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## Small and Narrowly Distributed Copper Nanoparticles Supported on Carbon Prepared by Surface Organometallic Chemistry for Selective Hydrogenation and CO<sub>2</sub> Electroconversion Processes

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Abstract: Copper nanoparticles (Cu NPs) are intensively investigated in recent years due to their promising catalytic properties, e.g. selective alkyne hydrogenation and CO<sub>2</sub> electrocatalytic reduction. While dispersing small supported Cu nanoparticles is relatively straightforward on most oxides, obtaining the corresponding small and well dispersed nanoparticles on carbon supports is more challenging because of weaker metal-support interactions resulting typically in larger particles and broader distribution. Here, we show that Surface Organometallic Chemistry can be applied on carbon support and allows the generation of small and narrowly dispersed Cu NPs (4.0 +/- 1.4 nm) supported on carbon. The thus-obtained Cu nanoparticles are catalytically active in the selective semihydrogenation of an alkyne and the hydrogenation of ethyl cinnamate into the corresponding saturated ester. Moreover, these Cu NPs dispersed on a conductive support catalyze the electroconversion of CO2 towards C1 (CO, HCOO<sup>-</sup>, CH4) and C2 (C<sub>2</sub>H<sub>4</sub>) reduction products, with high Cu-specific activity towards methane.

#### Introduction

Nanoparticles (NPs) prepared from earth-abundant and low-cost transition metals display catalytic properties towards a broad range of chemical processes employed both in industry and academia.<sup>[1]</sup> Size, shape, dispersion as well as the support play an important role in their final catalytic properties. Decreasing particle size - to increase dispersion (surface to volume ratio) and optimally use the metal - has led to a significant research effort, in particular since smaller particles are often associated with increased reactivity. Supported metal nanoparticles are specifically interesting in this regard because strong metalsupport interactions tend to favour high dispersion.<sup>[1b, 2]</sup> Among various metal nanoparticles, Cu nanoparticles<sup>[3]</sup> have received renewed interest for their applicability in organic transformations,<sup>[3-4]</sup> such as hydrogenations<sup>[5]</sup> or couplings,<sup>[6]</sup> and for their unique activity in the electroconversion of CO2 to valuable chemicals and fuels.<sup>[7]</sup> These catalytic properties together with the

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large earth-abundancy of Cu makes high dispersion of Cu NPs on support very appealing.

Our group has shown that surface organometallic chemistry (SOMC) is a powerful and general approach to generate small, narrowly-dispersed nanoparticles onto high surface area oxide supports.<sup>[8]</sup> This strategy relies on the controlled grafting of a molecular precursor, usually an organometallic compound, on an oxide support with a pre-defined OH density, followed by a reductive treatment under H<sub>2</sub> to generate supported particles. The thus-obtained nanoparticles have typically small size (1-10 nm range) that depends mainly on the metal and less on the support itself. For instance, this approach has been successfully applied to generate 2-5 nm particles of coinage metals as Cu<sup>[8a-d]</sup> but also Ag<sup>[8e]</sup> or Au<sup>[8f]</sup> on silica, alumina, zirconia, titania as well as tailored supports. In the specific case of Cu, we have shown that highly dispersed nanoparticles supported on silica (Cu/SiO<sub>2</sub>) efficiently catalyze the semihydrogenation of alkynes in the presence of organic ligands,<sup>[8c, d, 9]</sup> with performance reaching that of noble metal catalysts such as Lindlar Pd. We also discovered that Cu/SiO<sub>2</sub> can selectively catalyze the hydrogenation of the olefinic bond of  $\alpha,\beta$ -conjugated esters, whereas commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> or large Cu nanoparticles are inactive for that transformation, underlining the single behaviour of small and dispersed nanoparticles.<sup>[10]</sup>

In the past two decades, carbon materials have drawn attention as supports for heterogeneous catalysts,<sup>[11]</sup> because these materials are typically inert toward strongly acidic (or alkaline) conditions, in contrast to oxides that show poor stability under such conditions. Owing to their electronic conductivity, these supports are also particularly suited for electrocatalytic applications, as CO<sub>2</sub> electroconversion. We thus reasoned that the advantages offered by the carbon supports, the specific catalytic properties of copper nanoparticles and the superior metal optimization of small particles could be brought together using SOMC as a method of choice to generate small, well dispersed Cu nanoparticles on carbon. In this work, we demonstrate that SOMC can be transposed to carbon supports and used to produce small  $(4.0 \pm 1.4 \text{ nm})$  and dispersed Cu NPs supported on a common carbon support, carbon black. The resulting material (Cu/C<sub>B</sub>) is active in selective hydrogenations of unsaturated C-C bonds and, owing to the electronically conductive nature of the support, efficient in the electrocatalytic conversion of CO<sub>2</sub> to C<sub>1</sub> and C<sub>2</sub> reduction products.

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#### **Results and Discussion**

#### Preparation of carbon-supported Cu nanoparticles

Treatment of carbon-based materials under harsh oxidizing conditions allows the generation of surface groups such as, *inter alia*, hydroxyl or carboxyl groups (denoted here as -OH),<sup>[12]</sup> that could be exploited for SOMC. Here, carbon black is submitted to refluxing nitric acid followed by heat treatment at 200°C under high vacuum to generate the **C**<sub>B</sub> functionalized support (figure 1) displaying a preserved surface area (73 m<sup>2</sup>·g<sup>-1</sup>; figure S1) and a concentration of reactive surface -OH groups around 0.41 mmol<sub>OH</sub>·g<sup>-1</sup> (ca 3.4 OH·nm<sup>-2</sup>). This concentration of -OH groups is within the same order of magnitude as that of silica used in the SOMC preparation of supported Cu nanoparticles.<sup>[8a-c, 9a]</sup> Contacting **C**<sub>B</sub> for 24h with a toluene solution of [Cu<sub>n</sub>(Mes)<sub>n</sub>] (n = 4,5), a classical precursor for the SOMC routes to supported Cu nanoparticles.<sup>[8c, 9]</sup> affords [**Cu(Mes)**]/**C**<sub>B</sub> after washing and drying (figure 1).



