



Article Magnesium as a Methanation Suppressor for Iron- and Cobalt-Based Oxide Catalysts during the Preferential Oxidation of Carbon Monoxide

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Abstract: The preferential oxidation of CO (CO-PrOx) to CO₂ is an effective catalytic process for purifying the H₂ utilized in proton-exchange membrane fuel cells for power generation. Our current work reports on the synthesis, characterization and CO-PrOx performance evaluation of unsubstituted and magnesium-substituted iron- and cobalt-based oxide catalysts (i.e., Fe₃O₄, Co₃O₄, MgFe₂O₄ and MgCo₂O₄). More specifically, the ability of Mg to stabilize the MgFe₂O₄ and MgCo₂O₄ structures, as well as suppress CH₄ formation during CO-PrOx was of great importance in this study. The cobalt-based oxide catalysts achieved higher CO₂ yields than the iron-based oxide catalysts below 225 °C. The highest CO₂ yield (100%) was achieved over Co₃O₄ between 150 and 175 °C, however, undesired CH₄ formation was only observed over this catalyst due to the formation of bulk fcc and hcp Co⁰ between 200 and 250 °C. The presence of Mg in MgCo₂O₄ suppressed CH₄ formation, with the catalyst only reducing to a CoO-type phase (possibly containing Mg). The iron-based oxide catalysts did not undergo bulk reduction and did not produce CH₄ under reaction conditions. In conclusion, our study has demonstrated the beneficial effect of Mg in stabilizing the active iron- and cobalt-based oxide structures, and in suppressing CH₄ formation during CO-PrOx.

Keywords: CO-PrOx; iron-based oxides; cobalt-based oxides; magnesium effect; methane suppression

1. Introduction

Goal number seven in the United Nations Sustainable Development Goals is to "ensure access to affordable, reliable, sustainable and modern energy for all" [1]. The sustainability part of this goal is of great importance due to the challenges associated with the depleting fossil fuels and the negative impact that these have on the environment. Hydrogen (H₂) fuel cells are a potential sustainable energy source for mobile and stationary applications. Currently, H₂ is produced from hydrocarbons via a reforming and/or partial oxidation process, followed by a high- and a low-temperature water-gas shift (HTWGS and LTWGS) reaction. However, the main challenge associated with the use of fuel cells, in particular, proton-exchange membrane fuel cells (PEMFCs), is the carbon monoxide (CO) present (0.5-2 vol.%) in the H₂-rich reformate gas, which poisons the platinum (Pt)-based anode catalyst of the PEMFC [2]. The preferential oxidation of carbon monoxide (CO-PrOx) is considered as an effective and affordable H₂ purification process, where CO is oxidized by oxygen (O₂) to form carbon dioxide (CO₂), while minimizing/preventing the concurrent oxidation of H₂ to water (H₂O) [3].

CO-PrOx is typically carried out over noble metal-based catalysts, but due to the limited availability and economic impact of using noble metals, an alternative readily available and affordable class/type of catalyst is needed. In recent decades, researchers have focused on the development of base metals as catalysts for CO-PrOx with high CO oxidation activity and selectivity [4–7]. Iron (Fe) [7,8], nickel (Ni) [2,7,9], cobalt (Co) [7,8,10–13]



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and copper (Cu) [7,14,15] have been investigated for this purpose. The main challenge associated with using base metals is the phase dependency of their activity and selectivity, i.e., the metal oxide phase typically favors the oxidation of CO, while the metallic phase often favors CO hydrogenation to produce methane (CH₄) [11,16,17]. CO hydrogenation is not a desired CO-consuming route as it results in the consumption of the valuable H₂ that is required in the PEMFC [14,17].

Nyathi et al. [18] demonstrated an increase in the degree of reduction (DoR) of Co_3O_4 to metallic Co (Co⁰) and in the formation of CH₄ with an increase in the starting crystallite size of Co_3O_4 nanoparticles. The reduction of the Co_3O_4 phase was caused by the abundant H₂ in the feed (~50 vol.% in the study by Nyathi et al. [18]), which also causes the reduction of other base metal oxides used to catalyze CO-PrOx [7]. Other studies have shown that the reaction environment can influence the reduction onset temperature and DoR to Co⁰, where the presence of H₂O or O₂ delays the reduction onset and minimizes the DoR to Co⁰ [17,19–22].

