

In situ and *Operando* Characterisation in the Preferential Oxidation of Carbon Monoxide over Base Metal Oxide Catalysts: A Review

Thulani M. Nyathi,^{*,[a]} Mohamed I. Fadlalla,^[a] and Michael Claeys^{*,[a]}

Polymer electrolyte membrane fuel cells (PEMFCs) are the core technology of the steadily growing hydrogen (H_2) economy as they can convert chemical energy, in the form of H_2 , to electrical energy. If the H_2 is derived from (green) hydrocarbons, via steam reforming and the water-gas-shift reaction, then it would contain small amounts of carbon monoxide (CO, 0.5–2%), among other gases. CO poisons the platinum-based anode catalyst in the PEMFC, and the current recommendation is to decrease its concentration to below 0.01 % (or 100 ppm) in the H_2 -rich PEMFC feed. The preferential oxidation of CO (CO-PrOx) is a promising strategy for decreasing the CO concentration,

and base metal oxide catalysts have shown great potential in this regard. However, such catalysts tend to undergo physico-chemical changes that cause undesirable catalytic activity and selectivity changes. This review discusses the different base metal oxide catalysts that have been evaluated in CO-PrOx, while paying special attention to the various *in situ* and *operando* techniques that have been used to monitor the physicochemical changes of base metal oxides during operation. We conclude the review by highlighting the recent and possible future attempts of circumventing the undesired physicochemical changes of base metal oxides during CO-PrOx.

1. Introduction

The hydrogen (H_2) economy has gained considerable attention over the past few decades as it promises a carbon-lean route to producing electrical energy, using polymer electrolyte membrane fuel cells (PEMFCs), for stationary and mobile applications.^[1–4] The transition to a H_2 -based energy sector would require innovative ways of producing, storing, and transporting the H_2 gas to where it is required.^[5–7] In particular, the transportation of H_2 has proven to be challenging because it is expensive and unsafe to transport pressurised H_2 gas over long distances, and challenging to liquify the gas due to its very low boiling point (ca. -253°C). Therefore, one of the proposed strategies is to store and/or transport hydrogen as a liquid of different chemical identity (e.g., ammonia and hydrocarbons).^[5–7]

Hydrocarbons are the long-standing primary sources of H_2 and several technologies (e.g., steam reforming and the water-gas-shift (WGS) reaction) have been established to convert hydrocarbons to H_2 (and other carbon-based gases).^[7] For example, liquid methanol is regarded as the simplest and most suitable form of storing and transporting hydrogen.^[7–10] This is

also accompanied by the fact that methanol can be produced via low-temperature CO hydrogenation at an industrial scale and that great strides have been made in attempting to produce methanol from carbon dioxide (CO_2) and green H_2 . Although the steam reforming of methanol and subsequent WGS produce low amounts of CO_2 (relative to H_2), initially producing methanol from CO_2 (before methanol transportation) aids in the global efforts to establish net-zero carbon functionality.^[7–10] Therefore, liquid methanol or liquid hydrocarbons can be attractive storage and transportation forms of hydrogen if their initial production is achieved by reacting CO_2 with green H_2 . This would minimise the global reliance on the limited fossil fuel reserves for producing H_2 and transform the H_2 production chain into a more sustainable process that is less harmful to the environment.

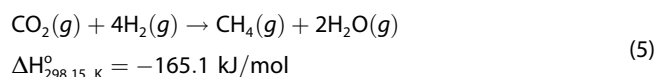
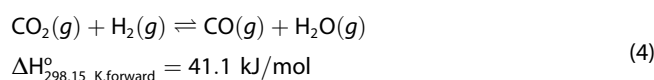
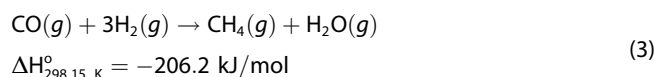
Hydrogen production from hydrocarbons produces other gases such as CO and CO_2 (0.5–2% and 15–25%, respectively) after carrying out steam reforming as well as the high- and low-temperature WGS reactions (Figure 1).^[1–4] If this gas mixture, containing 40–75% H_2 , is fed into a PEMFC, the performance of the platinum-based anode catalyst of the PEMFC is negatively affected by the adsorption of CO. More specifically, CO adsorption interferes with the dissociative adsorption of H_2 and the subsequent charge transfer processes that need to occur between the anode and cathode in the PEMFC. Therefore, the current recommendation is to decrease the CO content in the H_2 -rich PEMFC feed to below 0.01 % (or 100 ppm) to minimise the negative impact on the performance of the anode catalyst.^[1–4,11]

Several catalytic and non-catalytic processes have been proposed to achieve the required low levels of CO in the H_2 -rich PEMFC feed; however, the preferential oxidation of CO (CO-PrOx) is reported to be the most effective in this regard

[a] Dr. T. M. Nyathi, Dr. M. I. Fadlalla, Prof. M. Claeys
Catalysis Institute, Chemical Engineering Department
University of Cape Town
Building 54, c/o Madiba Circle and South Lane
Rondebosch, 7700 (South Africa)
E-mail: thulani.nyathi@uct.ac.za
michael.claeys@uct.ac.za

© 2024 The Authors. ChemCatChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

(Figure 1).^[3,4] This process involves oxidising CO to CO₂ (Equation 1) over a heterogeneous catalyst that can also minimise/prevent the oxidation of H₂ to H₂O (Equation 2). Noble metal-based catalysts have shown very good CO-PrOx activity and selectivity at temperatures below 175 °C but greatly facilitate H₂O formation above 175 °C. Furthermore, noble metals are becoming less attractive for this catalytic process because of their high cost. Base metal oxides are cheaper alternatives to noble metals and have shown comparatively good catalytic performance.^[3,4] However, the main drawback of base metal oxide catalysts is that they can undergo undesirable physico-chemical changes during CO-PrOx, such as reduction to their corresponding metallic form,^[12–17] which can change the conversion pathway of CO from oxidation to hydrogenation, forming methane (CH₄) instead of CO₂.^[12,15–17] Although CH₄ formation is achieved through CO conversion (Equation 3), relatively high amounts of valuable H₂ are also consumed. In a CO-PrOx feed containing CO₂ (15–25%), some studies have reported the occurrence of the reverse WGS (Equation 4) and CO₂ methanation (Equation 5).^[16,18–21] These two reactions further increase the unwanted consumption of valuable H₂, and in the case of the reverse WGS, the CO content can also increase.



It is important to note that the occurrence of the above-mentioned reactions depends on the feed composition, reaction temperature, and chemical phase of the catalyst (whether metallic or oxidic). A realistic CO-PrOx feed contains CO (0.5–2%), O₂ (0.25–4%), H₂ (40–75%), CO₂ (15–25%), and H₂O (*ca.* 10%);^[1–4] however, some of the research studies that are discussed in this review conducted the CO-PrOx reaction in the absence of CO₂ and H₂O in the feed for simplicity of the product analysis and to be able to discern the sole effect of H₂ (as the main competitor) on CO oxidation. The upper and lower reaction temperature limits for CO-PrOx are determined by the operating temperatures of the low-temperature WGS and PEMFC, respectively.^[1–4] The low-temperature WGS reaction is typically conducted between 200 and 300 °C, while the PEMFC is operated at approximately 80 °C. Therefore, the evaluation of CO-PrOx catalysts is often carried out between 50 and 350 °C to sufficiently cover the operating temperatures of the upstream and downstream processes. Furthermore, this means that an ideal CO-PrOx catalyst is one that can maintain CO conversions to CO₂ of at least 99% (to reach <100 ppm CO levels) within the abovementioned reaction temperature range.



Thulani Nyathi is a Junior Research Fellow (since 2021) at the Catalysis Institute of the University of Cape Town (UCT) and specialises in the synthesis, characterisation (*ex situ* and *in situ*), and evaluation of heterogeneous catalysts for carbon monoxide- and carbon dioxide-converting reactions. He received his MSc(Eng) and Ph.D. in Chemical Engineering from UCT in 2016 and 2021, respectively. His MSc(Eng) and Ph.D. projects were based on the preferential oxidation of carbon monoxide (CO-PrOx) where cobalt oxide-based catalysts were characterised using multiple (*quasi*) *in situ* and *operando* techniques, such as XRD, magnetometry, XAS, DRIFTS, and XPS, under different CO-PrOx reaction conditions.



Mohamed Fadlalla is currently a Senior Research Officer (since 2023) at the Catalysis Institute of UCT and works on various C₁ chemistry projects, in collaboration with multiple academic and industry partners, aiming at producing green and sustainable hydrocarbon chemicals and fuels, as well as producing carbon monoxide-free hydrogen for fuel cells. He received his MSc and Ph.D. from the University of KwaZulu-Natal on the heteroge-



neous aminohydroxylation reaction and oxidative dehydrogenation of *n*-Octane over molybdate-based catalysts in 2012 and 2015, respectively. He joined Prof. Claeys' research group at UCT in 2016 as a postdoctoral research fellow to work on C₁ chemistry.

Michael Claeys is a full Professor (since 2010) at the Catalysis Institute of UCT. He obtained his Ph.D. (with distinction) in Chemical Engineering from the Karlsruhe Institute of Technology in 1997, after which, he joined UCT as a postdoctoral fellow. His current research is focused on C₁ catalysis, with special emphasis on synthesis gas conversion and *operando* catalyst characterisation, often using *in-house* designed instruments, for example, a capillary-based reaction cell for XRD measurements and a low-frequency vibration sample magnetometer for performing magnetic measurements.

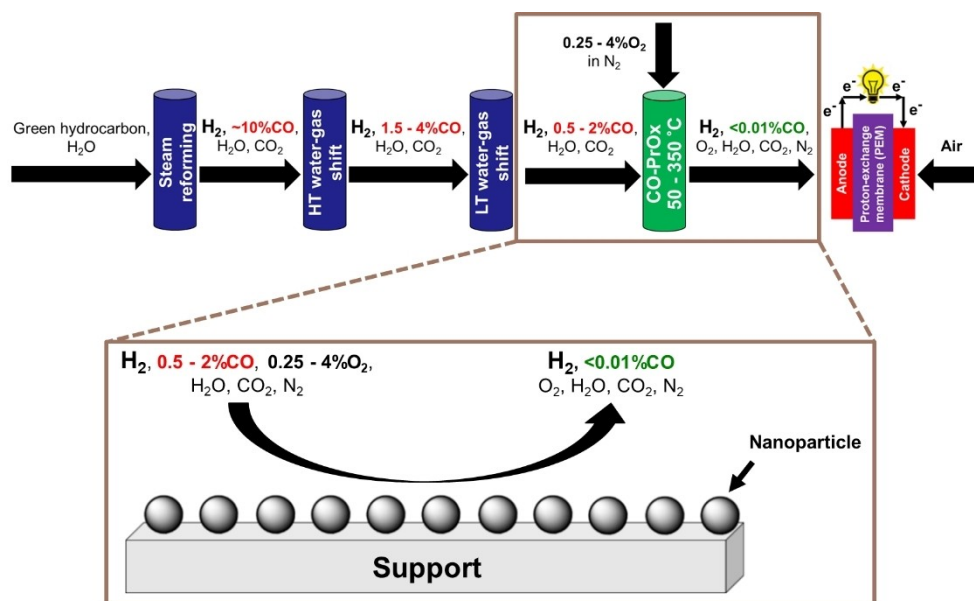


Figure 1. Processes involved in the production of H_2 -rich reformat gas (from a green hydrocarbon source) for electricity generation in a PEMFC. The production chain depicted shows a CO-PrOx unit existing between a low-temperature WGS unit and a PEMFC unit, with CO-PrOx being carried out over a supported heterogeneous catalyst.

