**Phenylacetylene Hydrogenation Coupled with
Benzyl Alcohol Dehydrogenation over Cu/CeO₂:
A Consideration of Cu Oxidation State**

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Abstract

We have examined the effect of copper oxidation state in the continuous gas phase coupled phenylacetylene hydrogenation (to styrene) with benzyl alcohol dehydrogenation (to benzaldehyde) over Cu/CeO₂. Analysis by H₂-TPR, XPS, XRD and STEM-EDX analyses demonstrates the generation of a range of Cu oxidation states (Cu⁰ (13-77%), Cu⁺ (13-74%), Cu²⁺ (0-55%)). The stepwise formation of styrene and ethylbenzene was promoted in the stand-alone phenylacetylene hydrogenation. An increase in Cu⁰/Cu⁺ (from H₂-TPR and XPS) enhanced H₂ chemisorption and styrene *TOF*, but with low hydrogen utilisation efficiency. The formation of benzaldehyde and toluene was promoted in the stand-alone dehydrogenation of benzyl alcohol, where benzaldehyde selectivity and *TOF* correlate with the concentration of Cu⁰. Full hydrogen utilisation, exclusive benzaldehyde/styrene formation and a (3-fold) greater styrene *TOF* (to attain 100% yield) was achieved in the coupled process, where hydrogenation/dehydrogenation activity correlates with Cu⁺/Cu⁰. This opens new directions for sustainable "hydrogen free" hydrogenations over *non*-noble Cu catalysts.

Key words: Coupling process, phenylacetylene hydrogenation, benzyl alcohol dehydrogenation, copper oxidation state, Cu/CeO₂.

1 Introduction

Hydrogenation products are an important class of chemicals often produced industrially in batch systems using pressurised (5-100 bar) *non-renewable* H₂ [1]. Coupling catalytic dehydrogenation with hydrogenation involves *in situ* hydrogen generation, transfer and utilisation [2]. It can be considered as a promising alternative that circumvents the requirement for external H₂ with the possible generation of two high value products. However, catalytic coupling processes have only been demonstrated for a limited number of molecular combinations to date, most notably the coupled reduction of aldehydes/ketones (*e.g.* furfural [3], acetophenone [4]) with dehydrogenation of aliphatic alcohols (*e.g.* 2-butanol, 2-propanol [5]). We are not aware of any report in the literature that involves -C≡C- bond transformation in tandem dehydrogenation-hydrogenation, the focus of this work. Two active sites are required for dehydrogenation and hydrogenation in the coupled system. Several catalysts have now been employed, primarily noble multi-metallic systems including bimetallic (*e.g.* Co-Ru [5] and Au-Cu [6]) and alloy catalysts (*e.g.* NiRuPtAu [7] and PdCu [3]). The use of a *non-noble* monometallic catalyst is an attractive consideration in the development of an effective catalyst, given the associated straightforward synthesis and low cost. However, there is a requirement for a bifunctional behaviour where the same metal promotes both steps. The metal oxidation state can control catalytic response [8]. Indeed, while metallic Au and Ag promote hydrogenation (*e.g.* nitroarenes [9,10]), the electron deficient counterparts (Au^{δ+} and Ag⁺) have been deemed active in the oxidative dehydrogenation of alcohols (*e.g.* benzyl alcohols, ethanol [11,12]). The use of monometallic catalysts in coupled dehydrogenation-hydrogenation is quite limited. Nevertheless, Jae *et al.* [13] examined the liquid phase coupled 2-propanol/5-(hydroxymethyl)furfural reaction over Ru/C and identified Ru⁰ and Ru⁴⁺ as the active species for dehydrogenation and hydrogenation, respectively. In a recent study, Reddy and co-workers [14] investigated the tandem 2-propanol/hydrocinnamaldehyde process using a series of oxide (SiO₂,

Al₂O₃, MgO and ZrO₂) supported Cu catalysts and attributed the differences in catalytic response to variations in copper dispersion and acid-base properties of the support. Copper promotes $\text{-C}\equiv\text{C-}$ bond hydrogenation [15] and alcohol dehydrogenation [16]. The active form of copper in alkyne hydrogenation still remains unknown and there is no general consensus regarding the copper oxidation state responsible for catalytic activity in alcohol dehydrogenation, *i.e.* Cu⁺ [17] and/or Cu⁰ [18] have been identified as the active species. The ultimate copper oxidation state is determined by the Cu precursor [19], synthesis method [19], activation conditions [20] and nature of the carrier [19]. It is difficult to establish an explicit link between dehydrogenation/hydrogenation response and Cu oxidation state from the available literature.

Herein, we have considered the continuous production of styrene, a precursor of polystyrene with an annual worldwide production of 1 million tonnes per year [21], *via* hydrogenation of phenylacetylene coupled with benzyl alcohol dehydrogenation to benzaldehyde, an important intermediate in the pharmaceutical and cosmetic industries [22] (**Figure 1**). The target styrene and benzaldehyde products can be readily separated by liquid-liquid extraction [23]. The industrial manufacturing of styrene by catalytic dehydrogenation of ethylbenzene over Fe-K-Cr oxide-based catalysts is inefficient due to (i) the multi-step nature of the process, (ii) catalyst deactivation and (iii) formation of propylene oxide as a by-product [24]. Gas phase catalytic hydrogenation of phenylacetylene has emerged as a viable alternative with a lower associated cost but over-hydrogenation (to ethylbenzene) is difficult to fully circumvent, notably at conversions >80% [25]. Commercial benzaldehyde production can involve hydrolysis of benzyl chloride or oxidation of benzyl alcohol using (toxic) chromium and manganese salts with production of hazardous waste [22]. Gas phase dehydrogenation of benzyl alcohol in N₂ at $P = 1$ atm offers clear economic and environmental advantages [22], but an exhaustive search through the literature unearthed only two studies using MgO [22] and hydrotalcite [26] supported copper catalysts, where toluene

was formed as a by-product.

Figure 1: Schematic reaction network for coupled process (framed) of benzyl alcohol dehydrogenation to target (I) benzaldehyde (with undesired C-O hydrogenolysis to (II) toluene) and phenylacetylene semi-hydrogenation to target (III) styrene (with undesired over-hydrogenation to (IV) ethylbenzene). *Note:* Solid arrows denote target reactions, dashed arrows indicate routes to undesired products while dotted arrows illustrate utilisation of hydrogen released from benzyl alcohol dehydrogenation in the hydrogenation of phenylacetylene and carbon-oxygen hydrogenolysis to toluene.

We provide in this work the first direct correlation between dehydrogenation-hydrogenation response and Cu oxidation state in the gas phase benzyl alcohol dehydrogenation coupled with phenylacetylene hydrogenation over a series of Cu/CeO₂ catalysts. We demonstrate that product distribution can be tuned by changing the Cu oxidation state and switching from the stand-alone (independent dehydrogenation and hydrogenation) to the coupled process.

2 Materials and Methods

2.1 Catalyst Preparation and Activation

The CeO₂ support and bulk CuO (Sigma-Aldrich, 99.99%) were used as received. Five

CeO₂ supported (1 and 15% wt.) Cu catalysts were synthesised by deposition-precipitation or standard impregnation and activated in flowing hydrogen (60 cm³ min⁻¹, 2 K min⁻¹ to 573-773 K; BOC, >99.99%). The metal content, preparation method and final temperature during hydrogen thermal treatment were selected in order to generate a series of catalysts with different Cu⁺/Cu⁰ molar ratio. The samples synthesised by deposition-precipitation or impregnation are denoted in this paper by the prefix "DP" and "IM", respectively, followed by the Cu content (1 or 15% wt.) with the associated activation temperature (573 or 773 K) specified in parentheses. DP1(573), DP15(573) and DP15(773) were synthesised (at 353 K) by drop wise addition of a sodium hydroxide solution (2 M, Fisher Scientific, ≥97%) to a suspension containing the CeO₂ carrier (3 g) and the metal precursor (Cu(NO₃)₂·3H₂O, 40-600 cm³, 1 × 10⁻² M, Sigma-Aldrich, 99%), kept under constant (650 rpm) agitation until pH = 10. The system was aged (353 K, 650 rpm, 4 h) to guarantee homogeneous deposition of Cu²⁺ species. The precipitate was extracted by filtration, washed (distilled water until pH = 7) and dried (45 cm³ min⁻¹ N₂, 393 K, *ca.* 12 h, BOC, >99.99%). IM1(773) and IM15(773) synthesis was based on standard impregnation with aqueous CuCl₂ (35-525 cm³, 2 × 10⁻² M, 4 g of CeO₂, Sigma-Aldrich, 99.99 %), where the slurry was heated (353 K, 650 rpm) until total evaporation; drying step as above. The catalyst precursors were sieved (75 μm, ATM fine test sieve), activated in H₂ (step as above) and passivated at room temperature (60 cm³ min⁻¹ 1% v/v O₂/N₂) for *ex situ* characterisation.