Iron has been reported as a dopant for the Cu-CeO₂ system used in CO-PrOx, where the addition of Fe resulted in improved activity and selectivity, especially at low reaction temperatures (60–100 °C) [23,24]. Qwabe et al. [8] reported on the use of Co₃O₄-Fe₂O₃ as a CO-PrOx catalyst, where the CO conversion increased with an increase in the Co₃O₄ content. Teng et al. [7] studied the performance of Fe₂O₃, CuFe₂O₄, NiFe₂O₄ and ZnFe₂O₄ in CO-PrOx and showed CuFe₂O₄ and NiFe₂O₄ to have the highest CO conversion (48.7%) and O₂ selectivity to CO₂ (35.9%), respectively. Furthermore, the metal oxides of Mn, Co, Ni and Fe have been used as carriers for Au-based catalysts in CO-PrOx [25,26].

Metals in groups I and II of the periodic table have been used as promoters of (non-) noble metal-based CO-PrOx catalysts [3,27–29]. For example, potassium (K) addition to Pt-based catalysts improves the activity (especially at low reaction temperatures) by weakening the CO–Pt interaction and changing the CO adsorption mode [30]. On the other hand, magnesium (Mg) addition to Pt-based catalysts results in increased catalytic performance due to an increase in the concentration of OH groups (caused by the increased Lewis basicity) and electron density on the surface of the catalyst [31]. Dongil et al. [28,29] studied the promotional effect of alkali metals (Li, Na, K and Cs) on CuO/CeO₂, reporting an increase in the ratio of Cu⁺ species-to-lattice oxygen species as a result of K addition, which resulted in an increase in the CO oxidation activity.

Fe₃O₄ and Co₃O₄ belong to the spinel structure group with a general formula of AB₂O₄. The spinel structure allows for tailoring the properties of the final catalyst (based on the selection of the cation(s) in the A and B sites) and ensures uniform mixing of the cations in the spinel structure. Due to this, spinel-based catalysts are studied in different catalytic processes [32], including the Fischer–Tropsch synthesis (FTS) [33,34] and WGS [35]. In this study, we aimed at exclusively placing Mg in the A site of Fe- and Co-based oxide spinel structures to produce MgFe₂O₄ and MgCo₂O₄, respectively, and thereafter study the effect of this inclusion on the physicochemical properties and CO-PrOx performance (under model/dry conditions) of the resulting Fe- and Co-based oxide catalysts.

2. Results and Discussion

2.1. Fresh Catalyst Characterisation

To determine the effect of Mg on the physicochemical properties of the Fe- and Cobased oxides, a number of ex situ characterization techniques were carried out. The crystallographic structure of the catalysts with and without Mg addition was determined via powder X-ray diffraction (PXRD). The obtained PXRD patterns in Figure 1a only show the reflexes of the targeted crystalline spinel structure in each sample, i.e., Fe₃O₄, MgFe₂O₄, Co₃O₄ and MgCo₂O₄. This points to the successful inclusion of Mg in the spinel structure of the Fe- and Co-based oxides. The inclusion of Mg resulted in the broadening of the reflexes of MgFe₂O₄ and MgCo₂O₄, indicating a decrease in the crystallite size upon addition of Mg. The relative crystallographic phase abundance and average volume-based crystallite size for each catalyst were determined via Rietveld refinement (in the software, TOPAS 5.0 [36]), indicating a decrease in the crystallite size of the Mg-bearing Fe- and Co-based oxides (Table 1), as well as confirming the sole presence of the targeted spinel phase in each catalyst (Table 1). It is important to note, all the refinement results in Table 1 have an associated weighted profile R-factor (Rwp) that is below 10%, indicating a good fit between the calculated and experimental PXRD patterns [36].



Figure 1. PXRD patterns of the (**a**) fresh and (**b**) CO-PrOx spent unsubstituted and Mg-substituted Fe- and Co-based oxides (obtained with a Co X-ray source ($K_{\alpha 1} = 0.178897$ nm)).

