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## Co<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> catalysts studied *in situ* during the preferential oxidation of carbon monoxide: the effect of different TiO<sub>2</sub> polymorphs†

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Co<sub>3</sub>O<sub>4</sub> nanoparticles were supported on different TiO<sub>2</sub> polymorphs, namely, rutile, anatase, and a 15:85 mixture of rutile and anatase (also known as P25), via incipient wetness impregnation. The Co<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> catalysts were evaluated in the preferential oxidation of CO (CO-PrOx) in a H<sub>2</sub>-rich gas environment and characterised *in situ* using PXRD and magnetometry. Our results show that supporting Co<sub>3</sub>O<sub>4</sub> on P25 resulted in better catalytic performance, that is, a higher maximum CO conversion to CO<sub>2</sub> of 72.7% at 200 °C was achieved than on rutile (60.7%) and anatase (51.5%). However, the degree of reduction (DoR) of Co<sub>3</sub>O<sub>4</sub> to Co<sup>0</sup> was highest on P25 (91.9% at 450 °C), with no CoTiO<sub>3</sub> detected in the spent catalyst. The DoR of Co<sub>3</sub>O<sub>4</sub> was lowest on anatase (76.4%), with the presence of Ti<sub>x</sub>O<sub>y</sub>-encapsulated CoO<sub>x</sub> nanoparticles and bulk CoTiO<sub>3</sub> (13.8%) also confirmed in the spent catalyst. Relatively low amounts of CoTiO<sub>3</sub> (8.9%) were detected in the spent rutile-supported catalyst, while a higher DoR (85.9%) was reached under reaction conditions. The Co<sup>0</sup> nanoparticles formed on P25 and rutile existed in the fcc and hcp crystal phases, while only fcc Co<sup>0</sup> was detected on anatase. Furthermore, undesired CH<sub>4</sub> formation took place over the Co<sup>0</sup> present in the P25- and rutile-supported catalysts, while CH<sub>4</sub> was not formed over the Co<sup>0</sup> on anatase possibly due to encapsulation by Ti<sub>x</sub>O<sub>y</sub> species. For the first time, this study revealed the influence of different TiO<sub>2</sub> polymorphs (used as catalyst supports) on the chemical and crystal phase transformations of Co<sub>3</sub>O<sub>4</sub>, which in turn affect its activity and selectivity during CO-PrOx.

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## 1. Introduction

Titanium(IV) oxide (or titania, TiO<sub>2</sub>) is a highly versatile material with applications in the manufacture of paint, paper, and plastic products as a pigmentation agent.<sup>1</sup> It is also used by the cosmetics industry as a sun-blocking agent in

sunscreen products.<sup>2</sup> Owing to its excellent capability to absorb sunlight, TiO<sub>2</sub> has found great use as a photocatalyst, for example, to produce carbon-free hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>) *via* water (H<sub>2</sub>O) electrolysis.<sup>3,4</sup> In other catalysed reactions, TiO<sub>2</sub> is employed as a support material that anchors active nanoparticles to minimise their growth in size (*i.e.*, sintering) and loss of chemical phase (*e.g.*, *via* reduction or oxidation).<sup>5–9</sup>

Depending on the catalytic process, strong nanoparticle-support interactions (NPSI) may have a negative impact on the performance of the catalyst as the active phase can be lost through reacting with TiO<sub>2</sub> to form Ti-containing mixed metal oxides such as titanates.<sup>6,7,9</sup> For example, the formation of cobalt titanates (*e.g.*, CoTiO<sub>3</sub>) has been observed in the Fischer-Tropsch synthesis (FTS) when operating Co/TiO<sub>2</sub> catalysts under high synthesis gas conversion environments because of the high H<sub>2</sub>O:H<sub>2</sub> partial pressure ratios realised.<sup>10–12</sup> In other cases, the surface of TiO<sub>2</sub> can be partially reduced to form Ti<sub>x</sub>O<sub>y</sub> species that subsequently migrate and encapsulate the reduced Co particles due to the surface energy of TiO<sub>2</sub> (*e.g.*, anatase: 0.44 J m<sup>−2</sup>) being lower than that of metallic Co (*e.g.*, face-centred cubic (fcc) Co<sup>0</sup>: 2.6 J m<sup>−2</sup>).<sup>13–15</sup> The encapsulation can also lead to the formation of cobalt titanates.<sup>7,10,16</sup>

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There are three well reported crystal forms or polymorphs of  $\text{TiO}_2$ , namely, rutile, anatase, and brookite. Rutile is the most stable of all the three polymorphs and can be produced in pure bulk form typically at high temperatures (600–800 °C) from either anatase or brookite.<sup>17</sup> Rutile and anatase are the widely utilised forms of  $\text{TiO}_2$  in the industries/fields mentioned earlier, and the application can either involve the pure form of one of the polymorphs or a mixture of both polymorphs. Owing to their different physical properties (such as surface area and porosity) and differences in the arrangement of atoms in their respective crystal lattices, the behaviours of rutile and anatase may also differ.<sup>1,18</sup>

For example, anatase is generally considered a better photocatalyst than rutile because of its greater charge transfer capability.<sup>19,20</sup> On the other hand, rutile-supported Co catalysts often exhibit a superior catalytic performance than that of their anatase-supported counterparts in the FTS.<sup>21,22</sup> The lower activity of anatase-supported Co catalysts may be caused by the encapsulation and/or loss of active Co *via* cobalt titanate formation, both of which are kinetically and thermodynamically more facile in  $\text{H}_2\text{O}-\text{H}_2$  environments when anatase is used as the support.<sup>10–12</sup> However, some researchers have reported improved catalytic performance when a mixture of rutile and anatase is employed, which has given rise to the wide range of nano-sized rutile–anatase mixtures being applied in various catalytic processes in recent years.<sup>4,21</sup>

In this study, we have supported cobalt(II,III) oxide ( $\text{Co}_3\text{O}_4$ ) nanoparticles *via* incipient wetness impregnation on rutile, anatase, and the commercially available mixture of rutile and anatase (at a 15:85 ratio) called “P25” (from Evonik Industries). The three supported catalysts were evaluated for activity, selectivity, and phase stability in the preferential oxidation of carbon monoxide (CO-PrOx) in a  $\text{H}_2$ -rich gas environment. CO-PrOx is an essential  $\text{H}_2$  ‘clean-up’ process that helps remove the trace amounts of CO (0.5–2%) that adsorb and deactivate the Pt-containing anode catalyst of proton-exchange membrane fuel cells (PEMFCs).<sup>23,24</sup>  $\text{Co}_3\text{O}_4$  is generally regarded as the most active phase of Co in the context of CO oxidation and CO-PrOx, which take place *via* the Mars–van Krevelen (MvK) mechanism.<sup>25,26</sup> Therefore, the loss of this oxide phase through reduction by the abundant  $\text{H}_2$  (40–75%) decreases the carbon dioxide ( $\text{CO}_2$ ) yield and selectivity in CO-PrOx. Moreover, the ultimate formation of  $\text{Co}^0$  changes the conversion pathway of CO from oxidation to hydrogenation, which produces undesired methane ( $\text{CH}_4$ ).<sup>27–33</sup>

Our previous study reported the effect of different support materials (*viz.*,  $\text{CeO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SiC}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$ ) on the performance and phase stability of  $\text{Co}_3\text{O}_4$  nanoparticles during CO-PrOx.<sup>32</sup> More specifically, we proposed that weak NPSI (*e.g.*, in  $\text{Co}_3\text{O}_4/\text{ZrO}_2$ ) allow for high  $\text{CO}_2$  yields to be achieved *via* the MvK mechanism, which relies on the high surface reducibility (and re-oxidation) of the nanoparticles. However, the weak NPSI

do not help stabilise the  $\text{Co}_3\text{O}_4$  phase against surface and bulk reduction as  $\text{Co}^0$  (and associated  $\text{CH}_4$ ) is formed at relatively low temperatures. On the other hand, strong NPSI (*e.g.*, in  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ ) helped stabilise the cobalt oxide phase and consequently limited  $\text{CH}_4$  formation. However, we further showed that a less reducible catalyst is less active for CO oxidation because the MvK cycle becomes kinetically hindered.

To the best of our knowledge, there has not been a study reporting the effect of different  $\text{TiO}_2$  polymorphs on the catalytic performance and phase stability of Co-based catalysts in the CO-PrOx reaction. Therefore, our current work involves the performance evaluation of  $\text{Co}_3\text{O}_4/\text{TiO}_2$  catalysts (where  $\text{TiO}_2$  = P25, rutile, or anatase) coupled with their *in situ* characterisation using powder X-ray diffraction (PXRD)<sup>34–36</sup> and magnetometry<sup>36,37</sup> during CO-PrOx. For the first time, we report a dependence of the catalytic performance of  $\text{Co}_3\text{O}_4$  on the polymorph of  $\text{TiO}_2$  used as the support. Furthermore, our *in situ* studies showed that certain chemical and crystallographic phase changes of  $\text{Co}_3\text{O}_4$  (leading to  $\text{CoO}$ ,  $\text{CoTiO}_3$ , fcc and/or hcp (hexagonal close-packed)  $\text{Co}^0$ ) may also be dependent on the type of  $\text{TiO}_2$  polymorph.

## 2. Experimental

### 2.1. Catalyst preparation

In the subsequent sections of the paper, the bare  $\text{TiO}_2$  supports used are referred to as “P25”, “rutile”, and “anatase”, while the  $\text{Co}_3\text{O}_4$ -loaded supports are referred to as “ $\text{Co}_3\text{O}_4/\text{P25}$ ”, “ $\text{Co}_3\text{O}_4/\text{rutile}$ ”, and “ $\text{Co}_3\text{O}_4/\text{anatase}$ ”.

The supported catalysts for this study were prepared *via* the incipient wetness impregnation of pre-calcined (300 °C) P25 (99.5% purity, Evonik Industries), rutile (99.5% purity, Merck), and anatase (99.7% purity, Merck) with an aqueous solution containing 1.2 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (reagent grade 98% purity, Merck) for every 1 mL of deionised water. The impregnated supports were dried overnight at 60 °C under a flow of nitrogen ( $\text{N}_2$ , 50 mL(NTP)  $\text{min}^{-1}$ ) and annealed for 60 min at 350 °C (heating rate: 2 °C  $\text{min}^{-1}$ ) under the same gas flow at atmospheric pressure<sup>38</sup> in a glass tube (I.D.: 15 mm, length: 240 mm; Lasec SA). In the case of rutile, two impregnation steps were conducted to achieve the targeted  $\text{Co}_3\text{O}_4$  loading of 10 wt% as this support had a low pore volume of 0.12  $\text{cm}^3 \text{g}^{-1}$  (Table 1). The calcined material obtained after the first impregnation was used for the second impregnation.