2.2 Catalyst Characterisation

The copper content was determined by atomic absorption spectroscopy (AAS, Shimadzu AA-6650 spectrometer, air-acetylene flame) from the extract in 25% v/v HNO₃/HCl. Temperature programmed reduction (H₂-TPR)/ desorption (H₂-TPD) and hydrogen chemisorption analysis (at 498 K) were carried out in the commercial CHEM-BET 3000 unit (Quantachrome Instrument, detector = TCD, software = TPR WinTM). H₂-TPR (17 cm³ min⁻¹,

5% v/v H₂/N₂, 2 K min⁻¹ to 573-773 K) was employed to determine the extent of Cu and CeO₂ reduction, and the amount of surface chlorine [19], *i.e.* profile curve fitting (software = CasaXPS 2.3.17) serves to quantify the amount of hydrogen consumed during each transition step ($\alpha = \text{Cu}^{2+} \rightarrow \text{Cu}^+$, $\beta = \text{Cu}^+ \rightarrow \text{Cu}^0$, $\gamma = \text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ and $\delta = 2\text{Cl}^* \rightarrow 2\text{HCl}$; Cl* indicates adsorbed chlorine on the catalyst surface) and extract the concentration of copper species (denoted Cu_{TPR}²⁺, Cu_{TPR}⁺ and Cu_{TPR}⁰), Ce³⁺ (Ce_{TPR}³⁺) and adsorbed chlorine (Cl_{TPR}^{*}). *Post* H₂-TPR, physisorbed hydrogen was removed by treatment in flowing N₂ (65 cm³ min⁻¹, 1.5 h) at the final activation temperature. Hydrogen consumption during activation was corrected using H₂-TPD (50 cm³ min⁻¹, N₂, 50 K min⁻¹ to 1073 K for 1 h; the profiles for the four Cu/CeO₂ catalysts are included in **Figure S.1** of the **Supplementary Information**) recorded in parallel directly after TPR to explicitly determine hydrogen utilised in the reduction of ceria. The samples were then cooled to room temperature and underwent hydrogen chemisorption by pulse (10-20 μl) titration. H₂ uptake reproducibility was better than $\pm 5\%$ and the values quoted in this work are the mean; there was no detectable hydrogen uptake on the ceria support alone.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Scienta ESCA 300 spectrometer using a monochromatic Al anode (K α 1486.6 eV, 10 kV, 20 mA). Before analysis, the Cu/CeO₂ catalysts were activated *in situ* in a pre-chamber under H₂ atmosphere (base pressure = 10⁻⁸ mbar, H₂ partial pressure = 10⁻⁶ mbar; 2 K min⁻¹ to 573-773 K) and subsequently subjected to ultra-high vacuum conditions (*ca.* 10⁻⁸ mbar). Full range survey (0–1100 eV) and high-resolution spectra (over the Cu 2*p*, Ce 3*d* core levels and Cu LMM Auger region) were collected; analyser pass energy = 150 eV. The Ce 3*d* u''' peak was calibrated at binding energy (B.E.) = 917 eV and used as an internal standard to compensate for charging effects [27]. Spectral curve fitting and quantification used the CasaXPS software, employing relative sensitivity factors provided by Scienta. The distribution of Cu and Ce

oxidation states was also derived from XPS curve fitting by fixing the B.E. for each Cu species (Cu^0 and Cu^+ ($\text{Cu } 2p_{3/2}$ B.E. ≤ 933 eV) and Cu^{2+} (>933 eV)) and Ce peaks (u''' peak B.E. = 917 eV with the $3d_{5/2}$ and $3d_{3/2}$ peaks separated by -18.3 ± 0.3 eV) according to reported literature [27,28], using the Gaussian-Lorentzian curves after subtracting a Shirley background with a full width at half maximum (fwhm) fixed at 2.6-3.6 eV over $\text{Cu } 2p_{3/2}$ [29] and 2.6-4.9 eV over $\text{Ce } 3d$ [30] regions. The concentration of Cu in different oxidation states derived from XPS data fit was compared with that determined according to the method described by Jasieniak and Gerson as reported in [31], *i.e.*

$$\text{Cu}_{\text{XPS}}^{2+} (\%) = \frac{B(1 + A_s/B_s)}{A + B} \times 100 \quad (1)$$

$$(\text{Cu}_{\text{XPS}}^0 + \text{Cu}_{\text{XPS}}^+) (\%) = \frac{A - (A_s/B_s)B}{A + B} \times 100 \quad (2)$$

where A and B are the experimental areas of the main and shake-up $2p$ peak of Cu^{2+} , respectively, while A_s/B_s represents the theoretical value for the ratio between the main and shake-up $2p$ peaks of pure Cu^{2+} (*i.e.* $\text{Cu}(\text{OH})_2$ $A_s/B_s = 1.57$; $\text{CuCl}_2 = 1.63$ [31]). It is important to note that the values for the distribution of Cu oxidation states extracted from curve fitting of experimental data and using the method of Jasieniak and Gerson did not exceed 5%, considered acceptable [31]; the values quoted in this study (*i.e.* $\text{Cu}_{\text{XPS}}^{2+}$, Cu_{XPS}^+ and Cu_{XPS}^0) are the mean. XPS data recorded from the Cu LMM region was used to calculate the modified Auger parameter α' , defined as the sum of the binding energy of the $\text{Cu } 2p_{3/2}$ and the kinetic energy of the Cu LMM peaks [31]. The distribution of copper oxidation states was also examined using the Wagner plot generated with data extracted from the analysis of the photoelectron and Auger electron regions. Reference data (*i.e.* B.E., K.E. and I') extracted from [31,32] for Cu^{2+} , Cu^+ and Cu^0 were also included in the plot to facilitate the elucidation of the surface copper species.

The (powder) X-ray diffractograms (XRD) were collected with a Bruker/Siemens D500 instrument (radiation = Cu K α , scan rate = 0.02° step⁻¹, range = 5° ≤ 2θ ≤ 85). Diffractograms were compared with the JCPDS-ICDD reference standards, *i.e.* Cu (004-0836), CeO₂ (043-1002) and CeClO (153-4659), for identification. Metal particle morphology was evaluated by probe corrected scanning transmission electron microscopy (STEM) using a FEI Titan Themis unit equipped with an energy dispersive X-ray (EDX) detector operated at an accelerating voltage of 200 kV. The scanned images were collected on a Fischione High Angle Annular Dark Field or FEI Annular Dark Field detector using the FEI TIA software (version 4.9 SP1) for data acquisition and analysis. Specimen preparation involved (dry) deposition on a holey carbon/Au (or Ni) grid (300 Mesh). The surface area-weighted mean copper nanocrystal size (d) was obtained from a measurement of up to 170 individual metal nanoparticles using the relationship:

$$d = \frac{\sum_i n_i \cdot d_i^3}{\sum_i n_i \cdot d_i^2} \quad (3)$$

where n_i is the number of particles of diameter d_i . Copper particle size distribution fitting was performed using Gaussian line shape functions. The identification of elements from EDX analysis was based on the Gatan DigitalMicrograph software (Bruker database), which revealed the presence of (i) Cu (signals at 0.93, 8.05 and 8.90 keV) from the supported metal phase, (ii) Au (2.20, 9.71) or Ni (0.85, 7.48, 8.27) from the grid and (iii) Ce (4.84-5.80) and O (0.53) from the support.

2.3 Catalyst Testing

Reactions (stand-alone hydrogenation of phenylacetylene in toluene under H₂, stand-alone dehydrogenation of benzyl alcohol under N₂ and coupled dehydrogenation/hydrogenation of benzyl alcohol/phenylacetylene under N₂) were carried

out in a (continuous) fixed-bed glass tubular reactor (i.d. = 15 mm, 433-573 K, 1 atm), after (*in situ*) catalyst activation under conditions of negligible mass/heat transfer constraints. The organic reactant(s) was(were) vaporised and reached reaction temperature in a preheating zone of (1 mm) borosilicate glass beads situated above the catalytic bed. The reaction temperature in the catalyst bed was monitored (continuously) with a thermocouple and kept constant (± 1 K) by mixing the Cu/CeO₂ catalyst (1-50 mg) with (75 μ m) ground glass. The organic reactant(s) was(were) fed into the reactor at a fixed calibrated flow rate (2×10^{-2} cm³ min⁻¹) *via* a glass air-tight syringe (Hamilton) and Teflon line with a microprocessor-controlled infusion pump (Model 100 kd Scientific). The stand-alone (uncoupled) reactions were conducted in a co-current flow of N₂ with benzyl alcohol (gas hourly space velocity (*GHSV*) = 3×10^3 h⁻¹, molar copper to reactant feed rate ($n/F_{\text{benzyl alcohol}}$) = $8 \times 10^{-5} - 4 \times 10^{-4}$ h) and H₂ with phenylacetylene (*GHSV* = 3×10^3 h⁻¹, $n/F_{\text{phenylacetylene}}$ = $2 \times 10^{-4} - 5 \times 10^{-2}$ h, H₂ content 80 times in excess to the stoichiometric requirement for the formation of styrene). Reactant conversion in the stand-alone reactions was varied by changing the n/F , altering the amount of catalyst while maintaining the total volume of the bed constant (884 mm³). The coupled reaction was conducted in N₂ (*GHSV* = 3×10^3 h⁻¹, $n/F_{\text{phenylacetylene}}$ = $9 \times 10^{-5} - 2 \times 10^{-4}$ h, Alkyne:Alcohol molar ratio = 1-191). The reactor effluent was condensed in a liquid N₂ trap for subsequent analysis, which was made by capillary gas chromatography (Perkin-Elmer Auto System XL, detector = FID, column = DB-1 J&W Scientific (length = 50 m, i.d. = 0.33 mm, film thickness = 0.20 μ m)). Qualitative analysis for the presence of HCl was carried out by flowing the gas through a two-necked gas-scrubbing bottle containing an aqueous NaOH solution (2×10^{-3} M, pH = 8.9) kept under constant agitation at 300 rpm with independent pH (Corning 440 pH Bench-meter) analysis. Before each run, the system was flushed with N₂. The reactants (benzyl alcohol (Acros organic, 99%) and phenylacetylene (Sigma-Aldrich, 98%)) and products/solvent (toluene (Sigma-Aldrich, 99.8%), benzaldehyde