Figure 1. Synthetic route for the preparation of Cu/CB and CuOx/CB.

Titration of the remaining precursor (excess) in the combined supernatant and washings infers the grafting of ca 0.66 mmole of [Cu(Mes)] unit per gram of CB, releasing mesitylene upon protonolysis, quantified to ca 0.30 mmol<sub>MesH</sub>·g<sup>-1</sup> in a separate NMR-scale grafting experiment in C<sub>6</sub>D<sub>6</sub>. These figures imply that ca 73% of the surface -OH groups reacted and that grafted Cu mesityl is present as multinuclear species ([Cum(Mes)m-1]-O-CB with m = 2-5; ca 5.4 Cu·nm<sup>-2</sup>), in line with what is found for silica.<sup>[8c,</sup> <sup>13]</sup> The substoichiometric amount of surface -OH groups reacted likely results from the steric bulkiness of grafted multinuclear Cu species. After slow oxidation in air, the resulting [Cu(Mes)]Ox/CB material was characterized by elemental analysis, transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX). Elemental analysis reveals a Cu loading of 3.96 wt%, confirming the immobilization of the copper precursor on C<sub>B</sub> surface, as also evidenced from EDX data (figure S2a). This Cu loading is also in good agreement with that calculated from titration of the unreacted [Cun(Mes)n] (ca 3.7 Cu wt%). TEM picture of [Cu(Mes)]Ox/CB does not show the substantial formation of copper/copper oxide nanoparticles (figure 2a) pointing to the high dispersion of Cu (small Cu clusters or discrete Cu sites) over the CB support upon grafting. [Cu(Mes)]/CB was then treated at 300 °C under a flow of hydrogen gas to give Cu/CB.



Figure 2. Representative HAADF-STEM images of a)  $[Cu(Mes)]O_x/C_B$ , b)  $CuO_x/C_B$  and c) particle size distribution at  $CuO_x/C_B$ .

This material was then further exposed to a slow oxidation in air, affording CuOx/CB (figure 1). Elemental analysis of CuOx/CB gives a Cu loading of 4.23 wt%, preserved from [Cu(Mes)]Ox/CB, and TEM images and EDX analysis of CuOx/CB (figures 2b and S2b, respectively) evidence the formation of small copper nanoparticles, which are well-dispersed over the  $C_B$  support. The particle size is ca. 4.0 ± 1.4 nm (figure 2c), higher than that found for Cu NPs prepared on SiO2-700 support using the same approach (1.2 ± 0.6 nm, 4.6 Cu wt%).<sup>[9a]</sup> Despite the lower dispersion of Cu on CB compared to SiO2-700 of higher surface area (73 vs 206 m<sup>2</sup>·g<sup>-1</sup>, respectively), the thus-obtained particles range among the smallest ones reported for Cu NPs on carbon supports,<sup>[3, 14]</sup> while maintaining a quite narrow size distribution and a marked Cu weight loading. These results further highlight the potentiality offered by the SOMC route to carbon-supported nanoparticles. To increase the Cu NPs loading on carbon black, we evaluated the possibility to use a second cycle of grafting of [Cun(Mes)n] and H2 treatment, taking Cu/C<sub>B</sub> as a starting material (figure S3). The resulting material contains an increased Cu loading, reaching 5.75 wt%, while preserving a high Cu dispersion and a rather small size for Cu NPs of 6.0 ± 1.8 nm (figure S4). The good retention of size for small supported (Cu) particles upon increasing metal loading was also observed with silica as a support[8b] and appears as an intrinsic property of the SOMC approach.[8i]

#### Alkyne hydrogenation

We then investigated the use of  $Cu/C_B$  in alkyne hydrogenation since the corresponding silica-supported Cu nanoparticles *via* SOMC showed good catalytic performances towards the semihydrogenation of alkynes.<sup>[8c, d, 9a]</sup> 1-Phenyl-1-propyne was used as a prototypical substrate (**S**, table 1a) with  $Cu/C_B$  (0.8 Cu mol%). The substrate **S** is fully converted within 24 h under mild conditions (at 60°C under 10 or 20 bar H<sub>2</sub>, respectively entries #1 and #2, table 1b), but yields the overhydrogenated alkane product **S**<sub>4H</sub> (table 1a), as observed with silica-supported copper nanoparticles **Cu/SiO**<sub>2</sub> (entry #9, table 1b). Decreasing the reaction temperature to 40°C limits the conversion of **S** to 98% and affords high selectivity (92%; entry #3, table 1b) to the desired semihydrogenated *cis*-olefin (*Z*)-**S**<sub>2H</sub> (table 1a). These results are in agreement with **S** inhibiting the overhydrogenation reaction, a process already evidenced for **Cu/SiO**<sub>2</sub> catalyst.<sup>[9a]</sup> 10 Cu/SiO2<sup>‡</sup>

IMes

20

60

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Table 1. a) Reaction scheme and b) conversions and overall selectivities for hydrogenation of **S** after 24 h of catalytic run (6.7  $\mu$ mol Cu, 0.8 Cu mol%, <sup>†</sup>except for **CuCu/C<sub>B</sub>** 1.1 Cu mol%). \*L/S = 1:50. <sup>‡</sup>9.3 mg material (6.7  $\mu$ mol Cu, 0.8 Cu mol%).