The bare support materials as well as the fresh and spent  $\text{TiO}_2$ -supported  $\text{Co}_3\text{O}_4$  catalysts were characterised *ex situ* using PXRD, scanning transmission electron microscopy coupled with electron energy loss spectroscopy (STEM-EELS),  $\text{N}_2$  physisorption, inductively coupled plasma-optical emission spectroscopy (ICP-OES), and X-ray absorption spectroscopy (XAS). The details pertaining to these *ex situ* techniques can be found under the section “*ex situ* catalyst characterisation” in the ESL.<sup>†</sup>

Table 1 *Ex situ* characterisation results for the fresh supported catalysts

Sample name	$d_{\text{PXRD}}^a$ (nm)	$d_{\text{STEM,v}}^b$ (nm)	$d_{\text{STEM,n}}^c$ (nm)	MSSA <sup>d</sup> ( $\text{m}^2 \text{g}^{-1}$ )	$v_{\text{pore}}^d$ ( $\text{cm}^3 \text{g}^{-1}$ )	Relative fraction of $\text{Co}_3\text{O}_4$ <sup>a</sup> (wt%)	$\text{Co}_3\text{O}_4$ loading <sup>e</sup> (wt%)
$\text{Co}_3\text{O}_4/\text{P25}$	$11.8 \pm 0.3$	$14.2 \pm 4.6$	$9.9 \pm 3.7$	$37.0$ (48.7)	0.19 (0.21)	$10.3 \pm 0.3$	9.4
$\text{Co}_3\text{O}_4/\text{rutile}$	$14.7 \pm 0.3$	$15.5 \pm 3.8$	$13.0 \pm 3.3$	$23.7$ (26.6)	0.08 (0.12)	$10.3 \pm 0.5$	9.8
$\text{Co}_3\text{O}_4/\text{anatase}$	$9.8 \pm 0.2$	$16.6 \pm 3.9$	$13.3 \pm 3.9$	$73.5$ (97.6)	0.23 (0.28)	$8.5 \pm 0.3$	9.9

<sup>a</sup> Average volume-based crystallite size and relative weight fraction (with associated errors) of  $\text{Co}_3\text{O}_4$ . <sup>b</sup> Average volume-based particle size and standard deviation. <sup>c</sup> Average number-based particle size and standard deviation. <sup>d</sup> Values in parentheses are for the corresponding bare support. <sup>e</sup> Calculated based on the concentration of Co determined using ICP-OES.

## 2.2. *In situ* catalyst characterisation and evaluation

**2.2.1. Reduction studies.** The reduction of the bare supports and supported  $\text{Co}_3\text{O}_4$  catalysts (*ca.* 0.012 g each) was performed at atmospheric pressure under a gas flow of 50%  $\text{H}_2$  in  $\text{N}_2$  (1.2 mL(NTP)  $\text{min}^{-1}$ ) in an in-house developed PXRD capillary-based reaction cell.<sup>34–36</sup> Reduction studies were also performed *via* conventional  $\text{H}_2$  temperature-programmed reduction (H<sub>2</sub>-TPR) under a flow of 5%  $\text{H}_2$  in Ar (50 mL(NTP)  $\text{min}^{-1}$ ) at atmospheric pressure using a sample of approximately 0.1 g. The experimental procedures for the PXRD-based reduction and H<sub>2</sub>-TPR studies, as well as the details for the data analysis can be found under the section “*in situ* catalyst characterisation” in the ESI.<sup>†</sup>

**2.2.2. Catalyst evaluation during CO-PrOx.** The bare supports and prepared catalysts were evaluated under model/dry CO-PrOx conditions (feed composition: 1% CO, 1%  $\text{O}_2$ , 50%  $\text{H}_2$ , and 48%  $\text{N}_2$ ) at atmospheric pressure in the PXRD reaction cell mentioned earlier and in an in-house developed *in situ* sample magnetometer.<sup>36,37</sup> We note that the evaluation of the bare supports did not involve *in situ* characterisation as the supports were not expected to undergo (bulk) phase changes and are not ferromagnetic (also see sections 3.2.1. and 3.3.). Furthermore, the reaction gas feed did not contain  $\text{H}_2\text{O}$  and  $\text{CO}_2$  as the effects of these gases have been reported in our previous publications.<sup>31,32</sup> The procedures followed for analysing the data obtained from the *in situ* techniques are detailed under the section “*in situ* catalyst characterisation” in the ESI.<sup>†</sup>

The magnetometer enables the detection of  $\text{Co}^0$  (with no distinction between fcc and hcp  $\text{Co}^0$ ) as it is the only ferromagnetic Co-based phase<sup>39</sup> among those that can be formed in the current study (*e.g.*,  $\text{Co}_3\text{O}_4$ ,  $\text{CoO}$ , and  $\text{CoTiO}_3$ ). However, the magnetometer is highly sensitive as very small amounts of  $\text{Co}^0$  (*ca.* 0.23 mg, which is equivalent to 0.1 wt% in this study) can be detected,<sup>30</sup> while PXRD requires relative amounts of  $\text{Co}^0$  (and of the other phases, *viz.*,  $\text{Co}_3\text{O}_4$ ,  $\text{CoO}$ , and  $\text{CoTiO}_3$ ) that are above 2–3 wt% for adequate detection.

The PXRD capillary reactor was loaded with approximately 0.012 g of catalyst each time, and while the magnetometry reactor was loaded with approximately 0.26 g. The reactors were heated from 50 to 450 °C at a rate of 1 °C  $\text{min}^{-1}$  while holding the temperature at every 25 °C for 60 min. The reaction feed was flowed at 1.2 mL(NTP)  $\text{min}^{-1}$  in the PXRD-based experiments and 25 mL(NTP)  $\text{min}^{-1}$  in the

magnetometry-based experiments to achieve a gas-hourly space velocity (GHSV) of 60 000 mL(NTP)  $\text{g}_{\text{Co}_3\text{O}_4}^{-1} \text{h}^{-1}$ , which is based on the  $\text{Co}_3\text{O}_4$  loadings determined using ICP-OES (Table 1).

The reactor effluent gas from the CO-PrOx experiments was sampled on-line every 5 min using a Varian CP-4900 micro-GC (Agilent) fitted with thermal conductivity detectors for detecting CO,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2$  in three different columns (see Table S1<sup>†</sup> for the identity of the columns and full set of parameters applied to achieve gas separation). The chromatographic analysis was operated using the Varian Galaxie Chromatography Data System (version 1.9.3.2). The relevant peak areas in each chromatogram were used to calculate the volumetric flow rates of each eluting gas using eqn (S1) and (S2).<sup>†</sup> The volumetric flow rates were subsequently used to calculate normalised gas outlet flow rates (eqn (S3)<sup>†</sup>), conversions/yields (eqn (S4) and (S5)<sup>†</sup>), and selectivities (eqn (S6)<sup>†</sup>). The formation of  $\text{H}_2\text{O}$  was inferred based on the results obtained using the abovementioned equations because  $\text{H}_2\text{O}$  could not be analysed in the micro-GC due to its prior condensation in a cold trapping vessel.

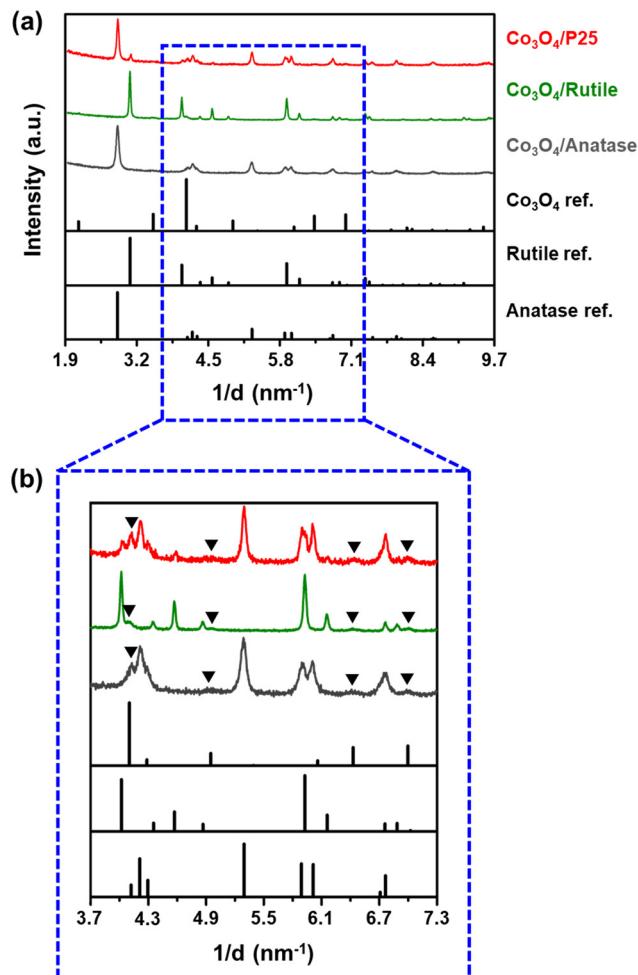
## 3. Results and discussion

### 3.1. *Ex situ* characterisation of fresh catalysts

Various *ex situ* characterisation techniques (*viz.*, PXRD, STEM-EELS,  $\text{N}_2$  physisorption, and ICP-OES) were employed to determine the physicochemical properties of the bare supports and fresh supported  $\text{Co}_3\text{O}_4$  catalysts. As mentioned earlier, the support material “P25” contains the rutile and anatase polymorphs at a 15:85 ratio, which was confirmed using Rietveld refinement in the TOPAS 5.0 software package<sup>40</sup> (see results in Fig. S3 and Table S3<sup>†</sup>). Additionally, this composition is qualitatively shown in the STEM-EELS Ti map of the bare P25 support (Fig. S4<sup>†</sup>), where the method ELNES (energy loss near edge structure) was used to distinguish the areas with rutile from those with anatase.

The diffraction patterns of the fresh catalysts are shown in Fig. 1 and those of the bare supports can be found in Fig. S5.<sup>†</sup> Despite the crystalline nature of the three supports used, most of the reflections from the  $\text{Co}_3\text{O}_4$  phase are visible in the diffraction patterns shown in Fig. 1(b) and do not overlap with those from the support materials. The presence of  $\text{CoTiO}_3$  was also considered (either





**Fig. 1** (a) PXRD patterns (radiation source:  $\text{Co K}\alpha_1 = 0.178897 \text{ nm}$ ) of the fresh supported catalysts and the reference reflection lines of  $\text{Co}_3\text{O}_4$ , rutile, and anatase as recorded in the ICDD PDF-2 database (see Table S2† for their PDF entry numbers). (b) Magnified short  $1/d$  range of the recorded PXRD patterns for clarity of the  $\text{Co}_3\text{O}_4$  reflections. The black triangles indicate the identified  $\text{Co}_3\text{O}_4$  reflections in each diffraction pattern.

with a cubic or rhombohedral crystal structure) but no reflections from this phase can be observed in the acquired diffraction patterns (Fig. S6†). Based on Rietveld refinement, the average volume-based crystallite sizes of  $\text{Co}_3\text{O}_4$  in the P25-, rutile-, and anatase-supported catalysts are  $11.8 \pm 0.3 \text{ nm}$ ,  $14.7 \pm 0.3 \text{ nm}$ , and  $9.8 \pm 0.2 \text{ nm}$ , respectively, while the relative weight fractions of  $\text{Co}_3\text{O}_4$  in each catalyst are  $10.3 \pm 0.3 \text{ wt\%}$ ,  $10.3 \pm 0.5 \text{ wt\%}$ , and  $8.5 \pm 0.3 \text{ wt\%}$ , respectively. It is worth noting that the relative weight fractions of  $\text{Co}_3\text{O}_4$  for the P25- and rutile-supported catalysts are close to 10 wt%, which is the targeted loading in this study. The low  $\text{Co}_3\text{O}_4$  weight fraction for the anatase-supported catalyst is likely a result of the excessive overlap of the  $\text{Co}_3\text{O}_4$  and anatase reflections. This excessive overlap causes the  $\text{Co}_3\text{O}_4$  reflections to be less visible, leading to a lower  $\text{Co}_3\text{O}_4$  weight fraction being estimated using Rietveld refinement. Other Rietveld refinement results,

based on the diffraction patterns in Fig. 1 (e.g., the fitted phases and  $R_{\text{wp}}$  values), can be found in Fig. S7 and Table S4.†

Bright-field STEM micrographs, corresponding Co maps (generated based on the Co L-edge), and derived number-based size distributions for each catalyst are shown in Fig. 2. The Co maps generally show a good distribution of the  $\text{Co}_3\text{O}_4$  particles over the various supports, but with some clustered particles also identifiable. For particle size analysis, only the Co-bearing entities that appear as single particles were measured to obtain number-based size distributions as well as average number- and volume-based particle sizes (see eqn (S8)–(S11)† and the results in Table 1). The average  $\text{Co}_3\text{O}_4$  particles sizes (on a number and volume basis) vary within a narrow range of approximately 3 nm among the three catalysts prepared, and the STEM-derived volume-based sizes are larger than the PXRD-derived volume-based sizes. This could indicate the presence of smaller  $\text{Co}_3\text{O}_4$  crystalline domains (detected using PXRD) that constitute the larger particles identified using STEM-EELS.<sup>41</sup>

The BET (Brunauer–Emmett–Teller) surface areas and BJH (Barrett–Joyner–Halenda) pore volumes of the bare and  $\text{Co}_3\text{O}_4$ -loaded supports are shown in Table 1. The surface areas and pore volumes of the supports decrease after supporting  $\text{Co}_3\text{O}_4$ , which is often observed with supported catalysts prepared using incipient wetness impregnation (as in the current study).<sup>32,42</sup> The decrease in the pore volume may indicate the presence of (most of the)  $\text{Co}_3\text{O}_4$  particles in the pores of each support. The ICP-OES-derived Co loading (in the form of  $\text{Co}_3\text{O}_4$ ) in each catalyst is close to the targeted 10 wt% loading and in agreement with the  $\text{Co}_3\text{O}_4$  relative weight fractions calculated using Rietveld refinement, especially for  $\text{Co}_3\text{O}_4/\text{P25}$  and  $\text{Co}_3\text{O}_4/\text{rutile}$  (Table 1).