(Fischer Scientific, $\geq 99\%$), ethylbenzene (Fluka, $\geq 99\%$) and styrene (Sigma-Aldrich, $\geq 99\%$) and the gasses (He, N₂, and O₂ (BOC, $>99.99\%$)) were used as supplied, without further purification. Data acquisition and analysis were carried out using the TurboChrom Workstation (version 6.3.2) chromatography data system. Calibration plots (not presented) were used to calculate reactant/product molar fractions (x_i). In a series of preliminary blank tests, there was negligible conversion by passing (i) each reactant in a stream of N₂ or H₂ over the (CeO₂) support alone or through the empty reactor or (ii) phenylacetylene in a stream of N₂ over the activated Cu/CeO₂ catalysts. Reactant (i) conversion (X_i) is defined by

$$X_i (\%) = \frac{[\text{Reactant}]_{i,\text{in}} - [\text{Reactant}]_{i,\text{out}}}{[\text{Reactant}]_{i,\text{in}}} \times 100 \quad (4)$$

and selectivity in terms of product "j" (S_j) is given by

$$S_j (\%) = \frac{[\text{Product}]_{j,\text{out}}}{[\text{Reactant}]_{i,\text{in}} - [\text{Reactant}]_{i,\text{out}}} \times 100 \quad (5)$$

where the subscripts "in" and "out" indicate "inlet" and "outlet" gas streams, respectively. Catalytic activity is also expressed as initial production rate (R , mol_{product} mol_{Cu}⁻¹ h⁻¹) defined as:

$$R (\text{mol}_j \text{ mol}_{\text{Cu}}^{-1} \text{ h}^{-1}) = \frac{F_i \times X_{i,0} \times S_j}{n} \quad (6)$$

where $X_{i,0}$ represents the initial conversion of reactant "i" determined from time on-stream measurements as described in detail in the **Supplementary Information (Figure S.2)** according to [33]. Turnover frequency (TOF , initial production rate per surface copper, h⁻¹) was obtained using the metal dispersion (D) derived from microscopy measurements according to:

$$TOF (\text{h}^{-1}) = \frac{R}{D} \quad (7)$$

Hydrogen utilisation efficiency in the stand-alone hydrogenation *vs.* coupled process was

assessed by:

$$\text{H}_2 \text{ utilisation efficiency} = \frac{\text{H}_2 \text{ supplied}}{\text{H}_2 \text{ consumed}} \quad (8)$$

where "H₂ supplied" is the molar hydrogen provided, either (i) *via* alcohol dehydrogenation or (ii) from an external gas cylinder supply, and "H₂ consumed" indicates the amount utilised in phenylacetylene conversion corrected with the surface hydrogen *post*-TPR from H₂-TPD; H₂ utilisation values >> 1 indicate low efficiency. Carbon mass balance and data reproducibility was better than ±10%.

3 Results and Discussion

3.1 Catalyst Characterisation

3.1.1 H₂-TPR/XPS/H₂ Chemisorption Analyses

Catalytic performance in dehydrogenation/hydrogenation reactions is dependent on the concentration of surface active sites. In the case of Cu/CeO₂, this is linked to the Cu⁰ and Cu⁺ concentration at the surface. In addition, the metal hydrogen uptake capacity is of practical importance in hydrogenation applications [34]. Hydrogen TPR measurements were conducted to examine the reducibility of the copper phase. The surface composition and chemical/electronic state of copper in the activated catalysts was determined by XPS analysis. The hydrogen uptake capacity of the Cu/CeO₂ catalysts was measured by hydrogen titration at reaction temperature (= 498 K).

The H₂ TPR profiles for the DP1 (**Ia**), DP15 (**Ib**), IM1 (**IIa**) and IM15 (**IIb**) catalysts are shown in **Figure 2**; hydrogen consumption and distribution of Cu oxidation states derived from curve fitting the H₂-TPR response is presented in **Table 1**. Each profile exhibits a broad positive peak (H₂ consumption) over the temperature range *ca.* 400-500 K (DP samples) and *ca.* 600-670 K (IM), which are close to the range of values reported (413-505 K (DP) [35,36] and 523-648 K (IM) [37,38]) for the conversion of Cu²⁺ into metallic Cu. A stepwise Cu²⁺ →

$\text{Cu}^+ \rightarrow \text{Cu}^0$ sequence has been proposed elsewhere [20] based on H_2 -TPR measurements where a mixture of the three copper species prevailed at $T \geq 580$ K [39]. The volume of hydrogen consumed exceeded (by a factor up to 2) the amount required for the formation of metallic copper in all the catalysts, but was significantly lower (up to a 96-fold) than that required for the reduction of $\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3$. This result is indicative of additional hydrogen consumption by (i) surface Cl species generated from the (CuCl_2) metal precursor [19] and/or (ii) the CeO_2 carrier, that can result in partial reduction, notably at the Cu-support interface [40].

Figure 2: H_2 -Temperature programmed reduction (H_2 -TPR) profiles for Cu/CeO_2 catalysts prepared by (I) deposition-precipitation (DP) and (II) impregnation (IM) with (a) 1% wt. and (b) 15% wt. Cu loading. *Note:* Raw data are shown as open symbols ($\circ$) while curve fitted and envelope are represented by solid and dashed lines, respectively. Hydrogen consumption peaks associated with $\text{Cu}^{2+} \rightarrow \text{Cu}^+$, $\text{Cu}^+ \rightarrow \text{Cu}^0$, $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ and $2\text{Cl}^* \rightarrow 2\text{HCl}$ transitions are represented by α , β , γ and δ , respectively.

Table 1. Physico-chemical properties of Cu/CeO₂ catalysts.

			DP1(573)	DP15 (573) (773)		IM1(773)	IM15(773)
Metal loading (%wt.)			1	15		1	15
H ₂ -TPR	H ₂ consumed (μmol g ⁻¹)	(Cu _{TPR} ²⁺ , %)	(-)	(50)		(-)	(20)
		α (Cu _{TPR} ⁺ , %)	80 ^a / 79 ^b (74)	655 ^a / 1180 ^b (14)		73 ^a / 78 ^b (23)	1049 ^a / 1180 ^b (66)
		β (Cu _{TPR} ⁰ , %)	21 ^a / 79 ^b (26)	470 ^a / 1180 ^b (36)		56 ^a / 78 ^b (77)	190 ^a / 1180 ^b (14)
		γ (Ce _{TPR} ³⁺ , %)	106 ^a / 11504 ^b (1)	1547 ^a / 9877 ^b (15)		180 ^a / 11504 ^b (2)	139 ^a / 9877 ^b (1)
		δ (Cl _{TPR} [*] , %)	-	-		-	1060 ^a / 2360 ^b (55)
XPS	B.E. (eV)	Cu _{XPS} ²⁺ (%)	-	934 (55)	934 (19)	-	935 (25)
		Cu _{XPS} ⁺ (%)	933 (74)	933 (13)	932 (51)	933 (23)	932 (62)
		Cu _{XPS} ⁰ (%)	930 (26)	932 (32)	930 (30)	931 (77)	930 (13)
<i>d</i> (nm) ^c			2	7	8	4	13
<i>D</i> (%) ^d			50	15	12	25	8

^aexperimental value; ^btheoretical amount of hydrogen required for transition step; ^cmean particle size from STEM analysis (see **Eqn. 3**); ^dcopper dispersion from STEM analysis. *Note:* Hydrogen consumption peaks during TPR associated with Cu²⁺→Cu⁺, Cu⁺→Cu⁰, Ce⁴⁺→Ce³⁺ and 2Cl*→2HCl transitions are represented by α, β, γ and δ, respectively, where * denotes adsorbed Cl.

The H₂-TPR profile for the DP1(573) sample (**Figure (Ia)**) presents, after deconvolution, a main peak at $T_{\max} = 446$ K, corresponding to the reduction of $\text{Cu}^{2+} \rightarrow \text{Cu}^+$, the hydrogen uptake associated with this signal matched (to $\pm 1\%$, **Table 1**) the amount required for the α transition. A peak at higher $T_{\max}$ ($= 454$ K) and lower intensity can be related to a partial reduction to metallic copper (*i.e.* $\text{Cu}^+ \rightarrow \text{Cu}^0$) [41]. The associated hydrogen consumption was significantly lower than the amount required for the full β transition (21 vs. 79 $\mu\text{mol g}^{-1}$; **Table 1**) and is consistent with a mixture of Cu^+ (74%) and Cu^0 (26%) *post* H₂-TPR. The presence of Cu^+ and Cu^0 species after thermal treatment in H₂ at 423-673 K was also observed by Dandekar *et al.* (for Cu/C) [42] and Kundakovic and Flytzani-Stephanopoulos (for Cu/CeO₂) [43]. An additional positive signal at 461 K can be attributed to partial reduction of the support, *i.e.* $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$; γ , with the occurrence of oxygen vacancies as a result of spillover hydrogen, *i.e.* migration of H to the ceria support. The degree of copper reduction appears to be sensitive to the strength of metal-support interactions [44] where surface defects on the carrier can stabilise transition metal nanoparticles, rendering them less susceptible to reduction [43]. While the presence of Cu^+ *post* H₂-TPR can be attributed to strong copper interaction with CeO₂ oxygen vacancies, there is also the possibility of a stabilisation of Cu^+ species *via* the redox equilibrium $\text{Ce}^{4+} + \text{Cu}^0 \leftrightarrow \text{Ce}^{3+} + \text{Cu}^+$ [45]. The H₂-TPR profile for the DP15(573) catalyst (**Figure (Ib)**) is very similar to that recorded for DP1(573) (*i.e.* peaks at $T_{\max}$ 442 ± 4 K, 451 ± 3 K and 464 ± 3 K), albeit a far greater difference between the experimental and theoretical hydrogen requirements for the (α , β , γ) transition steps, which results in a modified distribution of copper and Ce^{3+} species with different oxidation states ($\text{Cu}^{2+} = 50\%$, $\text{Cu}^+ = 14$, $\text{Cu}^0 = 36$, $\text{Ce}^{3+} = 15$; **Table 1**). The presence of Cu^{2+} and Cu^+ following activation in hydrogen at $T \geq 573$ K has been previously demonstrated by CO chemisorption [42], H₂-TPR [43] and XPS measurements [45] for oxide- (CeO₂ and ZrO₂) and carbon-supported Cu catalysts. The generation of larger copper

