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Published in:
CHEMSELECTROCHEM

DOI:
10.1002/celc.202100345

Published: 01/07/2021

Document Version
Publisher's PDF, also known as Version of record

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Please cite the original version:
Suominen, M., & Kallio, T. (2021). What We Currently Know about Carbon-Supported Metal and Metal Oxide Nanomaterials in Electrochemical CO2 Reduction. CHEMSELECTROCHEM, 8(13), 2397-2406. https://doi.org/10.1002/celc.202100345
What We Currently Know about Carbon-Supported Metal and Metal Oxide Nanomaterials in Electrochemical CO₂ Reduction

Milla Suominen* and Tanja Kallio*[a]

Electrochemical reduction of CO₂ is considered important in enhancing the circular-economy design; it can suppress harmful greenhouse-gas emissions while, combined with intermittent renewable energy sources, it can employ the surplus energy for production of important chemicals and fuels. In the process, electrocatalysts play an important role as the mediators of the highly active and selective conversion of CO₂. Transition and post transition metals and their oxides are an important electrocatalyst group. For practical reasons, these metals need to be applied as nanoparticles supported on highly conducting materials enabling fabrication of 3D electrodes. In this minireview, we focus on gathering our current knowledge on the effects which transition and post transition metal and metal oxide nanoparticles supported on different carbons may have on electrochemical reduction of CO₂. We focus on literature of studies conducted in aqueous conditions, under as similar conditions as possible, to ensure comparability. This approach enables us to highlight possible support effects and issues that complicate making conclusions on support effects.

1. Introduction

Electrochemical CO₂ reduction (CO₂R) is an appealing technique for lowering the concentration of atmospheric CO₂.[1] For large-scale CO₂ conversion, electrocatalysts need to operate selectively at low overpotentials for several thousands of hours. To achieve this milestone, electrocatalysts are designed and investigated; among them transition and post transition metals.[2,3] Main problems of CO₂R on these metals are high onset potentials, low activity, poor selectivity, and bad durability. To improve their performance, nanostructuring is utilized since nanomaterials possess a large surface area to bulk ratio and an abundance of low-coordinated sites offering more active sites. Unfortunately, nanoparticles are inherently vulnerable under reducing conditions and, additionally, the high price and scarcity of the most selective and active CO₂R electrocatalysts (Figure 1) requires supporting the nanoparticles on highly conductive materials, such as carbons. In this type of hybrid catalysts, the metal is expected to be the main contributor to catalytic activity but the support may also play its role:[4] it may promote the growth of certain size and shape of nanoparticles,[5] tune the electrochemical properties, inhibit the modification of metal chemical state or prevent agglomeration.[6]

Support effects have been reported for other catalytic reactions,[4] and CO₂R on transition and post transition metals has also been widely reviewed.[7–22] However, these reviews only briefly touch the issue of supporting effects, and reviews on carbon supported metals focus on several catalytic reactions, defect design, carbon shell tuning and single atom catalysts (SACs).[23] Herein, we focus strictly on carbon supported transition and post transition metal nanomaterials and their oxides towards CO₂R in aqueous conditions. Since these metals are readily oxidized and are likely in oxidized form prior to application of reductive potentials, both metal nanoparticles and their oxides are included. In the end, it has been shown that the active electrocatalyst is usually the reduced metal.[24,25] We have aimed to compare studies made under as identical conditions as possible keeping in mind the important methodology recommendations[17,26] to enable us to highlight possible support effects as well as issues that complicate our current understanding of support effects in CO₂R.

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1.1. Challenges of CO2R on Metals

CO2R takes place in the cathode. According to technoeconomic analyses, formic acid, propanol, ethylene and ethanol (EtOH) are profitable products,[17] while CO is an important intermediate in CO2R as well as a reactant in many follow-up reactions. The electrochemical reactions of these most important products along with their equilibrium potentials[28] are presented in (1)–(5), respectively.

\[
\begin{align*}
\text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^- & \rightarrow \text{HCOOH} \quad E^0 = -0.12 \text{ V} \\
3 \text{CO}_2 + 18 \text{H}^+ + 18 \text{e}^- & \rightarrow \text{C}_3\text{H}_6\text{O} + 5 \text{H}_2\text{O} \quad E^0 = 0.10 \text{ V} \\
2 \text{CO}_2 + 12 \text{H}^+ + 12 \text{e}^- & \rightarrow \text{C}_2\text{H}_4 + 4 \text{H}_2\text{O} \quad E^0 = 0.08 \text{ V} \\
2 \text{CO}_2 + 12 \text{H}^+ + 12 \text{e}^- & \rightarrow \text{C}_2\text{H}_6\text{O} + 3 \text{H}_2\text{O} \quad E^0 = 0.09 \text{ V} \\
\text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^- & \rightarrow \text{CO} + \text{H}_2\text{O} \quad E^0 = -0.10 \text{ V}
\end{align*}
\]

Water is a cheap and eco-friendly source of protons and electrons making aqueous electrolyzer designs highly desirable. However, the competing hydrogen evolution reaction (HER) affects the performance of the system.[99] In aqueous electrolyzer designs highly desirable. However, the competing hydrogen evolution reaction (HER) used, namely pyrolysis of metal-tetracyanoquinodimethane compounds, could result in formation of similar mixed catalysts which has not been excluded based on the presented results. For Fe, supported nanoparticles have been claimed to form syngas but on a closer look, the catalyst material is a very complex one making conclusions on support immensely difficult.[30] Since there are very few publications on this category of metals, not many conclusions can be made, and therefore, the remainder of this minireview will focus on the metals that are CO2R active.

