



Visualising Co nanoparticle aggregation and encapsulation in Co/TiO₂ catalysts and its mitigation through surfactant residues

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ABSTRACT

Due to the reducible nature of TiO₂, the encapsulation of cobalt nanoparticles (CoNPs) by reduced TiO_{2-x} is often reported to decrease their catalytic performance in reactions such as Fisher-Tropsch synthesis (FTS). Here, we show using HAADF-STEM imaging and electron energy loss spectroscopy (EELS) that a residual C₁₂E₄ surfactant used to prepare the CoNPs, remains on the surface of a TiO₂ rutile support, preventing the formation of Ti³⁺/Ti²⁺ oxides and therefore TiO_{2-x} migration. Furthermore, the presence of these surfactant residues prevents the coalescence and aggregation of CoNPs during catalyst preparation, maintaining the dispersion of CoNPs. As such, using C₁₂E₄ in the preparation of Co/TiO₂ can be considered beneficial for producing a catalyst with a greater number of active Co species.

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1. Introduction

A support, when used in heterogenous catalysis, is there primarily as a delivery medium of the active component often in the form of atoms, clusters or nanoparticles. More importantly, the interaction between the two can be optimised to improve dispersion, stability, tunability of the active component and even in some cases play a critical role in the catalytic process. The supports typically comprise both oxides (e.g. SiO₂, TiO₂, Al₂O₃, CeO₂, and zeolite) [1–3] and carbides (e.g. carbon and SiC) [4,5]. Among those, TiO₂-supported, cobalt nanoparticles (CoNPs) are widely reported in literature. [1,6,7,8,9,10,11] However, there is a big challenge to produce a Co/TiO₂ catalyst with desired performances since CoNPs often end-up encapsulated by reduced amorphous TiO_{2-x}. [8,9,10,11] This problem leads to the blockage of the active surface and is therefore inimical to the catalytic activity [8,10]. Encapsulation shows a dependency with TiO₂ polymorph [12–14], with anatase, typically possessing a high concentration of defects, being more susceptible to this phenomenon than rutile

[12,14]. An additional problem concerns the formation of metal-support compounds such as the non-reducible cobalt titanate, [15–17] leading to a loss of the active metallic cobalt for reactions. The mobility of Co and, in particular, the spreading of cobalt on the titania surface [18–20] exacerbates the formation of such titanate compounds. Fortunately, even this titanate formation can be mitigated against by the addition of small amounts of noble metals [21]. However, Melaet et al. [11] reported that cobalt oxide (CoO_x) can form a unique interface with TiO₂, which was more active than metallic Co/TiO₂ for Fisher-Tropsch synthesis and CO₂ hydrogenation. The above precis suggests that there is value in expending time and effort to mitigate encapsulation by TiO_{2-x} to develop better performing catalysts. Approaches for mitigating encapsulation include the application of a post-treatment reduction–oxidation–reduction (ROR) cycle to break and disperse the amorphous TiO_{2-x} layer [10]. An alternative strategy would be to inhibit the formation of TiO_{2-x} in the catalyst in the first place. Indeed, Hong, et al. [22] recently reported a novel approach applying a carbon nitride (C₃N₄) coating onto TiO₂ before adding the CoNPs, which subsequently showed improved FTS stability by stopping both CoNP agglomeration and encapsulation. A similar approach was adopted by Phaahlamohlaka, et al., but this time using mesoporous silica to obtain the sintering-resistant Co catalysts, although they did not

Abbreviations: SMSI, Strong Metal Support Interaction; HAADF-STEM, High-Angle Annular Dark Field-Scanning Transmission Electron Microscopy; H₂-TPR, H₂ Temperature Programmed Reduction.

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report whether the silica coating also inhibited the formation of a TiO_{2-x} layer [23].

The size of nanoparticles is another important parameter in catalytic research. For example, for FTS activity a typical critical size of CoNPs is determined to be 5–10 nm, [24–27] although no dependency on CoNP size is shown when the critical size is exceeded (i.e. > 10 nm) while below this, the activity shows a linear relationship with CoNP size. The size effects also affect the product selectivity [24,28,29] and nanoparticle stability [30,31]. The reasons for these nanoparticle size effects are not clear, but could be related to the size-dependent active sites contain more uncoordinated atoms but less B5 active sites in small NPs lead to adsorbates that are harder to remove [25,26,32]. In order to control the size of CoNPs (5–10 nm), various methods have been successfully employed, including for example, pre-synthesizing size-controllable NPs using reverse micelles [33–35], thermal decomposition [36], using organic solvents in place of water during impregnation [26,37], and modification of the support surface [38].

Here we report an alternative synthetic approach to mitigate CoNP aggregation and encapsulation, using a C_{12}E_4 surfactant. We demonstrate the impact of the C_{12}E_4 surfactant by preparing two similar catalysts, differing only in the point at which removal of the surfactant occurs; the early removal of the surfactant leading to aggregation of the CoNPs during preparation. We note that a similar ‘protective surfactant’ strategy has been successfully employed to prepare other types of catalysts, including a sintering-resistant Au/ TiO_2 catalyst for CO oxidation [39,40]. In that work, the authors observed that a polydopamine / oleylamine layer stops Au migration, preventing sintering via Ostwald ripening during calcination due to the formation of a strong metal-support interaction, with thermal decomposition of the surfactant leading to the formation of a protective carbon layer. Although this carbon layer can be removed by calcination, the strong interaction between Au and TiO_2 is maintained, ensuring a high Au dispersion which allows for optimal CO oxidation. A di-block poly(styrene)-block-poly(2-vinylpyridine) polymer is also widely reported to obtain uniform nanoparticle size although it is very expensive [41–43]. Due to the repulsion of ploy-styrene block in a reverse micelle, the nanoparticles can be individually maintained before and after depositing on a support. In contrast, our work here focused on the effect of surfactant on aggregation of CoNPs before calcination, reducibility of CoNPs and TiO_2 support during reduction, as well as improvement in CO reduction reaction *without* the formation of a carbon layer. The complex-like C_{12}E_4 derivatives formed during preparation coat the surface of size-controllable CoNPs and the titania support, which has a shielding effect that protects TiO_2 from being reduced and decorating the CoNPs. Even though the reducibility of the catalyst is lower, CO reduction is significantly enhanced.

2. Results and discussion

2.1. Identifying surfactant residues and determining their effect on the properties of the supported cobalt nanoparticles

Two types of catalysts were prepared using reverse micelle encapsulation. The first type of catalyst, labelled 5–15 %Co, contains 5–15 % wt. Co on TiO_2 deposited via inverse micelles and subsequently treated with acetone to break the micelles and remove surfactant. In the second type, 5–15 %Co@ C_{12}E_4 , since no acetone wash was performed, the micelle remains intact. The textural properties of calcined samples are found in Table S1, where a significant lower surface area is seen in 15 %Co due to the blockage by large amounts of surfactant residues.