Table 1. PXRD-derived average volume-based crystallite size and relative phase abundance (determined via Rietveld refinement), BET mass-specific surface area, as well as the SEM-EDS-derived cation composition for the fresh and spent unsubstituted and Mg-substituted Fe- and Co-based oxides.

| Catalyst | d _{crys, PXRD} , Fresh (nm) | Relative Phase Abundance, Fresh (wt.%) | BET Surface Area, Fresh (m²/g) | d _{crys, PXRD} , Spent (nm) | Relative Phase Abundance, Spent (wt.%) | Ratio of Fe or Co:Mg, Fresh * |
|----------------------------------|---|--|--------------------------------------|--|---|----------------------------------|
| Fe ₃ O ₄ | 6.9 ± 0.1 | 100 | 159 | 19.3 ± 0.4 | 100 | - |
| MgFe ₂ O ₄ | 2.1 ± 0.0 | 100 | 189 | 2.2 ± 0.0 | 100 | 2.2 |
| Co ₃ O ₄ | 28.2 ± 0.3 | 100 | 32 | 6.6 ± 0.2 (CoO), 25.7 \pm 7.1 (fcc Co ⁰), 3.0 \pm 0.2 (hcp Co ⁰) | $72.3 \pm 2.5 (CoO), 2.5 \pm 0.6 (fcc Co0), 25.2 \pm 2.6 (hpc Co0)) Co0)$ | - |
| MgCo ₂ O ₄ | 7.2 ± 0.1 | 100 | 77 | 7.7 ± 0.1 (CoO) | 100 | 2.3 |

* determined via SEM-EDS analysis.

The addition of Mg influenced the BET mass-specific surface area of the Fe-and Cobased oxide spinel structures (Table 1). The Fe-based oxide catalysts showed higher surface areas than those of the Co-based oxide catalysts. This was consistent with the Fe-based oxide catalysts displaying smaller crystallite sizes based on PXRD analysis. The addition of Mg caused an increase in the surface area of the resulting MgFe₂O₄ and MgCo₂O₄ catalysts (see Table 1). This was anticipated since Mg is a structural promoter that improves the dispersion of metal oxides [37]. It is important to note, although the crystallite sizes of Fe₃O₄ and MgCo₂O₄ are comparable, the observed difference in their BET surface area could be due to their differences in pore structure. The Fe or Co:Mg ratio in MgFe₂O₄ and MgCo₂O₄ is approximately 2, according to scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS)—also see Table 1. The discrepancy between the nominal and experimental ratios could be due to the detection limitations of the SEM-EDS technique [38]. The elemental maps for MgFe₂O₄ and MgCo₂O₄ (Figure 2) show a uniform distribution of the cations in both catalysts. This confirms the complete inclusion of Mg in the spinel structure by possibly substituting the divalent cations (i.e., Fe²⁺ or Co²⁺). One of the advantages of targeting the spinel structure is the possibility of achieving high loadings of the dopant in the final catalyst [39]. Moreover, the uniform distribution of Mg in the catalysts may result in an optimized effect of Mg during CO-PrOx due to its close proximity to Fe or Co [33,39].



Figure 2. SEM-EDS mapping of the cations in the fresh (**a**) MgFe₂O₄ and (**b**) MgCo₂O₄.

The CO-PrOx reaction is carried out under a reducing environment due to the high concentration of H₂ (typically between 40 and 75 vol.%) [5,6,40,41]. Nyathi et al. [16,17] showed that the performance of Co-based catalysts is phase dependent, i.e., the phases Co_3O_4 , CoO and Co^0 kinetically favor different reactions during CO-PrOx. For example, the authors showed the onset of CH₄ formation to coincide with the onset formation of Co^0 from Co_3O_4 . Therefore, it was important to first determine the reduction pathway for the unsubstituted and Mg-substituted Fe- and Co-based oxides using H₂ temperature-programmed reduction (H₂-TPR).

The H₂-TPR profile of Fe₃O₄ (Figure 3) shows two reduction peaks, the first one is between 200 and 350 °C, corresponding to the reduction of Fe₃O₄ to FeO, the second peak is between 360 and 700 °C, due to the reduction of FeO to metallic Fe (Fe⁰) [42]. The addition of Mg into the Fe-based oxide structure resulted in an increase in the area of the aforementioned peaks, indicating that Mg improves the dispersion of the Fe-based oxide particles [37]. This observation is also supported by PXRD (Figure 1a) and surface area analyses (Table 1). Furthermore, small crystallites are generally harder to reduce [18,20].



Figure 3. H₂-TPR profiles of the unsubstituted and Mg-substituted Fe- and Co-based oxides.