### 3.2. *In situ* reduction studies

**3.2.1. PXRD-based reduction.** The reducibility of the fresh  $\text{TiO}_2$ -supported catalysts was studied under a flow of 50%  $\text{H}_2$  in  $\text{N}_2$  at atmospheric pressure between 50 and 450 °C. This was coupled with *in situ* PXRD measurements taken every 5 min (or every 5 °C) throughout each experiment. The recorded diffraction patterns are plotted in Fig. 3(a) and 4(a) as a function of temperature but showing the on-top view of the diffraction patterns to allow for better visualisation of the appearing and disappearing reflections. Rietveld refinement was applied to calculate the relative weight fraction (Fig. 3(b) and 4(b)) and average crystallite size (Fig. 3(c) and 4(c)) of each Co-based phase formed. The weight fractions reported are on a Co basis, that is, the weight fraction of the support is not reported in each case.

It can be observed that the  $\text{Co}_3\text{O}_4$  crystallites supported on P25 and rutile reduce to  $\text{CoO}$  at 205 °C, while on anatase, this reduction step is first observed at 230 °C. Based on Rietveld refinement, the starting  $\text{Co}_3\text{O}_4$  crystallites supported on anatase have a smaller size than those supported on rutile

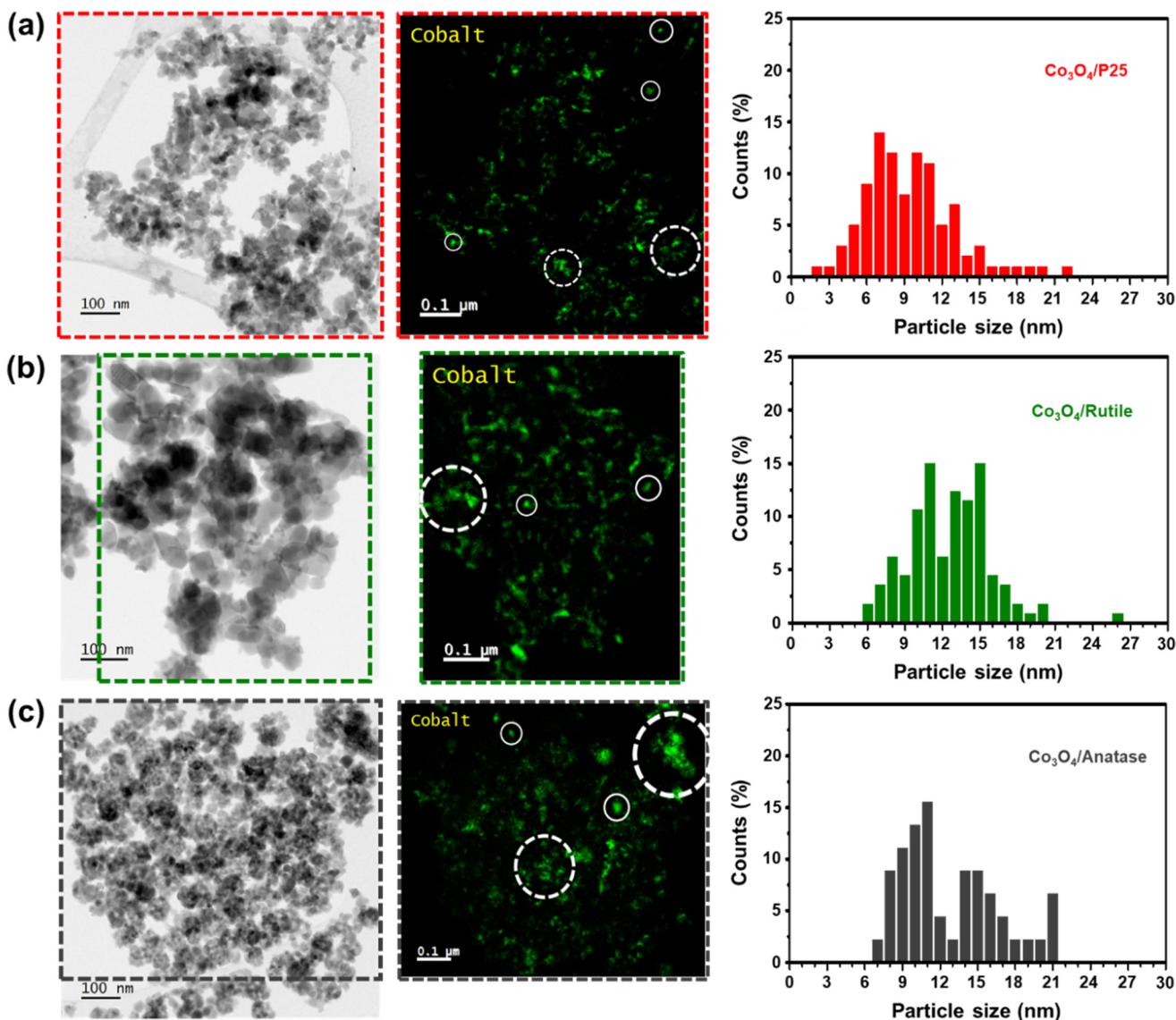


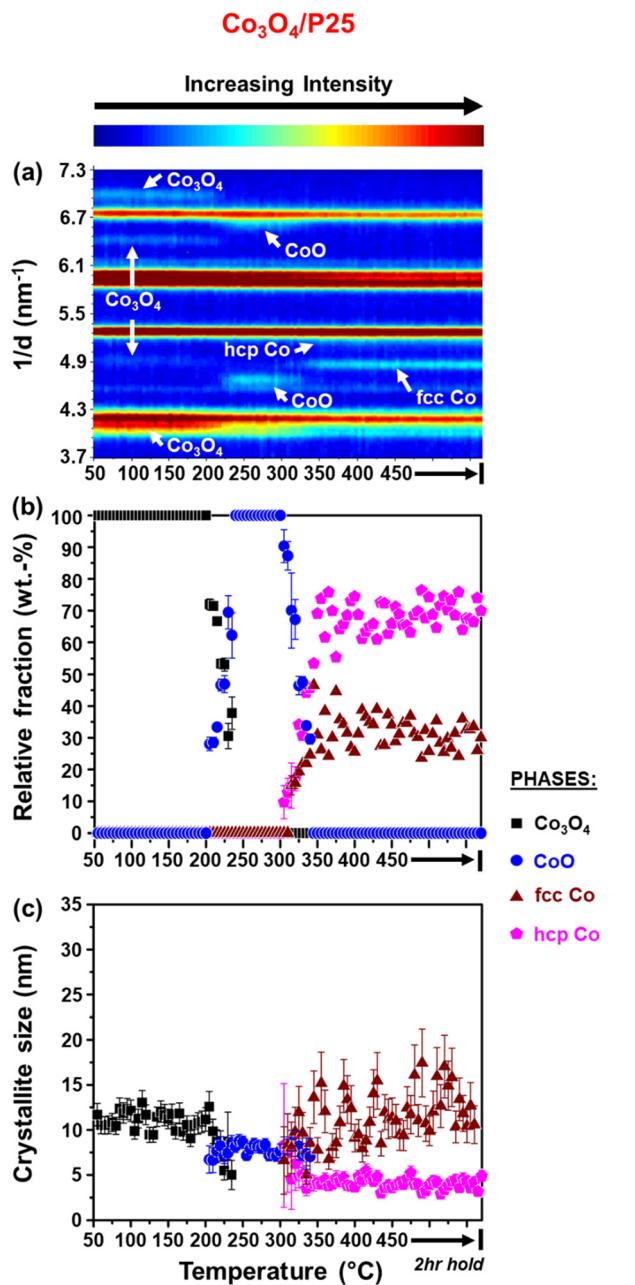
Fig. 2 (Left) Selected bright-field STEM micrographs of the fresh catalysts (a)  $\text{Co}_3\text{O}_4/\text{P25}$ , (b)  $\text{Co}_3\text{O}_4/\text{rutile}$ , and (c)  $\text{Co}_3\text{O}_4/\text{anatase}$ . (Middle) Corresponding STEM-EELS Co maps (generated based on the Co L-edge) showing the location of Co-bearing particles/clusters. (Right) Derived number-based size distributions. The solid white circles in the Co maps indicate the ‘single’ Co-bearing particles and the dashed white circles indicate ‘clusters’ of Co-bearing particles.

and P25 (Table 1 as well as Fig. 3(c) and 4(c)), which might explain their delayed reduction.<sup>43–45</sup> This may be further enhanced by the existence of stronger NPSI between  $\text{Co}_3\text{O}_4$  and anatase.<sup>7,10,16,21,22</sup> In general, the CoO crystallites formed are either similar (in the case of  $\text{Co}_3\text{O}_4/\text{anatase}$ ) or smaller than the starting  $\text{Co}_3\text{O}_4$  crystallites (as in the case of  $\text{Co}_3\text{O}_4/\text{P25}$  and  $\text{Co}_3\text{O}_4/\text{rutile}$ ), which indicates minimal or no sintering. The CoO crystallites supported on rutile reduce at 285 °C to fcc  $\text{Co}^0$  only, while the CoO crystallites on P25 and anatase reduce later at 305 °C to fcc and hcp  $\text{Co}^0$  (also see Fig. S8† for further evidence of hcp  $\text{Co}^0$  formation).