Calcination at 473 K in air of both samples should see the decomposition of the $\text{Co}(\text{OH})_2$ precipitate to form Co_3O_4 [33,44]. However, possibly due to the low temperature used for calcination, decomposition is incomplete (Fig. 1a) with both $\text{Co}(\text{OH})_2$ and Co_3O_4 observed to be present [45]. The sample was then subjected to reduction for 3 h at 623 K in 50 % H_2/He which saw the reduction of $\text{Co}(\text{OH})_2$ and Co_3O_4 to Co fcc (Fig. 1b). Fig. 2 shows the Fourier Transform Infrared Spectra (FTIR) of the heat-treated catalysts. In the calcined samples, there are bands present at 1120, 1724 and $\sim 2900 \text{ cm}^{-1}$ due to C–O, C=O and CH_2/CH_3 stretching modes, which are suggestive of the formation of the polymer-like species formed via ester polymerisation in the unwashed catalysts (5–15 %Co@ C_{12}E_4). Two bands can be assigned to C=O (1724 cm^{-1}) and COO^- (1590 cm^{-1}), respectively, and are more intense in the 15 %Co@ C_{12}E_4 than in the 5 %Co@ C_{12}E_4 sample [46]. Koizumi, et al. observed the same functional group formation from various glycol-containing compounds and proposed the formation of polymer-like complex species *via* ester polymerization during calcination at 400 K [46]. Hence, similar polymeric species are considered to be present in these samples after calcination or heating in H_2 . The presence of IR bands due to C=O, suggests that cross-linking has taken place to produce a polymer in addition to some residual surfactant; the presence of residual micelle can be seen particularly in the parts of the spectra where the C–O/CH stretches occur. Unsurprisingly, the unwashed catalysts, particularly the 15 %Co@ C_{12}E_4 , contain a large quantity of surfactant residues ($\sim 50\%$, estimated from the TGA data shown in Fig. S2a). Note also the presence of a sharp band at 1384 cm^{-1} in the 5–15 %Co catalysts due to residual nitrate [47]. It is thought that this nitrate remains encapsulated into the CoNPs in the washed catalysts and cannot be fully decomposed using the mild calcination conditions employed.

Fig. 3 & Figure S2 shows Thermal Gravimetric Analysis (TGA) data containing mass loss profiles for samples 5–15 %Co@ C_{12}E_4 and 5–15 %Co after calcination and after reduction for 3 h at 623 K in 50 % H_2/He . The weight loss occurring in all samples before 400 K is due to the loss of adsorbed water. For the calcined samples, the first derivative peaks after 600 K can be attributed to the decomposition of remaining C_{12}E_4 derivatives (Fig. 3b & S2b) whereas the weight losses after 1000 K comprise contributions derived from the reduction of cobalt oxide (i.e. $\text{Co}_3\text{O}_4 \rightarrow \text{Co}$). These TGA data also confirm therefore that residual C_{12}E_4 surfactant breaks down to yield polymeric compounds during calcination. For example, in Fig. 3b, the mass loss finished at $\sim 642 \text{ K}$ in pure C_{12}E_4 and in the physical mixture of rutile + C_{12}E_4 , whilst in the calcined rutile + C_{12}E_4 mixture or 5–15 %Co@ C_{12}E_4 samples, the mass loss continues beyond this temperature [46].

In contrast, for the samples that had undergone the reduction treatment the weight loss is minimal, indicating that only a very small amount of the surfactant remained on the sample. We estimate that $\sim 95 \text{ wt}\%$ of the surfactant is removed after reduction for the 5 %Co@ C_{12}E_4 sample (see Fig. 3a). This is also confirmed from analysis of the mass spectrometry (MS) traces in Figure S3, which show that significant mass loss of hydrocarbon species occurs between 50 and 100 min during the reduction treatment.

We propose that in samples that have not been subjected to reduction at elevated temperatures, the deposits remaining on the 5–15 %Co@ C_{12}E_4 surface would present some barrier between H_2 and the Co species preventing sample reduction (*vide infra*). Acetone washing however, removes the C_{12}E_4 compound in the sample (only $\sim 1\%$ remains in the fresh 5 %Co sample, according to Fig. 3a) enabling more facile cobalt oxide reduction. Increasing Co loading (15 %Co) leads to residual surfactant encapsulation in the aggregated CoNPs and is proposed to be the cause of the strong derivative peak at 513 and 701 K in Figure S2b; the first peak is thought to be the decomposition of residual $\alpha\text{-Co}(\text{OH})_2$ (in addi-

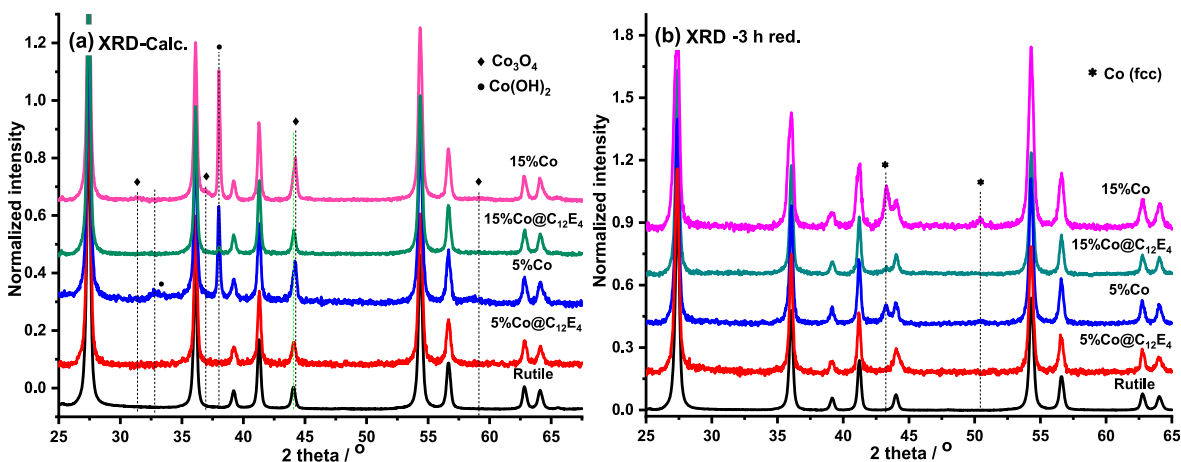


Fig. 1. XRD patterns of 5–15 %Co@C₁₂E₄ and 5–15 %Co catalyst before (a) and after (b) reduction at 623 K in 50 % H₂/He for 3 h. Note that for the samples where the micelle was removed before calcination (a) Co(OH)₂ and Co₃O₄ is detected whereas after reduction (b) the Co-fcc phase is observed.