nanoparticles on DP15(573) (vs. DP1(573)) *post* H₂-TPR is likely due to the higher metal loading [46]. The lower metal dispersion in DP15(573) leads to (i) inhibition of hydrogen diffusion in the Cu cluster and (ii) weak metal-support interactions linked to the small area of contact at the interface between the metal nanocrystals and the CeO₂ carrier which, in turn, hinders Cu²⁺ reduction and lowers the concentration of Cu⁺. The H₂-TPR profiles measured for the IM samples (**Figure 2(II)**) also exhibited three main peaks at $T \leq 658$ K but they were shifted to a significantly higher temperature (by ~ 185 K) relative to the DP catalysts. This suggests variations in metal-support interactions that can be linked to the different (i) metal precursor (Cu(NO₃)₂·3H₂O vs. CuCl₂) and (ii) preparation method (DP vs. IM). A surface Cl content > 1 ppb (>1 ppm for 1-4% wt. supported copper catalysts prepared *via* CuCl₂ impregnation [19]) has been demonstrated to facilitate Cu surface mobility with the formation of larger metal particles [47]. As the IM samples were prepared using CuCl₂, it is to be expected that these catalysts will bear larger metal nanoparticles, interacting weakly with the support and requiring higher reduction temperatures. Chen *et al.* [48], studying the hydrogen TPR of several Cu/CeO₂ samples reported a *ca.* 50 K increase in reduction temperature for samples *pre*-treated in different atmospheres (*i.e.* air, vacuum, hydrogen) and attributed this to a change in the electronic state of Cu nanoparticles that is dependent on metal dispersion with a shift to higher reduction temperature for bigger particles. Moreover, a stronger Cu/support interaction in the DP catalysts [19] improves the stabilisation of the excess electrons involved in the reduction step [49], lowering the temperature requirements. The H₂-TPR profile for the IM15(773) (**Figure 2(IIb)**) exhibits, in addition to the peaks at $T \leq 658$ K, signals at $T_{\max} = 670$ K, 678 K and 690 K, indicative of a multi-modal copper size distribution. The two H₂-TPR signals at 670 and 678 K can be tentatively attributed to α and β transitions, respectively, during the reduction of larger Cu nanoparticles [50]. The H₂-TPR signal at 690 K can be associated with the generation of HCl from CuCl₂ (*i.e.* δ transition)

linked to (i) Cl bonded to Cu and/or (ii) oxychloride species on the support. A similar rationale has been provided by Bond and co-workers [19] for the TPR hydrogen consumption peak recorded at $T_{\max} = 700$ K in their study of Cu/SiO₂ and Cu/Al₂O₃ prepared with CuCl₂ as metal precursor. The results from H₂-TPR analysis demonstrate the generation of supported Cu particles with oxidation states in the range Cu⁰ = 14-77%, Cu⁺ = 14-74% and Cu²⁺ = 0-50% (**Table 1**). The 1% wt. Cu/CeO₂ samples exhibit full reduction of Cu²⁺, whereas this step is hampered in the 15% wt. catalysts, which we attribute to inhibited hydrogen diffusion. Weak metal support interactions in IM (vs. DP) catalysts with increasing metal content (15% vs. 1% wt.) lowers Cu⁺ content. IM15(773) deviates somehow from this trend, where stabilisation *via* Cl⁻ complexation [19] results in a high concentration of copper (I).

The H₂-TPR measurements provide critical information on bulk characteristics which can differ greatly from surface properties [51]. The distribution of Cu oxidation states on the catalyst surface can be extracted from data fitting in the Cu 2*p* core level. However, the results can be compromised by the overlapping of copper species (*i.e.* Cu⁺ and Cu⁰) [52]. It has been demonstrated [52], that analysis of X-ray induced Auger transitions (*i.e.* electrons excited as a consequence of the relaxation process following the ejection of an electron from a core orbital) can serve as an additional measurement to investigate copper on the catalyst surface, where the spectra of Cu⁺ and Cu⁰ exhibit distinct peak(s) and shape. Surface copper and Ce³⁺ was examined by XPS analysis of the Cu 2*p*_{3/2} (**Figure 3(a)**), Cu LMM Auger (**Figure 4**) and Ce 3*d* regions (**Figure 3(b)**); the values derived from curve fitting of the XPS measurements are shown in **Table 1** and **Figure 5(I)**. XPS analysis of the 1% wt. loaded samples (DP1(573) (**Figure 3(Ia)**) and IM1(773) (**IVa**)) confirmed a total reduction of Cu²⁺ to generate a mixture of Cu⁺ and Cu⁰ species. In contrast, the 15% wt. catalysts (DP15(573) **Figure 3(IIa)**, DP15(773) (**IIIa**) and IM15(773) (**Va**)) exhibit an additional XPS signal at

943 ± 1 eV that can be related to the presence of Cu^{2+} , *i.e.* shake-up satellite peak that can be linked to the $\text{O } 2p \rightarrow \text{Cu } 3d$ transition [53].

Figure 3: XPS spectra for Cu/CeO_2 (I) DP1(573), (II) DP15(573), (III) DP15(773), (IV) IM1(773) and (V) IM15(773) and CeO_2 (VI) fresh (untreated) and (VII) thermally treated in H_2 to 773 K over the (a) $\text{Cu } 2p_{3/2}$ and (b) $\text{Ce } 3d$ regions (intensity expressed as normalised counts). *Note:* Raw data are showed as open symbol ($\circ$), curve fitted and envelope are represented as solid and dashed lines, respectively. The markers included in (b) illustrate the position of the $3d_{5/2}/3d_{3/2}$ levels for Ce^{4+} (v/u , v''/u'' and v'''/u''') and Ce^{3+} (v_0/u_0 and v'/u').

A greater Cu^{2+} content was recorded with increasing metal content (15 vs. 1% wt.), lower activation temperature (573 compared to 773 K) and for samples prepared by IM (vs. DP). The results in the Cu LMM kinetic energy region (K.E.) 900-930 eV for DP15(573) (**Ia**) and IM15(773) (**Ib**), as representatives, are depicted in **Figure 4**; Auger spectra of standards Cu^{2+} , Cu^+ and Cu^0 are included to illustrate the level of similarity. The Auger spectrum for the DP15(573) presents a main peak at K.E. = 918.1 eV that is characteristic of Cu^0 (K.E. = 918.6 eV, [31]), although the profile shape is similar to that of Cu^{2+} . On the other hand, the main signal for IM15(773) (915.1 eV) can be ascribed to Cu^+ (915.2 eV, [31]) although the response largely converges with the profile for Cu^{2+} . The results from the analysis in the LMM Auger region demonstrate that major contributions due to Cu^+ and Cu^0 for DP15(573) and IM15(773) catalysts, respectively, can be excluded. This is in agreement with the low concentrations of Cu^+ and Cu^0 (*i.e.* 13%, **Table 1**) extracted from the curve fitting of the XPS spectra. The Wagner plot can be used as an additional tool for the elucidation of copper oxidation states on the catalyst surface [32]. In this approach, the photoelectron binding energy (B.E.) is plotted as a function of the kinetic energy of the Auger electron (K.E.) and represented by lines with slopes of -1 intercepting α' (see **Materials and Methods** section) and -3 intercepting I' (*i.e.* initial state parameter; values in this work extracted from [32]). The values of K.E. and B.E. for the DP15(573) and IM15(773) samples in the Wagner plot (**Figure 4(II)**) were obtained from the survey spectra (see **Figure S.3** in **Supplementary Information**) and the high-resolution spectra (**Figure 4(I)** and **3(a)**). The results for DP15(573) suggest the presence of Cu^{2+} , (*i.e.* experimental data follows straight line with slope = -1 and $\alpha' = 1851.33$ eV [31]). In the case of IM15(773), the points fall in the region characteristic of Cu^+ species (*i.e.* straight line with slope = -3 and $I' = 3713.7$ eV). Moreover, the calculated value of $\alpha' = 1852.05 \pm 0.05$ eV for DP15(573) is close to that characteristic of Cu^{2+} , while that of IM15(773) ($\alpha' = 1847.30 \pm 0.10$ eV) suggests the presence of Cu^+

(1847.51 eV in CuCl [31]).

Figure 4: (I) XPS spectra over the Cu Auger LMM region for (a) DP15(573) and (b) IM15(773) Cu/CeO₂ (intensity expressed as normalised counts). (II) Cu 2p_{3/2}-Cu LMM Wagner plot including data reported in the literature (Cu²⁺ (X), Cu⁺ (+), Cu⁰ (*), [31]) and experimental values extracted from survey (open symbols) and high-resolution regions (solid symbols) of DP1(573) (△), DP15(573) (○, ●), DP15(773) (◇, ◆), IM1(773) (□) and IM15(773) (▽, ▼). *Note:* Raw data in (I) are presented as open symbols (○) while spectra for standards Cu²⁺, Cu⁺, Cu⁰ are denoted as solid, dashed and dotted lines, respectively. Solid and dashed-dotted lines in (II) represent modified Auger parameter (α') and initial state parameter (I'), respectively.

The predominance of Cu^{2+} and Cu^+ in DP15(573) and IM15(773), respectively, confirms the reliability of the distribution of copper oxidation states extracted from XPS data fitting in the $2p_{3/2}$ region. The presence of Cu^+ (DP1(573) and DP15(773)) and Cu^0 (IM1(773)) species was also proved for the rest of the samples by data inclusion in the Wagner plot, which further confirms the results from XPS fitting.

Consistent values for both measurements (H_2 -TPR and XPS) were obtained in the case of the low loading DP1(573) (*i.e.* $\text{Cu}^{2+} = 0\%$; $\text{Cu}^+ = 74$; $\text{Cu}^0 = 26$, **Table 1**) and IM1(773) (0; 23; 77). However, there are inconsistencies in those obtained with each method for the high loading samples. We should flag that there is a dearth of published work recording Cu oxidation states based on more than one analytical technique with XPS [28] or CO chemisorption [42] typically used. Nonetheless, there are reports in the literature that have considered a combination of XPS, XANES and EXAFS [54] or H_2 -TPR and O_2 -TPO measurements [55]. The discrepancy observed between H_2 -TPR and XPS data can be attributed to the type of information obtained with both methodologies. Indeed, H_2 -TPR is a "bulk" analytical technique while XPS is applicable for surface analysis. A source of disagreement can result from the information depth of the XPS measurements (*ca.* 3 nm [56]). This suggests copper nanoparticles >4 nm in the high loading Cu/CeO₂ catalysts, in agreement with previous studies [57,58] that have reported Cu nanocrystals of 8-18 nm for oxide (SiO₂, Al₂O₃) supported copper catalysts with similar loading (16-20% wt.) prepared by IM and DP. Although the combination of analytical methods employed in this work is complementary, catalytic reactions occur on the catalyst surface, consequently the distribution of Cu oxidation states based on XPS measurements was adopted in subsequent tests.