>99

73 (93:7)

27

<1

On the other hand, introducing 2%mol of tricyclohexylphosphine (PCy<sub>3</sub>) in the catalytic mixture allows reaching a selectivity of 84% towards (Z)- $S_{2H}$  at full conversion of S (entry #4, table 1b). The selectivity towards (Z)- $S_{2H}$  was further increased to 91% selectivity upon using the more efficient N-heterocyclic ligand IMes in place of PCy<sub>3</sub>, (entry #5, table 1b).<sup>[8d]</sup> The increased selectivity obtained with IMes originates from the competitive binding of this ligand on Cu NPs, which enables the adsorption of **S** and its conversion to  $S_{2H}$ , but adsorbs preferentially than the generated S<sub>2H</sub>, hindering overhydrogenation.<sup>[9a]</sup> Of note, under the same conditions Cu/SiO2 only provides 73% selectivity towards S<sub>2H</sub> at full conversion (entry #10, table 1b), likely because overhydrogenation is faster compared to Cu/CB, as suggested by H<sub>2</sub> uptake curves (figure S5). Besides, control experiments on bare  $C_B$  show no conversion of S (entries #7 and #8, table 1b) confirming that Cu NPs are the catalytic entities in Cu/CB. Interestingly, the morphology and size distribution of Cu NPs on Cu/CB are well retained after catalytic tests. After full conversion of S (24 h run), the Cu/CB catalyst exhibits a Cu NPs particle size of 5.5 ± 1.7 nm (Figure S6), very close to the initial value of 4.0 ± 1.4 nm. A similar size (4.8 ± 1.5 nm) is found when IMes is introduced as selectivity-driving ligand in the catalytic batch (Figure S7).

While the scope of this reaction was not investigated, we anticipate that such system will be active for the

semihydrogenation of related phenylalkyl- and diarylalkynes, since similar reactivity and selectivity patterns have been established with the silica-supported Cu NPs.<sup>[8c, 9a]</sup> Overall, the hydrogenation activity obtained here with **Cu/C**<sub>B</sub> further highlights the reach of the SOMC approach to generate catalytically active Cu NPs on carbon support.

#### Ethyl cinnamate hydrogenation

We also investigated the catalytic hydrogenation of  $\alpha,\beta$ conjugated esters to further compare the catatytic property of Cu/CB with respect to Cu/SiO2.[10] At 10 bar H2 and 60°C, the hydrogenation of the  $\alpha,\beta$ -conjugated ester ethyl cinnamate (S2, Table 2a) into the corresponding ethyl dihydrocinnamate S22H occurs, though with limited conversion within 24 h (30%; entry #1, table 2b). While increasing the H<sub>2</sub> pressure to 20 bars does not significantly improve the conversion (35%; entry #2, table 2b), increasing the temperature by only 20 °C, from 60 to 80 °C, greatly enhances the conversion to 85% at 24 h (entry #3, table 2b). Full conversion and high selectivity could be successfully achieved in doubling the loading in Cu/CB catalyst to 2.6 Cu mol% (entries #3-4, table 2b) or using the twice-loaded CuCu/CB catalyst (1.8 Cu mol% loading; entry #6, table 2b). The latter observation further shows the higher catalytic activity of CuCu/CB, which features a higher Cu loading. Note that the hydrogenation tested with only carbon C<sub>B</sub> (entry #7, table 2b) does not show any conversion, confirming that this reaction is catalysed by copper. We note that the activity observed here with Cu/CB reproduces well that observed with Cu/SiO2 under identical conditions (compare entries #5 and #8, table 2b).

Similar to what was found for **S** alkyne hydrogenation, the Cu NPs at **Cu/C**<sub>B</sub> are well retained in morphology and size ( $5.1 \pm 1.7 \text{ nm}$ ) upon catalytic conversion of **S2** (Figure S8).



b)

-,							
#	Catalyst	n( <b>S₂</b> ) (µmol)	m(cat) (mg)	P(H <sub>2</sub> ) (bar)	T (°C)	Conv. (%)	Carbon balance (%)
1	Cu/C <sub>B</sub>	500	10.0*	10	60	30	98
2	Cu/C <sub>B</sub>	500	10.0*	20	60	35	96
3	Cu/C <sub>B</sub>	500	10.0*	20	80	85	98
4	Cu/C <sub>B</sub>	250	10.0 <sup>†</sup>	20	80	>99	98
5	Cu/C <sub>B</sub>	500	20.0‡	20	80	>99	98
6	CuCu/C <sub>B</sub>	500	10.0§	20	80	>99	>99
7	Св	500	10.0	20	80	<1	98
8	Cu/SiO <sub>2</sub>	500	18.6 <sup>‡</sup>	20	80	>99	95

**Table 2.** a) Reaction scheme and b) conversion of **S2** after 24 h of catalytic run (\*6.7 µmol Cu, 1.3 Cu mol%; <sup>†</sup>6.7 µmol Cu, 2.6 Cu mol%; <sup>‡</sup>13.4 µmol Cu, 2.6 Cu mol%; <sup>§</sup>9.1 µmol Cu, 1.8 Cu mol%).

# which is attributed to catalytic H<sup>+</sup> reduction. By contrast, under CO<sub>2</sub>-saturated conditions, we observe an initial catalytic reduction that rises from potential shifted upward (around –1.86 V vs Fc<sup>+/0</sup>) compared to CO<sub>2</sub>-free conditions; this current is thus attributed to the specific electrocatalytic reduction of CO<sub>2</sub>. However, we note that the products actually evolved from CO<sub>2</sub> electroreduction can differ significantly between organic and aqueous electrolytes and further electrocatalytic tests were performed under fully aqueous conditions.



Figure 3. LSVs recorded at C<sub>B</sub>/GDL (black) and CuO<sub>x</sub>/C<sub>B</sub>/GDL (red) electrodes in a) CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> aqueous electrolyte and b) 0.1 M  $nBu_4PF_6$ MeCN (5%v water) under Ar (dashes) or CO<sub>2</sub> (lines) saturation.

The actual CO<sub>2</sub>ER activity of **CuO<sub>x</sub>/C<sub>B</sub>/GDL** was then assessed by potentiostatic electrolyses in CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> aqueous media, coupled with online analysis of gas-phase products (figure 4a). At low overpotentials (-0.4 to -0.6 V vs RHE), H<sub>2</sub> is the principal volatile product, as a result of the side-reduction of protons. From -0.6 V vs RHE down, evolution of CO is observed with increasing faradaic efficiency (F.E.) up to 5% at -1.1 V vs RHE (figure 4b). From -1.1 V vs RHE, C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub> are also evolved as CO<sub>2</sub>-reduction products with increasing F.E. as potentials are scanned downward (figures 4a,b).

