ and

1394–1392 cm⁻¹ can be assigned to mono- or tri-dentate carbonate species for samples revealing (100) faces of cerium oxide.^[28,29] Cu⁺-carbonyls are observed in the 2115–2099 cm⁻¹ zone.^[28,29] The formation of CO₂(g) is shown in the spectral zone at intermedial frequencies, which emerged in agreement with CO-oxidation activity. Cu⁺-carbonyl species at ~2110 cm⁻¹, which shifts gradually to the red-shift to ~2105 cm⁻¹ with the gradual increase of temperature up to 80 °C but doesn't disappear completely by the reduction of CO molecule. Because this Cu⁺ comes from the interfacial Cu²⁺ and is stabilized by the oxygen of adjacent CeO₂ molecule (Cu^{+/2+}-O-Ce^{3+/4+} moiety) otherwise, this type of observation is not possible.^[29,30]

We have performed the reaction, including the feed mixture of CO + H₂ + O₂. In-situ DRIFTS investigations were carried out between 25 and 80 °C with a 1:2:4 ratio of CO:O₂:H₂ to determine the critical intermediates on the surface of 2.8% Cu-CeO₂^{HT}. There three unique spectral areas were observed. Bands related to carbonate and bicarbonate species occurred in the region 1260–1800 cm⁻¹.^[30] The most powerful peaks in this spectral area are 1540 and 1650 cm⁻¹ are bi-dentate carbonates (Figure 13). Cu⁺-CO species are responsible for the bands ~2110 cm⁻¹.^[31] The reduction of Cu²⁺, induced by the support is linked to the creation of Cu⁺-CO species. The frequency of the carbonyl species is generally determined by the number of accessible surface-exposed Cu⁺ centres, CO content, and temperature.^[32] In the 2.8% Cu-CeO₂^{HT} catalyst, the development of interfacial Cu⁺ sites at the surface is stimulated and stabilized by CeO₂. Surface Cu⁺ entities must be stabilized by Ce⁴⁺/Ce³⁺ to prevent further reduction to Cu⁰.^[33] Bands at 2359 and 2336 cm⁻¹ demonstrate that CO₂ in gaseous form is generated, thus confirming CO oxidation (Figure 14).^[34]

Figure 14 depicts the Cu⁺-CO species area in greater detail. Adsorbed CO₂ and Cu⁺-CO species are found in the 2300–2400 cm⁻¹ and 2080–2140 cm⁻¹ areas, respectively.^[35] The concentration of Cu⁺-CO species dropped as the temperature raised, but the concentration of CO₂ continued to increase.

We have performed the reaction including the feed mixture of CO + H₂ + O₂ over 2.8% Cu-CeO₂^{comm}. In-situ DRIFTS tests were performed between 25 and 80 °C with a 1:2:4 ratio of CO:

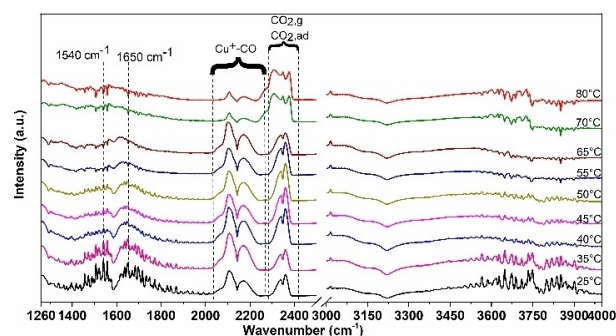


Figure 13. In-situ DRIFT study of 2.8% Cu-CeO₂^{HT} at 25–80 °C under CO + O₂ + H₂ flow after pre-treatment in O₂ at 450 °C.

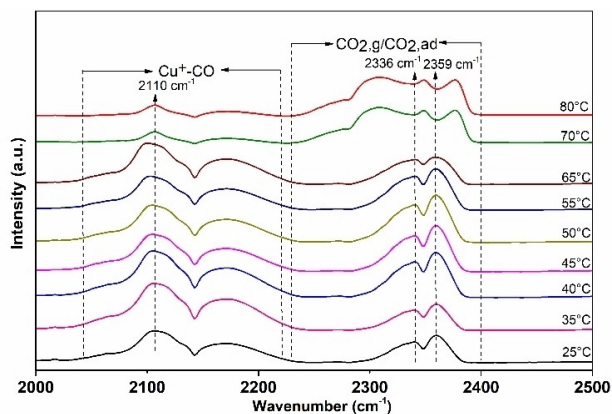


Figure 14. *In-situ* DRIFT study of 2.8% Cu-CeO₂^{HT} at 25–80 °C under CO + O₂ + H₂ flow after pre-treatment in O₂ at 450 °C.