The Ce 3d profile for the fresh (untreated) CeO₂ (**Figure 3(VIb)**) and hydrogen treated ((**VIIb**)) are similar and dominated by three spin-orbit doublets (peaks v/u , v''/u'' and v'''/u''' at

883 eV/901 eV, 888/907 and 899/917, respectively) that can be associated with the $3d_{5/2}/3d_{3/2}$ levels of Ce^{4+} [30]. Two additional spin-orbit doublets (peaks v_0/u_0 and v'/u' ; 880 eV/899 eV and 886/904) are also in evidence and can be attributed to the $3d_{5/2}/3d_{3/2}$ levels of Ce^{3+} [30]. The extracted surface concentration of Ce^{3+} (11 ± 1 %) matches the value quoted by Zhang *et al.* for bulk CeO_2 [30]. The equivalent XPS response was expected considering the higher (≥ 823 K) temperature requirement for the $Ce^{4+} \rightarrow Ce^{3+}$ reduction [59]. A comparison of the XPS spectra of Cu/CeO₂ (**Figure 3(Ib-Vb)**) with those of CeO₂ (**(VIb-VIIb)**) suggests that incorporation of Cu served to facilitate CeO₂ surface reduction with an increase (by up to 28%) in the concentration of Ce^{3+} . Enhancements of up to 40% in Ce^{3+} surface content has been reported *post*-Pd incorporation [60]. This can be tentatively attributed to spillover hydrogen on Cu/CeO₂ that can participate in a superficial reduction of the oxide carrier, a result that is consistent with H₂-TPR measurements. The correlation between concentration of Ce^{3+} and surface metallic copper (Cu_{XPS}^0 , %) is shown in **Figure 5(I)**, where there is a clear linear increase in Ce^{3+} density with increasing amount of Cu⁰ (0 $\rightarrow$ 77%).

Figure 5: Dependence of (I) surface Ce^{3+} content (Ce_{XPS}^{3+} , %) and (II) H_2 uptake ($\mu mol\ g_{Cu}^{-1}$) on surface Cu^0 concentration (Cu_{XPS}^0 , %) for (▲) DP1(573), (●) DP15(573), (◆) DP15(773), (■) IM1(773) and (▼) IM15(773). *Note:* The result for pure CeO_2 in (I) is represented as a symbol (*). Dashed lines provide a guide to aid visual assessment.

This tendency suggests H₂ adsorption at Cu⁰ sites, and finds agreement with theoretical work (density functional theory (DFT)) demonstrating that molecular hydrogen does not chemisorb on Cu²⁺ or Cu⁺, but occurs on Cu⁰ [61] *via* dissociative adsorption [62]. Hydrogen uptake measured at reaction temperature (498 K) on all the Cu/CeO₂ catalysts (1-147 μmol g_{Cu}⁻¹) was similar (1-158 μmol g_{Cu}⁻¹) to values reported previously for (Al₂O₃ and SiO₂) supported Cu catalysts [63,64], but far lower than the uptake for standard transition metal catalysts used in industrial hydrogenations (*e.g.* 2023 μmol g_{Pd}⁻¹ for Pd/Al₂O₃ [65]). This is consistent with the high energy barrier for H₂ dissociation due to the filled *d* band of copper [66]. The hydrogen chemisorption *vs.* Cu_{XPS}⁰ linear relationship shown in **Figure 5(II)**, where H₂ uptake capacity increases with increasing Cu⁰ surface content (13 → 77%), is further evidence for hydrogen chemisorption on metallic copper.

3.1.2 XRD/STEM-EDX

The morphology of the supported copper nanoparticles was examined by combined XRD (**Figure 6**) and STEM-EDX measurements (**Figures 7 and 8**). All the catalysts present diffraction peaks at $2\theta = 28.5^\circ$, 33.1° , 47.5° , 56.3° , 59.1° , 69.4° , 76.7° and 79.1° corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1) and (4 2 0) planes of CeO₂ with a cubic fluorite-type structure (JCPDS-ICDD reference 043-1002). The XRD patterns for the high loading Cu samples (DP15(573) **(II)**, DP15(773) **(III)** and IM15(773) **(V)**) present additional signals at $2\theta = 43.4^\circ$, 50.5° and 74.2° characteristic of (1 1 1), (2 0 0) and (2 2 0) planes of metallic Cu. The absence of Cu⁰ diffraction peaks in the 1% wt. Cu/CeO₂ catalysis (*i.e.* DP1(573) **(I)** and IM1(773) **(IV)**) can be linked to the low metal loading and/or the presence of small (<5 nm) Cu particles [67]. The intensity (*I*) and width (*W*) of the main Cu XRD peak ($2\theta = 43.4^\circ$) is sensitive to copper nanoparticle size where a higher *I/W* ratio is indicative of larger metal nanoparticles [67].

Figure 6: XRD patterns for activated (I) DP1(573), (II) DP15(573), (III) DP15(773), (IV) IM1(773) and (V) IM15(773) Cu/CeO₂ catalysts. *Note:* Peak assignment based on JCPDS-ICDD reference data: (□) CeO₂ (043-1002), (*) Cu (004-0836) and (Δ) CeClO (153-4659).

Taking the three high loading Cu/CeO₂ samples, the variation in I/W suggests the following sequence of increasing copper nanoparticle size: DP15(573) ($I/W = 50$ counts degree⁻¹) ~ DP15(773) (60) < IM15(773) (440). The XRD diffractogram pattern for IM15(773) exhibits additional signals at $2\theta = 12.9^\circ, 25.4^\circ, 30.9^\circ, 34.1^\circ, 40.8^\circ, 44.3^\circ, 51.7^\circ, 57.1^\circ, 76.9^\circ$

and 79.1° due to the (0 0 1), (1 0 1), (1 1 0), (1 0 2), (1 1 2), (2 0 0), (2 1 1), (2 1 2), (1 1 5) and (3 1 2) planes of CeClO. This result is in line with the report of Soria *et al.* [68], who demonstrated by electron paramagnetic resonance (EPR) analysis, using oxygen as a probe molecule, the formation of a cerium oxychloride layer *post* hydrogen thermal treatment to 773 K on the surface of Au/CeO₂ and Rh/CeO₂ prepared by impregnation using a chlorine containing metal precursor. The absence of detectable XRD signals for CeClO in IM1(773) (IV) can be attributed to the lower metal and Cl content.

Figure 7: (I) Representative STEM images with **(II)** associated particle distribution of **(a)** DP15(573) and **(b)** IM15(773) Cu/CeO₂ catalysts. *Note:* Black arrows in the **(Ia)** STEM image indicate isolated Cu nanoparticles.

STEM-EDX analysis (see micrographs for DP15(573) **(Ia)** and IM15(773) **(Ib)** in **Figure 7**, as representative samples) have revealed copper nanoparticles at the nanoscale (1-20 nm) for all the catalysts in this work. High magnification micrographs of individual nanoparticles **(I)** with associated EDX spectrum **(II)** on the surface of DP1(573) **(a)** and DP15(573) **(b)**, as representatives, in **Figure 8** demonstrate that the Cu component is present

as discrete nanoparticles with a pseudo-spherical morphology. Metal particle size distribution is illustrated by the histograms presented in **Figure 7(II)**; mean Cu diameters (d) are shown in **Table 1**.

Figure 8: (I) Representative high magnification STEM images with (II) associated EDX analysis of isolated Cu nanoparticle (dashed frame) on (a) DP1(573) and (b) DP15(573) Cu/CeO₂ catalysts.

The nature of the metal precursor, metal loading and preparation method are critical in determining the ultimate size distribution [69]. The mean diameter obtained from STEM analysis for DP1(573) (2 nm) and IM1(773) (4 nm) is consistent with the absence of XRD peaks characteristic of copper. Taking the same metal content and final activation temperature (*i.e.* 15% wt. and 773 K), the Cu/CeO₂ samples prepared by impregnation using CuCl₂ (*vs.* deposition precipitation with Cu(NO₃)₂·3H₂O) are characterised by a broader distribution of larger Cu particles, indicative of weaker copper-CeO₂ interactions. As expected, the samples with the higher metal content treated at increased activation temperature bear the larger Cu nanoparticles, which can be attributed to greater mobility and agglomeration of Cu species that results in a wider size distribution [69]. This trend is in agreement with the distribution of copper oxidation states from H₂-TPR and XPS measurements. The degree of heterogeneity

for the high loading samples is illustrated by the results for the IM15(773) catalyst (**Figure 7(IIb)**) with an apparent bimodal distribution of smaller (*ca.* 9 nm) and larger (*ca.* 14 nm) Cu nanocrystals, consistent with the four H₂-TPR peaks attributed to α and β transitions in **Figure 2(IIb)**.