These metals also produce different products based on their ability to bind the intermediates: Pd, Ag, Au, Zn and Ga mainly produce CO due to their weak binding energy towards intermediates whereas Cd, Hg, In, Ti, Sn, Pb and Bi mainly produce formic acid.[32] As an exception, Cu is able to produce more value added chemicals such as C2H4 and EtOH because of its unique adsorption energies to CO* and H+.[36] but selectivity on Cu is poor and supporting aims to improve this.

2. Carbon-Supported CO2R Nanocatalysts

Carbon-supported materials constitute the biggest group of supported electrocatalysts in CO2R. After all, carbon is a cheap, inert, chemically and electrochemically stable, and abundant material which we can obtain as bulk carbons (activated carbons, graphite) or nanocarbons (fullerenes, nanotubes, graphenes). Supporting on metal oxides[37–41] and carbides[41,42] has also been reported but to a lesser extent. It is worth to mention, however, that H2 formation tendency of the supporting carbide appears to affect CO2R activity of Pd.[42]

2.1. Effects of the Synthesis Route

To begin with, there are two main routes to produce supported nanoparticles: the in situ synthesis route where the metal precursor salt is converted into metal nanoparticles in the presence of the supporting material, and the ex situ route or physical adsorption method where nanoparticles are synthesized separately and the final hybrid material is produced by simple ultrasonication or mixing of the nanoparticles and support in a suitable solvent. Overall, the former method is more popular which is not surprising since it lowers the number of steps required to obtain a catalyst and often the supporting material can act as seed points for small, well-dispersed nanoparticles to grow from and prevent the harmful agglomeration which would normally take place if nanoparticles were synthesized without any additives. However, the route also leads to varying nanoparticle sizes and morphologies. Metal
loading is usually controlled by varying the amount of the metal salt precursor in the reaction mixture and increasing the metal loading generally leads to increased nanoparticle size as well as to agglomeration. Additionally, the size and morphology of the nanoparticles may vary between two different supports with same intended metal loading. For a given metal catalyst, those properties may affect CO₂R as often smaller, well-dispersed nanoparticles are reported to exhibit better performance over the larger or agglomerated ones. While in the absence of proper electrochemical surface area (ECSA) normalized results this conclusion remains ambiguous, we should keep in mind that there may be effects from nanoparticle size and morphology. Often the changes observed in CO₂R between supported or unsupported and between different supporting materials are directly attributed to support effects. However, often more than one variable is present, making conclusions on the underlying reasons behind different selectivity or activity on different supports difficult. Naturally, one could argue that the formation of an ideal nanoparticle in the presence of a certain support is a support effect as such but when the aim is to understand the mechanisms of CO₂R on different supports in order to rationally design novel catalysts, we desperately need variable-controlled studies on support effects, as well.

A good example of the size effect is an early study on supporting Cu on different carbons.[43,44] Hybrid materials 40 wt.% Cu on Vulcan carbon (VC) and 20 wt.% Cu on single walled carbon nanotubes (SWNT) with well-dispersed and small nanoparticles (8–13 nm and 15–25 nm, respectively) produced more C₂H₄ in comparison to CH₄ while 50 wt.% Cu on Ketjen black (KB) and 20 wt.% Cu/VC with agglomerated larger nanoparticles (70–80 nm and 70–130 nm, respectively) produced CH₄ and C₂H₄ at similar FEs.[43] Later, 20 wt.% of Cu was loaded on SWNT, reduced graphene oxide (rGO), onion-like carbon and VC with reduced changes in nanoparticle sizes (19 nm, 36 nm, 13 nm and 33 nm, respectively).[44] On 20 wt.% Cu/VC, the nanoparticle size is reduced from the previous work and now the product distribution is showing more C₂H₄ (ca. 40%) over CH₄ (ca. 25%) (Table 2). Changes in product distribution appear to have originated more from the nanoparticle size and distribution rather than from applying different carbon supports. Cu loading may also have played a role: by applying a higher loading of nanoparticles, critical changes in morphology may take place during CO₂R which favors C₂ and C₃ products.[45]

In the physical adsorption method, metal nanoparticles are separately formed primarily through chemical reduction routes. Although control over uniform nanoparticle size and distribution is easier, it does not come without problems. Use of capping agents or surfactants during nanoparticle synthesis is necessary to control the nanoparticle size and prevent agglomeration. Unfortunately, these additives themselves may be active in controlling the outcome of CO₂R. Intentional post modifications on Au[46] and Ag[47] nanoparticles, for example, have shown this. Hence, direct conclusions on support effects need to be made carefully if different surfactants are present.

Thus far, few have compared in situ and ex situ formed hybrid supported electrocatalysts. Indium oxides have been supported by both approaches on rGO[48] and VC,[49] and Bi₂O₃ nanosheets on multi-channel carbon matrix (MCCM).[50] In all these cases, the in situ grown hybrids exhibited higher FEs towards HCOOH than those formed by physical adsorption of the nanoparticles on the supporting carbon (Table 4). Between the differently synthesized In₂O₃ nanobelt hybrids there appeared to be an electronic interaction between the remaining oxygen functionalities on the rGO and the In₂O₃ nanobelts when the metal was formed on the support in situ but such interaction was missing for the physically adsorbed hybrid.[48] For the supported In₃O₇ nanoparticles, the reasons behind the differences were attributed to improved conductivity and increased ECSA,[49] while Bi₂O₃@MCCM and Bi₂O₃NPs/MCCM showed only a negligible shift between the binding energies of Bi 4f but the work function of the in situ synthesized hybrid material was lowered in comparison to Bi₂O₃NPs/MCCM. This indicates faster electron transfer in the former electrocatalyst and therefore improved catalytic activity.[50]