In the subsequent sections of this review, we discuss the various base metal oxide catalysts (*i.e.*, monometal and bimetal oxides of Co, Cu, Ni, Fe, Mn, *etc.*) that have been evaluated in the CO-PrOx reaction. The bimetal oxides can be in the form of composite oxides ($\text{M}_x\text{O}_y\text{-N}_x\text{O}_y$) or mixed metal oxides ($\text{M}_x\text{N}_y\text{O}_z$), where “M” and “N” are base metals. Special focus is placed on the different *in situ* and *operando* characterisation techniques that have been utilised to monitor any physicochemical changes of the base metal oxides under reaction conditions. Before the advancement of *in situ* and *operando* techniques, base metal oxide CO-PrOx catalysts were observed to lose activity and selectivity as a function of temperature, and in some cases, post-reaction *ex situ* characterisation would show that the catalysts had undergone some physicochemical change (*e.g.*, reduction, sintering, and/or metal-support compound formation).^[12,15,22] Linking the losses in catalytic activity and selectivity to the physicochemical changes observed after performing CO-PrOx is challenging because the temperature (and time) at which the physicochemical changes took place would remain unknown. Moreover, removing the catalyst from the CO-PrOx reaction environment for *ex situ* characterisation exposes it to air, which can change the chemical composition of the catalyst from what it was when the catalyst was still under the reaction environment. In recent years, various *in situ* and *operando* techniques have provided some of the required links between activity/selectivity and the physicochemical structure of the catalyst. These advanced analyses have also provided interesting mechanistic details related to some of the reactions (Equations 1–5) that can take place during CO-PrOx.

It is important to note that the terms *in situ* and *operando* refer to catalyst characterisation being performed during a chemical reaction.^[23,24] However, in this review, we use the term *operando* to describe CO-PrOx experiments that involved

catalyst characterisation coupled with reactor outlet gas analysis for determining catalytic activity and selectivity. In cases where catalyst characterisation was not coupled with reactor outlet gas analysis in the same CO-PrOx experiment, we use the term *in situ* to describe only the catalyst characterisation conducted under working conditions.

2. Cobalt Oxide Catalysts

Cobalt(II,III) oxide (Co_3O_4) and cobalt(II) oxide (CoO) have been extensively investigated in CO oxidation reactions carried out in the absence and presence of H_2 (with the latter also known as CO-PrOx). There remains some debate about which of these phases is the most active, but the majority of the existing literature claims the Co_3O_4 phase as most important for the oxidation of CO to CO_2 .^[20,25–27] Co_3O_4 contains one Co^{2+} ion for every two Co^{3+} ions in its bulk structure, and numerous studies have revealed Co^{3+} as exhibiting higher CO adsorption strengths (than Co^{2+}) and the oxygen anions bound to Co^{3+} as being more accessible for oxidising CO,^[25,28–30] in accordance with the Mars-van Krevelen (MvK) mechanism.^[31] The MvK mechanism is based on reduction-oxidation (‘redox’) chemistry, and in the context of CO oxidation, the Co^{3+} and Co^{2+} species form a redox pair as the Co_3O_4 surface cycles between being reduced by CO and subsequently re-oxidised by co-fed oxygen (O_2).

In the absence and presence of H_2 , the CO oxidation activity and selectivity of Co_3O_4 can be affected by the catalyst preparation method,^[32,33] particle size,^[17,34] particle shape,^[35,36] and the presence of a promoter^[37,38] or support.^[21,22,39–41] However, changes to the surface and bulk structure of Co_3O_4 have not been reported when CO oxidation is carried out in the

absence of H_2 . More specifically, in a feed containing an inert gas, CO, and excess O_2 (relative to CO), the surface and bulk structure of Co_3O_4 are protected from reduction by CO owing to the excess O_2 present. This way, the catalyst remains chemically intact and can reach/maintain 100% CO conversion over a wide temperature range, thus, confirming an effective MvK cycle over Co_3O_4 .^[20,26,27,34] In the presence of 40–75% H_2 , as in a typical reformate gas stream with co-fed O_2 (i.e., CO-PrOx), the progress of the CO oxidation reaction can be affected by the competitive adsorption of H_2 on the Co_3O_4 surface, resulting in H_2 oxidation to H_2O and a loss in CO_2 selectivity.^[16,20] At high reaction temperatures ($> 200^\circ\text{C}$), Co_3O_4 can reduce to CoO and ultimately metallic Co (Co^0).^[16,17,20,21,33,36,41] The reduction takes place because H_2 is present in great excess relative to O_2 ; therefore, when O_2 is fully consumed by the combination of CO and H_2 oxidation, Co_3O_4 becomes susceptible to reduction by the unreacted H_2 . This way, the Co^{3+} , and subsequently, the Co^{2+} species are lost, making it difficult for CO to be converted to CO_2 via the MvK mechanism.

In 2016, Lukashuk *et al.*^[16] showed the first evidence of Co_3O_4 reduction during CO-PrOx via *operando* X-ray absorption spectroscopy (XAS, Figures 2(a) and 2(b)) coupled with reactor outlet gas analysis via mass spectrometry (MS, Figures 2(c) and 2(d)). In their study, unsupported/unpromoted Co_3O_4 nanoparticles were observed to partially reduce to CoO and Co^0 at 300°C , with the amounts of CoO and Co^0 further increasing at the final reaction temperature of 350°C . Based on MS analysis, CH_4 formation (indicated by the green plot in Figure 2(c)) was

first seen at 300°C , and this reaction took place at the expense of CO_2 formation (indicated by the red plot in Figure 2(c)) because CO was starting to react more with H_2 and less with O_2 . It is worth noting that at 300°C , the catalyst composed of Co_3O_4 , CoO, and Co^0 (Figure 2(b)); however, the formation of CH_4 was attributed to the presence of Co^0 , implying that the metallic phase was likely present in the bulk structure and exposed on the surface of the catalyst. Metallic Co is a well-known methanation catalyst,^[42,43] and before the *operando* study by Lukashuk *et al.*,^[16] the formation of CH_4 over Co-containing CO-PrOx catalysts had been linked to Co^0 formation based only on post-reaction *ex situ* characterisation.^[12,19,22]

The effect of particle size on the performance and phase stability of Al_2O_3 -supported Co_3O_4 particles was first reported by Nyathi *et al.*,^[17] which involved *operando* catalyst characterisation based on bulk-sensitive X-ray diffraction (XRD) and magnetometry (see Figure 3). While XRD is a well-known characterisation tool, magnetometry is seldom used in heterogeneous catalysis. Briefly, magnetometry measures the magnetisation of ferromagnetic materials that are exposed to an external magnetic field.^[44] Metallic Co is ferromagnetic in nature,^[45] while the oxides of cobalt (viz., CoO and Co_3O_4) are antiferromagnetic.^[46,47] Therefore, Nyathi *et al.*^[17] used magnetometry to detect the formation of Co^0 during CO-PrOx by exploiting its magnetic susceptibility and calculated the degree of reduction (DOR) of Co_3O_4 to Co^0 based on a pre-derived Co-based instrument calibration. With a relatively high temporal resolution for the *operando* analyses (i.e., measurements taken

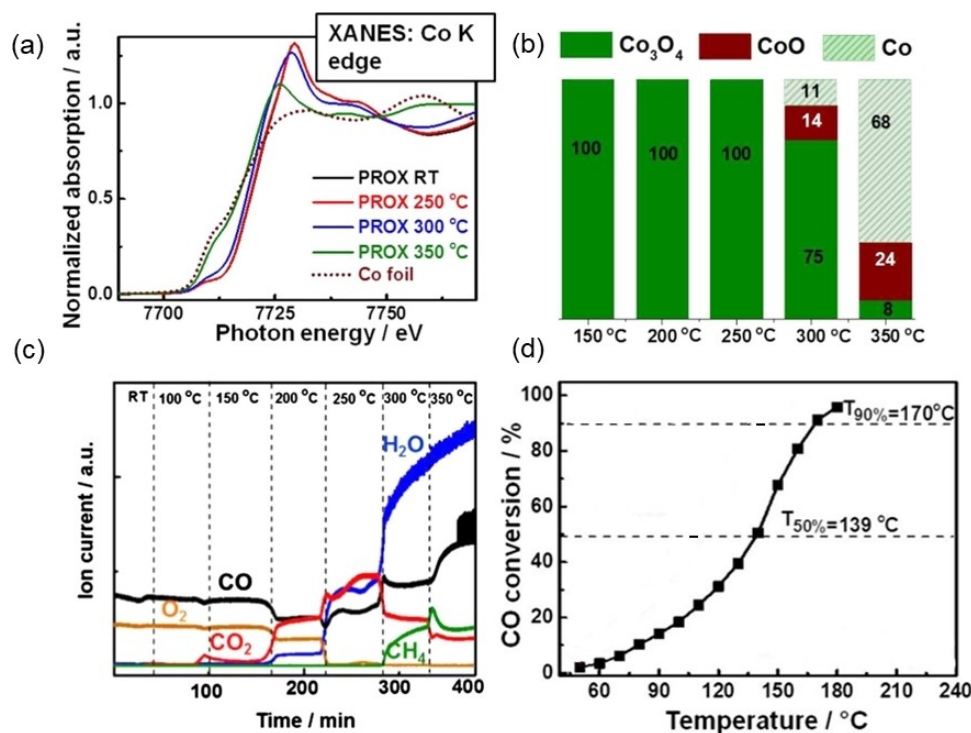


Figure 2. (a) XANES spectra at Co K-edge recorded during CO-PrOx (50 mL/min of 1% CO, 1% O_2 , 50% H_2 , and balance of He, at atmospheric pressure) over 2.5 mg of unsupported/unpromoted Co_3O_4 and (b) amount of reduced vs. oxidised cobalt calculated by linear combination fitting. (c) MS data acquired during *operando* XAS at the Co K-edge. (d) CO conversion over unsupported/unpromoted Co_3O_4 during CO-PrOx. The GC-FID (with methaniser) results in (d) were obtained from an evaluation performed in a stand-alone fixed-bed reactor under a 50 mL/min flow of 1% CO, 1% O_2 , 50% H_2 , and balance of He, at atmospheric pressure, over 20 mg of catalyst. Adapted from ref. [16] under the terms and conditions of the CC BY 4.0 license. Copyright © 2016 Elsevier.