In the case of Co_3O_4 , the H₂-TPR profile (Figure 3) shows two convoluted reduction peaks having temperature maxima (T_{max}) at ca. 260 °C and 340 °C, corresponding to the reduction of Co_3O_4 to CoO and then from CoO to Co^0 , respectively [16]. The addition of Mg to the Co-based oxide structure resulted in two resolved reduction peaks, with the first one observed between 190 and 220 °C, corresponding to the reduction of MgCo₂O₄ to a CoO-type phase containing Mg (possibly in the form Mg_{0.32}Co_{0.68}O). The second reduction peak was less intense and broad with a T_{max} at 600 °C, possibly representing the reduction of Mg_{0.32}Co_{0.68}O to an alloy phase in the form MgCo₂. The broadening of the second peak could also be due to Mg improving the dispersion and reducing the crystallite size of the Co-based oxide.

2.2. Spent Catalyst Characterisation

To determine the effect of the CO-PrOx reaction environment on catalyst phase stability, the spent catalysts were recovered after the CO-PrOx reaction and characterized via PXRD and SEM-EDS analysis. The PXRD results (Figure 1b), in the case of the Fe-based oxide catalysts, showed that the Fe₃O₄ (spinel) structure was dominant in the acquired diffraction patterns. However, in the case of the Co-based oxide catalysts, the PXRD results (Figure 1b) indicated the presence of CoO and the proposed Mg_{0.32}Co_{0.68}O phase as being dominant in the ex-Co₃O₄ and ex-MgCo₂O₄ catalysts, respectively. Moreover, face-centred cubic (fcc) Co⁰ and hexagonal close-packed (hcp) Co⁰ were detected in the ex-Co₃O₄ catalyst only, with relative phase abundances of 2.5 and 25.2 wt.%, respectively (see Table 1). These observations are in agreement with the H₂-TPR results (Figure 3), which showed an easier reduction of the Co-based oxides when compared with the Fe-based oxides.

A comparison in the crystallite sizes of the fresh and spent catalysts (see Table 1) shows that Fe_3O_4 and $MgCo_2O_4$ have comparable starting crystallite sizes, despite $MgCo_2O_4$ undergoing reduction to $Mg_{0.32}Co_{0.68}O$ during CO-PrOx. However, in the case of the Fe_3O_4 catalyst, the crystallite size increased by almost threefold, which could be due to

hydrothermal sintering as a result of the water produced during CO-PrOx [43]. In the case of the Co_3O_4 catalyst, the crystallite size decreased upon formation of the CoO and the hcp Co phases, while the crystallite size of the fcc Co phase was comparable with that of the starting Co_3O_4 phase, indicating a possible cleavage of the particles during CO-PrOx. This is in agreement with the findings reported by Nyathi et al. from their in situ PXRD-based CO-PrOx studies [16]. SEM-EDS analysis of the spent catalysts (Figure 4) shows a uniform distribution of the cations (i.e., Mg and Fe or Co), indicating that the cations remain in close proximity even after partial reduction (in the case of MgCo₂O₄). The Co:Mg ratio in the ex-MgCo₂O₄ catalyst remained as 2.3, while the Fe:Mg ratio was 2.2 in the ex-MgFe₂O₄ as determined by SEM-EDS analysis.



Figure 4. SEM-EDS mapping of the cations in the CO-PrOx spent (a) MgFe₂O₄ and (b) MgCo₂O₄.

2.3. CO-PrOx Performance Evaluation

Catalyst evaluation experiments were conducted between 50 and 250 °C at atmospheric pressure under a flow of 1% CO, 1% O₂, 50% H₂ and 48% N₂. Shown in Figure 5a–c are the CO, O₂ and H₂ conversions, respectively, then Figure 5d,e shows the CO₂ and CH₄ yields, respectively, and Figure 5f shows the O₂ selectivity to CO₂ for all four prepared catalysts. As mentioned in Section 3.3, water formation could not be measured as the water was condensed prior to the on-line micro-GC instrument.

The Co-based oxide catalysts (i.e., Co_3O_4 and $MgCo_2O_4$) displayed higher CO and O_2 conversions (Figure 5a,b), as well as higher CO₂ yields (Figure 5d) below 225 °C when compared with the Fe-based oxide catalysts (Fe₃O₄ and MgFe₂O₄). In CO-PrOx, Fe is often used as a promoter and not the main catalyst component as it is not very active for CO oxidation [7,8,44]. Based on the H₂-TPR profiles of the four catalysts (Figure 3), the Fe-based oxide catalysts required higher temperatures to reduce than the Co-based ones since they exhibited smaller crystallite sizes. Assuming the Mars–van Krevelen (MvK) mechanism for CO oxidation, which requires the catalyst surface to be easily reduced (and re-oxidised) [45–48], it is possible that the low CO oxidation activity of the Fe-based oxides was caused by their less reducible nature. This has also been proposed for other less reducible catalysts that displayed low CO oxidation activity during CO-PrOx [11,16,49].