2.2. Effects of Supporting on the Activity and Selectivity

2.2.1. N-Doped Carbon-Supported Catalysts

Carbons themselves, especially those with heteroatom doping, are also under scrutiny as possible metal-free electrocatalysts. Pristine carbon nanomaterials are inactive for CO₂R but doping with heteroatom or a co-doping strategy seems to improve their activity.[51] Four types of nitrogen groups, namely pyrrolic, pyridinic, graphitic and oxidized, are generated during N-doping, and the relative amount of these groups as well as the overall amount of nitrogen on the carbon varies depending on the level of doping, doping method and temperature.[32] The functionalities of the N-doped carbon materials vary depending on the relative amount of different nitrogen groups, and mainly pyridinic[32] and graphitic[53] nitrogen groups are speculated to act as active sites. Metal-free electrocatalysts are constrained to producing CO or formic acid only, and any mention of higher reduced products should be taken with the highest caution since the inherent problem of carbon materials is that they contain metal impurities[54,55] which originate from their synthesis.[56,57] Extensive purification procedures can be executed to ensure their removal.[55]

In the group of supported electrocatalysts, electronic interactions between the metal and the nitrogen functionalities have been speculated to induce the improved CO₂R activity and/or selectivity. N-doped carbon supported hybrid materials show promise in improving the activity for CO[56,58] and HCOOH[46,61] formation (Tables 3 and 4). Main reasons behind the improvement is the basicity of the nitrogen functional groups which results in electron abundance or deficiency on the metal surfaces resulting in stabilization of the intermediate species as well as improved adsorption of CO₂ on the nitrogen functional groups.

Steering the selectivity on N-doped carbon supported Cu nanomaterials is another thing entirely. The selectivity would appear to vary between ethylene and EtOH (Table 1) but often other products, such as H₂, are neglected in the discussions.
Ethylene formation has been reported to improve on N-doped porous carbon shell supported CuO nanoparticles (CuO/NCs).\(^6\) The improved selectivity towards ethylene over methane was attributed to the uniform dispersion of nanoparticles and improved adsorption of CO due to the pyridinic nitrogen on the catalyst surfaces, but it is noteworthy that FE for H\(_2\) is also improved on the N-doped hybrid catalyst (ca. 45%) in comparison to non-doped hybrid (ca. 35%) (−1.3 V\(_{\text{RHE}}\)). Cu particles supported on a butterfly wing derived porous carbon framework (CuPs/BCF)\(^6\) as well as 20 wt.% of dendritic-like CuO on N-doped carbons (CuO/NxC)\(^6\) also reported improved tendency to form ethylene.

Electrodeposited Cu nanoparticles on nitrogen containing carbon nanospikes (Cu/CNS), on the other hand, produced mainly EtOH.\(^6\) In a more recent study,\(^6\) improvement on carbon nanospikes (Cu/CNS), on the other hand, produced reported improved tendency to form ethylene.

### Table 1. Cu nanomaterials supported on N-doped carbons with main CO\(_2\)R products. Unless otherwise denoted, the electrolyte is 0.1 M KHCO\(_3\), potentials are reported against RHE, and the electrolysis has been conducted in an H-cell.

| Catalyst          | Total N [at.%] | Pyridinic N [%] | Pyrrolic N [%] | Graphitic N [%] | NP size [nm] | Cu loading [wt.%] | NP shape | Main product(s) | Ref. |
|-------------------|----------------|----------------|----------------|-----------------|--------------|-------------------|----------|-----------------|------|
| CuO/CS            | 1.68           | 20.7\(^a\)     | 65.0\(^b\)     | 14.2\(^c\)      | 150          | 3.24 at.%         | Spherical | CH\(_2\)CO, C\(_2\)H\(_4\) | \[62\] |
| CuO/NCs           | 2.34           | 35.6\(^a\)     | 51.5\(^a\)     | 12.9\(^a\)      |              | 2.16 at.%         | Cubic    | C\(_2\)H\(_4\) (25 %, −1.3 V\(_{\text{RHE}}\)) | \[64\] |
| Cu/PC             | –              | –              | –              | –               |              | 12.1              | Spherical | C\(_2\)H\(_4\) (31 %, −1.05 V\(_{\text{RHE}}\)) | \[66\] |
| Cu/NPC-700        | 8.5            | 30.5           | 28.8           | 29.1            | 5.3          | 19.7              | EthOH (50 %, −1.05 V\(_{\text{RHE}}\)) | \[67\] |
| Cu/NPC-800        | 8.4            | 40.8           | 15.9           | 32.7            | 5.2          | 19.8              | EthOH (65 %, −1.05 V\(_{\text{RHE}}\)) | \[68\] |
| Cu/NPC-900        | 7.1            | 27.9           | 9.7            | 40.3            | 5.4          | 20.2              | EthOH (44 %, −1.05 V\(_{\text{RHE}}\)) | \[69\] |
| CuPs/BCF          | –              | 49.7           | –              | 50.3            | 1−5 \(\mu\) m | –                 | Spherical | C\(_2\)H\(_4\) (64 %, −1.0 \(\mu\) V\(_{\text{RHE}}\)) | \[70\] |
| CuO/XC-72         | 0 wt.%         | –              | –              | –               | –            | 21.25             | Spherical | H\(_2\) (60 %, −1.25 V\(_{\text{RHE}}\)) | \[71\] |
| CuO/N,C-600 °C    | 12.1 wt.%      | 52.8           | –              | 18              | –            | 22.52             | Dendritic | C\(_2\)H\(_4\) (25 %, −1.15 V\(_{\text{RHE}}\)) | \[72\] |
| CuO/N,C-70 °C     | 9.72 wt.%      | 60.8           | –              | 10              | 50−100×7−15  | 22.13             | Spherical | C\(_2\)H\(_4\) (36 %, −1.25 V\(_{\text{RHE}}\)) | \[73\] |
| CuO/N,C-800 °C    | 6.5 wt.%       | 48.1           | –              | 23              | –            | 23.2              | Spherical | C\(_2\)H\(_4\) (30 %, −1.15 V\(_{\text{RHE}}\)) | \[74\] |
| Cu/CNS            | 5.1            | 26.07          | 24.59          | 36.88           | 5.4          | 20.2              | Spherical | C\(_2\)H\(_4\) (36 %, −1.2 \(\mu\) V\(_{\text{RHE}}\)) | \[75\] |

(a) Calculated based on the reported at.% of different nitrogen groups. (b) FE evaluated from figure. (c) Electrolyte was 0.2 M KHCO\(_3\). (d) Electrolyte was 0.1 M NaHCO\(_3\). (e) Cell configuration is elusive based on reported experimental information.