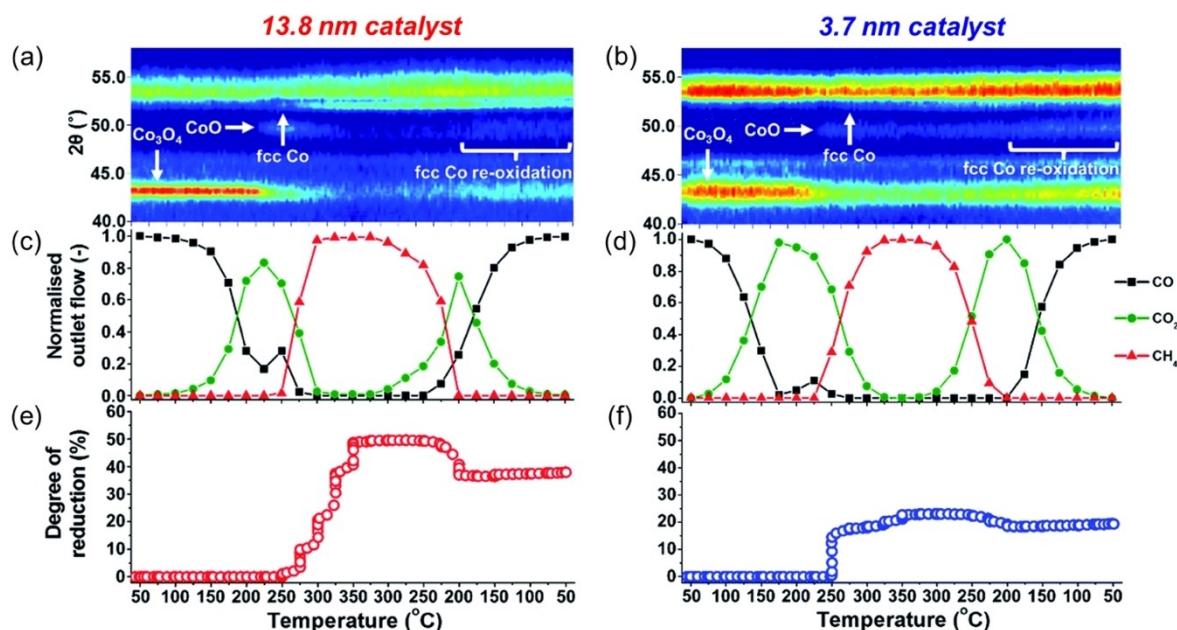


Figure 3. [(a) and (b)] On-top view of the XRD patterns acquired during CO-PrOx (1.5 mL/min of 0.9% CO, 0.9% O₂, 52.1% H₂, and balance of N₂, at atmospheric pressure) over a (left) 13.8 nm and (right) 3.7 nm Co₃O₄/Al₂O₃ catalyst (ca. 15 mg each). Changes in the [(c) and (d)] normalised outlet flow rates of CO, CO₂, and CH₄, as well as the [(e) and (f)] magnetometry-derived DORs of Co₃O₄ to Co⁰ during CO-PrOx (100 mL/min of 0.9% CO, 0.9% O₂, 52.1% H₂, and balance of N₂, at atmospheric pressure) over a (left) 13.8 nm and (right) 3.7 nm Co₃O₄/Al₂O₃ catalyst (ca. 1000 mg each). Adapted with permission from ref. [17]. Copyright © 2017 Royal Society of Chemistry.

every 5 min), the authors observed the stepwise reduction of Co₃O₄ to CoO, then CoO to face-centred cubic (fcc) Co⁰ under CO-PrOx conditions (Figures 3(a), 3(b), 3(e), and 3(f)). Interestingly, their study also showed a size dependency of the magnetometry-derived DOR of Co₃O₄ to fcc Co⁰ as the reaction temperature was increased from 50 to 350 °C. More specifically, large Co₃O₄ particles (13.8 nm) had reduced the most (DOR of up to ca. 46%), while small particles (3.7 nm) had reduced the least (DOR of up to ca. 22%). Nyathi *et al.*^[17] also observed that the onset temperature for CH₄ formation coincided with the onset temperature for fcc Co⁰ formation for both catalysts, confirming that Co⁰ is responsible for CO methanation during CO-PrOx. Upon cooling the reaction from 350 to 50 °C, the authors observed that the extent of bulk fcc Co⁰ reoxidation was highest when fcc Co⁰ was derived from larger Co₃O₄ particles (*i.e.*, the DOR decreased from ca. 46% to 38%). Furthermore, CH₄ formation decreased while CO₂ formation increased during reactor cooling, which may have been a kinetic effect caused by the decreasing reaction temperature and/or the surface reoxidation of metallic Co (which is undetectable using the bulk-sensitive XRD and magnetometer). Nonetheless, the study by Nyathi *et al.*^[17] (and a subsequent study by the same authors)^[33] showed great potential for catalyst regeneration to recover CO oxidation activity/selectivity. However, full catalyst regeneration may require intermittent substitution of the CO-PrOx feed mixture with air to convert metallic Co to Co₃O₄. Finally, the authors also showed that the smaller Co₃O₄ particles convert higher amounts of CO to CO₂ than the larger particles over a wider reaction temperature range, as seen in Figures 3(c) and 3(d). The authors postulated that the high amounts of CO₂ formed over the smaller Co₃O₄

particles was due to the exposure of a higher number of active Co³⁺ ions on the surface of the smaller particles.

Another important parameter that can affect the performance and phase stability of Co₃O₄-based catalysts is the CO-PrOx feed composition. The studies discussed above were performed in the absence of CO₂ and H₂O; however, a realistic CO-PrOx feed should contain these two gases.^[1–4] In a different study, Nyathi and co-workers^[20] showed the negative effect of co-feeding CO₂ and H₂O (individually and combined) on the conversion of CO to CO₂ over an unsupported Co₃O₄ catalyst, which had also been observed by other researchers using Co₃O₄^[48,49] as well as other metals^[50] and metal oxides.^[51] However, for the first time, the authors were able to show that co-feeding CO₂ and H₂O (individually and combined) helps delay the reduction of Co₃O₄ to CoO and Co⁰, and decreases the overall DOR of Co₃O₄, based on *operando* XRD and magnetometry analyses.^[20] The stabilising effect on Co₃O₄ was more pronounced in the presence of H₂O due to its stronger oxidising ability than that of CO₂. They also showed the occurrence of numerous side reactions, *viz.*, H₂ oxidation, CO and CO₂ methanation, as well as the forward and reverse WGS, and were able to link each side reaction with the phase of the catalyst (whether Co₃O₄, CoO, or Co⁰) that was responsible for its occurrence.

In situ diffuse reflectance infrared Fourier transform spectroscopic (DRIFTS) analysis provides valuable information regarding the type of species that are adsorbed on catalyst surfaces under reaction conditions. Furthermore, gases such as CO, CO₂, and CH₄ can be detected using DRIFTS. The Ozkan group^[49,52] reported the earliest *in situ* DRIFTS studies on CeO₂- and ZrO₂-supported Co₃O₄ catalysts during CO-PrOx. Regarding gas

analysis, the bands for gas-phase CO were observed to always decrease in intensity, while the bands for CO₂ would increase in intensity with an increase in reaction temperature, confirming the oxidation of CO to CO₂. At high temperatures ($\geq 300^\circ\text{C}$), the band for gas-phase CH₄ would emerge, while the CO₂ band would slightly decrease in intensity, suggesting the reduction of Co₃O₄ (and CoO) to the methanation-active Co⁰.^[52] Regarding surface-adsorbed species, different carbonates and formates were detected as a function of temperature.^[49,52] These carbonates and formates were formed after the adsorption and rapid oxidation of CO either by oxygen from the Co₃O₄ (or CoO) lattice or by dissociated oxygen species from gas-phase O₂. Three types of carbonates were identified: monodentate, bidentate, and polydentate carbonates. Monodentate and bidentate carbonates are low-temperature carbonates that gradually disappear upon increasing the reaction temperature. These carbonates were thought to have either desorbed as gas-phase CO₂ or further reacted into polydentate carbonates. Formates and polydentate carbonates were stable over a wide temperature range and, consequently, regarded as spectator species as they did not evolve in line with the consumption or formation of any gas-phase species. Similar observations were later made by other researchers when studying Co₃O₄-based catalysts during CO-PrOx using *in situ* DRIFTS.^[33,53]

Although less investigated, CoO is also regarded as a good CO-PrOx catalyst.^[12,53–56] CoO is a less oxidised form of cobalt when compared with Co₃O₄, which makes its phase purity/stability highly dependent on the gas environment that the sample is exposed to. For instance, in the presence of a high

concentration of O₂ or long exposures to O₂, CoO can oxidise to Co₃O₄ at relatively low temperatures.^[27,57] On the other hand, exposures to high concentrations of H₂ can cause CoO to reduce to Co⁰.^[12,53–56] The Zafeiratos group^[53,55,56] has performed various *in situ* and *operando* studies on CoO as a CO-PrOx catalyst, with selected results from one of their studies shown in Figure 4.^[55] Based on *operando* near-ambient pressure X-ray photoelectron spectroscopic (NAP-XPS) analysis, the surface composition of V-promoted CoO was shown to be impure between 50 and 350 °C, *i.e.*, CoO co-existed with one or two other Co-bearing phases (*viz.*, Co⁰ and/or Co₃O₄) on the catalyst surface during CO-PrOx. At low temperatures, CoO (labelled as 'Co²⁺' in Figure 4(a)) co-existed with small amounts of Co⁰, and at high temperatures, Co₃O₄ (labelled as 'Co^{2.67}' in Figure 4(a)) emerged at the expense of CoO. Good CO₂ selectivities were achieved below 250 °C (Figure 4(c)), and this was attributed to the presence of CoO as Co₃O₄ had not formed. Above 200 °C, CH₄ formation was observed, which was followed by Co₃O₄ formation at 300 °C. As mentioned earlier, CH₄ formation is often associated with the presence of Co⁰ on the catalyst surface, and the V-promoted CoO catalyst maintained small amounts of Co⁰ as a function of temperature (Figure 4(a)). However, Zafeiratos and co-workers proposed the possibility of cobalt oxides also playing a role in CO methanation through a mechanism that may be different to that observed over Co⁰.^[53,55,56] For example, CoO was recently shown to be active for CO₂ hydrogenation to C₁₊ hydrocarbons *via* the hydrogen-assisted mechanism that involves carbonates, formates, and formyl species as intermediates. On the other hand, Co⁰ was