O₂:H₂ so that the main intermediates on the surface of 2.8% Cu-CeO₂^{comm} under PROX conditions could be identified (Figure 15). From 25 to 65 °C, we didn't see any changes but when temperature reached 70 °C, we observed the increase of the intensity of the CO₂ peak. We can say that above 65 °C the catalyst becomes active, and it is less active than the hydrothermal ones.

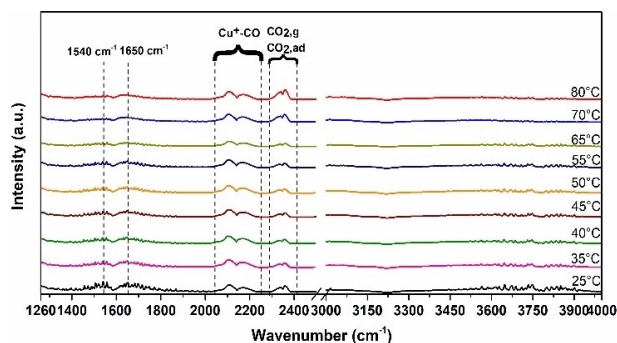


Figure 15. *In-situ* DRIFT study of 2.8% Cu-CeO₂^{comm} at 25–80 °C under CO + O₂ + H₂ flow after pre-treatment in O₂ at 450 °C.

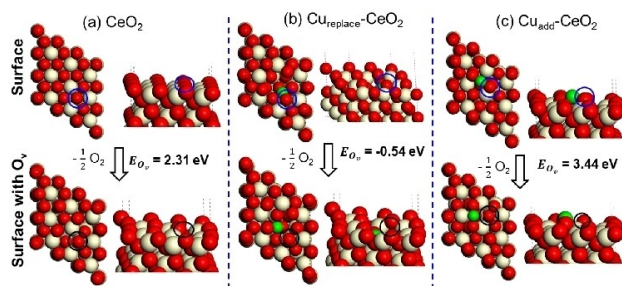


Figure 16. DFT optimized geometry of the non-defective (a) CeO₂, (b) Cu_{replace}-CeO₂ and (c) Cu_{add}-CeO₂(111) surfaces. The surfaces with oxygen vacancy shown in the bottom panel. The oxygen vacancy formation energy (E_{O_v}) for each of the three surfaces is given above. Color scheme: Cu (green), O (red), Ce (white) and the blue circle indicate the oxygen removed to create the oxygen vacancy. The position of oxygen is indicated with the black circle.

DFT calculation

The detail of the DFT calculation is given in the experimental section.^[36,37] The surface of CeO₂(111) is modelled using 3x3 supercell slab having three CeO₂ layers (9 atomic layers). The surface slabs are periodic in the xy plane, whereas they are separated in the z-direction by a vacuum of 20 Å (Figure 16(a)). The highly dispersed Cu/CeO₂ catalyst was modelled by replacing one Ce atom of the CeO₂(111) surface with a Cu atom to obtain Cu_{replace}-CeO₂ (Figure 16(b)) and by adding a Cu atom at the CeO₂(111) surface to obtain Cu_{add}-CeO₂ (Figure 16(c)). The defective surfaces with oxygen vacancy were created by removing the surface oxygen atom present at the Cu-CeO₂ interface. The exchange-correlation energy of the electrons is described by Perdew-Burke-Erberhof (PBE) parameterization of generalized gradient approximation (GGA).^[38] The core electrons were described using PAW potentials.^[39] The van der Waals dispersion corrections were incorporated using the Grimme DFT-D3 correction with Becke-Jonson damping.^[40] Kohn-Sham one-electron valence states are expanded using a plane-wave basis set truncated to cut-off energy of 396 eV. All the calculations were performed under spin-polarized condition, with Hubbard U_{eff} parameters of value 4.5 eV employed for Ce.^[41,42] The surface Brillouin zone is sampled using a 2x2x1 Monkhorst-Pack grid.^[43] For structure optimizations, the energy and force convergence criteria have been set to 1×10^{-6} eV and 0.05 eV/Å, respectively. The oxygen vacancy formation energy (E_{O_v}) of the adsorbate is calculated with respect to the surface and the gas phase reactant species, as follows:

$$E(O_v) = (E_{\text{surf-Ov}} + \frac{1}{2} E_{O_2, \text{gas}}) - E_{\text{surface}} \quad (1)$$

where E_{surface} , $E_{\text{surf-Ov}}$, and $E_{O_2, \text{gas}}$ denotes the energy of the non-defective surface, energy of an oxygen vacancy on a surface and the energy of an O₂ molecule in gaseous phase, respectively.