2.2.2. Covalent Modifications

In addition to doping, carbon can be modified by covalent attachment of functional groups. These can be used as mediators to not only improve the dispersibility of carbons but also as anchors for nanoparticle growth.\(^6\) Such defects may also result in interactions which may promote CO\(_2\)R. Such speculations was presented for Ag nanoparticles supported on cysteamine modified carbon and a covalency-aided reaction mechanism was proposed.\(^6\) XPS analysis showed an additional interaction, a Ag–S bond, in the Ag/C hybrid materials with the biggest changes taking place for the supported ~5 nm Ag nanoparticles. This catalyst exhibited approximately 300 mV lower onset potential for CO formation than Ag foil, and peak FE\(_{CO}\) was higher and reached at lower overpotential (84.4 % at ca. −0.7 V\(_{\text{RHE}}\)) than Ag foil (70.5 % at ca. −1.1 V\(_{\text{RHE}}\)). DFT calculations suggested that the size of the nanoparticles could not explain the changes but attributed it to the use of cysteamine anchoring agent: The formation of a Ag–S bond would result in stronger localization of electrons on the Ag surfaces thus stabilizing the important intermediates.

The effects of nitrogen are not always attributed to electronic effects but also to weaker interactions: Au nanoparticles physically adsorbed onto carbon nanotubes (CNTs) modified by first oxidizing (CNT-O) and then attaching an axial pyridine moiety on the tubes (CNT-O-Py) showed improved formation of CO over a hybrid supported on CNT-O (Table 3).\(^6\)
There was no evidence of a change in the valence state of Au, and DFT calculations suggested that a weak interaction, i.e., hydrogen bonding, between the pyridine and the COOH* intermediate would lower the activation energy barrier for the rate determining step.

2.2.3. Porous Carbon-Supported Catalysts

Carbons usually come with a complicated network of micro-, meso- and macropores. Introduction and reduction of CO₂ affects the pH of the electrolyte in the vicinity of the electrode material and under poor mass transport control, for example in a porous matrix, major fluctuations of the pH of the electrode microenvironment in comparison to the bulk electrolyte may take place affecting the activity and selectivity of CO₂R: Alkaline conditions are expected to suppress HER and enhance CO₂R for all the metal catalysts. Porosity may also affect the wettability of the catalyst material. Mere manipulation of the porosity affected CO₂R on metal free N-doped carbon electrodes. When applying very different materials with a range of porosities, more attention needs to be paid also to determining these properties.

The effect of porosity has been studied by depositing SnO₂ on mesopore rich activated carbon (SnO₂/AC) and micro- and macropore rich porous carbon (SnO₂/PC). The FE along with partial current density for HCOOH are both much higher on the porous carbon supported hybrid (Table 4). Different sized pores were concluded to affect both local pH and the mass transport of starting materials. Sn, Bi, Pb and Cd have been supported on mesoporous hollow kapok-tubes (MHKT), multi-walled carbon nanotubes (MWNTs) and rGO. Out of the supporting carbons, the MHKTs improved the j HCOOH in comparison to MWNTs and rGO for all the metal catalysts. Porosity may also affect the wettability of the catalyst material. Mere manipulation of the porosity affected CO₂R on metal free N-doped carbon electrodes. When applying very different materials with a range of porosities, more attention needs to be paid also to determining these properties.

2.2.4. Nanocarbons as Supports

Nanocarbons are excellent electric conductors and generated massive attention as future materials in several applications after their discovery. However, they also have in common high manufacturing costs which have slowed down their victory parade. It is only recently that the price for nanotubes has come down which now makes them candidates for electrocatalysis. Good electronic conductivity, chemical stability, ability to form porous 3D networks and possibilities for simple modifications are properties that are looked for in electrocatalysis. The improved electronic conductivity of the nanotubes in comparison to activated carbons has been attributed to lead to higher CO formation activities for Au nanoparticles supported on modified nanotubes and for a mixed configuration of Ag nanoparticles and MWNTs. Supported nanoparticles also appear to show higher activity than unsupported ones, but this comparison was made using geometric area normalized current densities.

For the metals which mainly produce either CO or HCOOH, supporting improves the selectivity to CO₂R but the main product usually remains unchanged and the activity increases. However, SnO₂ nanoparticles supported on differently modified supports on various carbons with product selectivity.