The formation of fcc  $\text{Co}^0$  only or both fcc and hcp  $\text{Co}^0$  during the reduction of cobalt oxides is common and may be influenced by the starting crystallite size (or size distribution) of cobalt oxide among other things.<sup>46</sup> Pure hcp  $\text{Co}^0$  is

thermodynamically stable above 20 nm, while fcc  $\text{Co}^0$  is stable below 20 nm.<sup>47,48</sup> In this study, the metallic crystallites formed on P25 and anatase are generally smaller than 20 nm (Fig. 3(c) and 4(c)), with the size of hcp  $\text{Co}^0$  (<5 nm) being smaller than that of fcc  $\text{Co}^0$ . It can also be seen that the fcc  $\text{Co}^0$  crystallites are larger than the starting  $\text{Co}_3\text{O}_4$  crystallites, especially on the anatase support. There is a possibility that the metallic crystallites on P25 and anatase are composed of (partially) intergrown domains of fcc and hcp  $\text{Co}^0$ , which may help stabilise the small hcp  $\text{Co}^0$  crystallites. Although the existence of intergrowth could not be confirmed using Rietveld refinement, this has been reported as a possible phenomenon by other researchers.<sup>31,46,49</sup>

We note that there is some degree of scatter in the Rietveld refinement data obtained for the co-existing fcc



**Fig. 3** (a) On-top view of the *in situ* PXRD patterns (X-ray source: Mo  $\text{K}\alpha_1 = 0.07093 \text{ nm}$ ) recorded during the reduction of  $\text{Co}_3\text{O}_4/\text{P25}$  (gas composition: 50%  $\text{H}_2$  and 50%  $\text{N}_2$ ; pressure: atmospheric; GHSV: 60 000 mL(NTP)  $\text{g}_{\text{Co}_3\text{O}_4}^{-1} \text{ h}^{-1}$ ). (b) Relative weight fractions (with error bars) and (c) average crystallite sizes (with error bars) of the different Co-based phases detected (excluding the support).

and hcp  $\text{Co}^0$  crystallites on P25 (Fig. 3(a) and (b)) and anatase (Fig. 4(a) and (b), right). This might be due to the inability to account for the possible (partial) intergrowth of the two  $\text{Co}^0$  allotropes.<sup>31</sup> Furthermore, there is extensive overlap between the PXRD reflections of anatase, rutile (in P25), as well as fcc and hcp  $\text{Co}^0$ , which could also contribute to the scatter in the data. Nonetheless, for the P25- and anatase-supported catalysts, the relative fraction of hcp  $\text{Co}^0$  is higher than that of fcc  $\text{Co}^0$ , with both catalysts exhibiting similar

average hept:fcc  $\text{Co}^0$  ratios at 450 °C (*i.e.*, 2.3 for  $\text{Co}_3\text{O}_4/\text{P25}$  and 1.8 for  $\text{Co}_3\text{O}_4/\text{anatase}$ ).

**3.2.2. Conventional  $\text{H}_2$ -TPR.**  $\text{H}_2$ -TPR experiments were also performed to study the reduction behaviour of the prepared catalysts and bare supports between 60 and 920 °C, and the results obtained are presented in Fig. 5(a). The  $\text{Co}_3\text{O}_4$  particles supported on P25 and rutile start reducing at a lower temperature (180 °C) than the particles supported on anatase (260 °C). This reduction trend is in line with the observations made during the PXRD-based reduction studies despite the differences in onset temperatures, which may be caused by the different experimental conditions applied (*e.g.*, different heating rates and concentrations of  $\text{H}_2$  – see the section “*in situ* catalyst characterisation” in the ESI†).

The reduction profile of each catalyst displays multiple peaks between 200 and 660 °C, with some of the peaks appearing as broad and convoluted. Nonetheless, the P25- and rutile-supported catalysts may have undergone a stepwise reduction where  $\text{Co}_3\text{O}_4$  first reduces to  $\text{CoO}$ , and then  $\text{CoO}$  reduces to  $\text{Co}^0$ .<sup>5,8,45,50</sup> The peak maxima at 270 °C for  $\text{Co}_3\text{O}_4/\text{rutile}$  and 280 °C for  $\text{Co}_3\text{O}_4/\text{P25}$  may be assigned to the formation of  $\text{CoO}$ . The temperature ranges of 300–540 °C for  $\text{Co}_3\text{O}_4/\text{rutile}$  and 320–450 °C for  $\text{Co}_3\text{O}_4/\text{P25}$  possibly represent the reduction to  $\text{Co}^0$ . However, the broad and convoluted nature of the reduction peaks in these temperature ranges may also suggest other contributing factors, such as particle size (or size distribution). In other words, different size  $\text{CoO}$  particles may be reducing at different temperatures, with larger particles reducing earlier.<sup>28,43,44</sup> It is also possible that some smaller  $\text{Co}_3\text{O}_4$  particles reduce within the abovementioned temperature ranges, and not below 300 °C.

The reduction profile of  $\text{Co}_3\text{O}_4/\text{anatase}$  displays a small peak maximum at 300 °C possibly due to the reduction of a small amount of large  $\text{Co}_3\text{O}_4$  particles. Between 330 and 490 °C,  $\text{Co}_3\text{O}_4/\text{anatase}$  also exhibits a broad reduction peak, which may be assigned to the reduction of relatively smaller  $\text{Co}_3\text{O}_4$  particles to form metallic  $\text{Co}$ .<sup>21,22</sup> There may be some other  $\text{CoO}_x$  or  $\text{Co}_x\text{Ti}_y\text{O}_z$  species reducing between 500 and 660 °C (Fig. 5(a) and S9†) due to the existence of strong NPSI in this catalyst. The *in situ* formation of  $\text{Co}_x\text{Ti}_y\text{O}_z$  could have been facilitated by the partial surface reduction of anatase, followed by the migration and reaction of  $\text{Ti}_x\text{O}_y$  with  $\text{CoO}_x$  species.<sup>7,10,16</sup> Fig. 5(b) shows a partial reduction of the bare anatase support (possibly occurring in two steps) between 220 and 730 °C as well as 730 and 920 °C, unlike the bare P25 and rutile supports. However, the  $\text{H}_2$  consumption of the bare anatase is almost negligible when compared with that of the supported  $\text{Co}_3\text{O}_4$  catalysts (Fig. 5(a)). The degree of reduction (DoR) to  $\text{Co}^0$  of each supported  $\text{Co}_3\text{O}_4$  catalyst was calculated using eqn (S12)–(S14)† and the results are presented in Table 2. The DoR trend is as follows:  $\text{Co}_3\text{O}_4/\text{P25}$  (92.5%) >  $\text{Co}_3\text{O}_4/\text{rutile}$  (90.3%) >  $\text{Co}_3\text{O}_4/\text{anatase}$  (85.5%), which suggests a higher proportion of unreduced Co-based oxides on the anatase support, likely due to the existence of strong NPSI.

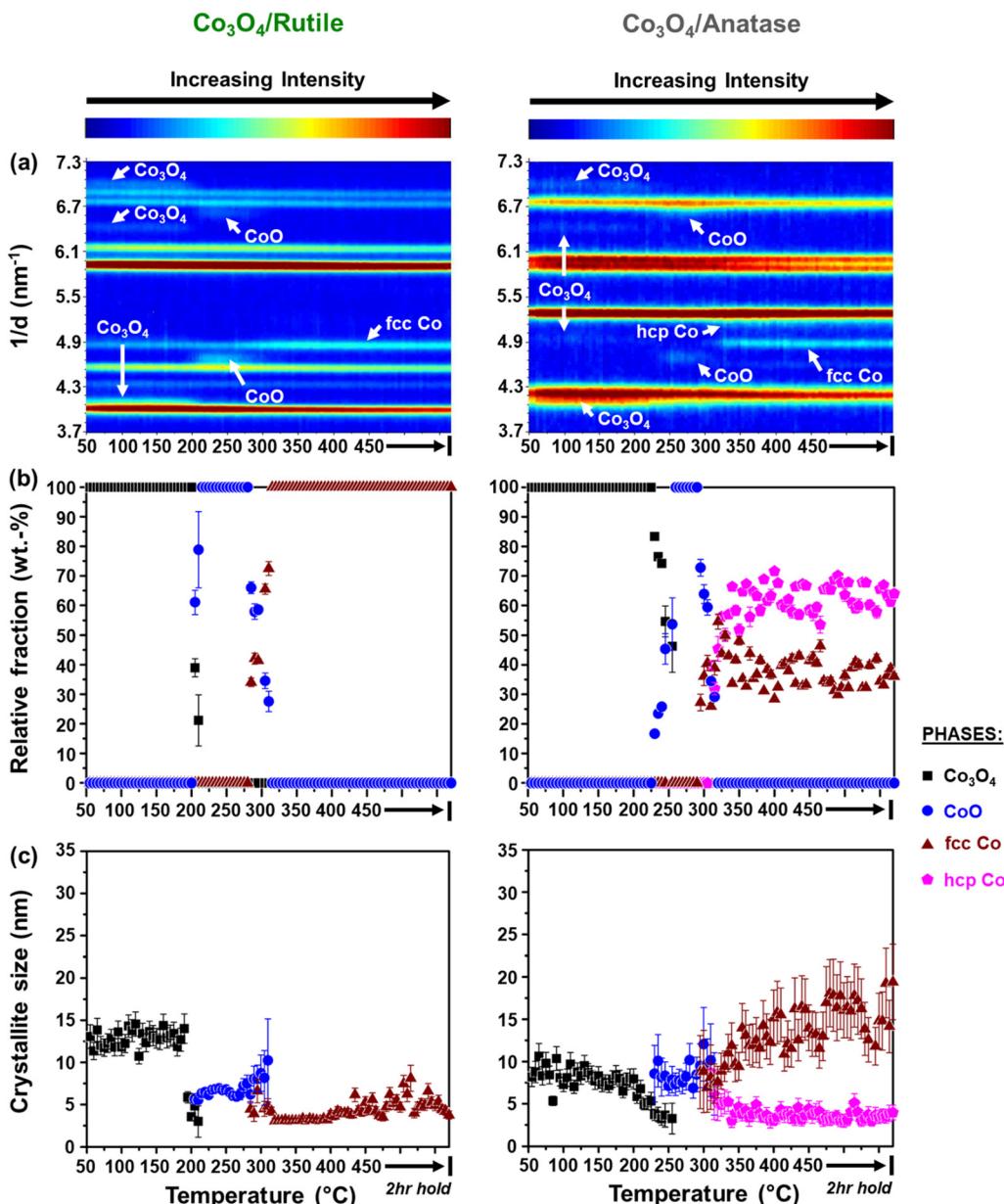


Fig. 4 (a) On-top view of the *in situ* PXRD patterns (X-ray source:  $\text{Mo K}\alpha = 0.07093 \text{ nm}$ ) recorded during the reduction of (left)  $\text{Co}_3\text{O}_4$ /rutile and (right)  $\text{Co}_3\text{O}_4$ /anatase (gas composition: 50%  $\text{H}_2$  and 50%  $\text{N}_2$ ; pressure: atmospheric; GHSV:  $60\,000 \text{ mL(NTP)} \text{ g}_{\text{Co}_3\text{O}_4}^{-1} \text{ h}^{-1}$ ). (b) Relative weight fractions (with error bars) and (c) average crystallite sizes (with error bars) of the different Co-based phases detected (excluding the supports).