To understand the effect of Cu on the formation of oxygen vacancy at the CeO₂ surface, DFT (Density Functional Theory) method was applied. Figure 16 (a) shows the geometry of CeO₂(111) optimized by DFT. The stable CeO₂(111) surface is oxygen terminated with Ce atoms forming the layer below, as can be seen in Figure 16 (a), where each Ce atom is connected to seven oxygen atoms. The oxygen vacancy in the CeO₂(111) surface was generated by taking away one surface oxygen atom, as shown in the bottom panel of Figure 16 (a). The formation of oxygen vacancy at the pure CeO₂(111) surface requires energy (E_{O_v}) that was calculated to be 2.31 eV. To understand the effect of Cu on the oxygen mobility of the CeO₂ surface, two Cu/CeO₂ surface models were studied here. The Cu_{replace}-CeO₂(111) surface is obtained by replacing one Ce atom at the CeO₂(111) surface with Cu (Figure 16 (b)), whereas Cu_{add}-CeO₂(111) surface is obtained by adding a Cu atom at the CeO₂ surface (Figure 16 (c)). In the Cu_{replace}-CeO₂(111) surface, the Cu atom move towards the second layer, breaking the octahedral symmetry in CeO₂, and form a square-planer like geometry where Cu is connected to four oxygen atoms, as can

be seen in Figure 16 (b). Due to the disruption of the lattice caused by the formation of the square-planer geometry by the Cu dopant, the oxygen vacancy formation at the Cu-CeO₂(111) surface become highly facile, as can be seen from the exothermic formation energy of oxygen vacancy -0.54 eV (Figure 16 (b), bottom panel). Similar negative oxygen vacancy formation energy was also obtained by Riley et al. for Ni doped CeO₂ catalyst.^[44] The spontaneous formation of oxygen vacancy was attributed to the charge balance as Ce⁴⁺ was replaced by Ni²⁺. Similar low oxygen formation energy was also calculated by Feng et al for Pt/Ga-CeO₂ catalyst system ($E_{O_v} = 0.09$ eV), where Ce⁴⁺ was replaced by Ga³⁺.^[45] The geometry of the Cu_{add}-CeO₂(111) surface, optimized by the DFT has been shown in Figure 16 (c). The Cu atom forms two Cu–O bonds with the CeO₂ surface and binds strongly to the surface. The oxygen vacancy in the Cu_{add}-CeO₂(111) metal-support interface was generated by pulling out one CeO₂(111) surface oxygen present at the Cu-CeO₂ interface, as shown in Figure 16 (c) bottom panel. The oxygen vacancy formation at the Cu_{add}-CeO₂ interface was found to be higher (3.44 eV) compared to the pure CeO₂(111) surface. This indicates the experimentally observed increase in the surface oxygen vacancy concentration ($I_{O_v}/I_{F_{2g}}$) in the Cu-CeO₂ catalyst compared to pure CeO₂, shown in Figure 7, is due to the insertion of Cu atom at the CeO₂ lattice, forming highly active Cu–O–Ce active site due to the disruption of lattice geometry. Easy oxygen vacancy formation increases the diffusion of lattice O₂ at the surface region, also observed experimentally in Figure 9 and 11. The easy formation of oxygen vacancy also expected to lower the light-off temperature for the CO PROX reaction, as observed experimentally in Figure 1.

The reaction occurs between the chemisorbed CO at the Cu²⁺-CeO₂ interface and nearby active oxygen. The CO molecule adsorbs at the active O-center of the Cu_{replace}-CeO₂ surface, forming CO₂ molecule as shown in Figure S3 (supporting information). The reaction energy for the CO adsorption at the Cu_{replace}-CeO₂ surface was calculated to be highly exothermic (-4.45 eV).