It can also be observed that the addition of Mg in the Fe- and Co-based oxide structure (i.e., $MgFe_2O_4$ and $MgCo_2O_4$) decreased the CO and O_2 conversions, as well as CO_2 yields below 250 °C. This decrease in the CO oxidation activity is consistent with the effect that Mg has on the reducibility of the catalysts (see H₂-TPR profiles in Figure 3), i.e., the addition of Mg makes the Fe- and Co-based oxide less reducible. The suppressed reducibility in the presence of Mg may have negatively affected the performance of the catalysts during CO-PrOx due to a less effective MvK mechanism.



Figure 5. CO-PrOx performance indicators: (**a**) CO conversion, (**b**) O_2 conversion, (**c**) H_2 conversion, (**d**) CO_2 yield, (**e**) CH_4 yield and (**f**) O_2 selectivity to CO_2 (plotted at temperatures where CO is converted to CO_2) as a function of reaction time and temperature. Feed composition: 1% CO, 1% O_2 , 50% H_2 and 48% N_2 , reaction pressure: atmospheric, GHSV: 60,000 mL/g_{cat}/h.

The Co₃O₄ catalyst exhibited superior activity amongst all catalysts tested, and maintained 100% CO conversion (Figure 5a) and CO₂ yield (Figure 5d) between 150 and 175 °C. The MgCo₂O₄ catalyst reached a maximum CO₂ yield of 84.2% at 200 °C, followed by Fe₃O₄ with a maximum CO₂ yield of 62.0% at 225 °C, and then by MgFe₂O₄ with a maximum yield of 52.1% at 250 °C. Ideally, the oxidation of H₂ should not take place during CO-PrOx as it decreases the amount of O₂ available for CO oxidation and decreases the amount of valuable H₂ for the PEMFC. However, the O₂ selectivity to CO₂ (Figure 5f) was below 100% for all catalysts and at all reaction temperatures, implying the concurrence of H₂ oxidation. This was also confirmed by the conversion of H₂ (Figure 5c), which was observed earlier over the Co-based oxide catalysts. An increase in the reaction temperature up to 250 °C kinetically favors H₂ oxidation and decreases the O₂ selectivity to CO₂, which is consistent with other studies reported in the literature [7,16,17,49].

The conversion of H₂ reached a maximum of approximately 3% at 250 °C over MgCo₂O₄, Fe₃O₄ and MgFe₂O₄, but reached almost 10% over Co₃O₄. The higher H₂ conversion over the Co₃O₄ catalyst is caused by CO methanation, which takes place in parallel with H₂ oxidation. The formation of CH₄ was indeed observed from 200 °C (Figure 5e) only over the Co₃O₄ catalyst. This implied that the Co₃O₄ phase had been (partially) reduced to Co⁰, which is often reported as the active phase for CO methanation [7,10,11,14,16–18,49]. The presence of Co⁰ in the ex-Co₃O₄ catalyst was also consistent with the H₂-TPR results, which showed a relatively easier reduction of this catalyst due to having large starting Co₃O₄ crystallites (20.8 nm according to PXRD). Furthermore, based on post-run ex situ PXRD analysis (Figure 1b), the ex-Co₃O₄ catalyst consisted of the phases CoO, fcc Co⁰ and hcp Co⁰, while the other spent catalysts did not contain any metallic phase (Co- or Fe-based), which explains why these catalysts did not form CH₄.