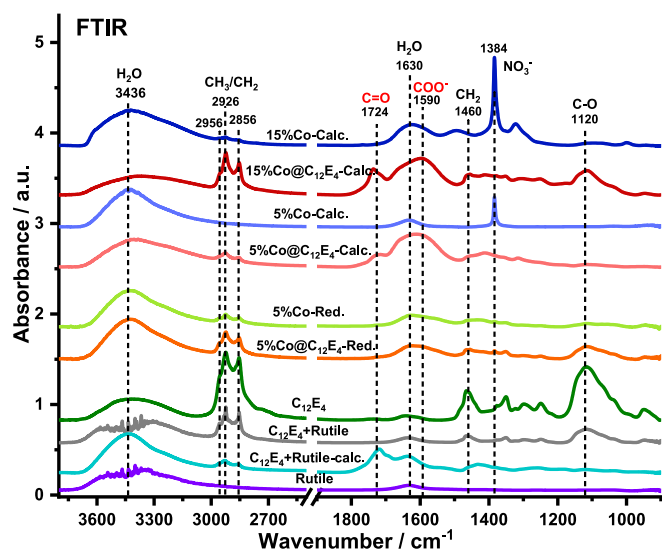


Fig. 2. Reference FTIR spectra for the components used to prepare the catalysts, plus those obtained from samples 5–15 %Co@C₁₂E₄ and 5–15 %Co after calcination and reduction. The unique absorption band at 1724 cm⁻¹ for 473 K calcined catalysts demonstrates the formation of complex-like C₁₂E₄ derivatives. Reduction in H₂ at 623 K for 3 h removes these compounds. Note, the band at 1384 cm⁻¹ disappears in 5 %Co after reduction, indicating decomposition of residual nitrate salt. For the reduced samples, the absorption at ~2900 and 1120 cm⁻¹ is mainly attributed to residual ethanol, which is used for isolation of reduced cobalt from air.

tion to decomposition of residual nitrate salt – see the MS response at *m/z* 28 & 46 after ~30 min in Figure S3f), while the second peak at 701 K is attributable to removal of the residual surfactant.

It is assumed that the initial CoNP size in all samples is broadly similar, since the same one-pot cobalt-micelle solution was used to prepare them. On close inspection of Fig. 4, the mean CoNP size in 5 %Co (10 nm) and 15 %Co (13 nm) is a little larger than that seen for the 5 %Co@C₁₂E₄ (8 nm) and 15 %Co@C₁₂E₄ (9 nm). We attribute the greater particle size seen in the former samples due to the addition of acetone which can break the micelles leading to movement of the Co species and partial aggregation of the CoNPs (Figure S4b). Interestingly, where a Scherrer analysis can be performed on the data shown earlier in Fig. 1b, there is a good correlation with the mean particle size as determined from the Transmission Electron Microscopy (TEM) images (~17 nm of metal CoNPs for 15 %Co, ~11 nm for 5 %Co, ~10 nm for 15 %Co@C₁₂E₄,

~9 nm for 5 %Co@C₁₂E₄). Furthermore, there is consistency in the observation that for samples 5–15 %Co the reflections appear narrower and indicative of larger crystallites (Fig. 1) compared to samples 5–15 %Co@C₁₂E₄.

The reducibility of the cobalt species and the samples in general was determined using H₂-TPR (in 10 % H₂/N₂) and shown in Fig. 5a. In the 5 %Co, there are two groups of H₂ consumption peaks before and after 700 K, corresponding to the reduction of Co₃O₄ and Co(OH)₂ to Co⁰ and CoTiO₃ to Co⁰, respectively [15,48,49,50]. Increasing cobalt loading to 15 wt% (15 %Co), sees significant differences in the reduction behaviour. Firstly, there is a small but unique double-peak before 560 K (~9 % relative to all the H₂-TPR peak area), which is equivalent to the TPR profile of unsupported CoNPs (Co₃O₄), [51,52] indicating the presence of aggregated CoNPs in this sample that are not strongly interacting with the TiO₂ support (see Fig. 5a insert). Additionally, a small bump (see *) just below 500 K in 5 %Co is seen and may be due to the aggregated NPs, but it contributes less to the signal (~5 % of signal intensity). The main consumption of H₂ for the 15 %Co sample in Fig. 5a comprises overlapping responses, corresponding to the delayed reduction of Co₃O₄ + Co(OH)₂ → Co⁰. [49,50] CoTiO₃ formation and reduction to Co⁰ is minimal in this sample based on the negligible H₂ consumption over 800 K, which indicates a weak interaction between cobalt and titania [53]. In contrast, the 5–15 %Co@C₁₂E₄ samples are difficult to reduce with only minor H₂ consumption observed at temperatures below 673 K and only two major peaks (corresponding to Co₃O₄/Co(OH)₂ and CoTiO₃ reduction to Co⁰) present in those samples above this temperature. This can be attributed to the effect of covering of the Co nanoparticles by the surfactant and/or the smaller NP size in the samples. Initially, the reduction of 5 %Co@C₁₂E₄ seems easier than the 15 %Co@C₁₂E₄ (see the high proportion of the H₂ consumption before 623 K in Fig. 5a, namely ~8.2 % for 5 %Co@C₁₂E₄ while only ~2.2 % for 15 %Co@C₁₂E₄). This could be due to the higher weight of surfactant coverage in 15 %Co@C₁₂E₄ (see Figure S2) and indeed support for this proposal can be seen in the form of the negative TCD response at 715 K that is thought to be due to the decomposition of the surfactant [54]. However, the second peak in 5 %Co@C₁₂E₄ centred at 845 K is higher than the peak seen in 15 %Co (810 K). It is proposed that a higher proportion of CoNPs in the 5 %Co@C₁₂E₄ sample are in contact with the titania surface than for the 15 %Co@C₁₂E₄ sample. This would then lead to more cobalt titanate (CoTiO₃) species, which are known to be more difficult to reduce than the cobalt oxides [15,48].

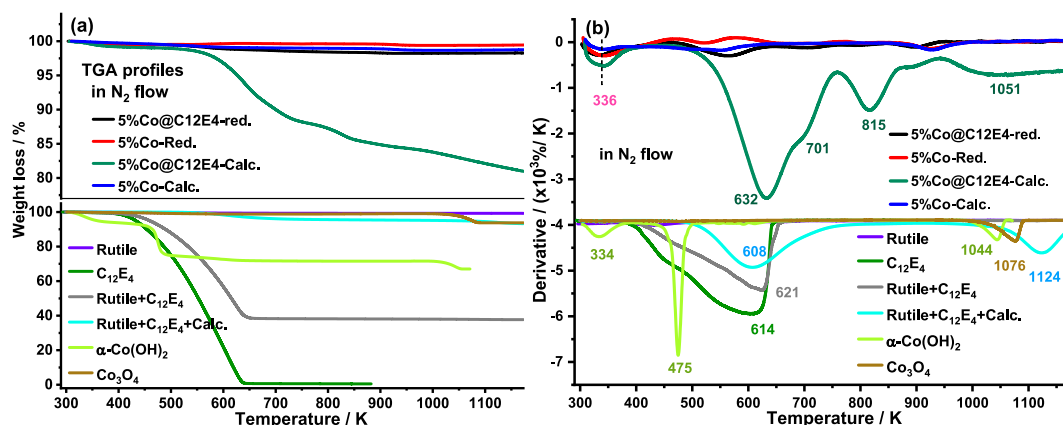


Fig. 3. TGA (a) and the corresponding first derivative (b) profiles of 5%Co@C₁₂E₄ and 5%Co catalysts with and without reduction.