| Catalyst | NP size [nm] | ECSA [m² g⁻¹] | E [V] | H₂ | CO | FE [%] | Electrolyte (Cell) | Ref. |
|----------|--------------|----------------|-------|-----|----|-------|-------------------|------|
| CSNP/ICP | 30–40        | 1.0 (vs. RHE)  | 19.8  | 7.5 | 2.4 | 48.7  | 0.1 M KHCO₃ (H-cell) | [73] |
| CSNP/Cu  | –            | 56.6           | 0.9   | 0.3 | 28.5|       |                   |      |
| Cu-foil  | –            | 46.7           | 0.5   | 18.7| 13.6|       |                   |      |
| Cu/SWNT  | ~ 19         | 2.8 ± 0.2      | –1.8 (vs. Ag/AgCl) | Ca. 20 | Ca. 5 | Ca. 15 | 0.1 M KHCO₃ (RDE) | [44] |
| Cu/rGO   | ~ 36         | 3.4 ± 0.1      | –      | Ca. 35 | Ca. 5 | Ca. 15 | 0.1 M KHCO₃ (RDE) | [44] |
| Cu/OLC   | ~ 13         | Negligible     | –      | Ca. 20 | Ca. 5 | Ca. 10 | 0.1 M KHCO₃ (RDE) | [44] |
| Cu/VC    | ~ 33         | 1.8 ± 0.1      | –      | Ca. 20 | Ca. 5 | Ca. 10 | 0.1 M KHCO₃ (RDE) | [44] |
| Cu/WC    | 70–130       | 0.7 ± 0.07     | –      | Ca. 20 | Ca. 5 | Ca. 10 | 0.1 M KHCO₃ (RDE) | [44] |

[a] ECSA determined by Pb underpotential deposition. [b] The values were evaluated from figures.

For Cu, ethylene formation is promoted in alkaline conditions. Cu supported on onion-like carbon (OLC) expressed ca. 60% FE towards ethylene while with same Cu loading (20 wt.%) nanoparticles supported on VC, SWNTs and rGO expressed ca. 40%, 35% and 30% FE to CH₄, respectively (Table 2). The improved ethylene formation on OLC was attributed to (1) OLC’s ability to produce large amount of *CO which could then spill to Cu, and (2) the unique porous structure of this nanocarbon which could result in an increase of local pH, known to be beneficial for ethylene formation. Improved selectivity to ethylene has also been noticed for electrospayed CuO on carbon paper. The same modification on Cu foil resulted in H₂ evolution rather than CO₂ reduction indicating a role for the support (Table 2). However, it has also been shown that Cu₂O nanocubes supported on VC shift their product selectivity more towards the C₁ products while higher ethylene formation was observed in unsupported cubes. Overall, however, the selectivity for CO₂R over HER improved after supporting in comparison to unsupported catalyst.

Table 2. Cu nanomaterials supported on various carbons with product selectivity.

ChemElectroChem 2021, 8, 2397–2406, www.chemelectrochem.org 2401 © 2021 The Authors. ChemElectroChem published by Wiley-VCH GmbH
MWNTs have shown high FEs towards CO (30–45%) in addition to formate.[80] In most reported studies within the formic acid producing metals, FEs for CO are usually < 10% and around 20% at best. The covalent modifications on the MWNTs were –OH, –COOH and –NH2.[82] The –NH2 modified hybrid exhibited highest efficiency for CO formation which was explained to occur due to an additional Sn–N interaction. However, FE CO were high for all the materials and solely the unsupported nanoparticles produced only trace amounts of CO. Since the other modified supports did not include nitrogen, selectivity was ascribed to the adsorption energies of the SnO nanoparticles on the different supports.

Graphene, on the other hand, offers a 2D platform for nanometal structures but is rarely applied due to the difficulties in producing high quality graphene. 15 nm Sn nanoparticles dispersed on commercial graphene showed FE HCOOH of approximately 61% at ca. 10 mA/cm² while unsupported 15 nm Sn nanoparticles exhibited FE HCOOH around 59% at ca. 8 mA/cm².[81] The supported nanoparticles show slightly higher ECSA and CO2 adsorption ability in comparison to the unsupported nanoparticles which could be the main reasons behind the small increase in FE for HCOOH and total current density observed. Loading same amount of similar sized SnO2 or Au nanoparticles[82] shows the superiority of graphene as supporting carbon over activated carbon and nanotubes (Tables 3 and 4).

Since the production of pure graphene is expensive, various nanoplatelets produced from graphite have been accepted as a compromise between the properties, manufacturing costs and easy handling of graphene. The most famous compromise is rGO synthesized by oxidation and subsequent reduction of graphite.[84] Between Cu supported on rGO, SWNT and VC, the selectivity varied very little although the rGO supported hybrid produced more H2 than the other catalysts which was attributed to the agglomerated nanoparticles on this hybrid.[44] In terms of current density, rGO supported material exhibited the highest current density in the beginning of the reduction reaction but the current decrease over time was also the greatest.[84] Cu/CuO nanomaterials electrodeposited on various substrates either in the presence or absence of GO in the electrodeposition solution were reported to improve the formation of ethylene over other possible products.[84] The origin of the change in selectivity was attributed more to the material synthesis procedure and its influence on the porosity of the hybrid catalyst material. Additionally, changes in morphology of the Cu/CuO deposits may also affect CO2R reaction in this work. Comparison of Cu nanoparticles supported on carbon black (CB), MWNTs and rGO in a polymer electrolyte membrane type cell resulted in improved selectivity to CO for the first two supports while Cu nanoparticles on rGO was reported to mainly produce HCOOH.[83] For Sn, Bi, Pb and Cd supported on MHKTs, MWNTs and rGO, the nanomaterials supported on rGO exhibit lower FEs and currents in comparison to the nanotubes independent of the metal under study.[71] rGO has also been shown to be poorer support than nitrogen doped rGO for SnO2 particles,[86] but supporting on rGO improved the formation of HCOOH on Bi in comparison to unsupported Bi.[87] With rGO one must also keep in mind that the origin of the graphite and the chosen oxidation and reduction methods all greatly affect the final rGO properties such as platelet size, remaining oxygen functionalities, trace amounts of impurities and porosity which may in turn affect electrocatalysis between different works.