### 3.3. *In situ* catalyst characterisation and evaluation

The activity and selectivity of the  $\text{TiO}_2$ -supported catalysts were evaluated under model/dry  $\text{CO-PrOx}$  conditions, which involved co-feeding 1%  $\text{CO}$ , 1%  $\text{O}_2$ , 50%  $\text{H}_2$ , and 48%  $\text{N}_2$  at a GHSV of  $60\,000 \text{ mL(NTP)} \text{ g}_{\text{Co}_3\text{O}_4}^{-1} \text{ h}^{-1}$ . The temperature was varied stepwise between 50 and 450 °C at atmospheric pressure while analysing the reactor effluent gas using online gas chromatography. Furthermore, the catalysts were characterised *in situ* using PXRD and magnetometry to monitor their chemical and crystallographic phase changes. Fig. 6(a) and 7(a) show the calculated relative weight fractions of the Co-based crystalline phases detected using PXRD, and

Fig. 6(b) and 7(b) show the crystallite sizes of the detected phases as a function of temperature for all three catalysts. The recorded diffraction patterns are plotted in Fig. S10.† Fig. 6(c) and 7(c) display the normalised gas outlet flow rates of  $\text{CO}$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ ; while Fig. 8(a)–(c) display a summary of the  $\text{CO}$  conversion to  $\text{CO}_2$  ( $X_{\text{CO-}\text{CO}_2}$ ),  $\text{O}_2$  selectivity to  $\text{CO}_2$  ( $S_{\text{O}_2-\text{CO}_2}$ ), and  $\text{CO}$  conversion to  $\text{CH}_4$  ( $X_{\text{CO-}\text{CH}_4}$ ), respectively. The magnetometry-derived DoR of  $\text{Co}_3\text{O}_4$  to  $\text{Co}^0$  is plotted in Fig. 6(d), 7(d), and 8(d) for all evaluated catalysts. The DoR was calculated using eqn (S15),† which is based on an instrument calibration curve (Fig. S2†). The  $X_{\text{CO-}\text{CO}_2}$  and  $X_{\text{CO-}\text{CH}_4}$  values for the bare  $\text{TiO}_2$  supports can be found in Fig. S11.†



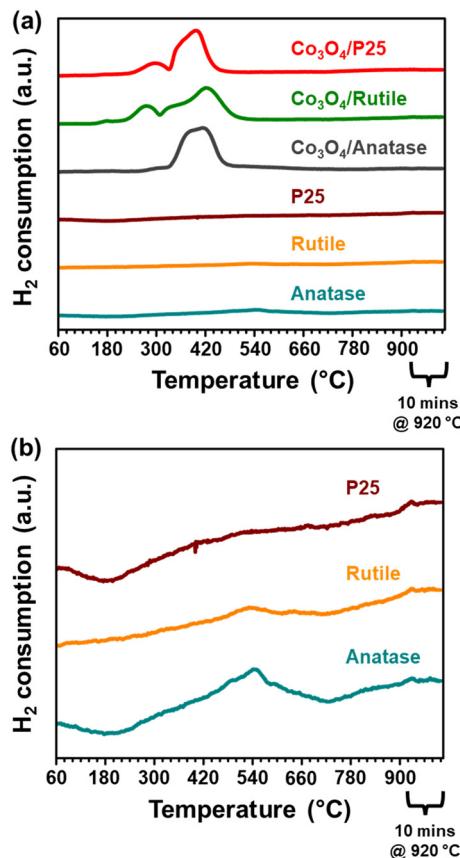


Fig. 5 Reduction profiles of the (a) Co<sub>3</sub>O<sub>4</sub>-loaded and bare TiO<sub>2</sub> support materials derived from H<sub>2</sub>-TPR performed in a 5:95 H<sub>2</sub>:Ar mixture at atmospheric pressure. (b) A re-plot of the reduction profiles of the bare support materials.

Table 2 Degree of reduction of each supported catalyst after H<sub>2</sub>-TPR

Sample name	DoR (%)
Co <sub>3</sub> O <sub>4</sub> /P25	92.5
Co <sub>3</sub> O <sub>4</sub> /rutile	90.3
Co <sub>3</sub> O <sub>4</sub> /anatase	85.3

Below 200 °C, the normalised outlet flow rates of CO and O<sub>2</sub> decrease while the outlet flow of CO<sub>2</sub> increases with increasing temperature, which confirms the oxidation of CO to CO<sub>2</sub> over all three catalysts. However, at 200 °C, the outlet flow of CO reaches a minimum (correspondingly, the  $X_{CO \rightarrow CO_2}$  reaches a maximum (Fig. 8(a))), while the outlet flow of O<sub>2</sub> continues to decrease until reaching zero at 225 °C for Co<sub>3</sub>O<sub>4</sub>/P25 (Fig. 6(c)) and 250 °C for Co<sub>3</sub>O<sub>4</sub>/rutile and Co<sub>3</sub>O<sub>4</sub>/anatase (Fig. 7(c)). According to eqn (1), half a mole of O<sub>2</sub> is required to convert one mole of CO to one mole of CO<sub>2</sub>. In the current experiments, a 1:1 CO:O<sub>2</sub> feed ratio was used, implying that the conversion of O<sub>2</sub> should ideally be half of the conversion of CO. However, the continued decrease in the outlet flow of O<sub>2</sub> suggests the simultaneous occurrence of H<sub>2</sub> oxidation (eqn (2)), which is a well-known competing reaction in CO-PrOx.<sup>23,24,27–33</sup> This is also confirmed by the  $S_{O_2 \rightarrow CO_2}$ , which is below 100% from 75 °C for all three

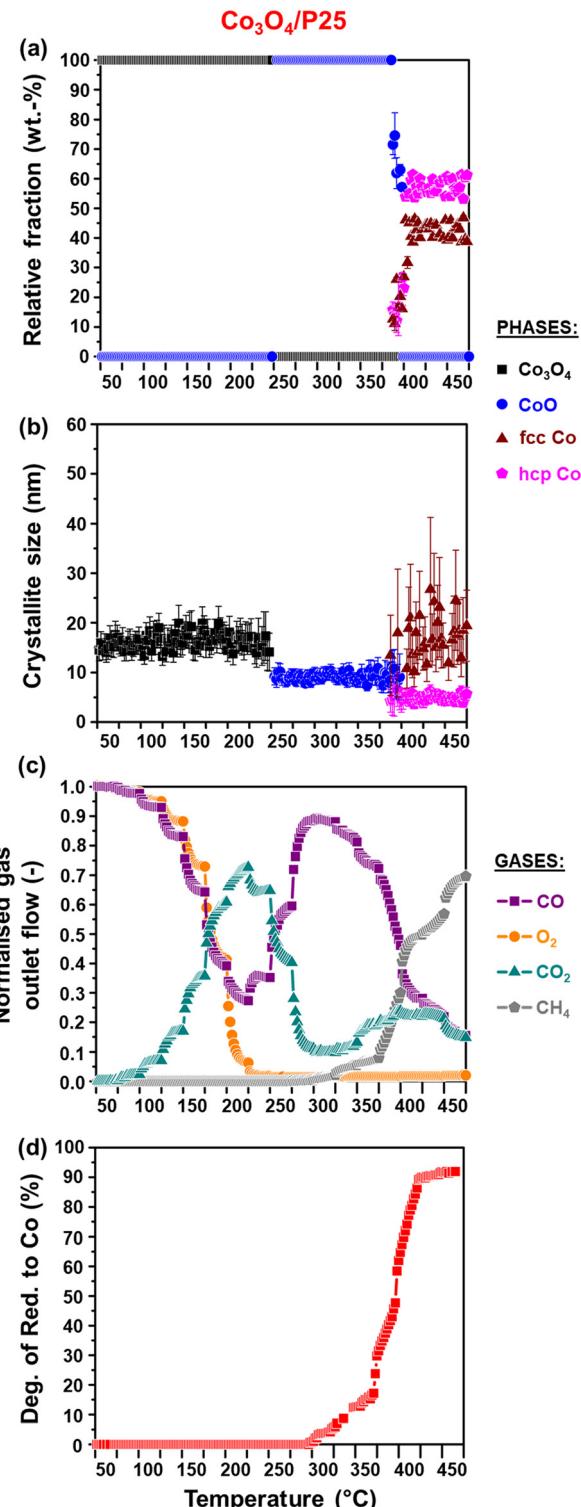
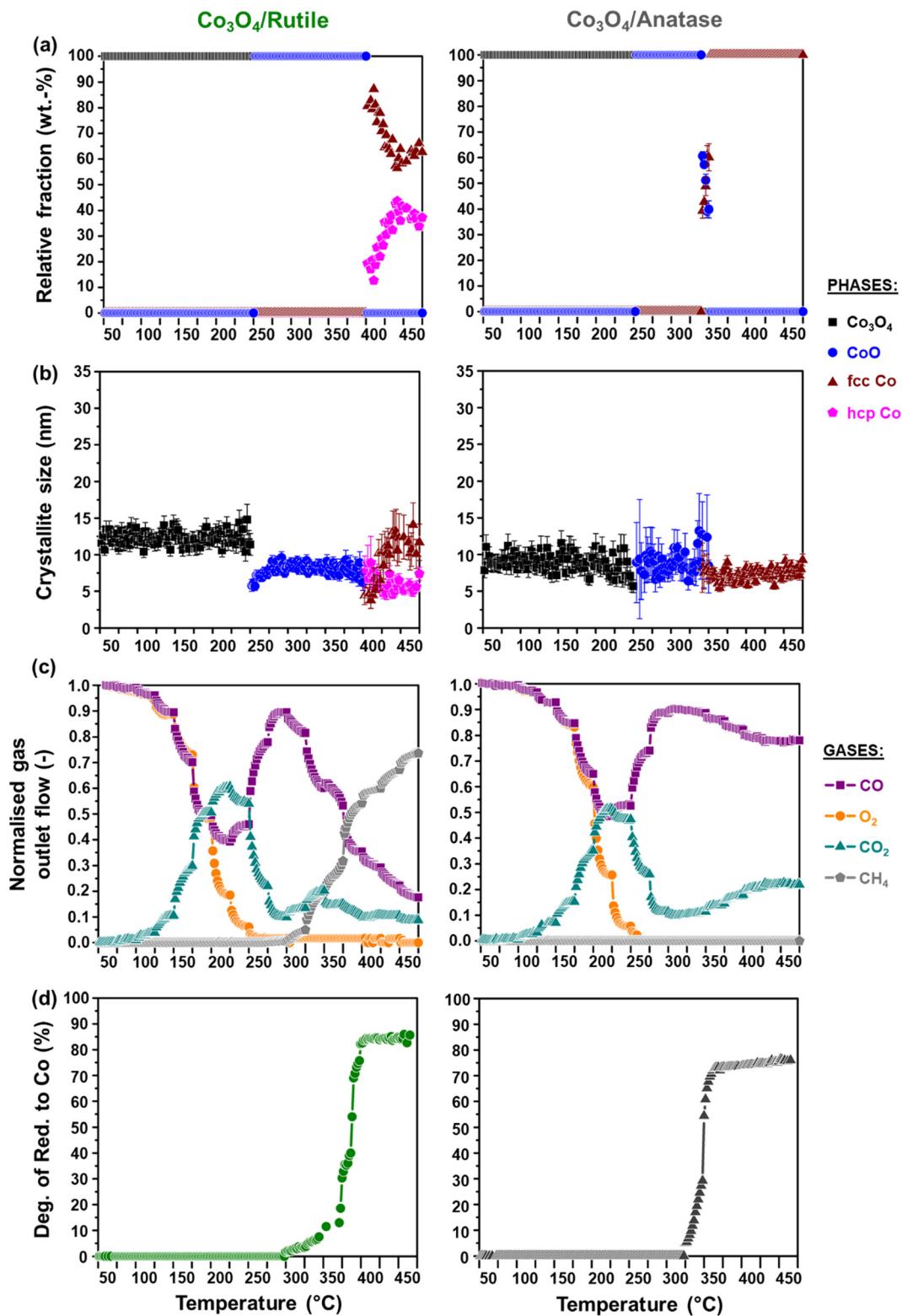