3.2 Catalytic Response

The characterisation measurements demonstrate the generation of a series of Cu/CeO₂ samples with copper oxidation states in the range Cu⁰ = 13-77%, Cu⁺ = 13-74% and Cu²⁺ = 0-55%. The impact of variations in the copper oxidation state on the tandem dehydrogenation-hydrogenation of benzyl alcohol with phenylacetylene has been considered. It has been demonstrated that Cu²⁺ is inactive in hydrogenation (*e.g.* isoprene conversion over 1% wt. Cu/ThO₂ [70]) and dehydrogenation reactions (*e.g.* ethanol transformation using 20% wt. Cu/Al₂O₃ [17]). In order to confirm the inactivity of Cu²⁺ in the catalytic conversion of benzyl alcohol and phenylacetylene, a (commercial) CuO was purchased and tested in the two (independent) reactions. CuO exhibited a lack of initial activity in both (dehydrogenation and hydrogenation) reactions. Based on these results, Cu⁰ and Cu⁺ were considered to establish the impact of metal oxidation state on catalytic performance. We first examine the catalytic response in the stand-alone phenyl acetylene hydrogenation, using an external hydrogen supply, and benzyl alcohol dehydrogenation (in N₂) over the five Cu/CeO₂ catalysts. A compilation of the studies in the open literature on hydrogenation of phenylacetylene and dehydrogenation of benzyl alcohol is presented **Table S.1** of the **Supplementary Information**; where pertinent, our results are related to the trends emerging from the tabulated studies.

3.2.1 Stand-alone Phenylacetylene Hydrogenation

The stand-alone phenylacetylene hydrogenation over all the catalysts generated styrene

and ethylbenzene as the only two products, with no evidence of ring reduction (to ethylcyclohexane) which has been observed for reaction over Pt/C [71]. The stepwise ($\text{-C}\equiv\text{C-} \rightarrow \text{-C=C-} \rightarrow \text{-C-C-}$ bond) hydrogenation of phenylacetylene to ethylbenzene through styrene as reaction intermediate is presented in **Figure 1** (steps **(III)** and **(IVb)**), which also includes a direct (parallel $\text{-C}\equiv\text{C-} \rightarrow \text{-C-C-}$ reduction) pathway (step **(IVa)**) [72]. At conversions $\leq 50\%$, reaction over all Cu catalysts generated styrene as the main product with secondary generation of ethylbenzene, consistent with the work of Merrill [73] working under high H_2 pressure (10 atm) using $\text{Cu/Al}_2\text{O}_3$. In contrast, under similar reaction conditions full hydrogenation to ethylbenzene was promoted over $\text{Au/Al}_2\text{O}_3$ [34]. In each case, we recorded a temporal loss of activity to attain a pseudo-steady state after *ca.* 2 h (see variation of phenylacetylene conversion ($X_{\text{phenylacetylene}}$) with time on-stream over DP1(573), as a representative, in **Figure 9(I)**).

Figure 9: Variation of **(I)** phenylacetylene conversion/styrene molar flow ($X_{\text{phenylacetylene}}$, %; F_{styrene} , mmol h^{-1}) and **(II)** benzyl alcohol conversion/ benzaldehyde molar flow ($X_{\text{benzyl alcohol}}$, %; $F_{\text{benzaldehyde}}$, mmol h^{-1}) with time on-stream (t , h) in stand-alone (Δ) and coupled process ($\blacktriangle$) over DP1(573). **(III)** Comparison of selectivity to styrene (S_{styrene} , %) (open bars) at specific $X_{\text{phenylacetylene}}$ (grey bars) over DP1(573), DP15(573), DP15(773), IM1(773) and IM15(773). *Note:* Dashed grey lines in **(I-II)** are the result of time scale fitting to obtain the initial $X_{\text{phenylacetylene}}$ according to the method described in the **Supplementary Information** section. *Reaction conditions:* $P = 1$ atm, $T = 498$ K.

Loss of activity in hydrogenation reactions over copper catalysts has been previously

reported and ascribed to carbon deposition [39] and/or strong reactant/product adsorption on Cu [74]. In order to gain some insight into the reaction mechanism, the dependence of styrene selectivity on phenylacetylene conversion was investigated. At similar levels of conversion, variations in the Cu^0/Cu^+ of the five catalysts in this work did not impact on product selectivity ($X_{\text{phenylacetylene}} = 15 \pm 1\% \rightarrow S_{\text{styrene}} = 93 \pm 2\%$, **Figure 9(III)**). In contrast, product distribution was sensitive to phenylacetylene conversion (**Figure 10(I)**).

Figure 10: (I) Styrene selectivity (S_{styrene} , %) as a function of phenylacetylene conversion ($X_{\text{phenylacetylene}}$, %) and (II) variation of benzaldehyde selectivity ($S_{\text{benzaldehyde}}$, %) with Cu^+/Cu^0 molar ratio in independent hydrogenation/dehydrogenation (open symbols) and coupled process (solid symbols) over ($\Delta, \blacktriangle$) DP1(573), ($\circ, \times$) DP15(573), ($\diamond, \blacklozenge$) DP15(773), ($\square, \blacksquare$) IM1(773) and ($\nabla, \blacktriangledown$) IM15(773) Cu/CeO₂ catalysts. *Note:* Solid lines provide a guide to aid visual assessment. *Reaction conditions:* $P = 1$ atm, $T = 498$ K, $X_{\text{benzyl alcohol}} \sim 6\%$.

We recorded formation of ethylbenzene in trace quantities ($S_{\text{ethylbenzene}} \leq 5\%$) at low phenylacetylene conversions ($\leq 3\%$) and a shift to preferential ethylbenzene generation at the expense of styrene with increasing phenylacetylene conversion ($X_{\text{phenylacetylene}} > 50\%$). These

results are consistent with a predominantly (stepwise) phenylacetylene $\rightarrow$ styrene $\rightarrow$ ethylbenzene mechanism following paths (III) and (IVb) in **Figure 1**, typical for hydrogenation of alkynes in gas phase operation [75]. It is important to state that, under similar reaction conditions the Cu/CeO₂ in this work delivered a 3 times greater specific styrene production rate [72] and enhanced selectivity (90% vs. 82% [76]) compared to Pd/Al₂O₃, a standard catalyst in industrial alkyne hydrogenation [25]. The effect(s) of copper oxidation state on the activity delivered by Cu/CeO₂ was considered at the same degree of conversion ($X_{\text{phenylacetylene}} = 5 \pm 2\%$) and the resultant variation of turnover frequencies (*TOF*, specific (per Cu surface atom) rate, see **Eqn. 7** and **Table 1**) with Cu⁰/Cu⁺ molar ratio is shown in **Figure 11(I)**.

Figure 11: Variation of turnover frequency (*TOF*, h⁻¹) as a function of (I) Cu⁰/Cu⁺ in stand-alone (open symbols) reactions and (II) Cu⁺/Cu⁰ in the coupled process (solid symbols) for styrene (solid lines) and benzaldehyde (dashed lines) production over (Δ,▲) DP1(573), (○,×) DP15(573), (◇,◆) DP15(773), (□,▤) IM1(773) and (▽,▼) IM15(773) Cu/CeO₂ catalysts. *Note:* Solid and dashed lines provide a guide to aid visual assessment. *Reaction conditions:* $P = 1$ atm, $T = 498$ K.

The experimentally determined specific rate increased linearly with increasing Cu^0/Cu^+ in the catalyst. A similar trend was observed by Filonenko and co-workers [77] using (Group 11) Au in the hydrogenation of CO_2 , where a decrease in Au^0 content was accompanied by a progressive decrease in activity. The opposite effect has also been recorded, with Ma *et al.* [55] reporting a concomitant increase in ester hydrogenation rate and Cu^+/Cu^0 ratio. The sequence of increasing activity over the Cu/CeO₂ catalysts (*i.e.* IM15(773) < DP1(573) < DP15(573) < DP15(773) < IM1(773)) mimics the increase in H₂ chemisorption capacity. The enhancement in hydrogen uptake that results from a greater Cu^0 content (**Figure 5(II)**) was accompanied by an elevated hydrogenation rate. We could find no comparable published study of phenylacetylene hydrogenation over supported copper. However, our results are consistent with experimental work that has demonstrated a zero order dependence in $-\text{C}\equiv\text{C}-$ bond coverage and identify H₂ splitting as the rate-limiting step for the gas phase hydrogenation of propyne over Cu catalysts [39]. In addition to catalytic activity/selectivity, hydrogen utilisation efficiency is a key parameter that must be optimised to ensure process sustainability. The limited H₂ chemisorption on Cu (*i.e.* at least 15 times lower compared to noble metals typically used in hydrogenations [65]) results in low H₂ utilisation efficiency (200-400 *vs.* 1 for reaction stoichiometry; see **Eqn. 8**) which represents a severe sustainability gap.

3.2.2 Stand-alone Benzyl Alcohol Dehydrogenation.

The consequence of changes in the copper oxidation state on the independent gas phase benzyl alcohol dehydrogenation was also investigated. All the Cu catalysts exhibited an essentially time invariant activity (see **Figure 9(II)** for DP1(573), as a representative), where benzaldehyde was the main product (up to 95%, path **(I)** in **Figure 1**), while toluene was generated as a secondary product *via* hydrogenolysis (path **(II)**). In contrast, deactivation in liquid phase dehydrogenation of benzyl alcohol over Pd/Al₂O₃ has been reported and

attributed to active site blockage due to adsorption of CO from decarbonylation [78]. Reaction selectivity can be assessed from **Figure 10(II)**, where benzaldehyde selectivity ($S_{\text{benzaldehyde}}$) is shown as a function of Cu^+/Cu^0 molar ratio. We observe a tendency of decreasing $S_{\text{benzaldehyde}}$ (95 $\rightarrow$ 85%) with increasing Cu^+/Cu^0 . Our results indicate a dependence of selectivity on copper oxidation state, which impacts on the benzyl alcohol adsorption/activation mechanism. There is limited evidence in the literature of a dehydrogenation selectivity dependence on copper oxidation state [22]. Cassinelli *et al.* [17] studying the dehydrogenation of ethanol over $\text{Cu}/\text{Al}_2\text{O}_3$ recorded a greater selectivity to ethyl acetate (*via* condensation) with increasing concentration of Cu^0 . Alcohol adsorption (through the polarised oxygen (O^{2-}) of the -OH group [79]) on Lewis acid sites [80] with hydrogen scission of the C-OH bond following a nucleophilic attack [81] generates toluene. Benzyl alcohol adsorption can also proceed at the Cu-oxide interface with the -OH functionality binding to the carrier and the α -hydrogen interacting with copper [80], to form benzaldehyde. The reaction follows a two-step mechanism where abstraction of the second (α)-hydrogen through a carbocation-type transition state [82] is rate determining [80]. From a consideration of the copper electronic properties, a (Lewis acid) positive charge (Cu^+) should facilitate interaction with the O^{2-} of the hydroxyl group, favouring hydrogenolysis (to toluene).