The small crystallite size of CeO₂ also indicates an increase in the Cu/CeO₂ interface area between the small Cu clusters CeO₂. As shown in the modelling work, the insertion of Cu in the CeO₂ surface (Cu_{replace}-CeO₂(111)) increases the propensity for oxygen vacancy formation. Hydrotreated 2.8% Cu-CeO₂^{HT} catalyst having small crystallites of CeO₂ is expected to have higher oxygen vacancy concentration, as seen in the Rietveld refined XRD analysis. The small crystallites of CeO₂ also increase the area % of other less stable CeO₂ surfaces like the CeO₂(110) surface.^[11] Similar to Cu_{replace}-CeO₂(111) surface, a Cu_{replace}-CeO₂(110) surface was modelled by replacing a Ce atom at the CeO₂(110) surface with Cu atom, shown in Figure S2 (supporting information). The oxygen vacancy formation energy at the Cu_{replace}-CeO₂(110) surface ($E_{O_v} = -0.46$ eV) was found to be similar to the Cu_{replace}-CeO₂(111) surface ($E_{O_v} = -0.55$ eV).

Conclusion

In conclusion, we found that the loosely bounded surface oxygen species reacts faster than other oxygen species. Then subsequently, lattice-oxygen (D1) reacts with CO with a concomitant increase of oxygen vacancy (D2), which are later filled up by the molecular oxygen. The formation of Cu²⁺-CeO₂ interface (Cu²⁺-O-Ce⁴⁺) is possible with the incorporation of Cu²⁺ into CeO₂ matrix (from line broadening of XRD and Raman Spectra and DFT calculation). O₂ activation occurs on the oxygen vacancies of CeO₂ (D2), and the diffusion of oxygen takes place into the lattice to regenerate the catalyst. This defect site is responsible for preferential oxidation of CO at low temperature when hydrogen is present in excess. The low-temperature PROX reaction with the maximum oxygen selectivity (100%) make the present catalyst suitable for practical polymer electrolyte membrane fuel cells application.

Instrumental techniques: An online gas chromatograph (Thermo Fischer Scientific, TRACE-GC 700) equipped with a TCD (thermal conductivity detector) and an Unibeads C column was used to ascertain the compositions of the emitted gases to separate CO₂, CO, O₂, and H₂O. Supposing the almost constant total volumes of the feed gas before and after reaction (< 1 vol.% change), the conversions of CO were measured according to the following equations:

$$\text{CO conversion (\%)} = \frac{n\text{CO}_{\text{in}} - n\text{CO}_{\text{out}}}{n\text{CO}_{\text{in}}} \times 100$$

where $n\text{CO}_{\text{in}}$ and $n\text{CO}_{\text{out}}$ are the GC peak areas of CO before and after the reactor, respectively. Diameter of 5 mm diameter and length of 11 cm were the dimensions of the quartz tube that was used as the reactor. Thermal mass flow controllers (TMFC) were used to control the flow of gases. Dimmerstat (continuously variable voltage auto-transformer) & heating tape was used to heat the whole tubing.

A PROTO X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu K α radiation source was used to detect the powder X-ray diffraction patterns. 0.5 degrees (2 θ) per minute rate of recording was used to detect the diffraction patterns in the 2°–80° region.

Inductively Coupled Plasma Atomic Emission Spectrometer (Model: PS 3000 uv, (DRE), Leeman Labs, Inc (USA)) was used to carry out the elemental analysis.

A JEOL JEM 2100 microscope was used to record the TEM images, and samples were prepared by putting in place an ethanol-dispersed sample on a Cu grid made of lacey carbon and coated with formvar.

In-situ Raman experiments were done in HORIBA Scientific instrument equipped with OLYMPUS confocal microscope, Labram detector made by CCD (charged coupled device) and LINKAM-CCR1000 cell (ceramic cell). Pre-treatment of the sample in 10 vol.% O₂/He mixture with a flow rate of 30 ml min⁻¹ was carried out before each test for 2 h and purging was done with He (20 ml min⁻¹) for additional 0.5 h. The spectra were recorded under 633 nm laser power (He/Ne power source).

An environmental reaction chamber with windows made of ZnSe installed in a Praying Mantis (Harrick) optical system at high temperature was used to execute the in-situ DRIFTS measurements. The species that were adsorbed gave spectra by subtraction of the spectrum after the pretreatment step.