### 2.3. Possible Support Effects and Mechanisms

Anchoring of the nanoparticle is the first important interaction between the support and the metal. Defects or dopants on the carbon serve as anchoring sites and enhance formation of well-dispersed small nanoparticles.[4] Similar results have been reported for carbon supported CO2R metal catalysts.[86,88] For an

| Table 3. Metal and metal oxide nanoparticles that mainly produce CO supported on carbons. Unless otherwise denoted, the potentials are reported against RHE, the current densities are reported against geometric area and the measurements have been conducted in an H-cell. |
| Support | Catalyst | NP size (nm) | ECSA (cm²/cm²) | E (V) | FE CO (%) | j CO (mA/cm²) | Electrolyte | Ref. |
|---|---|---|---|---|---|---|---|---|
| N-doped carbons | Au/C3N4 | – | 2636 (Cu UPD) | –0.45 | 90 | 2.5 mA/cm² | 0.5 M KHCO3 | [58] |
| Au/C | – | 2717 (Cu UPD) | –0.65 | Ca. 75 | – | – | – | – |
| Au/C3N4 | – | – | –0.85 | Ca. 90 | – | – | – | – |
| Au/C | – | – | –0.65 | Ca. 60 | – | – | – | – |
| Au-2@CN | 1.9 ± 0.3 | 0.69 (Au UPD) | –0.65 | 89 | 721 A/gAu | 0.5 M NaHCO3 | [59] |
| Au-4@CN | 4.7 ± 0.5 | – | – | 33 | 71.8 A/gAu | – | – | – |
| Au-6/CN | 6.7 ± 1.3 | 0.106 (Au UPD) | Ca. 40 | – | – | – | – | – |
| Au-6/VC | 6.8 ± 1.4 | 0.077 (Au UPD) | Ca. 30 | – | – | – | – | – |
| Au/Pt-CNT-O | 4.5 | – | –0.58 | 93 | 69 A/gAu | 0.1 M KHCO3 | [58] |
| Au/CNT-O | 4.0 | – | –0.78 | 89 | – | – | – | – |
| Au/CNTs | –3 | – | –0.55 | 70 | 7 mA/cm² | 0.5 M NaHCO3 | [78] |
| AuNPs | – | – | –0.58 | 70 | 7 mA/cm² | 0.5 M NaHCO3 | [78] |
| Nanotubes | | | | | | | | |
| Graphenes | | | | | | | | |
| Chevron-GNR/Au | 8 | 2.87 cm²/mg (Pb UPD) | –0.47 | 57.3 | 7.87 mA/cm² | 0.5 M KHCO3 | [83] |
| Cove-GNR/Au | 4.60 cm²/mg (Pb UPD) | –0.55 | 68.1 | 8.00 mA/cm² | 0.5 M NaHCO3 | [83] |
| KB/Au | 1.70 cm²/mg (Pb UPD) | –0.55 | 42.9 | 3.76 mA/cm² | 0.5 M NaHCO3 | [83] |

[a] The method used for ECSA determination is written inside the brackets after the value. Cu UPD = Cu underpotential deposition. Au UPD = reduction peak of Au. Pb UPD = Pb underpotential deposition. [b] The values were evaluated from figures. [c] The values were calculated based on reported information. [d] Activity at –0.87 V.
N-doped hybrid, the anchoring sites were speculated to be the graphitic nitrogen moieties by comparison of XPS spectra for support and hybrid catalysts.\cite{66}

One of the main support effects mentioned in literature is electronic interaction between the support and the metal which can be described as a metal-semiconductor interphase of the two.\cite{69} The size of the nanoparticles will affect the electronic interactions between the metal and the support\cite{63,69} which emphasizes the need to control nanoparticle size when aiming to reveal support effects. Graphene has a better ability to donate electrons than activated carbons and the improvements have been attributed to electronic interactions between the graphene and the metal.\cite{82,83} Similar electronic effects have been speculated for supported N-doped carbon materials, and the role of N-doping can be verified by quenching.\cite{53} We should also bear in mind, that where the dopant can interact with the metal, it also changes the polarization of the adjacent carbons and their reactivity and any curling or bending of carbon surfaces may also play a role.\cite{86} Out of the techniques that can reveal metal-support interactions via observing changes in binding energies, mainly XPS\cite{48,58,59,61,66,80,82,87,88} and XANES\cite{48,58,66} have been applied, but Raman could also be a powerful tool for studying support effects.\cite{90} and high-resolution transmission electron microscopy (HR-TEM) is a regularly used technique mainly to study the size and distribution of the nanoparticles but also the lattice fringes.

For example, Co$_3$O$_4$ nanocubes supported on reduced graphene and N-doped graphene, HR-TEM revealed a change in exposed surfaces depending on the supporting carbon,\cite{31} whereas Au supported on carbon and nitrided carbon,\cite{80} Bi on rGO\cite{87} or MWNTs\cite{98} and SnO$_2$ supported on differently modified MWNTs\cite{98} exhibited same crystallographic planes.

Spillover is a known effect in other fields of electrocatalysis\cite{4} and it has been speculated also for carbon supported Cu catalysts,\cite{44,66} but any experimental results have not been presented. For Cu bimetallic catalysts, \emph{in situ} Raman spectroelectrochemistry has been applied to reveal a spillover effect.\cite{91,92} Spillover of especially the CO$^*$ intermediate has been shown important for selectivity on Cu. As the N-doped carbons are known to produce CO while non-doped carbons will mainly be active towards hydrogen formation, spillover could explain at least partly the superior activity and selectivity of N-doped hybrid catalysts.