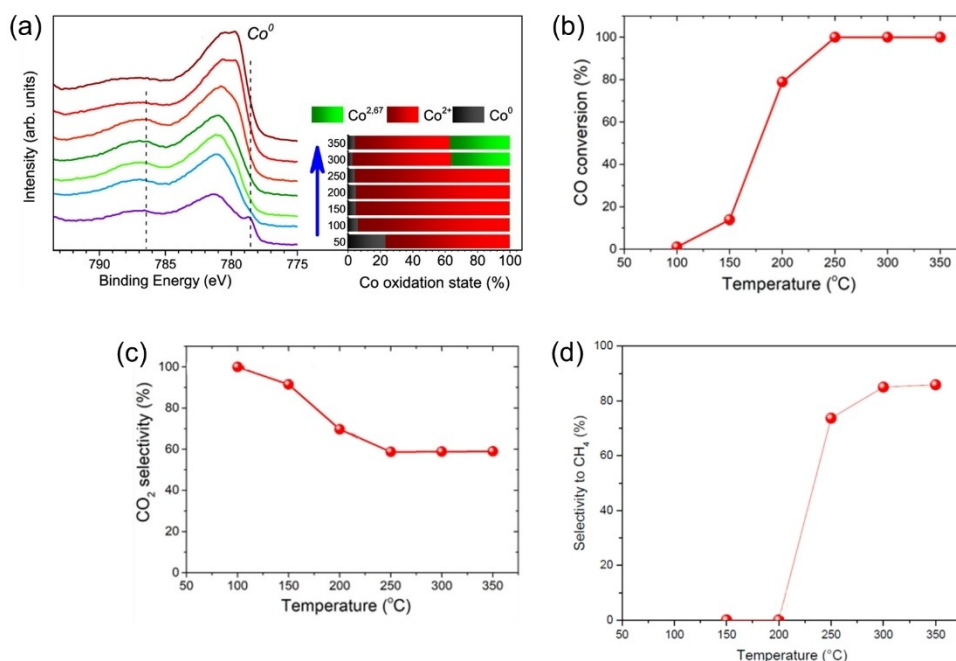


Figure 4. (a) *Operando* NAP-XPS Co 2p_{3/2} spectra recorded at different temperatures during CO-PrOx (30 mL/min of 1% CO, 1% O₂, 50% H₂, and balance of He, at 0.5 mbar pressure) over a V-promoted CoO_x (CoVO_x) catalyst. Note that the *operando* NAP-XPS experiment was coupled with MS analysis, however, the MS data were not presented in the original paper. (b) CO conversion, (c) CO₂ selectivity, and (d) CH₄ selectivity of a CoVO_x catalyst as a function of CO-PrOx reaction temperature. The GC-TCD results in (b–d) were obtained from an evaluation performed in a stand-alone fixed-bed reactor under a 50 mL/min flow of 1% CO, 1% O₂, 50% H₂, and balance of He, at atmospheric pressure, over 50 mg of catalyst. Adapted with permission from ref. [55]. Copyright © 2021 American Chemical Society.

shown to hydrogenate CO_2 via the direct CO_2 dissociation mechanism involving CO as a key intermediate.^[58]

3. Copper Oxide Catalysts

Gamarra *et al.*^[13] studied the effect of CO_2 on the performance and phase stability of a reverse-microemulsion-prepared $\text{Ce}_{0.8}\text{Cu}_{0.2}\text{O}_2$ catalyst via *operando* DRIFTS and XAS in the absence and presence of CO_2 in the CO-PrOx feed: (i) 1 % CO, 50 % H_2 , and 1.25 % O_2 , and (ii) 1 % CO, 50 % H_2 , 1.25 % O_2 , and 15 % CO_2 . The *operando* DRIFT spectra obtained under the absence and presence of CO_2 in the CO-PrOx feed, focusing on the wavenumber range from 2400 to 1800 cm^{-1} , are shown in Figures 5(a) and 5(b), respectively. In the absence of CO_2 in the feed (Figure 5(a)), the Cu^+ -carbonyl surface species was detected (at 2113 cm^{-1}) only in the temperature range of 30–110 °C. The formation of this species at 30 °C was thought to be a result of the reduction of Cu^{2+} species by CO on the surface of $\text{Ce}_{0.8}\text{Cu}_{0.2}\text{O}_2$, as was shown using XPS and EPR analyses in previous studies.^[59–61] The Cu^+ -carbonyl species was not observed above 110 °C due to its thermal decomposition. It is important to note that the decomposition of the Cu^+ -carbonyl coincided with the emergence of the band for gas-phase CO_2 .

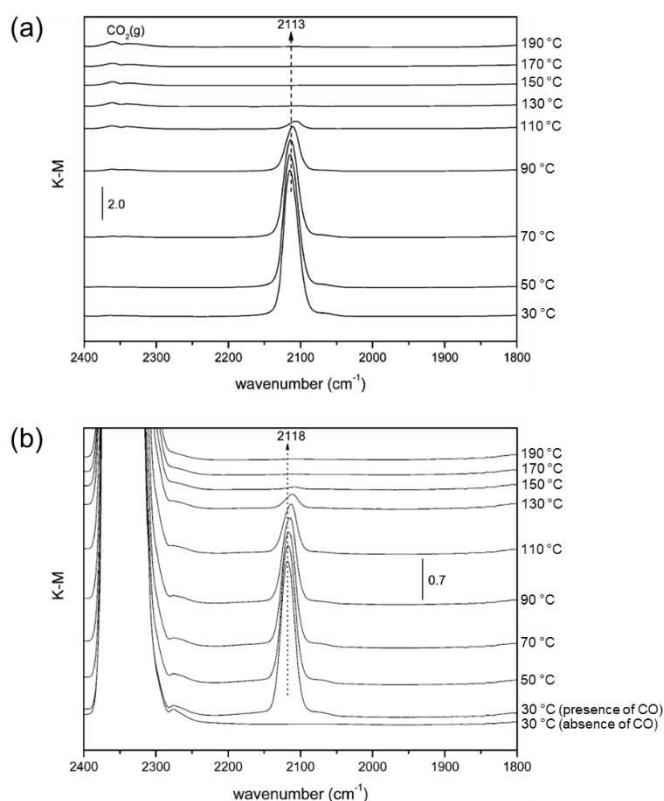


Figure 5. *Operando* DRIFT spectra recorded in the temperature window of 30–190 °C (every 20 min, at steady state of each reaction temperature) in the (a) absence and (b) presence of CO_2 in the CO-PrOx feed (*i.e.*, (a) 1 % CO, 1.25 % O_2 , and 50 % H_2 ; (b) 1 % CO, 1.25 % O_2 , 50 % H_2 , and 15 % CO_2). Both mixtures contained a balance of He) over a $\text{Ce}_{0.8}\text{Cu}_{0.2}\text{O}_2$ catalyst (*ca.* 100 mg), using a total feed gas flow rate of 100 mL/min. Adapted with permission from ref. [13]. Copyright © 2010 American Chemical Society.

Operando DRIFTS analysis was also conducted in the presence of CO_2 in the feed (Figure 5(b)). In this case, the Cu^+ -carbonyl band (at 2118 cm^{-1}) was only observed upon the interaction of the catalyst surface with CO at 30 °C, and the band remained visible up to 150 °C. However, the intensity of the Cu^+ -carbonyl band in the presence of CO_2 in the feed (when compared to the case with no co-fed CO_2) was lower at each temperature. These observations were attributed to the change in the reduction behaviour of the catalyst surface when CO_2 was present in the reaction feed. Therefore, the main effect of CO_2 addition in the reaction feed was the limitation of the reduction of CO-PrOx active Cu^{2+} species, as indicated by the decreased intensity of the Cu^+ -carbonyl band. This also suggested a decrease in CO oxidation activity since the intensity of the Cu^+ -carbonyl band is proportionally related to CO oxidation activity.^[61–65] During *operando* XAS, the CO conversion (Figure 6(a)) increased with reaction temperature up to *ca.* 175 and 210 °C in the absence and presence of CO_2 in the reaction feed, respectively, and decreased thereafter. This coincided with the temperatures at which the amount of Cu^{2+} species (which are active for CO oxidation) decreased in the catalyst (Figures 6(b) and 6(c), in the absence and presence of CO_2 in the reaction feed, respectively). The onset of H_2 oxidation was observed at *ca.* 120 and 140 °C in the absence and presence of CO_2 in the reaction feed, respectively, which coincided with the reduction of Cu^{2+} species (to Cu^+) that are not in close proximity with the CeO_2 support. However, the H_2 oxidation rate decreased above 190 °C because of the formation of less active Cu^+ species and/or the sintering of the Cu^+ species.^[63] Therefore, introducing CO_2 in the reaction mixture resulted in a decrease in H_2 oxidation activity due to the inhibited reduction of the Cu^{2+} species (Figure 6(c)), and a decrease in CO oxidation activity due to the formation of carbonate species that hinder the redox activity of the interfacial CuO-CeO_2 sites (which are active for CO oxidation), as determined using *operando* DRIFTS and XAS.^[13] This finding was in line with other reported studies that also applied *in situ* and *operando* analyses.^[64,66–70]

Martínez-Arias *et al.*^[71] showed that CO promotes the oxidation of H_2 at low temperatures as indicated by the onset temperature of hydroxyl species formation ($T=60$ °C), based on *operando* DRIFTS analysis. More specifically, CO partially reduces the interface between CuO and CeO_2 , then the partially reduced/defected interfacial sites catalyse the oxidation of H_2 . Furthermore, the Cu^+ -carbonyl band intensity was observed to decrease at the same temperature (*i.e.*, 60 °C) when H_2 was in the reaction feed (H_2 (50 %), CO (1 %), and O_2 (1.25 %) vs. CO (1 %) and O_2 (1.25 %), Ar was the balancing gas in both feed mixtures), possibly indicating the competitive adsorption of H_2 and CO on the partially reduced interfacial sites. This phenomenon (*i.e.*, CO-promoted H_2 oxidation) was also reported by Sedmak *et al.*,^[72] however, they observed the CO promotion from 107 °C instead of 60 °C. Kydd *et al.*^[73] showed (*via* CO adsorption, CO temperature-programmed reduction (TPR), and *operando* DRIFTS analyses) high selectivities to CO_2 (*via* CO oxidation) and H_2O (*via* H_2 oxidation) below and above 150 °C, respectively, over a 4 wt.-% Cu- CeO_2 catalyst prepared *via* flame spray pyrolysis. This is because Cu^+-CO species are stable

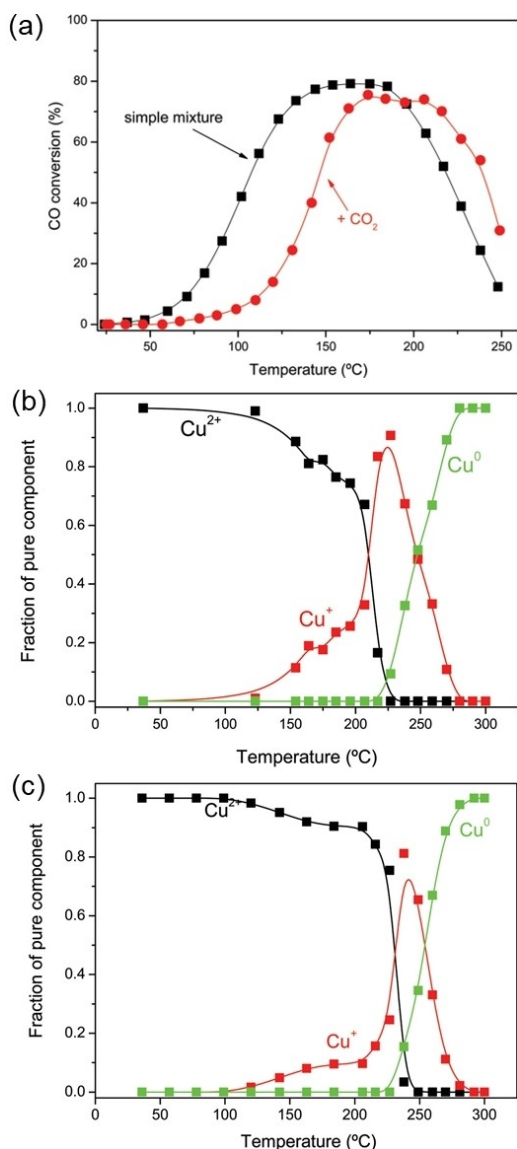


Figure 6. (a) CO conversions as well as the fraction of copper phases detected in the $\text{Ce}_{0.8}\text{Cu}_{0.2}\text{O}_2$ catalyst (ca. 100 mg) in the (b) absence and (c) presence of CO_2 . The reactor outlet gas was analysed via on-line MS. The *operando* XANES spectra (recorded at the Cu K-edge) used to obtain the results in (b) and (c) were acquired under different CO-PrOx feed mixtures (*i.e.*, (b) 1% CO, 1.25% O₂, and 50% H₂ ("simple mixture") and (c) 1% CO, 1.25% O₂, 50% H₂, and 15% CO₂, where He was the balancing gas in both mixtures), with a total feed gas flow rate of 100 mL/min. Adapted with permission from ref. [13]. Copyright © 2010 American Chemical Society.

below 150 °C, thus, preventing the adsorption and oxidation of H₂. Whereas above 150 °C, copper oxide starts to reduce to metallic Cu, thereby, destabilizing the Cu⁺-CO species and promoting H₂ oxidation to H₂O.