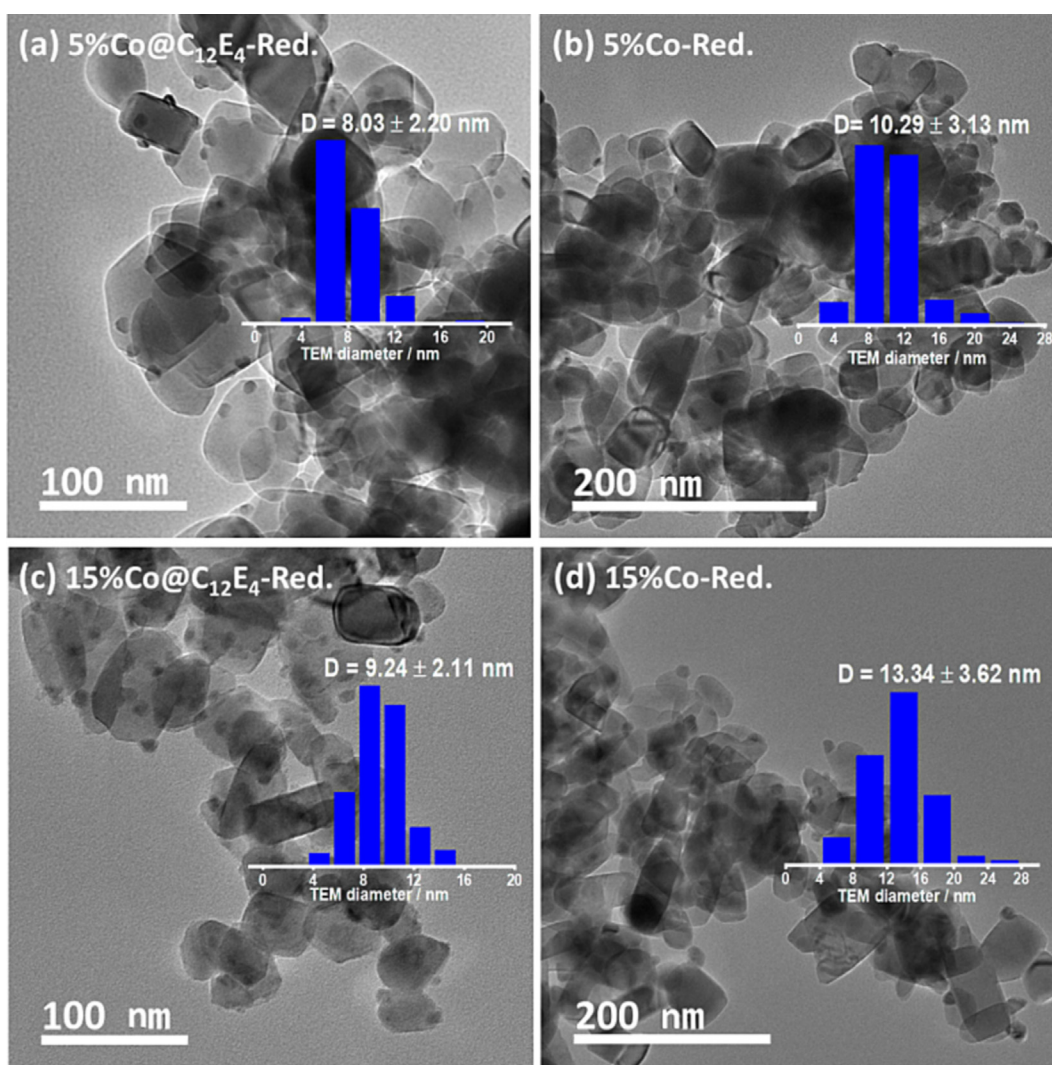


Fig. 4. TEM images and corresponding histograms of nanoparticle size distributions for 5–15 wt% Co loaded catalysts after reduction at 623 K in 50 % H₂/He for 3 h. The observed number of individual NPs is lower in the 5–15 %Co than in the 5–15 %Co@C₁₂E₄ catalysts, although the initial Co loading was the same.

The Degree of Reduction (DOR) of the samples is calculated based on their isothermal H₂-TPR (Fig. 5b). After 3 h at 623 K in 10 % H₂/N₂, the DOR values are: 45.7 % for 5 %Co@C₁₂E₄, 69.1 % for 5 %Co, 55.4 % for 15 %Co@C₁₂E₄ and 85.2 % for 15 %Co respectively. A slower decrease in H₂ consumption is observed for the

5–15 %Co@C₁₂E₄ samples during the isothermal period (at 623 K, particularly a jump centred at 90 min in 15 %Co@C₁₂E₄ in Fig. 5b), while H₂ consumption decays rapidly in the 5–15 %Co samples (e.g. TCD response from 38 to 0 within 45 min for 15 % Co, Fig. 5b). Hence the reduction process occurs to a significant

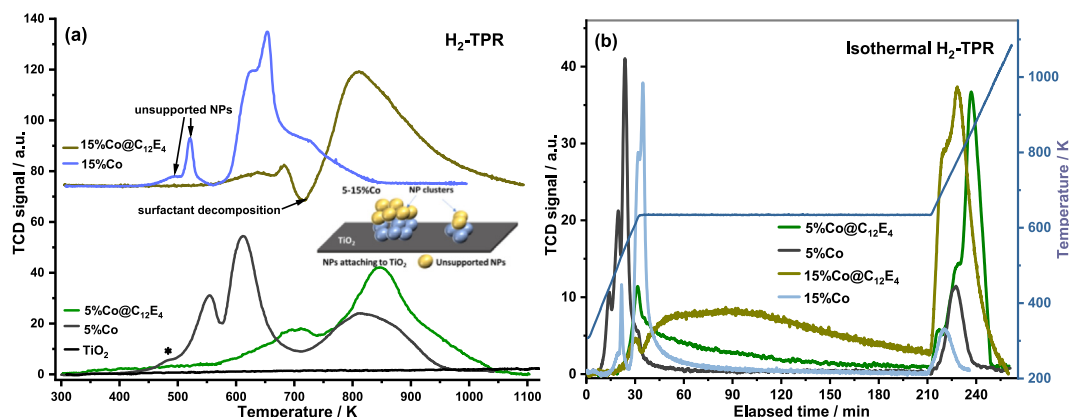


Fig. 5. H₂-TPR using a ramp rate of 10 K/min (a) and isothermal-H₂-TPR at 623 K for 3 h (b) profiles for cobalt catalysts heated in 10 % H₂/N₂ (50 mL/min).

extent during isothermal treatment for the 5–15 %Co@C₁₂E₄ catalysts, while it is negligible for the acetone-washed ones. As mentioned before, residual surfactant can be almost completely decomposed and removed after the 3 h reduction process, so the dominant factor affecting the DOR for 5–15 %Co@C₁₂E₄ would be the coverage of surfactant residue in the early stages of reduction (<1 h, including ramping) and the cobalt-titania interaction in the latter stages (after 1 h reduction). In contrast, for 5–15 %Co, the lack of surfactant residues renders the cobalt-titania interaction more noticeable.