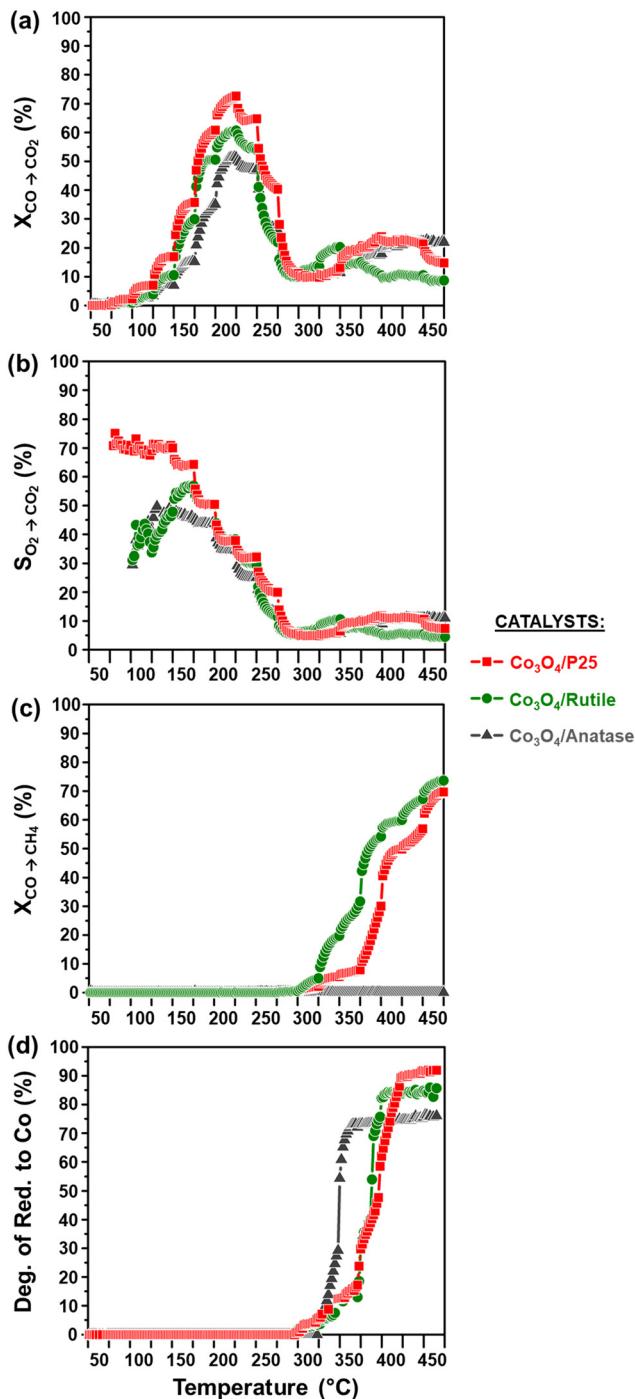
Fig. 6 (a) Relative weight fractions and (b) average crystallite sizes of the different Co-based phases detected using PXRD (excluding the support). (c) Normalised outlet flow rates of CO, O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>. (d) Magnetometry-derived DoR of Co<sub>3</sub>O<sub>4</sub> to Co<sup>0</sup> obtained for Co<sub>3</sub>O<sub>4</sub>/P25 during CO-PrOx (gas composition: 1% CO, 1% O<sub>2</sub>, 50% H<sub>2</sub>, and 48% N<sub>2</sub>; pressure: atmospheric; GHSV: 60 000 mL(NTP) g<sub>Co<sub>3</sub>O<sub>4</sub></sub><sup>-1</sup> h<sup>-1</sup>).

catalysts and continues to decrease as the reaction temperature is increased (Fig. 8(b)).



**Fig. 7** (a) Relative weight fractions and (b) average crystallite sizes of the different Co-based phases detected using PXRD (excluding the supports). (c) Normalised outlet flow rates of CO,  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ . (d) Magnetometry-derived DoR of  $\text{Co}_3\text{O}_4$  to  $\text{Co}^0$  obtained for (left)  $\text{Co}_3\text{O}_4$ /rutile and (right)  $\text{Co}_3\text{O}_4$ /anatase during CO-PrOx (gas composition: 1% CO, 1%  $\text{O}_2$ , 50%  $\text{H}_2$ , and 48%  $\text{N}_2$ ; pressure: atmospheric; GHSV: 60 000 mL(NTP)  $\text{g}_{\text{Co}_3\text{O}_4}^{-1} \text{h}^{-1}$ ).





**Fig. 8** (a) CO conversion to CO<sub>2</sub> ( $X_{CO \rightarrow CO_2}$ ), (b) O<sub>2</sub> selectivity to CO<sub>2</sub> ( $S_{O_2 \rightarrow CO_2}$ ), (c) CO conversion to CH<sub>4</sub> ( $X_{CO \rightarrow CH_4}$ ), and (d) magnetometry-derived DoR of Co<sub>3</sub>O<sub>4</sub> to Co<sup>0</sup> during CO-PrOx for all prepared catalysts. The  $S_{O_2 \rightarrow CO_2}$  was calculated at temperatures where both CO and O<sub>2</sub> were converted (see Fig. 6(c), 7(c), and 8(a)). (Gas composition: 1% CO, 1% O<sub>2</sub>, 50% H<sub>2</sub>, and 48% N<sub>2</sub>; pressure: atmospheric; GHSV: 60 000 mL(NTP) g<sub>Co<sub>3</sub>O<sub>4</sub></sub><sup>-1</sup> h<sup>-1</sup>).

A comparison of the CO oxidation activities of the evaluated catalysts shows that Co<sub>3</sub>O<sub>4</sub>/P25 is the most active catalyst over a wide temperature range (50 and 275 °C) and reaches a maximum  $X_{CO \rightarrow CO_2}$  of 72.7% at 200 °C, followed by Co<sub>3</sub>O<sub>4</sub>/rutile (60.7%) and Co<sub>3</sub>O<sub>4</sub>/anatase (51.5%) at the same temperature. The Co<sub>3</sub>O<sub>4</sub>/P25 catalyst also exhibits better

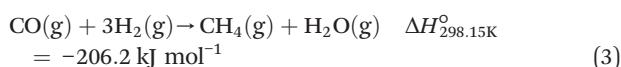
$S_{O_2 \rightarrow CO_2}$  values between 50 and 275 °C than the rutile- and anatase-supported catalysts. Although the catalysts do not reach the desired minimum  $X_{CO \rightarrow CO_2}$  of 99.9% (*i.e.*, decreasing the concentration of CO below 10 ppm),<sup>23,24</sup> P25 may still be a viable support for future catalyst development work in the context of CO-PrOx. This support composes of a mixture of rutile (15%) and anatase (85%), which has improved the activity of catalysts used in other catalytic processes.<sup>21</sup> The mixture of rutile and anatase is thought to result in relatively weaker interactions with Co<sub>3</sub>O<sub>4</sub> nanoparticles, making them easier to reduce.<sup>21,22</sup> Therefore, assuming the MvK mechanism for CO oxidation, which involves a surface reduction-oxidation (redox) cycle being undergone by Co<sub>3</sub>O<sub>4</sub>,<sup>25,26</sup> the higher activity of Co<sub>3</sub>O<sub>4</sub>/P25 may be due to the existence of weak NPSI that allow for an effective surface redox cycle.

Fig. S11(a)† shows the  $X_{CO \rightarrow CO_2}$  values plotted as a function of temperature for the three bare supports. It can be seen that the bare supports also exhibit some CO oxidation activity, with  $X_{CO \rightarrow CO_2}$  values that are below 10%. However, the Co<sub>3</sub>O<sub>4</sub>-loaded supports display much higher  $X_{CO \rightarrow CO_2}$  values than those of the bare supports, which emphasises the importance of the Co<sub>3</sub>O<sub>4</sub> phase. There may be contributions to the CO oxidation activity from each support, but this can be expected to be minor.

Based on the *in situ* PXRD measurements performed (Fig. 6, 7, and S10†), the Co<sub>3</sub>O<sub>4</sub> phase is stable between 50 and 225 °C in all three catalysts, which explains the overall increase in the  $X_{CO \rightarrow CO_2}$  values within this temperature range. However, it is possible that the slight decrease in the  $X_{CO \rightarrow CO_2}$  observed for all three catalysts from 225 °C (Fig. 6(c), 7(c), and 8(a)) is caused by the reduction of the Co<sub>3</sub>O<sub>4</sub> surface to CoO,<sup>27–32</sup> despite this being undetected using bulk-sensitive PXRD. Furthermore, the increase in the amount of O<sub>2</sub> converted *via* H<sub>2</sub> oxidation might also explain the decrease in the  $X_{CO \rightarrow CO_2}$  values from 225 °C. With reference to the MvK mechanism, the ultimate depletion of O<sub>2</sub> at 225 °C for Co<sub>3</sub>O<sub>4</sub>/P25 and 250 °C for Co<sub>3</sub>O<sub>4</sub>/rutile and Co<sub>3</sub>O<sub>4</sub>/anatase may have led to the onset formation of CoO at these temperatures as there was no O<sub>2</sub> available to stabilise (or regenerate) the active Co<sub>3</sub>O<sub>4</sub> phase.<sup>25,26</sup>

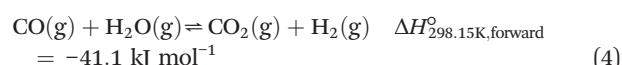
*In situ* PXRD adequately shows the formation of CoO at 250 °C in all three catalysts, which is later converted to fcc Co<sup>0</sup> on anatase (325 °C) and to fcc and hcp Co<sup>0</sup> on P25 (375 °C) and rutile (400 °C) (Fig. 6, 7, S10, and S12†). However, Co<sup>0</sup> (with no distinction between fcc and hcp Co<sup>0</sup>) is detected earlier in the magnetometer, that is, at 300 °C for the P25- and rutile-supported catalysts, and at 325 °C for the anatase-supported catalyst (see DoR plots in Fig. 6(d), 7(d), and 8(d)). As stated in section 2.2.2., the magnetometer is more sensitive than PXRD, which explains the earlier detection of Co<sup>0</sup> on P25 and rutile during the magnetometry-based experiments.<sup>28–32</sup> It can also be observed that within the temperature range where CoO exists in each catalyst, the amount of CO converted to CO<sub>2</sub> decreases with increasing temperature, indicating that CoO catalyses H<sub>2</sub> oxidation to a greater extent.<sup>27–32</sup>

Upon forming  $\text{Co}^0$ ,  $\text{CO}$  is converted to  $\text{CH}_4$ , which is an undesired  $\text{CO}$  conversion pathway because valuable  $\text{H}_2$  is being consumed (eqn (3)).<sup>27–33</sup> However, methanation only takes place over the fcc and hcp  $\text{Co}^0$  formed on P25 (max.  $X_{\text{CO} \rightarrow \text{CH}_4}$ : 69.7% at 450 °C) and rutile (max.  $X_{\text{CO} \rightarrow \text{CH}_4}$ : 73.7% at 450 °C), and not over the fcc  $\text{Co}^0$  formed on anatase (Fig. 8(c)). The bare P25 and rutile supports also exhibit  $X_{\text{CO} \rightarrow \text{CH}_4}$  values that are below 1%, with the anatase support displaying no methanation activity (Fig. 11(b)). At this stage, we propose that the metallic particles on anatase may be encapsulated by  $\text{Ti}_x\text{O}_y$  species, thereby blocking active sites on fcc  $\text{Co}^0$ , which has been observed for a reduced Co/anatase catalyst used in the FTS.<sup>16</sup> The encapsulation is thought to be driven by the more facile reduction of anatase (also see  $\text{H}_2\text{-TPR}$  profile in Fig. 5(b)), followed by the migration of  $\text{Ti}_x\text{O}_y$  species to the surface of fcc  $\text{Co}^0$  due to the significant differences in their surface energies (anatase: 0.44 J m<sup>-2</sup>, and fcc  $\text{Co}^0$ : 2.6 J m<sup>-2</sup>).<sup>13–15</sup> Evidence for Co encapsulation in this study, based on STEM-EELS analysis, is discussed in section 3.4.2.



Although considerable amounts of  $\text{CH}_4$  are formed between 300 and 450 °C over the  $\text{Co}^0$  allotropes on P25 and rutile,

there is also some  $\text{CO}_2$  being formed, with  $X_{\text{CO} \rightarrow \text{CO}_2}$  values that are less than 25% being achieved (Fig. 8(a)).  $\text{Co}^0$  is not known for catalysing  $\text{CO}$  oxidation but there is a possibility of an *in situ* water-gas shift (WGS) reaction taking place on the metallic surface, which first involves the formation of  $\text{H}_2\text{O}$  *via*  $\text{H}_2$  oxidation, followed by the reaction of this  $\text{H}_2\text{O}$  with  $\text{CO}$  (eqn (4)).<sup>29,31,32</sup> Additionally, the direct oxidation of  $\text{CO}$  could be taking place over the unreduced  $\text{CoO}$  in the P25- and rutile-supported catalysts<sup>51–53</sup> since they are not fully reduced even at 450 °C based on the magnetometry results (max. DoRs: 91.9% for  $\text{Co}_3\text{O}_4/\text{P25}$  and 85.9% for  $\text{Co}_3\text{O}_4/\text{rutile}$ ). The same could apply to the unreduced  $\text{CoO}$  present on anatase (max. DoR: 76.4% at 450 °C). At this stage, it is unclear if the encapsulated fcc  $\text{Co}^0$  particles on anatase catalyse the formation of  $\text{CO}_2$  *via*  $\text{CO}$  oxidation, the WGS, or any other reaction pathway.