From -1.3 V vs RHE, the current density among CO<sub>2</sub>-reduction products is mostly directed towards CH4 (figure 4c), which reaches 13 % F.E. at -1.6 V vs RHE (figure 4b). The increase in F.E. for C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub> correlates with a decrease in CO F.E. That observation is consistent with the current proposal that CO is a primary intermediate in the formation of C2H4 and CH4 over Cu electrocatalysts.<sup>[18]</sup> Beside volatile products, we also observed the production of HCOO<sup>-</sup> in an total F.E. of 14% as measured at the end of 4-hour electrolysis run at -1.0 V vs RHE (figure S12). Note that the Cu-free control electrode  $C_B/GDL$  yields  $H_2$  as the major volatile, with only traces of CO (< 1%; figures 4d and S13), unequivocally confirming that Cu NPs in CuOx/CB/GDL are responsible for the generation of the CO2 reduction products. At high overpotentials, the magnitude of the overall current density at  $C_B/GDL$  approaches that of the H<sub>2</sub> partial current density at CuO<sub>x</sub>/C<sub>B</sub>/GDL (figure 4d). This observation suggests that H<sup>+</sup> sidereduction at CuO<sub>x</sub>/C<sub>B</sub>/GDL mostly arises from the carbon black support and the gas diffusing layer and further underlines that Cu is crucial in that material to drive the conversion of CO2. Partial current densities obtained after subtraction of the background

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#### CO<sub>2</sub> electro-conversion

In order to investigate the electrochemical properties of the carbon-supported Cu NPs, we deposited the air-oxidized CuO<sub>x</sub>/C<sub>B</sub> material onto a gas diffusion layer (GDL) electrode using Nafion® as an ion-exchanging binding material, giving CuOx/CB/GDL electrodes. TEM picture and local EDX spectroscopy of the electrode top layer together confirm that Cu NPs are preserved after electrode templating (figure S9). The signatures of Nafion® are evident on the C 1s X-ray photoelectron spectrum (XPS) of the CuOx/CB/GDL electrode (peak at 292.5 eV for CF<sub>2</sub> groups;<sup>[15]</sup> see figure S10 and table S1), confirming the casting of the ionomer. To provide an estimate of the amount of electroactive Cu at CuOx/CB/GDL, we recorded cyclic voltammetry at this electrode in 1 M KOH aqueous electrolyte, after a reductive equilibration of the electrode at -1.3 V vs NHE (-0.47 V vs RHE) to convert CuO<sub>x</sub> layers into Cu. Upon scanning potential upward, a broad, ill-defined oxidation event is observed at around 0.04 V vs NHE (0.87 V vs RHE) as shown in figure S11a. Such event, which is not present on the blank C<sub>B</sub>/GDL electrode, is attributed to the oxidation of top Cu layers of the nanoparticles at the CV timescale. We assign this event to the oxidation of electroactive Cu(0) species at the NPs surface to Cu(I) and further Cu(II) species, namely soluble  $[Cu(OH)_2]^-$  and  $[Cu(OH)_4]^{2-}$  ions under the pH conditions used (pH = 14),<sup>[16]</sup> leading to the partial dissolution of the NPs. By integration of this wave, we obtain an upper estimate of the density of electroactive Cu species around  $\Gamma_{CV}(Cu) = 1.6 \ 10^{-8} \ \text{mol} \cdot \text{cm}_{\text{geom}}^{-2}$ . A similar density was found from CVs recorded in 0.5 M KHCO<sub>3</sub> electrolyte (figure S11b). The total density in Cu per geometric electrode area  $\Gamma_{tot}(Cu)$  is estimated around 2.6 10<sup>-7</sup> mol·cm<sub>geom</sub><sup>-2</sup> (see supplementary information), giving a dispersion in electrocatalytic Cu species of ca 0.06. For comparison, the density of surface Cu atoms estimated from the particle size obtained by TEM and assuming a spherical shape of the particles is found at ca  $\Gamma_{TEM}(Cu) = 6.8 \ 10^{-8} \ \text{mol} \cdot \text{cm}_{\text{geom}}^{-2}$  (see supplementary information). This coverage falls consistently within the same order as that obtained from CV, although with a higher value. Assuming a spherical shape for the particle size distribution obtained by TEM tends to give overestimate in Cu coverages,<sup>[8b]</sup> which can explain this higher value compared to CV estimate. In addition, part of the CuOx/CB domains may not be in electronic contact with the GDL back electrode, thus not addressed by the electroactive Cu coverage  $\Gamma_{CV}(Cu)$ .

Having established that Cu NPs at **CuO<sub>x</sub>/C<sub>B</sub>/GDL** can be electrochemically addressed, we studied their activity in CO<sub>2</sub> electroreduction, given the well-known ability of Cu nanoparticles to electrocatalyze this process.<sup>[7a, b, h, 17]</sup> In CO<sub>2</sub>-saturated KHCO<sub>3</sub> aqueous electrolyte, the linear scan voltammogram at **CuO<sub>x</sub>/C<sub>B</sub>/GDL** shows a catalytic reduction current that onsets around – 0.84 V vs NHE (– 0.43 V vs RHE), shifted more than 150 mV upward compared to the **C<sub>B</sub>/GDL** control electrode (figure 3a). Such shift suggests that Cu NPs present on **CuO<sub>x</sub>/C<sub>B</sub>/GDL** are electrocatalytically active. To further probe the origin of catalytic reductive processes, LSVs were recorded in 0.1 M *n*Bu<sub>4</sub>PF<sub>6</sub> MeCN electrolyte using water (5%v) as a proton source, in the absence or presence of CO<sub>2</sub> (figure 3b). In the CO<sub>2</sub>-free electrolyte, a reduction current onsets from ca –2.24 V vs Fc<sup>+/0</sup>,

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activity of **C**<sub>B</sub>/**GDL** shows that **CuO**<sub>x</sub>/**C**<sub>B</sub>/**GDL** has Cu-specific mass activity (using the total Cu loading  $\Gamma_{tot}(Cu)$ ) going from H<sub>2</sub> to predominantly CH<sub>4</sub> as potential is lowered (figures 4c and S14).