2.2. Visualising the Cobalt-Rutile interface

HAADF-STEM images for the samples 5 %Co@C₁₂E₄ and 5 %Co after reduction for 3 h at 623 K are shown in Fig. 6 a and b, and corresponding Electron Energy Loss Spectra (EELS) are shown in Fig. 6 c and d. The combined STEM/EELS is an insightful technique that allows us to obtain chemical and structural information with high (nm) spatial resolution [55]. From the STEM images, a single CoNP bound to the titania support is clearly observed and from this we can define sub-regions (red squares), labelled respectively from 1 to 8 in Fig. 6 a and b, from where EELS spectra were recorded in order to determine the local Ti and Co species. Only Ti⁴⁺ is detected in the 5 %Co@C₁₂E₄ sample in region 1 (Fig. 6a) which comprises the TiO₂ support, while in the corresponding 5 %Co sample, Ti³⁺ is the main component (see Table S2a for details of the Linear Combination Fitting (LCF) in region 1 of Fig. 6b). Note the nature of the TiO₂ environment (crystalline or non-crystalline) cannot simply be concluded from the visibility of lattice planes in Fig. 6a, b, as this is mainly caused by the orientation of the crystalline domains to the electron beam. Interestingly, both Ti³⁺ and Ti²⁺ are detected at the cobalt-titania interface in both samples (region 2 and Table S2a), although in the 5 %Co@C₁₂E₄ sample Ti⁴⁺ is present in minor amounts (~11 % Table S2a) at this interface. This localised reduction can be explained as an effect of the metallic cobalt promoting TiO₂ reduction to Ti₂O₃ or even to TiO via a H₂ spillover effect [56]. The more reduced TiO₂ in 5 %Co is also evidenced by a respective blue-shift of the Co 2p and red-shift of Ti 2p peaks in the XPS spectra shown in Figure S7.

Similarly, from the EELS spectra in Fig. 6d for the cobalt component, differences in composition can be observed, as determined from LCF analysis (with the results shown in Table S2b). As determined from the above TPR data, less metallic cobalt is determined to be present in the 5 %Co@C₁₂E₄ (~40 %) than in 5 %Co (~60 %). More specifically, regions 2 & 3 in the NP shown in Fig. 6 a & b contain 67 vs 89 and 9 vs 74 % metallic cobalt (Table S2b). The lower quantity of metallic cobalt in region 3 of 5 %Co@C₁₂E₄ is likely due

to surface oxidation during passivation (a flatter NP with a similar CoO_x layer is observed in Fig. 6b) while the low metal content at the interface (region 2) could be due to the strong interaction with TiO₂. The NPs featured in the two samples and depicted in Fig. 6 a & b are similar in width (~13 nm) and height (5–7 nm) and therefore under normal circumstances the DOR for both NPs would be expected to be similar. The fact that they are not, can be ascribed to the effect of the residual C₁₂E₄ surfactant (see Fig. 3). It not only suppresses cobalt oxide reduction but also inhibits H₂ spillover from cobalt to titania and therefore leads to a lower degree of TiO₂ reduction.

EELS spectra in several other regions of Fig. 6 a, b were also acquired and analysed. In regions 6 and 7 of Fig. 6a and regions 3–5 and 7 of Fig. 6b, Ti³⁺/Ti²⁺ species are also detected (Figure S5) although the spectra are noisy. However, no Ti species are seen in regions 3–5 of Fig. 6a and region 6 of Fig. 6b. Analysis of the elemental maps (Fig. 6 a1–a3 and b1–b3) also reveals no Ti on the surface of the CoNP. These observations contrast with findings in the literature where it has been reported that reduced TiO_{2-x} often forms a layer several nanometres thick to fully cover metal NPs [57–59]. Here, Ti³⁺/Ti²⁺ migration leads to decoration of the periphery of NPs at the interface with the support in both samples. This difference could be in part due to the use of the more stable rutile polymorph as opposed to the more common P25 or anatase [12]. It is clear that the decoration of Ti³⁺ in 5 %Co occurs to a greater extent than in 5 %Co@C₁₂E₄ with a high degree of TiO₂ reduction to Ti₂O₃/TiO confirmed in Fig. 6c and Table S2a.

A further examination of the cobalt-titania interaction in the two samples (but from different regions to Fig. 6) was also performed via analysis of the Fast Fourier Transform (FFT) patterns extracted from HAADF-STEM images (Fig. 7). The support of 5 %Co@C₁₂E₄ (region 4 in Fig. 7a) displays a rutile TiO₂ structure (d-spacing 1.7 Å / {2 1 1} planes) and again the FFT patterns show no evidence of (crystalline) TiO_{2-x} on the CoNPs (regions 1 ~ 3, 5); note however that in Fig. 6a, Ti³⁺/Ti²⁺ species are seen at the periphery of the NPs (see EELS spectra in region 6, 7, Figure S5a). However, for 5 %Co in Fig. 7b a corundum Ti₂O₃ structure (region 4 in Fig. 7b) is determined from the FFT patterns (d-spacing 2.7 Å / {10–14}, 2.2 Å / {2–1–13}). Note that Ti₂O₃ is seen at the periphery of the CoNP in Fig. 7b, while it is not detected in similar profiled regions (2 & 5) of Fig. 7a for the 5 %Co@C₁₂E₄ sample. Further evidence of Ti₂O₃ migration to the surface of CoNPs can be seen from the FFT patterns (region 2 of Fig. 7b). The crystal phases of cobalt present in both samples are determined to be either cobalt oxide or metallic cobalt, although the latter is present in lower quantities in 5 %Co@C₁₂E₄ (Fig. 7a) than 5 %Co (Fig. 7b). This is in line with the linear combination fitting results of EELS cobalt spectra in