Unlike magnetometry, the PXRD measurements indicate a complete reduction of  $\text{CoO}$  to  $\text{Co}^0$  in all three catalysts at 450 °C (Fig. 6, 7, and S10†). As mentioned earlier, PXRD requires higher amounts of crystalline material for adequate detection, so it is possible that the remaining unreduced  $\text{CoO}$  is below the detection limit of PXRD (typically 2–3 wt%). Nonetheless, PXRD provides important crystallographic information (*e.g.*, a distinction between fcc and hcp  $\text{Co}^0$  can be made), making it a suitable complementary technique to magnetometry. It is worth mentioning that during the PXRD-based reduction studies,  $\text{Co}_3\text{O}_4$  ultimately reduced to fcc and hcp  $\text{Co}^0$  only on P25 and anatase (Fig. 3 and 4), while during CO-PrOx,  $\text{Co}_3\text{O}_4$  reduces to both allotropes only on P25 and rutile.

Ślawiński *et al.*<sup>46</sup> and Nyathi *et al.*<sup>31</sup> have shown that the formation of fcc and hcp  $\text{Co}^0$  (with different ratios) can be influenced by the gas environment. Although this effect was not investigated in-depth, the idea is that different reducing environments may cause the reduction to occur at different temperatures and reduction rates. Consequently, the metallic particles formed can also differ in size, leading to the formation of particles with crystalline domains of either one or both allotropes of Co. Additionally, the strength of the NPSI may influence the reduction of cobalt oxide particles (*i.e.*,  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$ ) depending on their size and the type of support used.<sup>10,30,32,45</sup> Therefore, the formation of fcc and hcp  $\text{Co}^0$  on anatase (during the PXRD-based reduction studies only) and rutile (during CO-PrOx only) might have been caused by the different gas environments and the nature of the interactions between these supports and the  $\text{Co}_3\text{O}_4/\text{CoO}$  particles. Moreover, these effects may have also resulted in the higher hcp  $\text{Co}^0$  content relative to fcc  $\text{Co}^0$  on P25 (hcp:fcc ratio: 1.3 at 450 °C), while more fcc Co than hcp  $\text{Co}^0$  is formed on rutile (hcp:fcc ratio: 0.5 at 450 °C) during CO-PrOx (Fig. 6(a) and 7(a)). Similar to the PXRD-based reduction experiments, Rietveld refinement could not be used to confirm fcc-hcp  $\text{Co}^0$  intergrowth, but the occurrence of this phenomenon cannot be ruled out.<sup>31,46,49</sup>

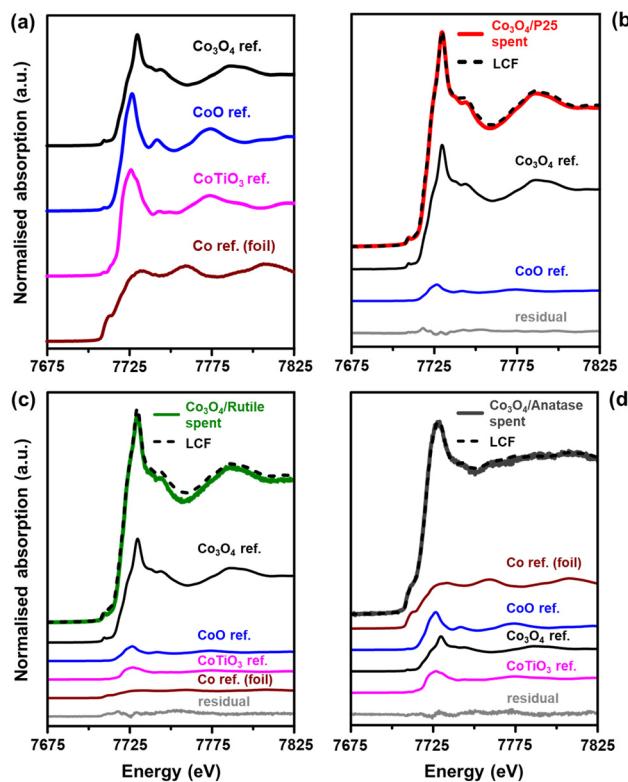


Fig. 9 Normalised XANES spectra of the (a) reference compounds and (b)–(d) spent samples obtained after performing CO-PrOx. The results from the LCF are also included in (b)–(d). The fitted reference components in (b)–(d) are scaled according to their contribution to the LCF.

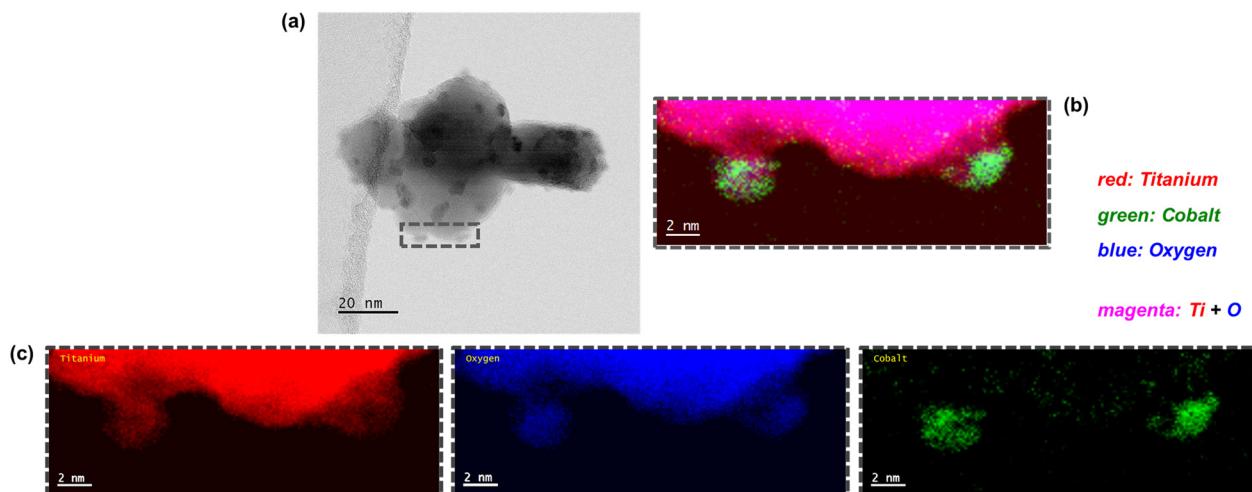


Fig. 10 (a) Bright-field STEM micrograph, (b) magnified STEM-EELS composite map showing the regions with Ti, O, and Co, and the (c) corresponding magnified STEM-EELS maps of the individual elements present in the spent  $\text{Co}_3\text{O}_4$ /anatase catalyst.

The reduction of  $\text{Co}_3\text{O}_4$  on all support materials leads to the formation of  $\text{CoO}$  crystallites of similar sizes (on anatase) or smaller sizes (on P25 and rutile) than the starting  $\text{Co}_3\text{O}_4$  crystallites (Fig. 6(b) and 7(b)), indicating minimal or no sintering. On anatase, the fcc  $\text{Co}^0$  crystallites are also similar in size as the  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$  crystallites, further confirming no significant crystallite growth. However, the fcc  $\text{Co}^0$  crystallites formed on P25 and rutile are larger than the crystallites of  $\text{CoO}$ , while heptagonal  $\text{Co}^0$  is smaller than  $\text{CoO}$ . As observed during the magnetometry studies, the P25- and rutile-supported catalysts achieved higher DoRs than the anatase-supported catalyst (Fig. 6(d), 7(d), and 8(d)), which may suggest the existence of weaker NPSIs in the highly reduced catalysts.<sup>10,30,32,45</sup> It is also possible that the sintering of fcc  $\text{Co}^0$  on P25 and rutile is a result of the weak NPSIs.<sup>54</sup>

### 3.4. *Ex situ* characterisation of spent catalysts

**3.4.1. XAS measurements.** *Ex situ* XAS measurements were conducted primarily to determine the presence of mixed metal oxides (such as  $\text{CoTiO}_3$ ) in the spent catalysts. Since  $\text{CoTiO}_3$  is not ferromagnetic,<sup>55</sup> it would not be detected using magnetometry. Although  $\text{CoTiO}_3$  is detectable using PXRD, the *in situ* diffraction patterns obtained for all catalysts during CO-PrOx did not show any reflections from this phase (Fig. S10†), possibly due to its formation in small amounts and/or small crystallite sizes.

The normalised XANES (X-ray absorption near edge structure) spectra of the reference compounds  $\text{Co}_3\text{O}_4$ ,<sup>44</sup>  $\text{CoO}$ ,<sup>56</sup>  $\text{CoTiO}_3$ ,<sup>57</sup> and  $\text{Co}^0$  (or Co foil)<sup>58</sup> are presented in Fig. 9(a). These reference compounds were synthesised according to the procedures outlined in the cited literature. The first derivatives of the XANES spectra for the reference compounds (Fig. S13†) also help to show the differences in their spectral features. Fig. 9(b)–(d) shows the XANES spectra of the spent catalysts together with the linear combination fit (LCF) and the individual fitted components, which have been scaled according to their contribution to the LCF. The phase compositions of the spent samples (based on the LCF) are presented in Table 3 together with the *R*-factors. It is worth mentioning that the quantities of the Co-based phases reported in Table 3 are on a Co basis because only the Co K-edge was measured. Therefore, the amounts of the different Co-based phases can be expected to be much lower than those presented in Table 3 after factoring in the proportion of the support, which is at least 90 wt% according to ICP-OES analysis.

The results of the LCF generally indicate a high concentration of  $\text{Co}_3\text{O}_4$  in each spent sample, whereas the *in situ* PXRD experiments showed the complete disappearance of this phase to  $\text{CoO}$  and  $\text{Co}^0$  during CO-PrOx (Fig. 6, 7, and S10†). Therefore, the presence of  $\text{Co}_3\text{O}_4$  in the spent samples analysed using XAS is likely due to the re-oxidation of the  $\text{CoO}$

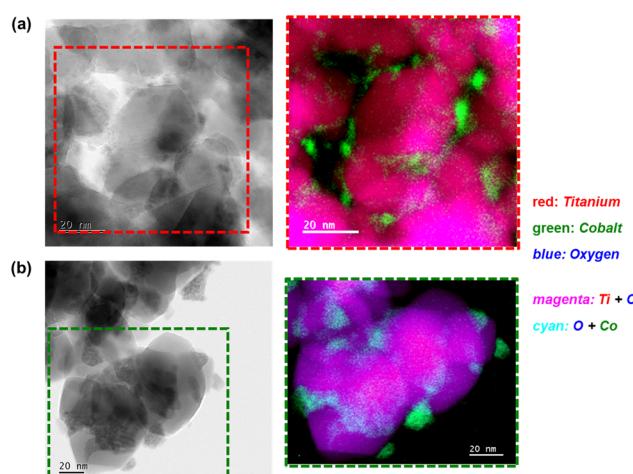


Fig. 11 (Left) Bright-field STEM micrographs and the (right) magnified STEM-EELS composite maps showing the regions with Ti, O, and Co in the spent (a)  $\text{Co}_3\text{O}_4$ /P25 and (b)  $\text{Co}_3\text{O}_4$ /rutile catalysts.