Figure 4. a) Total current density (black squares, left scale) and faradaic efficiencies for gas-phase products (dots, right scale) at  $CuO_x/C_B/GDL$ . b) Zoom on faradaic efficiencies for CO<sub>2</sub>-reduction gas-phase products at  $CuO_x/C_B/GDL$ . c) Background-subtracted Cu-mass partial current densities at  $CuO_x/C_B/GDL$ . d) Total (black) and H<sub>2</sub> partial (wine) current densities at  $C_B/GDL$  (triangles) and  $CuO_x/C_B/GDL$ . (squares). Conditions: CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> aqueous electrolyte (pH = 7). Colors: all gas-phase products (gray), all gas-phase CO<sub>2</sub>-reduction products (navy), H<sub>2</sub> (wine), CO (blue), CH<sub>4</sub> (green) and C<sub>2</sub>H<sub>4</sub> (purple).

This high specific activity for H<sub>2</sub> and CH<sub>4</sub> is a consistent feature within precedent reports on small Cu NPs (< 10nm)<sup>[7a, b, 17c]</sup> and is proposed to arise from low-coordinated Cu surface sites.<sup>[19]</sup> We observe here that the CH<sub>4</sub> specific current density continuously increases in magnitude with increasing overpotential at CuO<sub>x</sub>/C<sub>B</sub>/GDL (-540 A·g<sub>Cu</sub><sup>-1</sup> at -1.6 V vs RHE), whereas it plateaus or decays for unsupported Cu NPs.<sup>[7a, b, 17c]</sup> Among the few reports on CO2ER catalyzed by Cu NPs supported on high surface area carbon,<sup>[20]</sup> Baturina and co-workers observed that relatively small Cu NPs (8-13 nm) on Vulcan carbon black (40 wt% Cu)<sup>[20a]</sup> have high activity towards C-products at low potentials but produce a mixture of mostly C2H4 and CH4 (ca 47 and 30 % overall F.E., respectively, at -1.6 V vs RHE). At the same potential, CuOx/CB/GDL displays lower overall F.E. towards C-products but predominantly evolves CH4 within C-products (F.E.  $(CH_4) = 13\%$  vs F.E. $(C_2H_4) = 4\%$ ). This difference can be explained by a much higher Cu loading for Cu NPs on Vulcan carbon<sup>[20a]</sup> (40 vs 4.2 wt% Cu for CuO<sub>x</sub>/C<sub>B</sub>/GDL), given that increasing Cu loading is known to promote activity towards Cproducts and C-C couplings, thus C2+ products.<sup>[7a, h, 21]</sup> The low Cu

loading at CuOx/CB/GDL thus corroborates its moderate overall F.E. for C-products and its high intrinsic selectivity for CH4 within C-products, also favoured by high Cu dispersion. We note that subsurface Cu atoms remaining partially oxidized under electroreductive conditions and possibly impacting activity, as debated in the literature,  $^{\left[ 21\right] }$  may be present at our  $\textbf{CuO}_{x}/\textbf{C}_{B}/\textbf{GDL}$ electrode, although we did not address this point in further details. Long-term electrolyses over 24 hours show a gradual decay of the activity towards CO2 reduction (figure S15). To understand the origin of this decay, we analysed by TEM the CuOx/CB material at several durations of electrolysis. After a 1-hour electrolysis at -1.0 V vs RHE, we observed Cu nanoparticulate species of ca 1-3 nm (figure S16a,b) together with the formation of larger cubeshape nanoparticles of ca 20 nm (figure S16c-e), possibly grown from this small Cu NPs (figure S16f). Interestingly, longer electrolyses lead to the gradual disappearance of the larger cubic nanoparticles towards more of the 1-3 nm Cu nanoparticles (after 4-hour electrolysis; figures S17-19) and further nanometric clusters (after 24-hour electrolysis; figure S20). Consistent with this behaviour, Hwang and co-workers have recently reported a similar observation that small Cu-based nanoparticles first agglomerate into larger cube-shaped nanoparticles, which further undergo fragmentation back into smaller Cu NPs.<sup>[7k]</sup> Electrolyses at lower potential (-1.4 V vs RHE) also led to the re-dispersion of Cu into smaller Cu NPs (1-3 nm) after 4 and 24 hours (figures S21,22). We note that the presence of potentially low-coordinated Cu sites at these nanoparticles also correlates with the high Cu mass activity observed for H2 and CH4.[19, 22] Overall, reconstruction of Cu NPs under electrocatalytic conditions into more dispersed Cu species having higher intrinsic activity for H<sub>2</sub> evolution explains the observed decrease in selectivity towards CO<sub>2</sub> reduction products. While Cu loading is known to directly affect the reconstruction of Cu NPs under electrocatalytic conditions,<sup>[7h]</sup> we propose that the moderate Cu loading at CuOx/CB favours re-dispersion of the initial Cu NPs into smaller ones. Also, strong interactions with surface groups present on the CB support, such as alcohol- or ketone-type moieties evidenced on the C 1s and O 1s XPS spectra<sup>[23]</sup> of CuO<sub>x</sub>/C<sub>B</sub>/GDL electrode (figure S10, table S1) may further stabilize these small Cu NPs.