3. Experimental Section

3.1. Catalyst Synthesis

The unsubstituted and Mg-substituted Fe- and Co-based oxide catalysts were synthesised via a co-precipitation method adopted from Fadlalla et al. [33]. In the case of $MgFe_2O_4$, a magnesium nitrate solution ($Mg(NO_3)_2$, Merck, (Darmstadt, Germany) 99%, Johannesburg, South Africa) and iron(III) nitrate solution (Fe(NO₃)₃.9H₂O, Merck, \geq 98%, Johannesburg, South Africa) were mixed in a Fe:Mg molar ratio of 2. The resulting mixture of the nitrate solutions (heated to near boiling) was added in one step to a sodium hydroxide solution (also heated to near boiling, NaOH, Merck, \geq 97%, 0.64 M, Johannesburg, South Africa) to initiate the precipitation process. The synthesis mixture was aged for 1 h at 95 °C, while magnetically stirred at 350 rpm, after which, the mixture was allowed to cool naturally to room temperature, and a black precipitate was recovered and washed repeatedly with double-distilled liquid H₂O until neutral pH (pH 7) was reached. The precipitate was then dried overnight at 120 °C, thereafter calcined at 450 °C for 5 h in stagnant air, with a heating rate of 1.5 °C/min. The Fe₃O₄, Co₃O₄, and MgCo₂O₄ were synthesised using the same procedure. However, in the case of Fe_3O_4 , a solution of iron(III) nitrate (Fe(NO₃)₃.9H₂O, Merck, ≥98%, Johannesburg, South Africa) and iron(II) chloride (FeCl₂, Merck, \geq 98, Johannesburg, South Africa), at a Fe³⁺/Fe²⁺ ratio of 2, was used.

3.2. Catalyst Characterisation

The influence of magnesium on the physicochemical properties of the Fe- and Cobased oxide structures was determined using powder X-ray diffraction (PXRD), nitrogen (N₂) physisorption, scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), and H₂ temperature-programmed reduction (H₂-TPR). The PXRD measurements were conducted in a Bruker D8 Advance Laboratory X-ray diffractometer (Bruker AXS, Karlsruhe, Germany) equipped with a LYNXEYE XE detector. The X-rays were generated from a Co source (K_{α1} = 0.178897 nm) and filtered with a Ni filter. The measurements were carried out using a step size of 0.018°, a time per scan of 0.02 s within a 20 range of 20–120°, giving a total analysis time of 35 min. Before the N₂ physisorption analysis, the samples (ca. 100 mg) were dried under vacuum at 150 °C overnight in a Micromeritics sample preparation (FlowPrep 060, Micromeritics, Atlanta, GA, USA) instrument. The surface area of the samples was measured at liquid nitrogen temperature, with N₂ as the adsorbate, and determined by the Brunauer–Emmett–Teller (BET) method [50].

For the SEM-EDS analysis, the samples were first placed on a copper grid coated with carbon, and then sample imaging was performed with a FEI Nova NanoSEM 230 instrument (FEI, Oregon, OR, USA) equipped with an Oxford X-Max detector.

A Micromeritics AutoChem 2920 instrument (Micromeritics, Atlanta, GA, USA) equipped with a thermal conductivity detector (TCD) was utilised to conduct the H₂-TPR analysis. The catalyst sample (ca. 0.05 g) was placed in a U-shaped quartz tube reactor between two pieces of quartz wool. The sample was heated to 120 °C for 1 h under a flow of pure Ar (50 mL (NTP)/min) to remove any physisorbed molecules on the catalyst surface and/or pores. Thereafter, the sample was cooled to 60 °C, followed by a change from Ar to 5% H₂ in Ar (50 mL (NTP)/min), after which, the temperature was raised from 60 to 920 °C at a rate of 10 °C/min. The consumption of H₂ was measured every 0.1 min during the temperature ramp from 60 to 920 °C.

3.3. CO-PrOx Catalyst Evaluation

The catalysts were evaluated under model/dry CO-PrOx conditions involving 1% CO, 1% O₂, 50% H₂ and 48% N₂ being flowed through a $\frac{1}{4}$ -inch U-shaped stainless steel fixed-bed reactor (Swagelok, Ohia, OH, USA) at atmospheric pressure. Although H₂O and CO₂ are also components of a typical CO-PrOx feed, these gases were not co-fed as their effects have been reported in our previous publications [16,17]. The mass of catalyst loaded in the reactor was 25 mg, which was diluted with 225 mg of mesoporous SiC (1 mm extrudates crushed below 150 µm (SiCAT, Germany)). The feed mixture was flowed through the diluted catalyst at 25 mL(NTP)/min, resulting in a gas-hourly space velocity (GHSV) of 60,000 mL(NTP)/g_{cat}/h. The reactor was heated from 50 to 250 °C at a rate of 1 °C/min, while holding the temperature every 25 °C for 60 min. The lower and upper limits of the reaction temperature represent the operating temperatures for the PEMFC (60–80 °C) and the LTWGS process (200–300 °C) [5,40,41].