Supporting Information Summary

Material Characterizations, instrumentation and DFT calculation techniques are shown in detail in supporting information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: In-situ Raman • In-situ DRIFT • Interface • mixed oxide • oxygen vacancy

- [1] Trovarelli, C. de Leitenburg, M. Boaro, G. Dolcetti, *Catal. Today* **1999**, *50*, 353–367.
- [2] A. Trovarelli, *CATAL REV* **1996**, *38*, 439–520.
- [3] Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science* **2003**, *301*, 935–938.
- [4] J. Li, Y. Han, Y. Zhu, R. Zhou, *Appl. Catal., B* **2011**, *108–109*, 72–80.
- [5] D. Vovchok, C. J. Guild, J. Llorca, W. Xu, T. Jafari, P. Toloueinia, D. Kriz, I. Waluyo, R. M. Palomino, J. A. Rodriguez, S. L. Suib, S. D. Senanayake, *Phys. Chem. Chem. Phys.* **2017**, *19*, 17708–17717.
- [6] M. Efstathiou, S. Y. Christou in *Catalysis by Ceria and Related Materials, Investigation of the Oxygen Storage and Release Kinetics of Model and Commercial Three-Way Catalytic Materials by Transient Techniques*, Imperial College Press, London, **2013**, 139.
- [7] E. Mamontov, T. Egami, R. Brezny, M. Koranne, S. Tyagi, *J. Phys. Chem. B* **2000**, *104*, 11110–11116.
- [8] X. Liu, K. Zhou, L. Wang, B. Wang, Y. Li, *J. Am. Chem. Soc.* **2009**, *131*, 3140–3141.
- [9] T. Taniguchi, T. Watanabe, N. Sugiyama, A. K. Subramani, H. Wagata, N. Matsushita, M. Yoshimura, *J. Phys. Chem. C* **2009**, *113*, 19789–19793.
- [10] Y. M. Choi, H. Abernathy, H.-T. Chen, M. C. Lin, M. Liu, *ChemPhysChem* **2006**, *7*, 1957–1963.
- [11] M. Nolan, G. W. Watson, *J. Phys. Chem. B* **2006**, *110*, 16600–16606.
- [12] Q. Wan, F. Wei, Y. Wang, F. Wang, L. Zhou, S. Lin, D. Xie, H. Guo, *Nanoscale* **2018**, *10*, 17893–17901.
- [13] T. X. T. Sayle, F. Caddeo, X. Zhang, T. Sakthivel, S. Das, S. Seal, S. Ptasińska, D. C. Sayle, *Chem. Mater.* **2016**, *28*, 7287–7295.
- [14] S. T. Hossain, E. Azeeva, K. Zhang, E. T. Zell, D. T. Bernard, S. Balaz, R. Wang, *Appl. Surf. Sci.* **2018**, *455*, 132–143.
- [15] R. D. Shannon, *Acta Cryst. A* **1976**, *32*, 751–767.
- [16] P. Bera, K. R. Priolkar, P. R. Sarode, M. S. Hegde, S. Emura, R. Kumashiro, N. P. Lalla, *Chem. Mater.* **2002**, *14*, 3591–3601.
- [17] S. Adak, J. Rabeah, R. Ranjan, T. S. Khan, M. K. Poddar, R. K. Gupta, T. Sasaki, S. Kumar, A. Bordoloi, C. S. Gopinath, A. Brückner, R. Bal, *Appl. Catal., A* **2021**, *624*, 118305.
- [18] D. Gamarra, G. Munuera, A. B. Hungria, M. Fernández-García, J. C. Conesa, P. A. Midgley, X. Q. Wang, J. C. Hanson, J. A. Rodríguez, A. Martínez-Arias, *J. Phys. Chem. C* **2007**, *111*, 11026–11038.
- [19] S. Agarwal, B. L. Mojet, L. Lefferts, A. K. Datye in *Catalysis by Materials with Well-Defined Structures, Ceria Nanoshapes-Structural and Catalytic Properties* (Eds.: Z. Wu, S. H. Overbury) Elsevier Academic Press, Amsterdam, **2015**, 44.
- [20] B. M. Reddy, G. K. Reddy, L. Katta, *J. Mol. Catal. A: Chem.* **2010**, *319*, 52–57.
- [21] S. Deshpande, S. Patil, S. V. Kuchibhatla, S. Seal, *Appl. Phys. Lett.* **2005**, *87*, 133113.