#### Conclusions

We successfully translated the SOMC strategy to prepare narrowly-dispersed and small (ca 4 nm) Cu nanoparticles on carbon black. We demonstrated that these carbon-supported Cu NPs are active for the semihydrogenation of a prototypical alkyne (1-phenyl-1-propyne). The use of a ligand (e.g. IMes) permits to reach high selectivity for the desired *cis*-olefin at full conversion of the starting alkyne. We also showed that the **Cu/C**<sub>B</sub> material can efficiently catalyze the selective hydrogenation of  $\alpha$ , $\beta$ -conjugated esters like ethyl cinnamate into ethyl dihydrocinnamate under mild conditions. This activity in selective hydrogenations parallels that of the counterpart silica-supported Cu NPs and demonstrates the successful translation of the SOMC route to generate catalytically active Cu NPs on carbonaceous material. Besides, taking advantage of the electronic conductivity brought by the carbon

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support, Cu NPs obtained by SOMC and templated within an  $CuO_x/C_B/GDL$  electrode assembly can be electrochemically addressed. The electrode is competent for the electroconversion of CO<sub>2</sub> to carbonaceous products as CO, HCOOH, C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub> under fully aqueous conditions. The partial reconstruction of the Cu NPs observed upon electrocatalytic turnover namely yields discrete Cu species, possibly responsible for the high Cu-specific activity towards H<sub>2</sub> and CH<sub>4</sub>.

Demonstrating the SOMC route to Cu NPs on carbon reconciles the innate properties of this support (electronic conductivity, hydrolytic stability) with the high dispersion of supported metallic nanoparticles at its surface. We anticipate that the approach can be straightforwardly expanded to produce supported nanoparticles of different metals and on alternative carbon supports. Expanding the library of supports available for SOMC to carbon materials and more broadly to electronic conductors will open new opportunities in the application scope of supported, well-dispersed NPs towards various catalytic conversions, including electrocatalysis. We are currently investigating this direction.

#### **Experimental Section**

General procedures. Unless otherwise noted, all experiments were conducted with dry, oxygen-free solvents using standard Schlenk techniques or in N2 or Ar-filled gloveboxes and reagents were obtained from commercial suppliers and used as received. Toluene and pentane were purified by passage through double solvent purification alumina columns (MBraun). CO2 (quality 48) was purchased from Pangas. Carbon black (acetylene, 50% compressed, 99.9+%, surface area 75 m<sup>2</sup>·g<sup>-1</sup>, bulk density 80-120 g·L<sup>-1</sup>) was purchased from Alfa-Aesar. Gas diffusion layer (GDL 39 BC) was graciously provided by SGL CARBON GmbH Company. Anion-exchanging membrane (Fumasep® FAA-3-PK-130) was purchased from Fumatech. Tricyclohexylphosphine was purchased from Aldrich and recrystallized from pentane. 1-Phenyl-1-propyne and ethyl cinnamate were purchased from Sigma-Aldrich, degassed by three freeze-pumpthaw cycles and then high-vacuum transferred in Rotaflo-type Schlenk vessels, stored in a glove-box over 3 Å molecular sieves and passed over activated alumina just before use. IMes (1,3-bis(2,4,6trimethylphenyl)imidazol-2-ylidene) was synthetized by a procedure adapted from the literature.<sup>[24]</sup> [Cu<sub>5</sub>(Mes)<sub>5</sub>] toluene was prepared according to procedures from the literature.[25] Cu/SiO2 (4.6 Cu wt%) was prepared as reported previously.[9a]

**Characterization methods.** Elemental analysis of the supported material was performed by the Mikroanalytisches Labor Pascher, Remagen, Germany. Liquid-state NMR spectra were recorded on a Bruker DPX-300 instrument operating at the denoted spectrometer frequency given in MHz for the specified nucleus. The <sup>1</sup>H and <sup>13</sup>C chemical shifts are calibrated with the residual solvent peak. Electron microscopy (HAADF-STEM and EDX) was performed at the ScopeM facility on a HD2700CS (Hitachi) instrument or on a Talos F200X (Thermo Fischer Scientific) instrument both operated at an acceleration voltage of 200 kV. Samples for electron microscopy were dry-casted on Cu mesh grids (Lacey C only; 300 mesh Cu; TED PELLA INC.) unless otherwise noted for Au grids (UC-A on Lacey; 300 mesh Au; TED PELLA INC.) X-ray photoelectron spectroscopy measurements were performed at ca. 2·10<sup>-9</sup> mbar in a VG ESCALAB 220iXL spectrometer (Thermo Fisher Scientific) using focused monochromatized Al K<sub>a</sub> radiation (1486.6 eV) with a beam size of ca. 500

μm<sup>2</sup>. The spectrometer was pre-calibrated by performing measurement on a clean silver surface, whereby the Ag  $3d_{5/2}$  peak was aligned to a binding energy of 368.25 eV with a full width at half-maximum of 0.78 eV at a pass energy of 30 eV. Spectra were recorded with a dwell time of 50 ms, using a pass energy of 30 eV and in 0.05 eV binding energy steps. Spectra were acquired with a take-off angle of 90°. C 1s, respectively O 1s, spectra were calibrated by adjusting the binding energy of the C sp<sup>2</sup> contribution to 284.8 eV, respectively of the C=O contribution to 531.1 eV. Nitrogen adsorption isotherms were recorded on a Bel-Mini apparatus (BEL Japan, Inc.) at 77 K. Approximately 100 mg of the samples were loaded into cells. Prior to the adsorption measurement, the samples were evacuated under vacuum (ca. 10<sup>-3</sup> mbar) at R.T. for 1 h then at 200 °C for 2 h. Data were fitted according to a BET isotherm to obtain the total surface area.

**Preparation of C**<sub>B</sub>. Carbon black (4.4 g) was first refluxed in 100 ml HNO<sub>3</sub> fuming solution for 24 hours, to generate reactive surface groups.<sup>[11a]</sup> The material was filtered on a filter paper, washed with large portions of distilled water, then ethanol and dried under high vacuum (10<sup>-5</sup> mbar) at 200 °C for 24 hours to yield the activated carbon support **C**<sub>B</sub>. Titration of the activated support **C**<sub>B</sub> with [Mg(Bn)<sub>2</sub>(THF)<sub>2</sub>] gave a density of reactive protic groups of ca 0.41 mmol<sub>group</sub>·g<sup>-1</sup>. The surface area measured using nitrogen adsorption-desorption isotherms is 73 m<sup>2</sup>·g<sup>-1</sup> (figure S1).