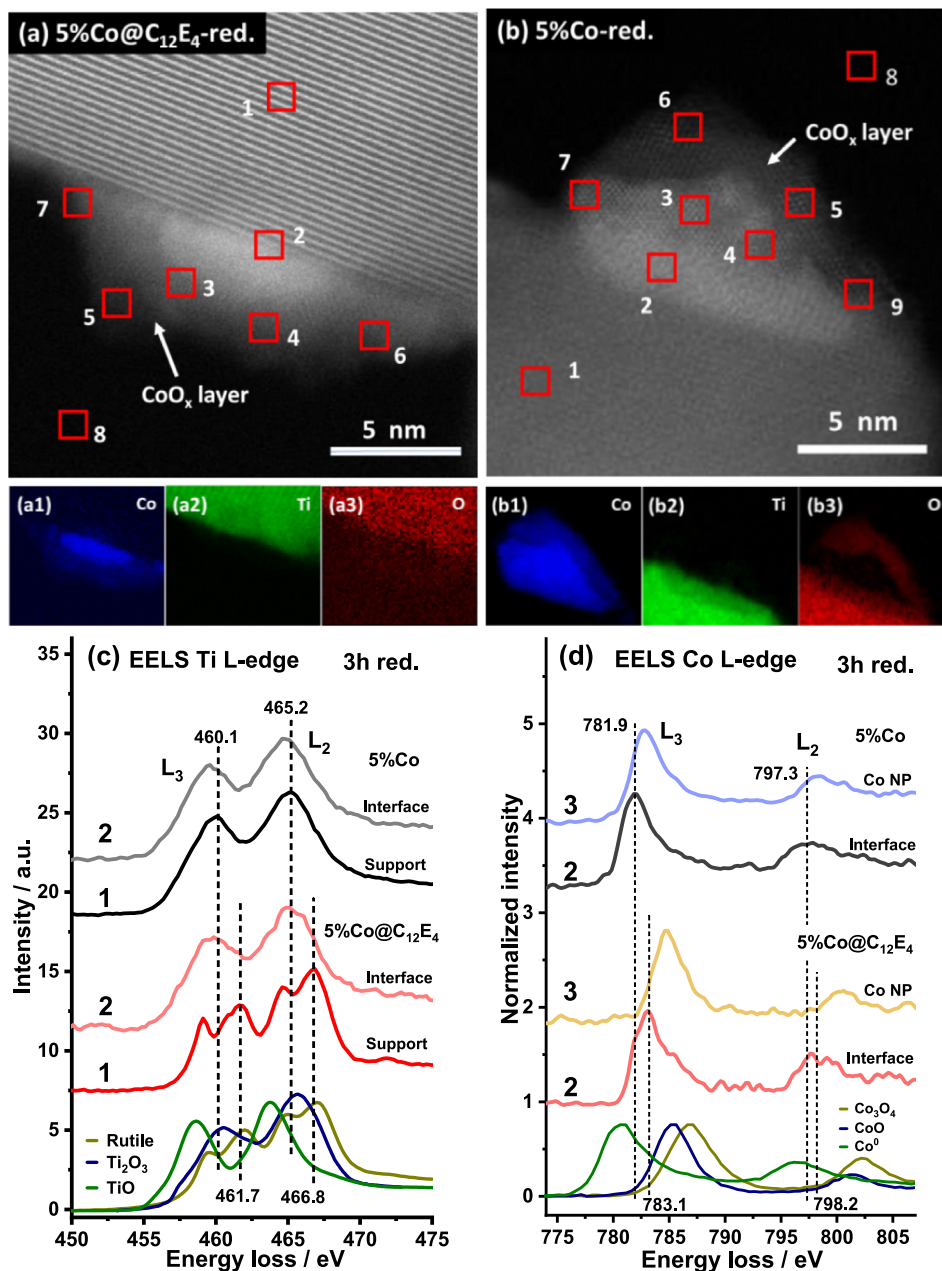


Fig. 6. (a, b) HAADF-STEM images and EELS elemental maps (a1–a3; b1–b3) of the reduced catalysts (3 h, 623 K) with corresponding single point L-edge EELS spectra shown for Ti (c) and Co (d) respectively. The reduced catalysts were passivated with 1 % O₂/He at 303 K for 30 min, hence the presence of a CoO_x layer on the CoNPs.

Table S2b and DOR values from TPR in Fig. 5, and partially due to the NPs being more highly dispersed. The presence of more reduced Co in 5 %Co sample also suggests the TiO_{2-x} layer to be crystalline, which can inhibit gas diffusion [58,60] and protect the reduced cobalt from oxidation during passivation. In contrast, the TiO_{2-x} in 5 %Co@C₁₂E₄ is amorphous and permeable, allowing the contact between gas molecules and NPs and which we propose allows for oxidation of NPs during passivation [58,60]. We propose that the presence of highly dispersed cobalt and low prevalence of Ti³⁺/Ti²⁺ in 5 %Co@C₁₂E₄ are both attributable to the effects of surfactant residues present after calcination.

2.3. Rationalising the differences in CO conversion

A summary of the CO reduction performance of the two types of catalyst under ambient conditions (493 K, H₂/CO = 2, 1 bar) are given in Table S3; note the low conversions obtained allow us com-

pare the catalytic performance. As can be seen in the table, although the CO conversions drop with time, it is clear that the Cobalt Time Yield/Turnover Frequencies (CTY/TOFs) in 5 %Co@C₁₂E₄ are observed to be ~ 4 times higher than in 5 %Co throughout the reaction. A tripling of the cobalt loading to 15 wt% leads to a narrowing of the activity gap (the 15 %Co@C₁₂E₄ CTY/TOFs are only ~ 2 times greater than the 15 %Co sample). When comparing the effects of reduction time, it is noteworthy that the 5 %Co@C₁₂E₄ samples show improved CTY/TOFs with increased reduction time whereas the 5 %Co samples exhibited a worsening in performance. Based on these data it is possible to identify the differences in performance to be due to the amount of active component (i.e. DOR), CoNP size and morphology, etc. The DOR value reflects the amount of metallic cobalt (fcc) present; the component which is considered active and responsible for CO conversion (i.e. 5–15 %Co@C₁₂E₄ samples < 55 % vs 5–15 %Co samples > 69 % reduction). We note however, that in Co/TiO₂ catalysts it has been reported that the

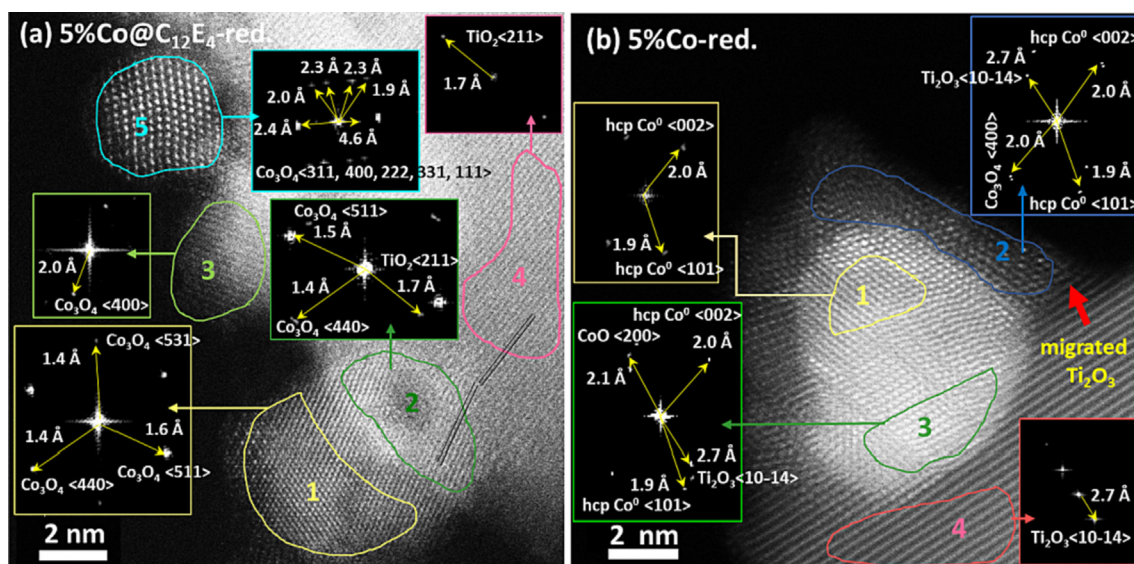


Fig. 7. HAADF-STEM images of the reduced catalysts and their corresponding fast Fourier transform patterns in marked regions for (a) 5%Co@C₁₂E₄-red and (b) 5%Co-red. The reduced catalysts were passivated with 303 K 1 % O₂/He for 30 min before being imaged. In (a) Co₃O₄ is present in regions 1, 3, 5; whilst TiO₂ is the sole component in region 4, whilst region 2 contains a mixture of these oxides. In (b) Co⁰ is seen in region 1; Ti₂O₃ in region 4, and mixture of Co⁰, CoO/Co₃O₄ and Ti₂O₃ in regions 2 and 3. Note changes in the Co or TiO₂ lattice-spacing caused by the metal-support interaction were not detected. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