Gamarra *et al.*^[61] used *operando* DRIFTS analysis to study the effect of the synthesis method (*i.e.*, impregnation vs. reverse microemulsion-coprecipitation) and Cu content in their catalysts during CO-PrOx (*i.e.*, 1% CO, 1.25% O₂, 50% H₂, and a balance of He). The reverse microemulsion-coprecipitation method produced a solid solution of copper-cerium oxide with the formula $\text{Ce}_{1-x}\text{Cu}_x\text{O}_2$ (where $x=0.05, 0.1, \text{ and } 0.2$), while the

impregnation method yielded ceria-supported copper oxide catalysts in the form of xCuO/CeO_2 (where $x=0.5, 1, \text{ and } 5 \text{ wt.}\%$). The *operando* DRIFTS analysis showed the presence of hydroxyl species, carbonates (*e.g.*, mono- and poly-dentate), formate, and Cu⁺-carbonyl species. Generally, formate species formation is linked with WGS activity;^[74,75] however, formate formation was not accompanied by an increase in the CO₂ band intensity in the study by Gamarra *et al.*,^[61] which indicated that the catalysts used were not WGS-active (also reported in previous work).^[76] The catalyst prepared *via* the reverse microemulsion-coprecipitation method showed higher Cu⁺-carbonyl band intensities and higher CO oxidation activity than the catalyst prepared *via* impregnation. The higher CO oxidation activity of the catalyst prepared *via* reverse microemulsion-coprecipitation was due to (i) the presence of the $\text{Ce}_{1-x}\text{Cu}_x\text{O}_2$ phase only in this catalyst and (ii) the smaller size of its copper-cerium oxide particles, which both facilitated the reduction of Cu²⁺ species (when compared with the larger CeO₂-supported CuO particles produced *via* impregnation).^[77,78] Furthermore, the reduction of Cu²⁺ and generation of oxygen vacancies on the CeO₂ support also led to the activation and subsequent oxidation of H₂ to H₂O.^[61] It is important to note that the increase in copper content resulted in an increase in CO and H₂ oxidation activity.

Hornés *et al.*^[14] studied the performance and phase transformation of $\text{Cu}_{0.2}\text{Ce}_{0.8}\text{O}_2$ and an inverse CeO₂/CuO catalyst *via operando* XRD (Figure 7) under a CO-PrOx mixture of CO (1%), O₂ (1.25%), H₂ (50%), and Ar (47.75%). Focusing on the inverse CeO₂/CuO catalyst, the CO conversion (Figure 7(a)) increased with reaction temperature, reaching 100% CO conversion at ca. 365 K (92 °C) and maintained up to ca. 425 K (152 °C), with the CO₂ selectivity also reaching 100% between 335 and 365 K (62–92 °C, Figure 7(a)). Between 300 and 475 K (27 and 202 °C), the inverse catalyst maintained the CuO phase (Figure 7(b)), indicating that this phase was responsible for converting CO to CO₂. The inverse CeO₂/CuO catalyst started to reduce to CeO_{2-x}/Cu and a small amount of Cu₂O above 475 K (or 202 °C; Figure 7(b)). This reduction behaviour was also observed during the reduction of unsupported/unpromoted CuO particles under pure H₂^[79] and pure CO.^[80] Furthermore, the size of the CeO₂ lattice was observed to slowly increase with increasing reaction temperature from 300 to 475 K (*i.e.*, 27 to 202 °C) due to thermal expansion; however, above 475 K (202 °C), the size of the CeO₂ lattice increased rapidly (Figure 7(b)). The reduction of CeO₂ to CeO_{2-x} and rapid expansion of the CeO₂ lattice coincided with the reduction of CuO, indicating a strong interaction between CuO and CeO₂. Upon reduction of the inverse catalyst, H₂ oxidation became the dominate reaction as indicated by the decrease in CO conversion (Figure 7(a)).

Furthermore, López Cámara *et al.*^[81] studied the effect of zinc doping on the performance of an inverse CeO₂/(Cu–Zn)O (Cu:Zn atomic ratio of 9:1) catalyst, when compared with an undoped CeO₂/CuO (Ce:Cu atomic ratio of 4:6) counterpart, under a CO-PrOx environment with 1% CO, 1.25% O₂, 50% H₂, and He as the balancing gas. Both catalysts showed similar CO conversions below 150 °C, while above this temperature, the

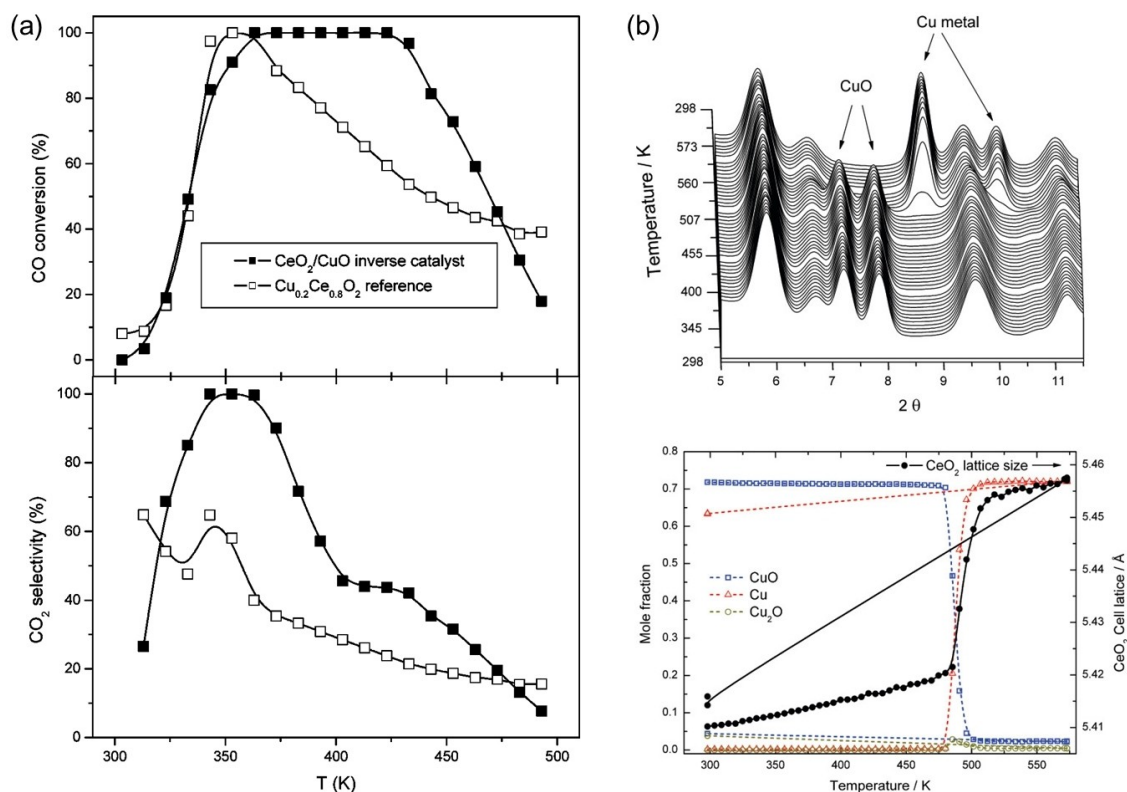


Figure 7. (a) CO conversions and CO_2 selectivities for the $\text{Cu}_{0.2}\text{Ce}_{0.8}\text{O}_2$ and inverse CeO_2/CuO catalysts. The reactor outlet gas was analysed using on-line MS. (b) Time-resolved *operando* XRD patterns of the inverse CeO_2/CuO catalyst recorded during CO-PrOx (1% CO, 1.25% O_2 , 50% H_2 , and a balance of Ar) at a space velocity of 1000 $\text{mL/g}_{\text{cat}}/\text{min}$. Also shown are the phase composition and lattice parameter data obtained by analysing the XRD patterns using Rietveld refinement. Adapted with permission from ref. [14]. Copyright © 2010 American Chemical Society.

$\text{CeO}_2/(\text{Cu}-\text{Zn})\text{O}$ catalyst exhibited higher CO conversions (Figure 8(a)). The CO_2 selectivity was higher over the $\text{CeO}_2/(\text{Cu}-\text{Zn})\text{O}$ catalyst at all reaction temperatures (Figure 8(b)). These results demonstrated that Zn doping had a positive effect on CO conversion and CO_2 selectivity. *Operando* XRD analysis was conducted to determine the correlation between catalyst phase and reactant consumption/product formation. Figures 8(c) and 8(d) show the consumption of CO and O_2 as well as the formation of CO_2 and H_2O , while Figures 8(e) and 8(f) show the XRD-derived catalyst phase composition results. The inclusion of Zn in the CeO_2/CuO catalyst increased the onset reduction temperature of CuO from ca. 110 to 145 °C (see Figures 8(e) and 8(f)). This finding was also confirmed by *in situ* XAS (specifically XANES) analysis, where the formation Cu^+ and Cu^0 was observed at higher temperatures in the presence of Zn. In the presence of the CuO and Cu_2O phases, there was no H_2 oxidation, and O_2 was only consumed *via* CO oxidation to CO_2 . However, the formation of metallic Cu closely coincided with the onset of H_2 oxidation to H_2O and the decrease in CO_2 formation. For CeO_2/CuO (Figure 8(c)) and $\text{CeO}_2/(\text{Cu}-\text{Zn})\text{O}$ (Figure 8(d)), H_2O formation was observed from ca. 160 and 180 °C, respectively. This finding indicated that CuO and Cu_2O are selective to CO oxidation while metallic Cu is selective to H_2 oxidation. It is worth noting that methane formation was not observed. *In situ* DRIFTS analysis at different temperatures showed that the presence of Zn stabilised a high concentration

of interfacial Cu^+ species (this was also observed by Zou *et al.*^[82]), which are active for CO oxidation,^[63] resulting in the observed higher CO oxidation activity of $\text{CeO}_2/(\text{Cu}-\text{Zn})\text{O}$ above 150 °C. Moreover, the introduction of Zn led to a decrease in the crystallite size of CuO, which increased the onset reduction temperature of CuO and decreased the crystallite size of CeO_2 , resulting in the modification of the CuO– CeO_2 interface. These results were also observed by Zou *et al.*^[82] over $\text{Cu}_1\text{Zn}_1\text{Ce}_9\text{O}_2$ using *in situ* DRIFTS. In the same study,^[82] the authors also investigated the effect of Fe and Mn addition and concluded that both dopants deteriorated the CO oxidation activity by facilitating the reversible desorption of CO over $\text{Cu}_1\text{Fe}_1\text{Ce}_9\text{O}_2$, as well as the strong adsorption of CO over $\text{Cu}_1\text{Mn}_1\text{Ce}_9\text{O}_2$. Moreover, $\text{Cu}_1\text{Mn}_1\text{Ce}_9\text{O}_2$ had a poor redox property, which also negatively affected the CO oxidation activity.