**Preparation of Cu/C<sub>B</sub> and CuO<sub>x</sub>/C<sub>B</sub>.** A mixture of  $[Cu_5(Mes)_5]$ -toluene (0.54 g, 0.54 mmol, 2.68 mmol<sub>cu</sub>) and activated carbon black **C**<sub>B</sub> (1.44 g, ca 0.59 mmol<sub>group</sub>) in 30 mL toluene was stirred for 24 hours at room temperature. The mixture was then filtered on a glass frit, washed twice with 10 mL toluene, then once with 10 mL pentane and dried under vacuum to afford [**Cu(Mes)**]/**C**<sub>B</sub>. [**Cu(Mes)**]/**C**<sub>B</sub> was then submitted to hydrogenation under a flow of H<sub>2</sub> using the following temperature program: from R.T. to 300 °C at 60 °C·h<sup>-1</sup>, then 12 h at 300 °C. The reactor was then evacuated under high-vacuum at 300 °C for 4 h, to afford the **Cu/C**<sub>B</sub> material, which was stored in an Ar-filled glovebox. Upon slow exposure to air, [**Cu(Mes)**]/**C**<sub>B</sub> yields [**Cu(Mes)**]**O**<sub>x</sub>/**C**<sub>B</sub> and **Cu/C**<sub>B</sub> yields **CuO**<sub>x</sub>/**C**<sub>B</sub>.

**Preparation of CuCu/C<sub>B</sub> and CuCuO<sub>x</sub>/C<sub>B</sub>**. The grafting/hydrogenation procedure was repeated a second time on the **Cu/C<sub>B</sub>** material. Briefly, a mixture of [Cu<sub>5</sub>(Mes)<sub>5</sub>]-toluene (80 mg, 80 µmol, 400 µmol<sub>cu</sub>) and **Cu/C<sub>B</sub>** (0.2 g) in 10 mL toluene was stirred for 24 hours at room temperature. The mixture was then filtered on a glass frit, washed twice with 5 mL toluene, then once with 5 mL pentane and dried under vacuum. The obtained material was submitted to hydrogenation under a flow of H<sub>2</sub> using the following temperature program: from R.T. to 300 °C at 60 °C·h<sup>-1</sup>, then 12 h at 300 °C. The reactor was then evacuated under high-vacuum at 300 °C for 4 h, to afford the **CuCu/C<sub>B</sub>** material, which was stored in a Ar-filled glovebox. Slow oxidation by exposure to air yields the **CuCuO<sub>x</sub>/C<sub>B</sub>** material, for which a Cu loading of 5.75 wt% was found by elemental analysis.

**Preparation of CuO<sub>x</sub>/C<sub>B</sub>/GDL electrodes.** 5 mg of **CuO<sub>x</sub>/C<sub>B</sub>** were dispersed in a solution 100 mL ethanol containing 50 µL of Nafion 5 wt%. The solution was sonicated for around 30 minutes. The final solution was then filtered on a gas diffusion layer (GDL) support of surface 12.6 cm<sup>2</sup> (disc). The obtained **CuO<sub>x</sub>/C<sub>B</sub>/GDL** material was then sliced into pieces to prepare electrodes, the working area of which was delimited to 1 cm<sup>2</sup> geometric using epoxy glue. Samples for TEM imaging and XPS analysis were prepared by scratching with a plastic spatula the side of the electrode where **CuO<sub>x</sub>/C<sub>B</sub>** is deposited.

Alkyne hydrogenation. Hydrogenation studies were performed on an 8parallel reactor autoclave (Endeavour, Biotage) operated inside a glove box. The H<sub>2</sub> feed was passed through activated Cu/Al<sub>2</sub>O<sub>3</sub> sorbent (BASF) and activated 4-Å molecular sieves. Stock solutions of substrates in

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toluene (1 M), ligands in toluene (10 mM) and tridecane (100 mM) in toluene were prepared using volumetric flasks. GC analysis was performed on Shimadzu-QP 2010 Ultra equipped with parallel FID and MS detectors using an HP-5 column, N2 as a carrier gas (30 mL·min<sup>-1</sup>) and the following temperature program: ramp of 15 °C min-1 from 70 °C to 260 °C and then holding at 260 °C for 15 min. In a typical experiment, the glass liner reactors were charged with 10.0 mg of material unless otherwise noted, 800 µL of 1M substrate (800 µmol) solution and 800 µL of a 100 mM tridecane (internal standard) solution or 800  $\mu L$  of a mixture of substrate (1M; 800 µmol) and tridecane (100 mM) and, for corresponding experiments, 1600 µL of a 10 mM ligand L solution (n(L) = 16 µmol; L/S ratio of 1:50). The glass liners were then filled with toluene until a total volume of 4400 µL was reached. 400 µL of the thusly prepared initial mixtures were then aliquoted and submitted to GC analysis. The reaction media were then set to the desired pressures and temperatures and stirred at 500 rpm for 24 h. At the end of the catalytic run, 400 µL of the final reaction mixtures were drawn and analyzed by GC. Areas of GC peaks were normalized against the area of the tridecane peak. Comparison of normalized areas of initial mixture with that of final ones allowed to determine conversions and selectivities, using the same response factors for all substrates. All carbon balances were found >99%. Hydrogen consumption curves are reported in moles of H<sub>2</sub> consumed per volume of batch solution. Post-activity samples for TEM imaging were collected at the end of catalytic runs. The supernatant solution was removed, the spent material dried under vacuum and stored in glovebox before slow exposure to air.