interface between the Co NPs and TiO₂ is more active, than the Co NPs themselves [11]. We propose therefore that the 5–15 % Co@C₁₂E₄ catalysts possess a larger CoO_x-TiO₂ interface than the 5–15 %Co samples and hence are both more difficult to reduce whilst being more active [11]. When considering the effect of CoNP size in isolation, the larger crystallite sizes (10 and 13 nm respectively) observed in 5–15%Co catalysts indicate that the active surface area for CO conversion should be lower in these samples than those seen in 5–15 %Co@C₁₂E₄ (8–9 nm). Note that differences in intrinsic CO reduction activity should be ignored, as the average NP size is above the critical size range (5–10 nm) reported in literature [24,26]. Another principal cause for lower performance in our TiO₂ supported catalysts is due to a manifestation of the strong metal support interaction (SMSI) effect leading to Co NP decoration with Ti³⁺/Ti²⁺ species [61,62]. According to the HAADF-STEM images shown in Fig. 7, the sub-oxides TiO_{2-x} observed on 5%Co are crystalline and likely impermeable, blocking the contact between syngas and NPs. The presence of C₁₂E₄ derivatives (polymers) on the 5–15 %Co@C₁₂E₄ catalysts appears to prevent TiO₂ from being reduced to TiO_{2-x} and migrating onto the CoNPs, thereby leaving a clean and open surface for CO reduction; this according to TGA which suggested reduction removes all C₁₂E₄ and their derivatives. Therefore, these data indicate that surfactant-coated catalysts can exhibit better CO reduction performance. Indeed, from Table S3, the surfactant coated 5–15 % Co@C₁₂E₄ catalysts exhibit a greater TOF during an ambient pressure CO reduction test. This indicates a combination of smaller NP size, lower degree of CoNP aggregation and extent of Ti³⁺/Ti²⁺ coverage accounts for the differences in performance in surfactant coated 5–15 %Co@C₁₂E₄ samples.

3. Summary and conclusion

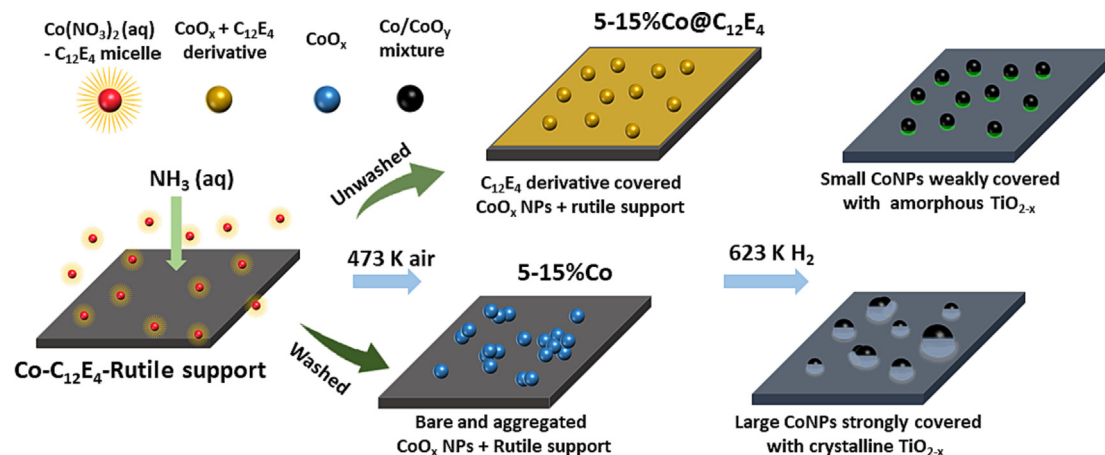
The purpose of this work is to demonstrate how residual C₁₂E₄ surfactant used in catalyst preparation can prevent both CoNP aggregation during preparation and TiO₂ reduction and migration during pre-reduction treatment. Although coverage by TiO_{2-x} species of the CoNPs occurs to some extent in both samples, for 5–15 %Co@C₁₂E₄ the TiO_{2-x} that forms is determined to be

amorphous, permeable and does not cover the NPs so such an extent; thus it can be considered as decoration to the Co NPs [8]. In contrast, the TiO_{2-x} present on the samples where the surfactant was removed before heating, excessive coverage of the Co NPs was observed, by crystalline and impermeable Ti₂O₃ (See Scheme 1). We note that this phase has not been previously identified. This suggests that there is scope to optimise the interaction between the Co NPs and TiO₂ although there is also a risk that too much TiO₂ migration can be problematic even for the rutile polymorph. Critically, it is the surfactant residue that remains after initial thermal treatment that mitigates the titania reduction and encapsulation [60], although as shown here this can be removed by prolonging reduction time or increasing temperature [13]. We note however that this latter treatment needs to strike a balance between being sufficient to effect surfactant removal whilst not leading to excessive titania reduction/Co NP coverage. This study demonstrated that the conditions used here (e.g. 50 % H₂/He, 623 K, 3 h) is beneficial for producing a more active catalyst although there is likely scope for further optimisation of these conditions. This method is of course not limited to the preparation of Co NPs on TiO₂ and may be translated to the preparation of the same CoNPs on other reducible supports (e.g. Nb₂O₅ [10]) else used for the supporting of other metal (Au [13], Rh [58], etc.) NPs thereby expanding the application of surfactant encapsulation to optimise the performance of a catalyst. Catalysts with size-controlled NPs can be easily obtained using this method by simply varying the amount of precursor during NPs preparation. Lastly, the protection of titania reduction by a surfactant can also be applied to some conventional methods for catalyst preparation such as impregnation, for example coating the dried or calcined samples with surfactant (with further heating treatment) before reduction.

4. Methods

4.1. Catalyst preparation

With reference to previously used pentaethylene glycol dodecylether (C₁₂E₅), [33] here an affordable tetraethylene glycol monododecyl (C₁₂E₄, Brij[®] L4, Sigma-Aldrich) was chosen as an



Scheme 1. (Top) Surface $C_{12}E_4$ residues prevent the CoNPs from aggregating and rutile from being reduced. In addition, the gold-coloured sheet in the 473 K calcined 5–15 % $Co@C_{12}E_4$ sample represents the residual $C_{12}E_4$ on the surface, while in the 5–15 % Co sample, the aggregated NPs were shown as blue spheres. TiO_{2-x} migrates in the 5–15 % Co sample and forms a crystalline and impermeable surface (grey solid semicircles), while the partial coverage seen in 5–15 % $Co@C_{12}E_4$ occurs (top depiction) to a lower extent whilst retaining an amorphous and permeable character, (green colour).