Specific benzaldehyde production rate (*TOF*) was calculated and the Cu^0/Cu^+ dependence is illustrated in **Figure 11(I)** where a linear correlation is in evidence. The use of Cu/CeO_2 catalysts in the *non*-oxidative gas phase dehydrogenation of benzyl alcohol resulted in a significantly greater activity (by up to a factor of 16) relative to reactions over supported Au [80,83] and Pd [83] catalysts with comparable metal size (2-12 nm) in both, gas and liquid phase operation. The Cu^0 rich catalyst (IM1(773); $\text{Cu}^0/\text{Cu}^+ = 3.4$) delivered a specific dehydrogenation rate that was twice that recorded for the lower content system (IM15(773); 0.3). This result suggests that Cu^0 stabilises the rate determining transition complex with a

resultant increase in reactivity, *i.e.* repulsion between positively charged Cu^+ and the cationic transition state results in elevated intrinsic dehydrogenation efficiency with enhanced Cu^0/Cu^+ content ($0.3 \rightarrow 3.4$). This result finds agreement in the work of Kon *et al.* [84] who, studying the *non-oxidative* dehydrogenation of 2-octanol over $\text{Re}/\text{Al}_2\text{O}_3$, demonstrated enhanced activity with increasing Re^0 concentration. A greater dehydrogenation (*vs.* hydrogenation) activity is essential to ensure sufficient hydrogen supply in the coupling system. The results in this section confirm that this prerequisite is met by all the catalysts where hydrogen produced was at least 5 times greater than that consumed in the phenylacetylene hydrogenation step.

3.2.3 Coupled Benzyl Alcohol Dehydrogenation with Phenylacetylene Hydrogenation

The results presented in sections 3.2.1 and 3.2.2 demonstrate that undesired full hydrogenation to ethylbenzene (path **(IV)** in **Figure 1**) and hydrogenolysis to toluene (path **(II)**) were promoted in the stand-alone hydrogenation of phenylacetylene and dehydrogenation of benzyl alcohol, respectively, over the Cu/CeO_2 catalysts. In contrast, the selectivity response is striking in that the five copper catalysts promoted the sole formation of the two target products, styrene and benzaldehyde, in the coupled process. The generation of styrene (from phenylacetylene transformation in N_2 atmosphere) demonstrates effective use of the hydrogen generated *in situ* from the dehydrogenation of benzyl alcohol. We could find no comparable study in the literature where a switch in selectivity was observed for standard *vs.* coupled alkyne hydrogenation with alcohol dehydrogenation. Nonetheless, Nagaraja and co-workers [18] studying the tandem dehydrogenation-hydrogenation of cyclohexanol-furfural over bulk $\text{Cu-MgO-Cr}_2\text{O}_3$ reported enhanced selectivity to cyclohexanone (from 75 to 100%) and furfuryl alcohol ($50 \rightarrow 100\%$) relative to the stand-alone reactions, but the authors did not elaborate further. Product distribution was largely insensitive to variations in $X_{\text{phenylacetylene}}$ (**Figure 10(I)**) and copper oxidation state (**Figure 10(II)**) where 100%

selectivity of both target products was maintained. We associate this switch in selectivity (from full to partial hydrogenation) towards styrene generation to the low H₂:phenylacetylene molar ratio, close to stoichiometry in the coupling process (vs. 80:1 mol_{H₂} mol_{phenylacetylene}⁻¹ in stand-alone hydrogenation). In support of this, Bridier *et al.* [39] studying the gas phase hydrogenation of propyne over a series of (Al₂O₃, SiO₂ and hydrotalcite) supported Cu catalysts reported absence of triple bond over-hydrogenation (to propane) at inlet H₂:propyne <8. The suppressed hydrogenolysis to toluene can be tentatively linked to the presence of phenylacetylene as a hydrogen acceptor. Likewise, studying the same reaction over Cu/hydrotalcite by adding CO₂ to the feed Gurram *et al.* [26] recorded a simultaneous decrease in toluene generation and a 2-fold increase in benzaldehyde selectivity, attributed to consumption of *in situ* generated H₂ in the dehydrogenation step *via* reverse water gas shift reaction.

Under similar reaction conditions, reactant conversion in the coupled process, shown in **Figure 9(I)** ($X_{\text{phenylacetylene}}$) and **(II)** ($X_{\text{benzyl alcohol}}$), exhibit a similar time on-stream dependence to that observed in the stand-alone (hydrogenation and dehydrogenation) reactions, albeit greater phenylacetylene conversion and lower dehydrogenation activity in the coupling system. The generation of activated atomic hydrogen (from benzyl alcohol dehydrogenation) serves to circumvent the activation of molecular hydrogen (rate determining in the stand-alone hydrogenation [39]), thereby increasing hydrogenation activity. The lower dehydrogenation conversion in the coupled process can be tentatively linked to competition for (copper) adsorption sites that must result in a displacement of benzyl alcohol from the surface by phenylacetylene. Our premise is in accordance with the reported higher (~10 kcal mol⁻¹) desorption energy barrier from Cu for acetylene [85] relative to ethanol and isopropanol [86]. Coupled dehydrogenation-hydrogenation can also proceed through direct hydrogen transfer (*i.e.* the -C≡C- bond in the alkyne is attacked by the α-hydrogen in the

alcohol) following a mechanism similar to the Meerwein–Ponndorf–Verley (MPV), with a requirement for having the two active sites for dehydrogenation and hydrogenation in close proximity [87]. The MPV mechanism was initially proposed for homogeneous systems where good results have been established in the liquid phase tandem hydrogenation of carbonyl compounds with alcohols [87]. Nonetheless, there has been several published studies [87,88] where it has been successfully employed in gas and liquid phase coupling processes over (metal supported) heterogeneous catalysts. Benzyl alcohol dehydrogenation in the coupled process following a MPV-like mechanism cannot be ruled out. Nonetheless, inhibited hydrogen removal in the direct (*vs.* stepwise) process has been demonstrated elsewhere [89] and is consistent with the decrease in dehydrogenation activity for the coupled (*vs.* stand-alone) process.

The extracted styrene and benzaldehyde *TOF* (from conversions *vs.* time on-stream profiles, **Figure 9**) were used to establish the dependence between hydrogenation/dehydrogenation activity and copper oxidation state in the coupled process. The results are presented in **Figure 11(II)** where a linear correlation with respect to Cu^+/Cu^0 concentration for both reactions is in evidence. There are reports in the literature that demonstrate (*via* UV-PES and IR spectroscopy) alkyne adsorption on both metallic [85] and electron deficient [90] copper sites. In the case of (Pt-group) metals with high H_2 chemisorption capacity (*i.e.* $\text{H}_2/\text{Metal mol ratio} \geq 1$ [91]), it has been proposed that $-\text{C}\equiv\text{C}-$ bond adsorption/activation is rate determining in phenylacetylene hydrogenation [91]. The ceria supported Cu^+ facilitates adsorption/activation of the (electron-donating) $-\text{C}\equiv\text{C}-$ group in phenylacetylene through an electrostatic interaction (alkyne σ -donation followed by copper π -backdonation [92]) where a higher concentration of electron deficient copper results in an increased specific hydrogenation rate. Phenylacetylene adsorption on Cu^+ limits the number of active sites available for the adsorption of benzyl alcohol at the hydroxyl oxygen and

serves to suppress hydrogenolysis to toluene (**Figure 10(II)**). It should be noted that IM15(773) with the highest chlorine content (**Table 1**) deviates somehow from the general trend. We tentatively attribute the lower hydrogenation activity over IM15(773) to consumption of the available hydrogen in the conversion of Cl to HCl, consistent with the findings of Ordóñez *et al.* [93] who showed a decrease of (toluene) hydrogenation activity that was accompanied by the release of HCl from the catalyst surface. In order to test this premise, we monitored the pH of an aqueous NaOH trap before, during and after reaction where the solution pH progressively decreased (from 8.9) to reach 7.5 after 3 h as a result of HCl produced [94]. A similarly greater *TOF* with increasing Cu^+/Cu^0 ratio was recorded for the dehydrogenation of benzyl alcohol in the coupled process (**Figure 11(II)**). We envision a surface mechanism where phenylacetylene is adsorbed on Cu^+ sites while benzyl alcohol is activated (*via* the -OH group) on $\text{Ce}^{4+}\text{-O}^{2-}$ in close proximity to the copper nanoparticles. The uncoordinated α -hydrogen of the alcohol attacks [79] the activated triple bond which removes the hydroxyl hydrogen (from benzyl alcohol) in a concerted fashion to form a (six-membered cyclic) activated complex yielding the simultaneous formation of styrene and benzaldehyde. An increase in Cu^+ content on the catalyst surface results in enhanced dehydrogenation activity. A similar mechanism was proposed by Wang *et al.* [95] for the liquid phase coupled 1-octanol dehydrogenation with styrene hydrogenation over $\text{Cu/La}_2\text{O}_2\text{CO}_3$, although the authors did not identify the copper oxidation state active in the tandem process.