Since pH has been shown to affect CO$_2$R, carbons are known to be porous, and it is known that in confined spaces pH can change drastically, we could consider pH an indirect support effect. However, there are no experimental results that can

| Support | Catalyst | NP size [nm] | ECSA [mF cm$^{-2}$] | E [V] | $\text{FE}_{\text{HCOOH}}$ [%] | $\text{J}_{\text{HCOOH}}$ [mA/cm$^2$] | Electolyte | Ref. |
|---------|----------|--------------|---------------------|------|-------------------------------|------------------|----------|------|
| N-doped carbons | SnO$_2$/0.14@N-rGO | 3.9 ± 0.3 | 225.5 cm$^2$ | −0.8 | 78 | 16.6 mA/cm$^2$ | 0.5 M NaHCO$_3$ | 98 |
| | SnO$_2$/0.14@rGO | 7 | 167.3 cm$^2$ | 26 | | | | |
| | Sn-CF1000 | 0.5–3 μm | 65 | −0.8 | 4.7 mA/cm$^2$ | 0.1 M KHC0$_3$ | 98 |
| | Bi/NPC | 20 | −1.5 (vs. SCE) | 92.0 | 14.4 mA/cm$^2$ | 0.1 M KHC0$_3$ | 98 |
| | Bi-NP | − | −1.6 (vs. SCE) | 85.9 | 5.6 mA/cm$^2$ | | |
| Nanotubes | SnO$_2$@MWCNT | − | 6.4 | −0.82$^a$ | 55 | 0.5 M KHC0$_3$ | 98 |
| | SnO$_2$@MWCNT-COOH | − | 12.8 | 7.2 mA/cm$^2$ | | | | |
| | SnO$_2$@MWCNT-NH$_2$ | − | 10.4 | 6.8 mA/cm$^2$ | | | | |
| | SnO$_2$@MWCNT-OH | − | 9.7 | 61 | | | | |
| | SnO$_2$ | − | − | 52 | | | | |
| | Bi NPs@MWCNTs | −4.4 | − | −0.83$^a$ | 95.2 | 10.2 mA/cm$^2$ | 0.5 M KHC0$_3$ | 98 |
| Graphenes | Nano-SnO$_2$/graphene | − | 5 | −1.8 (vs. SCE) | 93.6 | 248.9 A/g$^a$ | 0.1 M NaHCO$_3$ | 92 |
| | Nano-SnO$_2$/CB | − | − | 86.2 | 108.6 A/g$^a$ | | | |
| | Bi/rGO | − | 2 | 55.8 | 98 | 0.1 M KHC0$_3$ | 97 |
| | Bi-PVP | − | 30.0 | 92 | | | | |
| | In$_2$O$_3$/rGO | − | 25.5 m$^2$/g | 84.6 | 22.17 mA/cm$^2$ | 0.1 M KHC0$_3$ | 98 |
| | In$_2$O$_3$/rGO | − | 41.4 m$^2$/g | 61.9 | | | | |
| | In$_2$O$_3$/C | − | 34.6 m$^2$/g | 48.2 | 6.95 mA/cm$^2$ | | | |
| Porous carbons | Sn@MHKts | −25 | 22.6 | −1.0 | 95 | 30.8 mA/cm$^2$ | 0.5 M KHC0$_3$ | 71 |
| | Sn@MWNts | − | 16.1 | 86 | Ca. 18 A/cm$^2$ | 0.1 M NaHCO$_3$ | 98 |
| | Sn@rGO | − | 75 | | 75 | Ca. 13 A/cm$^2$ | 0.1 M NaHCO$_3$ | 98 |
| | Sn$_2$O$_3$/PC | 4.8 ± 1.0 | 0.004 | −0.86 | 92 | 29 mA/cm$^2$ | 0.5 M KHC0$_3$ | 70 |
| | Sn$_2$O$_3$/AC | 4.4 ± 0.8 | 0.003 | 56 | 4 mA/cm$^2$ | | | |
| | Bi$_2$O$_3$ NPs@MCCM | − | −1.256 | 93.8 | − | 0.1 M KHC0$_3$ | 90 |
| | Bi$_2$O$_3$ NPs@MCCM | − | − | Ca. 80$^a$ | | | | |
| | Bi$_2$O$_3$ NPs@SCM | − | − | Ca. 90$^a$ | | | | |
| | In$_2$O$_3$/rC | 6–18 | 9.4 | −0.9 | 87.6 | 12.9 mA/cm$^2$ | 0.5 M KHC0$_3$ | 99 |
| | In$_2$O$_3$/C | 8.8 | 78 | 9.9 mA/cm$^2$ | | | | |
| | In$_2$O$_3$ | 6–22 | 1.2 | 79 | 2.7 mA/cm$^2$ | | | |

[a] The values were calculated based on reported information. [b] The values were evaluated from figures.
corroborate changes in pH with changes in CO}_2R selectivity and/or activity but most discussions on pH effects are speculations based on previous knowledge. This is not a surprise since pH inside the material cannot be simply measured. Recent in situ spectroelectrochemical results\(^{[93]}\) give hope that we could monitor pH in situ and obtain experimental insights into pH effects of carbon supported CO}_2R electrocatalysts.

Possible routes to the 2 electron reduction products CO and formate are fairly simple at least in comparison to the possible routes that end in the formation of the 12 electron products C}_2H}_4 and EtOH.\(^{[17]}\) These reduction pathways have been probed through studying the reduction of possible intermediates as well as by probing the surface adsorbed species in situ during CO}_2R. The studies on supported electrocatalysts reviewed in this work mainly apply theoretical calculations to conclude on possible changes in the binding of intermediates. Although, theoretical calculations can provide useful insights, combining them with experimental results can paint a more realistic picture. CO reduction has been applied on one occasion, and it was found that the pyridinic N would be able to produce a higher CO coverage favorable for the formation of EtOH over C}_2H}_4.\(^{[90]}\) More such experimental work aiming to elucidate mechanisms on carbon supported electrocatalysts is welcomed.