Copper-based catalysts, containing CuO_x or metallic Cu, are known to be inactive for CO and CO_2 methanation. Therefore, H_2 oxidation is the only reaction that can consume H_2 during CO-PrOx, especially at high reaction temperatures, due mostly to the formation of metallic Cu.^[61,71,81] Therefore, an active, selective, and stable copper-based catalyst in CO-PrOx must undergo limited-to-no reduction to metallic Cu to limit/prevent H_2 oxidation.

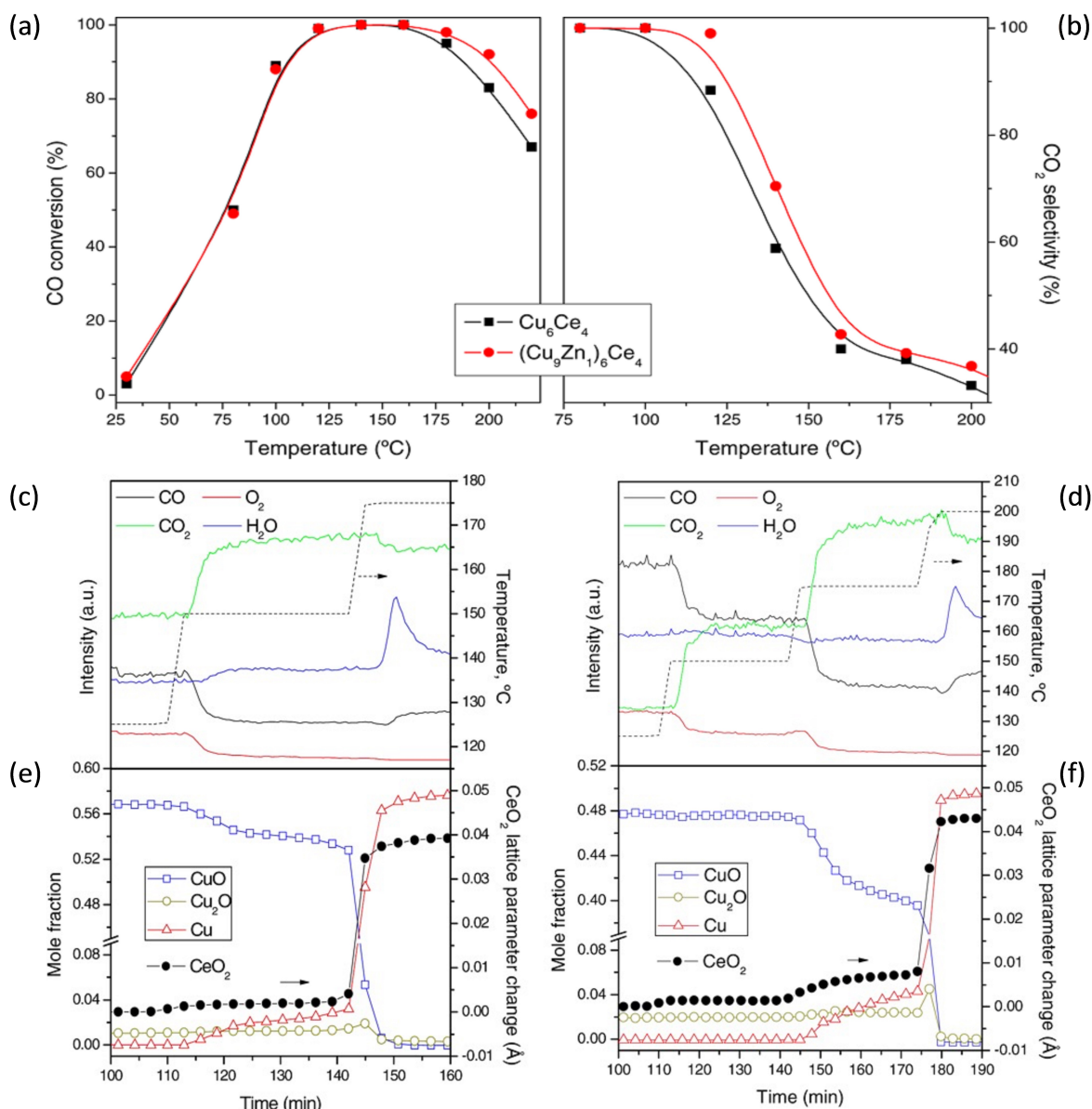


Figure 8. CO-PrOx performance evaluation of CeO_2/CuO and $\text{CeO}_2/(\text{Cu-Zn})\text{O}$ under 1% CO, 1.25% O_2 , 50% H_2 , and He as the balancing gas (space velocity: 1000 mL/g_{cat}/min), coupled with *operando* XRD analysis. Figures (a) and (b) show the CO conversion and CO_2 selectivity over both catalysts, respectively. Figures (c) and (d) show the consumption of CO and O_2 as well as the formation of CO_2 and H_2O over CeO_2/CuO and $\text{CeO}_2/(\text{Cu-Zn})\text{O}$, respectively, measured using a quadrupole mass spectrometer. Figures (e) and (f) show the phase composition results obtained after applying Rietveld refinement (in the GSAS software) on the *operando* XRD patterns acquired as a function of reaction temperature during CO-PrOx for CeO_2/CuO and $\text{CeO}_2/(\text{Cu-Zn})\text{O}$, respectively. Adapted with permission from ref. [81]. Copyright © 2014 American Chemical Society.

4. Other Base Metal Oxide Catalysts

Although Co- and Cu-based oxide catalysts are the most investigated in the CO-PrOx reaction, there are other base metal oxides (e.g., oxides of Fe, Ni, and Mn) that have recently piqued the interest of researchers as potential CO-PrOx catalysts. For instance, the performance of Fe-based oxides in CO-PrOx has been shown to depend on (i) their chemical phase (Fe_2O_3 vs. Fe_3O_4), where Teng *et al.*^[12] showed Fe_2O_3 to be CO-PrOx inactive, while Fadlalla *et al.*^[38] showed Fe_3O_4 to achieve a maximum CO conversion to CO_2 of approximately 62% at 225 °C; (ii) the nature of the substituent in the ferrite structure

($\text{M}_x\text{Fe}_{3-x}\text{O}_4$), where Teng *et al.*^[12] showed that the substitution of Co, Cu, Ni, Mn, or Zn alters the CO conversion and CO_2 selectivity during CO-PrOx. However, they did not evaluate the unsubstituted Fe_3O_4 under the same reaction conditions, hence, there is no reference point to adequately determine the effect of each substituent. Fadlalla *et al.*^[38] showed that substituting Mg in the ferrite structure results in a decrease in CO conversion and CO_2 selectivity relative to that of unsubstituted Fe_3O_4 . Qwabe *et al.*^[83] demonstrated that increasing the Co content in an Fe-based oxide catalyst improves the conversion of CO and selectivity to CO_2 . Furthermore, the catalyst with a hydrotalcite-like structure showed better CO-PrOx performance than its

counterpart that was prepared *via* a conventional coprecipitation method. Generally, Fe-based oxide catalysts have limited-to-no CO methanation activity, with the exception of those that contain Co^[12] or Ni,^[84] which is possibly due to the easier reduction of the catalyst (surface) when Co or Ni is present in the Fe-based oxide structure.

Ni-based oxide catalysts have also been investigated as potential CO–PrOx catalysts.^[12,15,85,86] For example, Malwadkar *et al.*^[15] showed that NiO/CeO₂ achieves CO conversions of up to ca. 90 % at 200 °C, and that the CO conversion decreases above a NiO content of 10 wt.-% because of the formation of large NiO particles that have a weak interaction with the CeO₂ support. However, as the CO conversion increased with increasing reaction temperature, the CO₂ selectivity decreased because H₂ was being oxidised concurrently. No methane formation was detected regardless of the catalyst composition. The performance of the NiO/CeO₂ catalyst in CO–PrOx was improved by adding Cu (to yield a CuO–NiO/CeO₂ catalyst) owing to the synergistic effect of the dispersed Cu species and the oxygen vacancies on the CeO₂ support.^[87] In other investigations, unsupported^[12] and Al₂O₃-supported NiO^[86] attained CO conversions of up to ca. 23 % and 8 %, respectively, with methane formation reported over the unsupported catalyst only. Therefore, it is important to note that the main drawbacks of Ni-based oxide catalysts are their high H₂ oxidation activity as well as high CO and CO₂ methanation activity,^[88] therefore, further research is required to overcome these drawbacks to maximise the potential of these catalysts in the CO–PrOx reaction.

Mn-based oxide catalysts are also reported to have CO–PrOx activity. Their activity is dependent on the chemical phase, where Mn₃O₄ can achieve four-fold higher CO conversions than Mn₂O₃ and MnO₂, while no CO is converted over MnO.^[12] Arena *et al.*^[89] showed that a MnCeO_x catalyst, with a high number of exposed Mn⁴⁺ species, achieves CO and H₂ conversions of up to 100 % and ~1 %, respectively, at 150 °C. It is worth noting that both studies did not report methane formation, possibly indicating that Mn-based catalysts are not active for CO and CO₂ methanation.

Although Fe-, Ni-, and Mn-based oxides are reported as potential catalysts for CO–PrOx, there is still significant room for their development to overcome the drawbacks associated with their application. Furthermore, research on these base metal oxides is still in the initial stages, hence, there are no *in situ* or *operando* studies reported on them to date, to the best of our knowledge.

5. Summary and Outlook

Hydrocarbons (especially in liquid form) remain viable sources of hydrogen for electrical energy generation in PEMFCs. However, for H₂ production and utilisation to remain sustainable and eco-friendly, hydrocarbons must initially be produced from captured CO₂ and green H₂ before storage and transportation.^[7–10] This means that CO–PrOx, as a final “cleaning” step for fuel cell H₂, will remain relevant in the foreseeable

future because of the continued production of H₂ from green hydrocarbons. In this review, we presented a variety of promising base metal oxide catalysts for the CO–PrOx reaction and highlighted the critical role of *in situ* and *operando* characterisation in improving our understanding of base metal oxides under working conditions. It was pointed out in several cases that losing the oxide form of the base metal either changes the conversion pathway of CO from oxidation to hydrogenation or changes the conversion pathway of O₂ from CO oxidation to H₂ oxidation. Such changes to the conversion pathway of CO and/or O₂ result in the undesired high consumption of valuable H₂ that is needed in the PEMFC.