The catalytic results suggest that the production of styrene and benzaldehyde in the stand-alone and coupled processes is favoured predominantly by Cu^0 and Cu^+ , respectively. This has been accounted for in terms of a change in (i) the rate-determining step in the hydrogenation (*i.e.* activation of H_2 *vs.* $\text{-C}\equiv\text{C-}$ bond in the stand-alone and coupled reactions, respectively) and (ii) dehydrogenation mechanism (*i.e.* stepwise *vs.* concerted α -hydrogen elimination for stand-alone and tandem processes, respectively). Our results find agreement

with reported modified catalytic response in hydrogenation of furaldehydes over Ru-catalysts, where metallic [96] and electron deficient [13] ruthenium species were identified as the active sites in the stand-alone and coupled reactions, respectively. Moreover, alcohol dehydrogenation in tandem processes over catalysts in which the active sites for dehydrogenation and hydrogenation are in close proximity, predominantly follow a MPV mechanism, where alcohol $\rightarrow$ hydrogen-acceptor hydride transfer is rate-determining [79]. We must stress that a switch from stand-alone hydrogenation to the coupled dehydrogenation-hydrogenation process (without external hydrogen supply) resulted in full phenylacetylene $\rightarrow$ styrene conversion, *i.e.* 100% yield of the target vinyl monomer, with a remarkably greater (two orders of magnitude) hydrogen utilisation. This exceeds the highest yields reported for gas phase hydrogenation of phenylacetylene (*ca.* 31% using Pd/Al₂O₃ [72]) and commercial production of styrene through ethylbenzene dehydrogenation (*ca.* 70% [97]). DP1(573) delivered the highest specific hydrogenation rate with almost full hydrogen utilisation and, therefore, it was employed for further analyses.

The H₂/alkyne ratio is key in determining the rate of alkene production where changes in hydrogen partial pressure affect available hydrogen on the surface. With the aim of further enhancing overall catalyst performance, we examined the effect of modifying the Alcohol:Alkyne molar feed ratio; the results obtained are presented in **Table 2**.

Table 2. Effect of Alcohol:Alkyne molar ratio on dehydrogenation of benzyl alcohol to benzaldehyde and hydrogenation of phenylacetylene to styrene turnover frequency (*TOF*, h⁻¹; **Eqn. 7**) and H₂ utilisation efficiency (**Eqn. 8**) in the coupled process over the Cu/CeO₂ DP1(573) catalyst. *Reaction conditions:* *T* = 498 K, *P* = 1 atm, *n* = 1 × 10⁻³ mmol.

		Alcohol:Alkyne					
		0.1	1	18	31	95	191
<i>TOF</i> (h ⁻¹)	Dehydrogenation	70	110	490	530	660	1030
	Hydrogenation	100	115	375	275	150	118
H ₂ utilisation efficiency (-)		1.0	1.0	1.2	2.2	5.3	10.4

In each case, we achieved full selectivity to the target products (benzaldehyde and styrene). At Alcohol:Alkyne = 0.1 the amount of hydrogen generated in the dehydrogenation step is not sufficient to account for the recorded hydrogenation rate (*i.e.* 70 vs. 100 h⁻¹). Alkyne hydrogenation can be enhanced by contributions due to spillover hydrogen (*i.e.* atomic hydrogen generated during activation *via* dissociative adsorption of H₂ on supported metal sites that can migrate to the support). H₂-TPD is a practical analysis that can be used to quantify spillover hydrogen. The greater than expected styrene *TOF* can be correlated with surface available hydrogen where H₂-TPD is related to phenylacetylene consumption rate, closing the balance of H₂ utilisation efficiency (*i.e.* 1 vs. 0.8). An increase in Alcohol:Alkyne (1 → 18) served to elevate hydrogen generated in the dehydrogenation step (step **(I)**, **Figure 1**) and styrene *TOF* (from 115 to 375 h⁻¹) with 1.0-1.2 hydrogen utilisation efficiency. Reaction at greater Alcohol:Alkyne (31 → 191) further enhanced hydrogen production to attain a similar *TOF* to that achieved in the stand-alone dehydrogenation (*i.e.* 1030 vs. 1046 h⁻¹). This result further confirms reactant competition with inhibited stepwise conversion of benzyl alcohol, in the presence of phenylacetylene. Nonetheless, at high Alcohol:Alkyne ratio (≥31) we observed a decrease in styrene production where full hydrogen utilisation could not be maintained. The carbonyl group in benzaldehyde bears a higher electron density than the -C≡C- bond in phenylacetylene [98], with a consequent stronger interaction with Cu⁺ sites on CeO₂. The higher production of benzaldehyde (at increased benzyl alcohol *TOF*) must decrease the number of active sites available for -C≡C- adsorption/activation (rate limiting in the hydrogenation step of the coupled process), lowering styrene *TOF*. The less effective hydrogen utilisation can be linked to low phenylacetylene surface coverage, where the amount of hydrogen generated is greater than that required for full transformation to styrene. We have achieved a significantly higher specific styrene production rate in the coupled process relative to reported value for stand-alone hydrogenation over Cu catalysts (375 h⁻¹ vs.

0.2 h⁻¹ [99]).

The applicability of pseudo-first order kinetic treatment can be tested using the relationship [33]:

$$\ln \left[\frac{1}{(1 - X_{i,0})} \right] = k \cdot \left(\frac{n}{F_i} \right) \quad (9)$$

where n/F_i (s) represents the Cu molar ratio in the catalyst bed to reactant "i" (*i.e.* phenylacetylene or benzyl alcohol) inlet flow rate. The $\ln[1/(1 - X_{i,0})]$ vs. n/F_i linear relationship for the coupled hydrogenation **(Ia)** and dehydrogenation **(Ib)** steps shown in **Figure 12**, confirms adherence to pseudo-first order behaviour. The sole formation of styrene and benzaldehyde was maintained in the 433-575 K temperature range.

Figure 12: (I) Pseudo-first order kinetic plot and (II) Arrhenius relationship for (a) hydrogenation of phenylacetylene to styrene and (b) dehydrogenation of benzyl alcohol to benzaldehyde in coupled process over DP1(573). *Note:* Solid (hydrogenation) and dashed (dehydrogenation) lines in (I) and (II) are the result of pseudo-first order kinetic and Arrhenius equation data fit, respectively. *Reaction conditions:* $P = 1 \text{ atm}$, $T = 433\text{-}573 \text{ K}$.

The Arrhenius plots for the hydrogenation **Figure 12(IIa)** and dehydrogenation **(IIb)** reactions in the coupled process delivered apparent activation energies of $\Delta E_{a \text{ hydrogenation}} = 75 \text{ kJ mol}^{-1}$ and $\Delta E_{a \text{ dehydrogenation}} = 59 \text{ kJ mol}^{-1}$, comparable with those obtained in the stand-alone reactions ($\Delta E_{a \text{ hydrogenation}} = 88 \text{ kJ mol}^{-1}$, $\Delta E_{a \text{ dehydrogenation}} = 44 \text{ kJ mol}^{-1}$; see **Figure S.4** in the **Supplementary Information**). We could not find any reported activation energy for a comparable phenylacetylene-benzyl alcohol coupling system in the literature. However, the apparent values obtained are similar to those recorded for phenylacetylene hydrogenation (using an external hydrogen supply) over Pd/C [100] (55 kJ mol^{-1}) and alcohol (ethanol [101] and propanol [86]) dehydrogenation over carbon- and SiO_2 -supported Cu catalysts ($50\text{-}115 \text{ kJ mol}^{-1}$). We recorded a lower activation energy in the dehydrogenation step, further demonstrating that hydrogen generation is not rate determining in phenylacetylene $\rightarrow$ styrene transformation. Future work will consider long term stability and heat utilisation to establish feasibility for industrial implementation.

4. Conclusions

The results in this study support the following conclusions:

- i. Activation in hydrogen of 1 and 15% wt. Cu/CeO₂ prepared by deposition-precipitation and impregnation over the temperature range 573-773 K generated supported Cu nanoparticles (2-13 nm) with oxidation states in the range $\text{Cu}^0 = 13\text{-}77 \%$, $\text{Cu}^+ = 13\text{-}74 \%$ and $\text{Cu}^{2+} = 0\text{-}55\%$ as confirmed by XPS, XRD and STEM-EDX measurements.
- ii. The H₂-TPR results are consistent with a stepwise $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$ transformation with complete reduction of Cu^{2+} for the low loading samples bearing small (2-4 nm) metal nanoparticles. Inhibited H₂ diffusion and weak metal support interactions for larger (7-13 nm) copper nanocrystals in the high loading Cu/CeO₂ catalysts results in a mixture of Cu^{2+} ,

Cu^+ and Cu^0 species *post* H_2 -TPR; the presence of bigger metal particles increases the temperature requirements for the reduction of the copper phase.

- iii. The generation of styrene and ethylbenzene *via* partial- and full-hydrogenation was observed in the stand-alone gas phase hydrogenation of phenylacetylene with low H_2 utilisation efficiency. Although the copper oxidation state did not impact significantly on product distribution, we demonstrate a greater turnover frequency (*TOF*) over samples with increased Cu^0/Cu^+ attributed to elevated hydrogen uptake capacity.
- iv. Benzyl alcohol dehydrogenation produced benzaldehyde (over metallic copper) and toluene (*via* C-OH hydrogenolysis over Cu^+).
- v. The coupled dehydrogenation-hydrogenation of benzyl alcohol with phenylacetylene over all the Cu/CeO_2 catalysts resulted in the sole formation of the targets benzaldehyde and styrene products. An increase in Cu^+/Cu^0 was accompanied by an enhanced specific styrene and benzaldehyde production rate (*TOF*). We can account for this response on the basis of variations in the rate-determining step (in hydrogenation) and reaction mechanism (in dehydrogenation) for the coupled *vs.* stand alone processes. Reaction exclusivity was maintained over the temperature range 433-573 K ($\Delta E_{\text{a hydrogenation}} = 75 \text{ kJ mol}^{-1}$ and $\Delta E_{\text{a dehydrogenation}} = 59 \text{ kJ mol}^{-1}$) to attain 100% yield of styrene.
- vi. Full hydrogen utilisation and greater (up to 3-times) styrene *TOF* was recorded in the coupled dehydrogenation-hydrogenation process relative to the stand-alone reaction. Our results establish a basis for the development of a sustainable hydrogen-free continuous process for the production of high value alkenes/ketones using a *non-noble* copper catalyst.

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