**Ethyl cinnamate hydrogenation**. The procedure for the hydrogenation of ethyl cinnamate is identical to that for alkyne hydrogenation except for the following alterations: a stock solution containing the substrate (1 M) and tridecane (100 mM) in toluene as an internal standard was prepared. The glass liner reactors were charged with the desired amount of material (typically 10.0 mg), of substrate solution (typically 500 µL; 500 µmol) and filled with toluene to reach a total volume of 4400 µL. 400 µL of the thusly prepared initial mixtures were then aliquoted and submitted to GC analysis. The reaction media were then set to desired pressures and temperatures and stirred at 500 rpm for 24 h. At the end of the catalytic run, 400 µL of the final reaction mixtures were aliquoted and analyzed by GC. GC analysis was performed with the following temperature program: 8 min at 40 °C, then ramp of 20 °C ·min<sup>-1</sup> to 200 °C followed by a ramp of 40 °C ·min<sup>-1</sup> to 260 °C and then holding at 260 °C for 4.5 min.

Electrochemical investigation. Electrochemical experiments were carried out with an Autolab PGSTAT 128N potentiostat/galvanostat. Experiments were conducted at room temperature (24 ± 1 °C), using a Pt wire counter electrode and a AgCl/Ag (in KCl 3M), respectively a AgNO<sub>3</sub>/Ag (10 mM in 0.1 M nBu<sub>4</sub>PF<sub>6</sub> MeCN), reference electrode for experiments conducted in aqueous, respectively organic, electrolyte. Potentials measured in aqueous electrolyte were referenced against the normal hydrogen electrode (NHE) and reversible hydrogen electrode (RHE) using conversion from the literature.[26] Potentials measured in organic electrolyte were referenced versus an internal Fc+/0 reference added at the end of the experiment. Cyclic voltammetries (CV) and linear sweep voltammetries (LSV) were performed in a single compartment cell using 1 M KOH or 0.5 M KHCO3 aqueous electrolytes or 0.1 M nBu4PF6 MeCN with H<sub>2</sub>O 5%v electrolyte, under Ar or CO<sub>2</sub>-saturated conditions. Unless otherwise noted, CVs and LSVs were recorded at 100 mV·s<sup>-1</sup>. Potential-dependence of currents and evolved products was evaluated under potentiostatic conditions in a two-compartment cell. The compartment containing the working and reference electrodes was separated from that containing the counter electrode by a porous glass frit or by a Fumasep FAA-3-PK-130 anion-exchanging membrane. A mass flow meter (Bronkhorst EL-Select), was used to control the flow of CO2 flushed through the electrolyte. Prior to electrolysis, CO2 (20 mL·min<sup>-1</sup>)

was bubbled first in the counter electrode compartment for 30 min then in the working electrode compartment for 30 min. Potentiostatic electrolyses were conducted for 1 h and under a constant flow of CO<sub>2</sub> (20 mL·min<sup>-1</sup>) flushing the electrolyte at the working electrode compartment. The outlet stream directly fed the injection loops of an in-line gas chromatographmass spectrometer (GC-MS) for analysis of gas-phase products. In a typical experiment, the first electrolysis was recorded at -1.6 V vs RHE, and following ones at potentials incremented by 0.1 V up to -0.4 V vs RHE. Identification and quantification of the gas-phase products was realized by in-line GC-MS (Agilent Technologies 7890 gas chromatograph coupled to an Agilent Technologies 5977B MSD mass spectrometer) setup. The outlet stream of the electrochemical cell flushed injection loops of two parallel lines and samplings are realized every 30 min. The first line was eluted with Ar carrier gas on a Porapak Q column followed by a GScarbonplot column to a thermal conductivity detector (TCD) followed by a Ni-catalyst methanizer used to methanize the CO fraction and bypassed otherwise and finally to a flame ionization detector (FID). The other line fed a split-splitless port that injected in the split mode with He carrier gas on a GS-Carbonplot capillary column plugged to a mass selective detector (MSD) operated in the scan mode in the m/z range 0-100. Elution was realized using the following temperature program: 40 °C for 2 min, then ramp to 150°C at 55°C ⋅ min<sup>-1</sup> and 150°C for 3 min. The in-line GC-MS system was calibrated with gas standards containing known molar ratios (0.1, 1 or 10% each) of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> in CO<sub>2</sub> (balance gas). Long-term electrolyses were performed with CuOx/CB/GDL at -1.0 V and -1.4 V vs RHE, using a CO<sub>2</sub> flow of 20 mL·min<sup>-1</sup>. Investigation of gas-phase products were performed as described above. At the end of an electrolysis, the working electrode was immediately disconnected and dried under a flow of Ar. The side of the electrode where CuOx/CB was deposited was scratched using a plastic spatula and the resulting black powder deposited on TEM grids for imaging. Samples of electrolyte were aliquoted from the cathodic and anodic compartments for characterization of liquid-phase products. Liquid-phase products were analysed and quantified using nuclear magnetic resonance (NMR) spectroscopy. Samples were prepared by mixing 380 uL of analyte with 40 uL D<sub>2</sub>O and 8  $\mu\text{L}$  of a 0.5 M DMSO (standard) aqueous solution in a NMR tube, according to a procedure modified from the literature.<sup>[27]</sup> Quantification was performed on a 400 MHz Bruker spectrometer using a water suppression (CW) NMR sequence.

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**Keywords**: Supported copper nanoparticles • surface organometallic chemistry • carbon support • alkyne

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semihydrogenation • selective hydrogenation • CO<sub>2</sub> electroreduction

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Carbon-supported copper nanoparticles prepared *via* surface organometallic chemistry are active catalysts in selective hydrogenation and CO<sub>2</sub> electroconversion.

#### Expanding support for SOMC route to Cu NPs



Christos K. Mavrokefalos, Nicolas Kaeffer\*, Hsueh-Ju Liu, Frank Krumeich, Christophe Copéret\*

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Small and Narrowly Distributed Copper Nanoparticles Supported on Carbon Prepared by Surface Organometallic Chemistry for Selective Hydrogenation and CO<sub>2</sub> Electroconversion Processes