Several measures have been taken to stabilise base metal oxides during CO–PrOx. For instance, anchoring Co₃O₄ on support materials such as Al₂O₃, TiO₂, and SiO₂ improves the reduction resistance of Co₃O₄ and delays the formation of undesired CH₄.^[21,22,33,41] The improved reduction resistance is attributed to the existence of strong Co₃O₄-support interactions. Similarly, Lukashuk *et al.*^[16] promoted Co₃O₄ with 10 wt.-% CeO₂ and observed the delayed formation of metallic Co at 350 °C (Figure 9(a)), instead of 300 °C as in the case of unpromoted Co₃O₄ (Figure 9(b)). The addition of CeO₂ also enhanced the conversion of CO to CO₂ below 180 °C (Figure 9(c)). Zhong *et al.*^[56] improved the phase stability and CO conversion to CO₂ over CoO by adding a small amount of MnO_x (to give a Mn:Co atomic ratio of 0.1). However, at a high Mn:Co atomic ratio of 8.31, the CO conversion to CO₂ significantly decreased even below that of the MnO_x-free CoO catalyst, despite exhibiting greater phase stability owing to the presence of excess MnO_x.

In the case of copper-based catalysts, Hornés *et al.*^[14] and Gamarra *et al.*^[61] demonstrated, *via operando* XRD and XAS, that the CuO phase is responsible for the conversion of CO to CO₂ during CO–PrOx, while the Cu₂O and metallic Cu phases (formed after the partial and complete reduction of CuO, respectively) are selective to H₂ oxidation to H₂O. Furthermore, the strength of the interaction between CuO and CeO₂ was found to be crucial for the oxidation of CO to CO₂ because of the redox properties of the interface between CuO and CeO₂. The presence of CO₂ (15 %) in the CO–PrOx feed over Ce_{0.8}Cu_{0.2}O₂ results in the retardation of Cu²⁺ reduction and the stabilisation of the Cu⁺-carbonyl surface species. One or both of these observations could be the reason for the delayed formation of CO₂ *via* CO oxidation that is observed when CO₂ is also present in the CO–PrOx feed.^[13]

In the case of the iron-based catalysts, researchers have shown that the CO–PrOx performance of this class of catalysts can be tailored. For example, the conversion of CO to CO₂ can be improved by doping metals such as cobalt into the iron oxide structure,^[83] while the conversion of CO to CH₄ can be suppressed by doping metals such as magnesium into iron oxide.^[38] In the case of nickel-based catalysts, their CO conversion to CO₂ can be improved by increasing the content of NiO on a support material such as CeO₂,^[15] while their CO and CO₂ methanation activity is influenced by the presence and nature of the support material used.^[12,86] Manganese-based catalysts have shown great promise, for example, by achieving

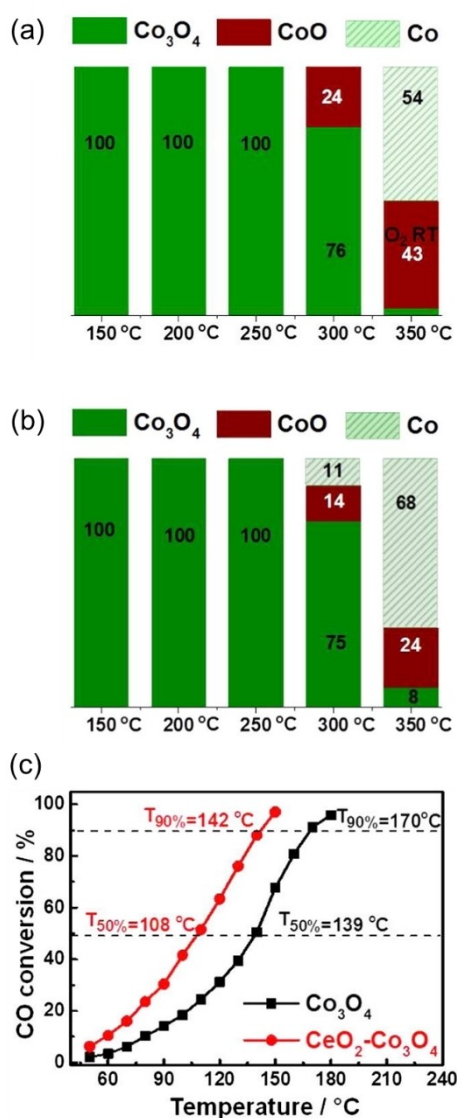


Figure 9. Amount of reduced vs. oxidised cobalt calculated via linear combination fitting of XANES spectra. The processed XANES spectra were recorded at the Co K-edge during CO-PrOx (50 mL/min of 1% CO, 1% O₂, 50% H₂, and balance of He, at atmospheric pressure) over 2.5 mg of (a) CeO₂-promoted Co₃O₄ (CeO₂-Co₃O₄) and (b) unpromoted Co₃O₄. (c) Comparison of CO conversion over Co₃O₄ and CeO₂-Co₃O₄ during CO-PrOx. The GC-FID (with methaniser) results in (c) were obtained from evaluations performed in a stand-alone fixed-bed reactor under a 50 mL/min flow of 1% CO, 1% O₂, 50% H₂, and balance of He, at atmospheric pressure, over 20 mg of catalyst. Adapted from ref. [16]. under the terms and conditions of the CC BY 4.0 license. Copyright © 2016 Elsevier.

100% CO₂ selectivity when Mn is incorporated in the CeO₂ lattice.^[89] However, we note that further fundamental studies are needed to develop active, selective, and stable CO-PrOx catalysts that are based on iron, nickel, manganese, or a combination thereof.

Stabilising the chemical phase of base metal oxides and enhancing their CO oxidation activity and selectivity in CO-PrOx remains a crucial task, and it has become apparent that an ideal CO-PrOx catalyst will likely compose of two or more metal oxides, either through the use of a strongly interacting oxide

support material or the addition of relatively small amounts of an oxidation promoter(s). Catalyst promotion may be in the form of mixed metal oxides (M_xN_yO_z)^[12,25] or composite oxides (M_xO_y-N_xO_y).^[16,56] Although limiting the composition of the final CO-PrOx catalyst to only base metal oxides makes the catalyst more affordable, promoting base metal oxides with small amounts of noble metals might also prove to be beneficial, especially in terms of catalytic activity and selectivity.^[86,90–92]

Acknowledgements

The financial support from the National Research Foundation's Thuthuka programme (grant numbers: TTK2204041915 and UID129833) and the University of Cape Town's University Research Committee is gratefully acknowledged.

Conflict of Interests

The authors declare no conflict of interest.

Keywords: CO-PrOx · base metal oxides · catalytic performance · physicochemical changes · *in situ* and *operando* characterisation

- [1] T. V. Choudhary, D. W. Goodman, *Catal. Today* **2002**, *77*, 65–78.
- [2] A. F. Ghenciu, *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 389–399.
- [3] E. D. Park, D. Lee, H. C. Lee, *Catal. Today* **2009**, *139*, 280–290.
- [4] A. Mishra, R. Prasad, *Bull. Chem. React. Eng. Catal.* **2011**, *6*, 1–14.
- [5] D. Teichmann, W. Arlt, P. Wasserscheid, *Int. J. Hydrogen Energy* **2012**, *37*, 18118–18132.
- [6] M. Aziz, A. T. Wijayanta, A. B. D. Nandiyanto, *Energies* **2020**, *13*, 3062.
- [7] R. Hren, A. Vujanović, Y. Van Fan, J. J. Klemes, D. Krajnc, L. Čuček, *Renewable Sustainable Energy Rev.* **2023**, *173*, 113113.
- [8] S. Golunski, *Platinum Met. Rev.* **1998**, *42*, 2–7.
- [9] N. Edwards, S. R. Ellis, J. C. Frost, S. E. Golunski, A. N. J. van Keulen, N. G. Lindewald, J. G. Reinkingh, *J. Power Sources* **1998**, *71*, 123–128.
- [10] M. Bowker, *ChemCatChem* **2019**, *11*, 4238–4246.
- [11] R. K. Ahluwalia, Q. Zhang, D. J. Chmielewski, K. C. Lauze, M. A. Inbody, *Catal. Today* **2005**, *99*, 271–283.
- [12] Y. Teng, H. Sakurai, A. Ueda, T. Kobayashi, *Int. J. Hydrogen Energy* **1999**, *24*, 355–358.
- [13] D. Gamarra, M. Fernández-García, C. Bolver, A. Martínez-Arias, *J. Phys. Chem. C* **2010**, *114*, 18576–18582.
- [14] A. Hornés, A. B. Hungria, P. Bera, A. L. Cámara, M. Fernández-García, A. Martínez-Arias, L. Barrio, M. Estrella, G. Zhou, J. J. Fonseca, J. C. Hanson, J. A. Rodriguez, *J. Am. Chem. Soc.* **2010**, *132*, 34–35.
- [15] S. Malwadkar, P. Bera, M. S. Hegde, C. V. V. Satyanarayana, *React. Kinet. Mech. Catal.* **2012**, *107*, 405–419.
- [16] L. Lukashuk, K. Föttinger, E. Kolar, C. Rameshan, D. Teschner, M. Hävecker, A. Knop-Gericke, N. Yigit, H. Li, E. McDermott, M. Stöger-Pollach, G. Rupprechter, *J. Catal.* **2016**, *344*, 1–15.
- [17] T. M. Nyathi, N. Fischer, A. P. E. York, M. Claeys, *Faraday Discuss.* **2017**, *197*, 269–285.
- [18] M. L. Brown Jr, A. W. Green, G. Cohn, H. C. Andersen, *Ind. Eng. Chem.* **1960**, *52*, 841–844.
- [19] M. P. Woods, P. Gawade, B. Tan, U. S. Ozkan, *Appl. Catal. B* **2010**, *97*, 28–35.
- [20] T. M. Nyathi, N. Fischer, A. P. E. York, M. Claeys, *ACS Catal.* **2020**, *10*, 11892–11911.
- [21] T. M. Nyathi, M. I. Fadlalla, N. Fischer, A. P. E. York, E. J. Olivier, E. K. Gibson, P. P. Wells, M. Claeys, *Appl. Catal. B* **2021**, *297*, 120450.
- [22] Z. Zhao, M. M. Yung, U. S. Ozkan, *Catal. Commun.* **2008**, *9*, 1465–1471.
- [23] B. M. Weckhuysen, *Chem. Commun.* **2002**, *2*, 97–110.
- [24] M. A. Bañares, *Catal. Today* **2005**, *100*, 71–77.