### 2.4. Are We Improving the Durability?

One of the major drawbacks of using transition and post transition metals for CO}_2R is their poor durability under continuous operation. Improving the durability is named as one important goal in supporting the nanometals. However, there does not seem to be any common guidelines for such measurements and as a result the information on the durability of supported nanoparticles is poor. For example, the time applied for the long-term studies varies between 1 h and 1 day (24 h), in most studies only one material is tested for a longer period, and often post-mortem analysis of the catalyst material has not been conducted to give information on the possible degradation mechanisms. There also appears to be some discrepancy whether supporting on carbon improves the durability or not: One study claims that the ability to retain the original morphology on a carbon support would be improved over supporting on nanostructured copper foil,\(^{[75]}\) while another has shown that Cu cubes retain their shape and valence state better when supported on Cu foil rather than on carbon.\(^{[94]}\) A recent work shows that CuO cubes supported on carbon gradually disintegrate and the product selectivity changes from C}_1 products to C}_2 products while unsupported nanocubes remained stable over 40 h of electrolysis.\(^{[76]}\) It has also been reported that N-doping of the graphene oxide support prevents the Cu nanocubes from disintegrating.\(^{[95]}\) Poor state of durability testing of Cu materials within the field of CO}_2R has been recently critically reviewed.\(^{[96]}\) Although the review in question only focuses on Cu, same problems apply to all the other metals.

### 3. Conclusions and Outlook

Although studying the effects of supporting nanoparticles on carbons is an age old field,\(^{[4]}\) research into the effects supporting may have on CO}_2R of transition and post transition metal nanoparticles is still in infancy. The use of a support material seems to improve the selectivity towards CO}_2R over HER for CO and HCOOH forming metals and the N-doped carbon supports would appear to bring about the highest improvements. Our understanding on steering the selectivity on Cu is hindered by lack of variable controlled studies as well as lacking physico-chemical characterizations of one or more of the reference materials. Current results suggest that nitrogen doping and changes of pH in the porous support material would steer the reduction products towards either ethylene or EtOH but due to the existence of several variables and missing information, definitive conclusions cannot be drawn. Applying a support also seems to improve the activity at first sight but upon a closer look there are major issues in the determination of ECSA. This is yet crucial for the comparison of hybrid electrocatalyst performances. Finally, although improving durability is always named as one important parameter to improve by supporting, the methodology is severely lacking and conclusions on improved durability cannot be drawn if only the best performing catalyst is tested. Based on our analysis of the literature, we suggest focusing on following issues in the future so that consistent information about carbon support effects in CO}_2R could be obtained:

1. **Focus on the Use of Reference Materials:** To make conclusions on support effects, the reference materials need special attention. Naturally, comparison to unsupported nanocatalysts as well as comparison between in situ and ex situ synthesized hybrids is welcomed but comparison also to polycrystalline metals might be a good idea if applicable. When unsupported or supported nanocatalysts on other supports are compared, better control over the nanoparticle size, morphologies and loading will help our understanding of support effects. Naturally, this is not a simple task but when a risk exists for other effects than support this should be acknowledged. Finally, support effects cannot be concluded if reference material properties are insufficiently reported. The aim should be to report the FEs and partial current densities for all the catalysts – not only for the best performing ones – and for all the products.

2. **Focus on the Physicochemical Characterizations:** Carbon is not a simple material; single sample can have varying porosities and highly ordered and disordered regions. These may play an important role in the product selectivity due to changes in pH in confined spaces. Additionally, the adsorption and desorption of CO and the intermediates on the support may play a crucial role in activity if more starting material is available for the reduction. The situation becomes more difficult when heteroatom doping of carbon is included and the changes in selectivity or activity are attempted to ascribe for the different nitrogen groups. Applying the physico-chemical analysis on all the materials should be applied to gain insights on possible reasons...
behind the change in activity and/or selectivity. We suggest analyzing BET surface areas, porosities, wettability, and CO₂ and/or CO adsorption/desorption behavior. For N-doped materials, total nitrogen content and share of different moieties should be reported preferably at.% for better comparison between different catalysts.

(3) Common Guidelines for Durability Testing: Durability needs to be reported not only for the best performing hybrid catalyst but also for the reference materials. This includes appropriate pre- and postmortem analyses since the product distribution may not change but the structure may suffer significant changes. Secondly, we should have common guidelines for these tests in order to properly compare between different materials as was suggested in Ref. [96]. We suggest 100 h of chronopotentiometry in the potential where the highest FE for CO₂R products was detected.

(4) Focus on ECSA Determination: With hybrid electrocatalysts, proper determination of ECSA becomes even more vital. ECSA is often determined by double layer capacitance (CSDL) which, in the case of porous carbon supported materials, mainly originates from the support and can be used as an indication of surface area but probably not as a direct indication of the active sites. Underpotential deposition (UPD) or adsorption/desorption of small molecules should be favored as they reveal more information about the amount of metal in the hybrid. Applying more than one method (for example CSDL and UPD) should be considered.

(5) Elaboration of Mechanisms: Spectroelectrochemistry has been applied to elaborate CO₂R mechanisms on polycrystalline materials. They can be a powerful tool for studying hybrid catalysts, as well, but so far supported hybrid materials have not been studied in situ to the best of our knowledge. For example, these techniques could open possibilities to monitor the microenvironment inside a porous carbon or reveal possible spillover effects. Another good tool for mechanistic studies is the reduction of important intermediates, such as CO. Information can also be obtained by quenching desired functionalities to reveal active sites or by leaching the nanoparticles.[32]

Acknowledgements

We thank Jane and Aatos Erkko foundation (the USVA project) and Academy of Finland (Aalto University Profi 5) for financial support. We thank Md Noor Hossain for discussions.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: electrochemical CO₂ reduction · supported nanoparticles · transition metals · post-transition metals · carbon