The products of the reaction were analysed using on-line gas chromatography (GC) in a Varian CP-4900 micro-GC (Agilent Technologies, California, CA, USA) fitted with TCDs for analysing CO, O_2 , H_2 , CO_2 , CH_4 and N_2 in three different columns (i.e., two molecular sieve 5Å PLOT columns (20 m and 10 m long), and a PoraPLOT Q 10 m column). The water formed during the experiments could not be quantified as it was condensed in a cold trapping vessel (kept at room temperature) before the other gases were sampled by the micro-GC. The Varian Galaxie Chromatography Data System (version 1.9.3.2, Varian, California, CA, USA) was used to conduct the chromatographic analysis. The inlet and outlet flow rates of each gas were used to calculate the CO, O_2 and H_2 conversions (Equations (1)–(3), respectively), CO_2 and CH_4 yields (Equations (4) and (5), respectively) and O_2 selectivity to CO_2 (Equation (6)). From these equations and the knowledge of the reactions that can occur during CO-PrOx, the formation of water was inferred.

$$X_{CO} (\%) = \frac{v_{CO, in} - v_{CO, out}}{v_{CO, in}} \times 100 = \frac{v_{CO_2, out} + v_{CH_4, out}}{v_{CO, in}} \times 100$$
(1)

$$X_{O_2}(\%) = \frac{v_{O_2, in} - v_{O_2, out}}{v_{O_2, in}} \times 100 = \frac{0.5 \cdot [v_{CO_2, out} + v_{H_2, in} - v_{H_2, out} - (3 \cdot v_{CH_4, out})]}{v_{O_2, in}} \times 100$$
(2)

$$X_{H_2}(\%) = \frac{v_{H_2, in} - v_{H_2, out}}{v_{H_2, in}} \times 100 = \frac{2 \cdot (v_{O_2, in} - v_{O_2, out}) - v_{CO_2, out} + (3 \cdot v_{CH_4, out})}{v_{H_2, in}} \times 100$$
(3)

$$Y_{CO_2}(\%) = \frac{v_{CO_2, out}}{v_{CO, in}} \times 100 = \frac{v_{CO, in} - v_{CO, out} - v_{CH_4, out}}{v_{CO, in}} \times 100$$
(4)

$$Y_{CH_4}(\%) = \frac{v_{CH_4, out}}{v_{CO, in}} \times 100 = \frac{v_{CO, in} - v_{CO, out} - v_{CO_2, out}}{v_{CO, in}} \times 100$$
(5)

$$S_{O_2 \to CO_2}(\%) = \frac{v_{CO_2, out}}{2 \cdot (v_{O_2, in} - v_{O_2, out})} = \frac{v_{CO, in} - v_{CO, out} - v_{CH_4, out}}{v_{CO, in} - v_{CO, out} + v_{H_2, in} - v_{H_2, out} - (4 \cdot v_{CH_4, out})}$$
(6)

where X = conversion, Y = yield, S = selectivity and v = volumetric flow rate.

4. Summary and Conclusions

This study aimed at determining the effect of Mg on the physicochemical properties and catalytic performance of Fe- and Co-based oxide catalysts during CO-PrOx under model reaction conditions (i.e., with no H_2O or CO_2 being co-fed). Our results showed that Mg was successfully doped into the Fe- and Co-based oxides since only the reflexes of the targeted spinel structures were observed in the acquired PXRD patterns. The inclusion of Mg may have occurred via the substitution of the divalent ions (Fe²⁺ or Co²⁺) in each spinel structure.

Regarding CO-PrOx performance, the following observations were made: (i) the conversion of CO, O_2 and H_2 increased with an increase in reaction temperature, where the Co-based oxide catalysts exhibited higher conversions than the Fe-based oxide catalysts within the temperature window studied (i.e., 50–250 °C). (ii) The addition of Mg to the oxide spinel structures resulted in a decrease in the conversion of CO, O_2 and H_2 , however, (iii) the addition of Mg prevented CH₄ formation and minimized cobalt oxide reduction since CH₄ and Co⁰ formation were only observed for the Co₃O₄ catalyst. Furthermore, no CH₄ formation and metal oxide reduction were observed for the Fe-based oxide catalysts. Based on our current findings, we believe that Mg can be used to prevent/suppress the reduction of other (base) metal oxide catalysts and their propensity to produce CH₄ under CO-PrOx reaction conditions.

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