**Table 3** Results obtained after performing linear combination fitting on the normalised XANES spectra

Sample name	Co <sub>3</sub> O <sub>4</sub> (%)	CoO (%)	CoTiO <sub>3</sub> (%)	Co <sup>0</sup> (%)	R-Factor (-)
Co <sub>3</sub> O <sub>4</sub> /P25 spent	88.9 ± 0.9	11.1 ± 0.6	—	—	0.003
Co <sub>3</sub> O <sub>4</sub> /rutile spent	73.0 ± 6.1	9.8 ± 3.6	8.9 ± 4.5	8.3 ± 1.2	0.010
Co <sub>3</sub> O <sub>4</sub> /anatase spent	21.3 ± 0.7	21.8 ± 1.5	13.8 ± 1.8	43.2 ± 2.5	0.002

and Co<sup>0</sup> during the long storage times (6–12 months) of the samples in a non-inert environment prior to the XAS measurements. However, since determining the presence of mixed metal oxides using XAS was of primary importance, these oxides would remain stable during sample storage and therefore, should still be detectable.<sup>10,57</sup>

The Co<sub>3</sub>O<sub>4</sub>/P25 spent catalyst underwent extensive re-oxidation as the XANES spectrum mostly exhibits features similar to those of Co<sub>3</sub>O<sub>4</sub> between 7700 and 7825 eV (Fig. 9(b)). The LCF also confirmed the presence of 88.9 ± 0.9% Co<sub>3</sub>O<sub>4</sub> and 11.1 ± 0.6% CoO, with no traces of CoTiO<sub>3</sub>. The spectrum of the rutile-supported spent catalyst (Fig. 9(c)) is also dominated by features of the Co<sub>3</sub>O<sub>4</sub> phase (73.0 ± 6.1%), but also shows an edge shift of approximately 1.5 eV to the left, relative to the main edge of the Co<sub>3</sub>O<sub>4</sub> reference (which is at 7723 eV). This left shift is indicative of Co species of lower oxidation state, that is, below +3. Indeed, there are also relatively small amounts of CoO (9.8 ± 3.6%), CoTiO<sub>3</sub> (8.9 ± 4.5%), and Co<sup>0</sup> (8.3 ± 1.2%) in the Co<sub>3</sub>O<sub>4</sub>/rutile spent catalyst. In these three phases, Co is either in the +2 or 0 oxidation state.

The XANES spectrum of Co<sub>3</sub>O<sub>4</sub>/anatase (Fig. 9(d)) exhibits different features from those observed in the spectra of Co<sub>3</sub>O<sub>4</sub>/P25 and Co<sub>3</sub>O<sub>4</sub>/rutile. There is a pronounced pre-edge feature at 7710 eV, which indicates the presence of Co<sup>0</sup>, and the edge and white line have shifted to the left by approximately 3 eV relative to the edge and white line of the Co<sub>3</sub>O<sub>4</sub> reference (which are at 7723 and 7730 eV, respectively). The white line and the spectral features between 7750 and 7825 eV for Co<sub>3</sub>O<sub>4</sub>/anatase appear to be less intense (Fig. 9(d)). These observations further indicate the presence of relatively high amounts of Co<sup>0</sup> (43.2 ± 2.5%) in this spent sample. There is also CoO (21.8 ± 1.5%), Co<sub>3</sub>O<sub>4</sub> (21.3 ± 0.7%), and CoTiO<sub>3</sub> (13.8 ± 1.8%) indicated by the LCF.

The presence of CoTiO<sub>3</sub> in the Co<sub>3</sub>O<sub>4</sub>/rutile and Co<sub>3</sub>O<sub>4</sub>/anatase spent catalysts is in good agreement with the low magnetometry-derived DoRs reached by these samples (85.9% and 76.4%, respectively) at 450 °C during CO-PrOx when compared with Co<sub>3</sub>O<sub>4</sub>/P25 (91.9%), which did not form CoTiO<sub>3</sub>. We note that CoTiO<sub>3</sub> was not observed in any supported catalyst during the PXRD-based *in situ* reduction or CO-PrOx experiments. This may have been a result of the CoTiO<sub>3</sub> amounts being below the detection limit of the PXRD instrument. Nonetheless, the higher content of CoTiO<sub>3</sub> in Co<sub>3</sub>O<sub>4</sub>/anatase is possibly due to the high reduction susceptibility of anatase (also see H<sub>2</sub>-TPR profile in Fig. 6(b)) followed by the migration and reaction of Ti<sub>x</sub>O<sub>y</sub> with CoO<sub>x</sub> species.<sup>7,10,16</sup> Rutile is generally less susceptible to reduction, which might explain the lower amounts of CoTiO<sub>3</sub> formed in Co<sub>3</sub>O<sub>4</sub>/rutile. The more facile formation of CoTiO<sub>3</sub> in Co<sub>3</sub>O<sub>4</sub>/

anatase is also supported by thermodynamic calculations (based on bulk phases), which show lower values for the change in the Gibbs free energy ( $\Delta G$ ) and partial pressure ratio of H<sub>2</sub>-to-H<sub>2</sub>O ( $p_{H_2}/p_{H_2O}$ ) as a function of temperature than for Co<sub>3</sub>O<sub>4</sub>/rutile (Fig. S14 and S15†). The P25 support is a 15:85 mixture of rutile and anatase, which is thought to make the support (or the anatase fraction) more stable under reduction conditions.<sup>21,22</sup> This could explain the absence of CoTiO<sub>3</sub> in the Co<sub>3</sub>O<sub>4</sub>/P25 spent sample.

**3.4.2. STEM-EELS analysis.** The spent catalysts were also studied using STEM-EELS to determine changes in particle size in comparison with the fresh catalysts. Fig. 10 and 11 show the bright-field micrographs of the three spent samples as well as the corresponding elemental maps showing regions with Ti, O, and Co. PXRD measurements carried out during CO-PrOx indicated the presence of fcc and hcp Co<sup>0</sup> crystallites at 450 °C that vary between 10 and 25 nm for the fcc phase, and between 5 and 10 nm for the hcp phase, among the three evaluated catalysts (Fig. 6(b) and 7(b)). Although the spent samples that were analysed using STEM-EELS likely underwent re-oxidation during storage, the particles shown in Fig. 10 and 11 are mostly below 10 nm, which is smaller than the starting Co<sub>3</sub>O<sub>4</sub> particles (Table 1).

The exact cause of the size discrepancy between PXRD and STEM-EELS (especially regarding fcc Co<sup>0</sup>) remains unknown. However, it is possible that there exists a small number of large particles that were not identified using STEM-EELS, but were detected using PXRD, resulting in larger average sizes for fcc Co<sup>0</sup> based on PXRD. Furthermore, in the absence of fcc-hcp Co<sup>0</sup> intergrowth, the small particles identified using STEM-EELS could be hcp Co<sup>0</sup> (although this is thermodynamically less feasible<sup>47,48</sup>), or could have been derived from hcp Co<sup>0</sup>, in the case of re-oxidation during sample storage.<sup>31</sup>

Interestingly, some of the small Co-bearing particles located on the edge of the large anatase particles have been encapsulated by Ti<sub>x</sub>O<sub>y</sub> species (Fig. 10 and S16†). This is not observed in the STEM-EELS micrographs of the Co<sub>3</sub>O<sub>4</sub>/P25 and Co<sub>3</sub>O<sub>4</sub>/rutile spent samples (Fig. 11). The encapsulation of CoO<sub>x</sub> particles by anatase-derived Ti<sub>x</sub>O<sub>y</sub> species is well-known under reducing conditions,<sup>7,10,16</sup> but this is being observed after CO-PrOx for the first time in this study. In section 3.3., it was proposed that the absence of CH<sub>4</sub> in the CO-PrOx product stream of Co<sub>3</sub>O<sub>4</sub>/anatase (Fig. 7(c)) was due to the encapsulation of Co<sup>0</sup> (or more generally, CoO<sub>x</sub> species). Therefore, the detection of Ti<sub>x</sub>O<sub>y</sub>-encapsulated Co-bearing particles using STEM-EELS could explain the absence of CH<sub>4</sub> formation over the partially reduced anatase-supported catalyst. Furthermore, it has been reported that the encapsulation of CoO<sub>x</sub> particles by Ti<sub>x</sub>O<sub>y</sub> species may lead to



the formation of  $\text{CoTiO}_3$ .<sup>7,10,16</sup> This phase was detected in relatively high amounts ( $13.8 \pm 1.8\%$ ) in the  $\text{Co}_3\text{O}_4$ /anatase spent sample using XAS.

## 4. Conclusions

The presented study investigated the effect of different  $\text{TiO}_2$  polymorphs (rutile, anatase, and a 15:85 mixture of rutile and anatase (also commercially known as P25)), used as supports, on the chemical and crystallographic phase transformations of  $\text{Co}_3\text{O}_4$  during dry CO-PrOx. The phase changes were detected *in situ* using PXRD and magnetometry as a function of temperature, while *ex situ* XAS and STEM-EELS analyses of the spent catalysts provided further complementary information on the phase changes that occurred. Furthermore, on-line gas product analysis was coupled with the *in situ* characterisation to evaluate catalytic performance. It was shown that supporting  $\text{Co}_3\text{O}_4$  on P25 results in high CO conversions to  $\text{CO}_2$ , with a maximum conversion of 72.7% achieved at 200 °C. Owing to the high concentrations of  $\text{H}_2$  in the feed (50%), the reduction of  $\text{Co}_3\text{O}_4$  to  $\text{Co}^0$  and ultimately to  $\text{Co}^0$  took place in all three catalysts, which caused a loss in the  $\text{CO}_2$  yield and selectivity. The DoR of  $\text{Co}_3\text{O}_4$  to  $\text{Co}^0$  was highest on P25 (91.9% at 450 °C), while the DoR (76.4% at 450 °C) and  $\text{CO}_2$  yield (51.5% at 200 °C) was lowest on anatase. Assuming the MvK mechanism for CO oxidation, which depends on surface reduction (and re-oxidation), the high CO oxidation activity of  $\text{Co}_3\text{O}_4$ /P25 could be a result of its high surface reducibility. Furthermore, the high surface and bulk reducibility (as determined *via in situ* characterisation for the latter) of  $\text{Co}_3\text{O}_4$ /P25 could be due to the existence of weak interactions between the  $\text{Co}_3\text{O}_4$  nanoparticles and P25 support.

The  $\text{Co}^0$  formed on P25 and rutile existed in the fcc and hcp crystal forms at elevated temperatures during CO-PrOx, while only fcc  $\text{Co}^0$  was formed on anatase. The average larger size of  $\text{Co}^0$  crystallites, relative to the size of  $\text{CoO}$  crystallites, on P25 and rutile may have led to the formation of (partially) intergrown crystalline domains of fcc and hcp  $\text{Co}^0$ . This sintering may have also been a result of the weaker NPSIs in  $\text{Co}_3\text{O}_4$ /P25 and  $\text{Co}_3\text{O}_4$ /rutile when compared with the NPSIs in  $\text{Co}_3\text{O}_4$ /anatase. The formation of  $\text{CoTiO}_3$  was confirmed in the anatase (13.8%) and rutile (8.9%) supported spent catalysts *via ex situ* XAS, while the presence of  $\text{Ti}_x\text{O}_y$ -encapsulated  $\text{CoO}_x$  particles was only observed in the anatase-supported spent catalyst *via ex situ* STEM-EELS. The encapsulation of  $\text{CoO}_x$  particles may have occurred because of the relatively high reducibility of the anatase support, which forms highly mobile  $\text{Ti}_x\text{O}_y$  species that migrate to the surface of the  $\text{CoO}_x$  particles. In the case of the encapsulated fcc  $\text{Co}^0$  particles on anatase,  $\text{CH}_4$  formation did not take place (even at 450 °C) as the required surface active sites may have been blocked. On the other hand,  $\text{CH}_4$  formation was observed over the fcc and hcp  $\text{Co}^0$  on P25 and rutile, possibly because of minimal or no encapsulation.

## Conflicts of interest

There are no conflicts to declare.

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