- [25] K. Omata, T. Takada, S. Kasahara, M. Yamada, *Appl. Catal. A* **1996**, *146*, 255–267.
- [26] L. Lukashuk, N. Yigit, R. Rameshan, E. Kolar, D. Teschner, M. Hävecker, A. Knop-Gericke, R. Schlögl, K. Föttinger, G. Rupprechter, *ACS Catal.* **2018**, *8*, 8630–8641.
- [27] L. Lukashuk, N. Yigit, H. Li, J. Bernardi, K. Föttinger, G. Rupprechter, *Catal. Today* **2019**, *336*, 139–147.
- [28] D. Perti, R. L. Kabel, G. J. McCarthy, *AIChE J.* **1985**, *31*, 1435–1440.
- [29] P. Broqvist, I. Panas, H. Persson, *J. Catal.* **2002**, *210*, 198–206.
- [30] F. Zasada, W. Piskorz, J. Janas, J. Gryboś, P. Indyka, Z. Sojka, *ACS Catal.* **2015**, *5*, 6879–6892.
- [31] P. Mars, D. W. van Krevelen, *Chem. Eng. Sci.* **1954**, *3*, 41–59.
- [32] C.-B. Wang, C.-W. Tang, S.-J. Gau, S.-H. Chien, *Catal. Lett.* **2005**, *101*, 59–63.
- [33] T. M. Nyathi, N. Fischer, A. P. E. York, D. J. Morgan, G. J. Hutchings, E. K. Gibson, P. P. Wells, C. R. A. Catlow, M. Claeys, *ACS Catal.* **2019**, *9*, 7166–7178.
- [34] V. Iablokov, R. Barbosa, G. Pollefeyt, I. Van Driessche, S. Chenakin, N. Kruse, *ACS Catal.* **2015**, *5*, 5714–5718.
- [35] Y. Teng, Y. Kusano, M. Azuma, M. Haruta, Y. Shimakawa, *Catal. Sci. Technol.* **2011**, *1*, 920–922.
- [36] M. Khasu, T. Nyathi, D. J. Morgan, G. J. Hutchings, M. Claeys, N. Fischer, *Catal. Sci. Technol.* **2017**, *7*, 4806–4817.
- [37] O. A. Bulavchenko, T. N. Afonassenko, S. S. Sigaeva, A. V. Ivanchikova, A. A. Saraev, E. Y. Gerasimov, V. V. Kaichev, S. V. Tsybulya, *Top. Catal.* **2020**, *63*, 75–85.
- [38] M. I. Fadlalla, T. M. Nyathi, M. Claeys, *Catalysts* **2022**, *12*, 118.
- [39] C.-B. Wang, C.-W. Tang, H.-C. Tsai, M.-C. Kuo, S.-H. Chien, *Catal. Lett.* **2006**, *107*, 31–37.
- [40] C.-B. Wang, C.-W. Tang, H.-C. Tsai, S.-H. Chien, *Catal. Lett.* **2006**, *107*, 223–230.
- [41] T. M. Nyathi, M. I. Fadlalla, N. Fischer, A. P. E. York, E. J. Olivier, E. K. Gibson, P. P. Wells, M. Claeys, *Catal. Sci. Technol.* **2023**, *13*, 2038–2052.
- [42] T. Herranz, X. Deng, A. Cabot, J. Guo, M. Salmeron, *J. Phys. Chem. B* **2009**, *113*, 10721–10727.
- [43] A. Tuxen, S. Carenco, M. Chintapalli, C.-H. Chuang, C. Escudero, E. Pach, P. Jiang, F. Borondics, B. Beberwyck, A. P. Alivisatos, G. Thornton, W.-F. Pong, J. Guo, R. Perez, F. Besenbacher, M. Salmeron, *J. Am. Chem. Soc.* **2013**, *135*, 2273–2278.
- [44] J.-A. Dalmon, in *Catal. Charact. - Phys. Tech. Solid Mater.* (Eds.: B. Imelik, J. C. Vedrine), Springer US, Boston, MA, **1994**, 585–609.
- [45] V. Sechovský, in *Encycl. Mater. Sci. Technol.* (Eds.: K. H. J. Buschow, R. W. Cahn, M. C. Flemings, B. Ilshner, E. J. Kramer, S. Mahajan, P. Veyssière), Elsevier Science Ltd, **2001**, 5018–5032.
- [46] C. G. Shull, W. A. Strauser, E. O. Wollan, *Phys. Rev.* **1951**, *83*, 333–345.
- [47] W. L. Roth, *J. Phys.* **1964**, *25*, 507–515.
- [48] Q. Guo, Y. Liu, *React. Kinet. Catal. Lett.* **2007**, *92*, 19–25.
- [49] P. Gawade, B. Bayram, A.-M. C. Alexander, U. S. Ozkan, *Appl. Catal. B* **2012**, *128*, 21–30.
- [50] S. Monyanon, S. Pongstabodee, A. Luengnaruemitchai, *J. Chinese Inst. Chem. Eng.* **2007**, *38*, 435–441.
- [51] D. H. Kim, J. E. Cha, *Catal. Lett.* **2003**, *86*, 107–112.
- [52] M. M. Yung, Z. Zhao, M. P. Woods, U. S. Ozkan, *J. Mol. Catal. A* **2008**, *279*, 1–9.
- [53] L. Zhong, T. Kropp, W. Baaziz, O. Ersen, D. Teschner, R. Schlögl, M. Mavrikakis, S. Zafeiratos, *ACS Catal.* **2019**, *9*, 8325–8336.
- [54] J. Cai, Z. Liu, K. Cao, Y. Lang, S. Chu, B. Shan, R. Chen, *J. Mater. Chem. A* **2020**, *8*, 10180–10187.
- [55] L. Zhong, M. Barreau, V. Caps, V. Papaefthimiou, M. Haevecker, D. Teschner, W. Baaziz, E. Borfecchia, L. Braglia, S. Zafeiratos, *ACS Catal.* **2021**, *11*, 5369–5385.
- [56] L. Zhong, M. Barreau, D. Chen, V. Caps, M. Haevecker, D. Teschner, D. H. Simonne, E. Borfecchia, W. Baaziz, B. Šmíd, S. Zafeiratos, *Appl. Catal. B* **2021**, *297*, 120397.
- [57] M. Wolf, N. Fischer, M. Claeys, *Catal. Today* **2016**, *275*, 135–140.
- [58] I. C. ten Have, J. J. G. Kromwijk, M. Monai, D. Ferri, E. B. Sterk, F. Meirer, B. M. Weckhuysen, *Nat. Commun.* **2022**, *13*, 324.
- [59] A. Martínez-Arias, M. Fernández-García, O. Gálvez, J. M. Coronado, J. A. Anderson, J. C. Conesa, J. Soria, G. Munuera, *J. Catal.* **2000**, *195*, 207–216.
- [60] A. Martínez-Arias, A. B. Hungria, M. Fernández-García, J. C. Conesa, G. Munuera, *J. Phys. Chem. B* **2004**, *108*, 17983–17991.
- [61] 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.
- [62] A. Martínez-Arias, A. B. Hungria, M. Fernández-García, J. C. Conesa, G. Munuera, *J. Power Sources* **2005**, *151*, 32–42.
- [63] D. Gamarra, C. Belver, M. Fernández-García, A. Martínez-Arias, *J. Am. Chem. Soc.* **2007**, *129*, 12064–12065.
- [64] D. Gamarra, A. Martínez-Arias, *J. Catal.* **2009**, *263*, 189–195.
- [65] C. S. Polster, H. Nair, C. D. Baertsch, *J. Catal.* **2009**, *266*, 308–319.
- [66] G. Avgouropoulos, T. Ioannides, C. Papadopolou, J. Batista, S. Hocevar, H. Matralis, *Catal. Today* **2002**, *75*, 157–167.
- [67] J. W. Park, J. H. Jeong, W. L. Yoon, Y. W. Rhee, *J. Power Sources* **2004**, *132*, 18–28.
- [68] G. Avgouropoulos, T. Ioannides, H. Matralis, *Appl. Catal. B* **2005**, *56*, 87–93.
- [69] F. Mariño, C. Descorme, D. Duprez, *Appl. Catal. B* **2005**, *58*, 175–183.
- [70] G. Avgouropoulos, T. Ioannides, *Appl. Catal. B* **2006**, *67*, 1–11.
- [71] A. Martínez-Arias, A. B. Hungria, G. Munuera, D. Gamarra, *Appl. Catal. B* **2006**, *65*, 207–216.
- [72] G. Sedmak, S. Hocevar, J. Levec, *J. Catal.* **2003**, *213*, 135–150.
- [73] R. Kydd, D. Ferri, P. Hug, J. Scott, W. Y. Teoh, R. Amal, *J. Catal.* **2011**, *277*, 64–71.
- [74] T. Shido, Y. Iwasawa, *J. Catal.* **1993**, *141*, 71–81.
- [75] G. Jacobs, E. Chenu, P. M. Patterson, L. Williams, D. Sparks, G. Thomas, B. H. Davis, *Appl. Catal. A* **2004**, *258*, 203–214.
- [76] X. Wang, J. A. Rodríguez, J. C. Hanson, D. Gamarra, A. Martínez-Arias, M. Fernández-García, *J. Phys. Chem. B* **2006**, *110*, 428–434.
- [77] M. Fernández-García, A. Martínez-Arias, J. C. Hanson, J. A. Rodríguez, *Chem. Rev.* **2004**, *104*, 4063–4104.
- [78] D. Gamarra, A. Hornés, Z. Koppány, Z. Schay, G. Munuera, J. Soria, A. Martínez-Arias, *J. Power Sources* **2007**, *169*, 110–116.
- [79] J. Y. Kim, J. A. Rodríguez, J. C. Hanson, A. I. Frenkel, P. L. Lee, *J. Am. Chem. Soc.* **2003**, *125*, 10684–10692.
- [80] X. Wang, J. C. Hanson, A. I. Frenkel, J.-Y. Kim, J. A. Rodríguez, *J. Phys. Chem. B* **2004**, *108*, 13667–13673.
- [81] A. L. Cámara, V. C. Corberán, L. Barrio, G. Zhou, R. Si, J. C. Hanson, M. Monte, J. C. Conesa, J. A. Rodríguez, A. Martínez-Arias, *J. Phys. Chem. C* **2014**, *118*, 9030–9041.
- [82] H. Zou, S. Chen, Z. Liu, W. Lin, *Powder Technol.* **2011**, *207*, 238–244.
- [83] L. Q. Qwabe, H. B. Friedrich, S. Singh, *J. Mol. Catal. A* **2015**, *404–405*, 167–177.
- [84] P. T. A. Santos, A. C. F. M. Costa, R. H. G. A. Kiminami, H. M. C. Andrade, H. L. Lira, L. Gama, *J. Alloys Compd.* **2009**, *483*, 399–401.
- [85] C. A. Chagas, E. F. de Souza, R. L. Manfro, S. M. Landi, M. M. V. M. Souza, M. Schmal, *Appl. Catal. B* **2016**, *182*, 257–265.
- [86] Z. Mohamed, V. D. B. C. Dasireddy, S. Singh, H. B. Friedrich, *Appl. Catal. B* **2016**, *180*, 687–697.
- [87] C. A. Chagas, M. Schmal, *Int. J. Hydrogen Energy* **2022**, *47*, 8858–8866.
- [88] J. A. Gómez-Cuaspud, M. Schmal, *Int. J. Hydrogen Energy* **2013**, *38*, 7458–7468.
- [89] F. Arena, F. Ferrante, R. Di Chio, G. Bonura, F. Frusteri, L. Frusteri, A. Prestianni, S. Morandi, G. Martra, D. Duca, *Appl. Catal. B* **2022**, *300*, 120715.
- [90] T. Cwele, N. Mahadevaiah, S. Singh, H. B. Friedrich, A. K. Yadav, S. N. Jha, D. Bhattacharyya, N. K. Sahoo, *Catal. Sci. Technol.* **2016**, *6*, 8104–8116.
- [91] L. Q. Qwabe, V. D. B. C. Dasireddy, S. Singh, H. B. Friedrich, *Int. J. Hydrogen Energy* **2016**, *41*, 2144–2153.
- [92] L. Q. Qwabe, H. B. Friedrich, S. Singh, *J. Environ. Chem. Eng.* **2019**, *7*, 102827.

Manuscript received: February 9, 2024
Revised manuscript received: May 3, 2024
Accepted manuscript online: May 7, 2024
Version of record online: June 24, 2024