alternative surfactant. 5.00 g $C_{12}E_4$ mixing with 26.67 g *n*-hexane (Sigma-Aldrich) were put into a 303 K water bath and stirred at 500 rpm for 2 h to form reverse micelles solution. Then 0.96 g cobalt nitrate hexahydrate (Sigma-Aldrich, > 98 %) in 0.44 g DI water was added and kept stirring for another 1 h under the same conditions. After that, 3.70 g rutile TiO_2 (50 m^2/g , Sigma-Aldrich, 6 h 773 K air calcination before use) was added in the above solution and continuing stirring for another 1 h. Then the system was added with 28 wt% NH_3 (aq) (0.41 g, Sigma-Aldrich) to generate solid NPs and kept stirring for 1 h. Next, splitting the above green mixture into two portions, one portion was dropwise added with > 80 mL acetone (Sigma-Aldrich) to break micelles. The acquired precipitation and liquid mixture was filtered to remove hexane and $C_{12}E_4$ and then washed for 3–5 times by acetone before drying at 373 K for 12 h and calcining at 473 K for > 5 h [33,63]. The generated catalyst was denoted as 5 % Co . The other portion before calcination was heated to 323 K to evaporate hexane and then the obtained sample was referred to 5 % $Co@C_{12}E_4$. Both cobalt loadings in above catalysts were 5 wt%, but decreasing the amounts of rutile, the 15 wt% cobalt loading catalysts were prepared and denoted as 15 % Co and 15 % $Co@C_{12}E_4$, respectively. Sample reduction, normally, was conducted in a HIDDEN CATLAB Microreactor with the condition of 50 % H_2/He flow (20 mL/min), 623 K for 3 h. The reduced samples were either passivated by 1 % O_2/He (303 K, 50 mL/min, 30 min) or protected in pure ethanol before further characterisation.

4.2. UV–vis

The changes of cobalt nitrate- $C_{12}E_4$ micelles in hexane during adding NH_3 (aq) was characterised using a SHIMADZU UV-1800 UV–vis spectrometer in the wavelength range from 300 to 900 nm with a spectral resolution of 2 nm. The measurement conditions were at room temperature and atmosphere and using a pure hexane solvent as reference.

4.3. FTIR

Organic groups residing on above calcined catalysts were studied by FTIR. Before measurement, all the samples were dried at 373 K for 1 h. After cooling down to room temperature, each of the catalysts was diluted with KBr powder, and pressed into 1 mm thick pellets. FTIR measurements were carried out in a

Nicolet iS10 spectrometer under transmission mode with spectral resolution of 4 cm^{-1} .

4.4. TGA

~10 mg sample was analysed in a TGA Q50 V20.13 Build 39 instrument with 50 mL/min N_2 flow. Temperature was ramped from room temperature to 1273 K (10 K/min). Specifically, the reduced samples were obtained with the reduction treatment in catalyst preparation (section 1) but without protection during sample transfer. Then first derivative profiles were obtained by processing the TGA (weight loss) profiles with origin Pro 2019.

4.5. TEM/STEM

Before measurement, the samples were reduced using the above mentioned conditions but with an additional passivation process (303 K, 1 % O_2/He). Reduced catalysts were quickly dispersed using ethanol and an ultrasonic bath (10 min) and then the supernatant was dropped onto a copper TEM grid (mesh size 200) with a carbon film. Next, the sample was dried in air at room temperature and TEM imaging was conducted using a JEOL JEM2100 TEM 200 kV instrument (RCaH). HAADF-STEM and dual-EELS were performed using a JEOL ARM200CF microscope (ePSC, Diamond Light Source) operated at 200 kV. FFT patterns and EELS spectra were extracted from exact regions (i.e. region 1 for pure TiO_2 support, region 2 for cobalt- TiO_2 interface, region 3–7 for different parts of a CoNP and region 8 for background) shown in Fig. 6 and Fig. 7. The TEM/STEM images and FFT patterns were analysed using the ImageJ software (version 1.52e) [64,65]. The NP size is averaged from manually measuring over 100 NPs. The selected EELS spectra were background corrected by using a Gatan DigitalMicrograph software (version 3.30.2016.0) and the EELS references were from EELSDB and EELDC database.

4.6. XRD

A Rigaku Miniflex X-ray diffraction (XRD) instrument (Cu $K\alpha_1$, 45 kV, 2θ 20–70°, step 0.01°, speed 0.2 s°) with fixed divergence slits at ISIS neutron and muon light source was used for measurement. The samples were also reduced at 623 K for 3 h in 50 % H_2/He flow (20 mL/min) and then cooled down to 303 K but quickly moved into ethanol without passivation. Reduced samples measurement was protected by the ethanol solvent and used a low

noise Si background holder while the calcined samples were a standard XRD run at room temperature. The loading of samples on the pucks is just ensuring the sample is finely ground and has a nice flat surface with respect to the puck edge.

4.7. H₂-TPR

Reducibility of the catalysts was tested by employing an Anton Paar ChemBET Pulsar chemisorption analyzer. The H₂-TPR procedures were: pre-treating catalysts in pure He flow (50 mL/min) at 393 K for 30 min then cooling down to 303 K with changing gas to 10 % H₂/N₂ (50 mL/min) and lastly ramping to 1073 K (10 K/min). The outlet gases were analysed by a Thermal Conductivity Detector (TCD) detector. Particularly, the DOR calculations were conducted at an isothermal temperature step of 623 K for 3 h as part of the experiment. DOR calculations were based on the H₂ consumption ratios at temperatures ≤ 623 K versus the total temperature range in the H₂-TPR profiles.

4.8. XPS

XPS analysis for the reduced samples with passivation (same as that for STEM/TEM) was performed on a Thermo Fisher Scientific NEXSA spectrometer at HarwellXPS. This XPS was equipped with a micro-focused monochromatic Al X-ray source (72 W, 400 μm). Data were recorded at pass energies of 50 eV for Co 2p and O 1 s scans with 0.1 eV step size. The samples were measured under the vacuum of 10⁻⁹ mbar and room temperature with a charge neutralisation mode. The recorded data were analysed by CasaXPS (version 2.3.19PR1.0) [66]. The binding energy was calibrated by using C 1 s (284.8 eV).

4.9. Activity for CO reduction

Ambient pressure CO reduction activity was tested on the HIDDEN CATLAB Microreactor. 150 mg powder catalyst was loaded in a quartz tube reactor (using quartz wool to stop catalyst moving) and then reduced in 50 % H₂/He (20 mL/min) at 623 K for 1/3/5 h. After that, the catalyst was cooled down to 423 K and switched to syngas (H₂ 3.3 mL/min; 10 % CO/He 16.7 mL/min). Lastly, the temperature was ramped to 493 K and kept for > 1.5 h. The outlet gases before and after reaction were recorded by using an equipped mass spectrometer (MS) with m/e equal to 2, 4, 15, 18, 26, 27, 28, 41, 43, 44, 57, 58, 71. The CO conversions were calculated based on the MS CO calibrated intensity (m/e = 28) changes. Note all the fragments' intensities (i.e. m/e = 2, 15, 18 ... 71) were calibrated by the inert standard gas He (m/e = 4).

$$\text{CO conversion} = \frac{I_{\text{CO}}(\text{initial}) - I_{\text{CO}}(\text{FTS})}{I_{\text{He}}(\text{initial})} \times 100\%$$

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper: [Andrew Beale reports a relationship with Finden Ltd that includes: consulting or advisory, employment, equity or stocks, funding grants, non-financial support, and travel reimbursement].

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcat.2023.02.002>.

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