- [22] E. Sartoretti, C. Novara, F. Giorgis, M. Piumetti, S. Bensaid, N. Russo, D. Fino, *Sci. Rep.* **2019**, *9*, 1–14.
- [23] S. Sun, D. Mao, J. Yu, Z. Yang, G. Lu, Z. Ma, *Catal. Sci. Technol.* **2015**, *5*, 3166–3181.
- [24] Q. Zou, Y. Zhao, X. Jin, J. Fang, D. Li, K. Li, J. Lu, Y. Luo, *Appl. Surf. Sci.* **2019**, *494*, 1166–1176.
- [25] C. Andriopoulou, A. Trimpalis, K. C. Petallidou, A. Sgoura, A. M. Efstathiou, S. Boghosian, *J. Phys. Chem. C* **2017**, *121*, 7931–7943.
- [26] V. V. Pushkarev, V. I. Kovalchuk, J. L. d'Itri, *J. Phys. Chem. B* **2004**, *108*, 5341–5348.
- [27] J. F. Xu, W. Ji, Z. X. Shen, W. S. Li, S. H. Tang, X. R. Ye, D. Z. Jia, X. Q. Xin, *J. Raman Spectrosc.* **1999**, *30*, 413–415.
- [28] D. Gamarra, G. Munuera, A. B. Hungria, M. Fernández-García, J. C. Conesa, P. A. Midgley, X. Q. Wang, J. C. Hanson, J. A. Rodríguez, A. Martínez-Arias, *J. Phys. Chem. C* **2007**, *111*, 11026–11038.
- [29] P. Bera, A. L. Cámara, A. Hornés, A. Martínez-Arias, *J. Phys. Chem. C* **2009**, *113*, 10689–10695.
- [30] A. Martínez-Arias, A. B. Hungria, M. Fernández-García, J. C. Conesa, G. Munuera, *J. Phys. Chem. B* **2004**, *108*, 17983–17991.
- [31] S.-C. Yang, S. H. Pang, T. P. Sulmonetti, W.-N. Su, J.-F. Lee, B.-J. Hwang, C. W. Jones, *ACS Catal.* **2018**, *8*, 12056–12066.
- [32] S. Yao, K. Mudiyanse, W. Xu, A. C. Johnston-Peck, J. C. Hanson, T. Wu, D. Stacchiola, J. A. Rodriguez, H. Zhao, K. A. Beyer, K. W. Chapman, P. J. Chupas, A. Martínez-Arias, R. Si, T. B. Bolin, W. Liu, S. D. Senanayake, *ACS Catal.* **2014**, *4*, 1650–1661.
- [33] A. Martínez-Arias, D. Gamarra, A. Hungria, M. Fernández-García, G. Munuera, A. Hornés, P. Bera, J. Conesa, A. Cámara, *Catalysts* **2013**, *3*, 378–400.
- [34] X. Guo, R. Zhou, *Catal. Sci. Technol.* **2016**, *6*, 3862–3871.
- [35] J. Lu, J. Wang, Q. Zou, D. He, L. Zhang, Z. Xu, S. He, Y. Luo, *ACS Catal.* **2019**, *9*, 2177–2195.
- [36] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, *6*, 15–50.
- [37] Materials Data on CeO₂ by Materials Project. Persson, Kristin, United States. <https://materialsproject.org/materials/mp-20194/>, **2020**.
- [38] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [39] D. Vanderbilt, *Phys. Rev. B* **1990**, *41*, 7892–7895.
- [40] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- [41] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, *Phys. Rev. B* **1998**, *57*, 1505–1509.
- [42] J. L. F. Da Silva, M. V. Ganduglia-Pirovano, J. Sauer, V. Bayer, G. Kresse, *Phys. Rev. B* **2007**, *75*, 045121.
- [43] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188–5192.
- [44] C. Riley, S. Zhou, D. Kunwar, A. De La Riva, E. Peterson, R. Payne, L. Gao, S. Lin, H. Guo, A. Datye, *J. Am. Chem. Soc.* **2018**, *140*, 12964–12973.
- [45] Y. Feng, Q. Wan, H. Xiong, S. Zhou, X. Chen, X. I. Pereira Hernandez, Y. Wang, S. Lin, A. K. Datye, H. Guo, *J. Phys. Chem. C* **2018**, *122*, 22460–22468.

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