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Insights into the mechanism of electrocatalytic CO2 reduction and concomitant catalyst degradation pathways

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High-pressure CO electroreduction at silver produces ethanol and propanol

Reducing CO_2 to long-chain carbon products is attractive considering such products are typically more valuable than shorter ones. However, the best electrocatalyst for making such products from CO_2, copper, lacks selectivity. By studying alternate C2+ producing catalysts we can increase our mechanistic understanding, which is beneficial for improving catalyst performance. Therefore, we investigate CO reduction on silver, as density functional theory (DFT) results predict it to be good at forming ethanol. To address the current disagreement between DFT and experimental results (ethanol vs. no ethanol), we investigated CO reduction at higher surface coverage (by increasing pressure) to ascertain if desorption effects can explain the discrepancy. In terms of product trends, our results agree with the DFT-proposed acetaldehyde-like intermediate, yielding ethanol and propanol as C2+ products – making the CO_2 electrochemistry of silver very similar to copper at sufficiently high coverage.

2.1. Introduction

Few electrocatalytic systems are known to be capable of generating carbon-coupled products from the CO_2 reduction reaction (CO2RR) and/or the CO reduction reaction (CORR).[1–4] Out of these, copper is by far the most capable electrocatalyst for making C2+ molecules, yielding ethylene,[5, 6] ethanol[7] and n-propanol[8] as its primary multi-carbon products.[3, 9] Other catalysts (in aqueous media) include molybdenum disulfides[10], enzymatic nitrogenases with a vanadium/molybdenum active center[11] (and its organo-metallic homologues[12]), bimetallic palladium/gold nanparticles[13], heteroatom (N, B) doped nanoparticles[14–16], transition-metal (Ni, Fe) doped carbon xerogels[17], certain surfaces when coated with functionalized films,[18, 19] nickel/gallium alloys,[20] nickel phosphides,[21] and metallic nickel and silver.[22–24] However, these non-copper catalysts exhibit comparatively low (on the order of a few %) faradaic efficiencies (FEs) for C2+ products.

As for the currently existing theories on the C-C coupling mechanism, an in-depth review concerning non-copper systems has recently been published by Zhou and Yeo[25], whilst comprehensive reviews regarding the mechanism on copper can be found in e.g. [26–29], with a review by Fan *et al.*[30] comparing mechanisms on a per-product basis. For comprehensibility, summaries of the main theories for making C2 and C3 products on metallic Cu in aqueous media are also provided in the supporting information in schemes A-C2 to I-C2 (with, where applicable, reaction paths to C3 products in accompanying schemes A-C3 to J-C3).

To increase molecular-level understanding of the formation mechanism for C2+ products, Hanselman *et al.* carried out Density Functional Theory (DFT) calculations on CO reduction to C2 products for various transition metal surfaces (including silver), suggesting two reaction pathways: one to ethylene and one to ethanol, bifurcating from a surface intermediate that is one hydrogen short of acetaldehyde.[31] This mechanism, where acetaldehyde is the precursor to ethanol, agrees with experiments on copper single-crystal electrodes.[32] Their DFT calculations indicate that, among nine transition-metal surfaces, only copper has a reasonably low onset potential for ethylene formation whilst ethanol has a slightly later onset. The former agrees well with literature as copper is reported to yield reasonable FE towards C_2H_4 at overpotentials of a few hundred mV[6, 33, 34], although experimentally no large differences are observed between the formation onsets of ethylene and ethanol.[5, 35, 36] Importantly, their calculations also indicate silver should have a lower onset potential for ethanol formation than copper whilst being incapable of producing ethylene. In chemical terms, silver is seemingly too noble to break the last C-O bond.

This prediction is, however, in apparent disagreement with experimental studies as the maximum reported FE of CO_2 to ethanol is ca. 0.1% on silver vs. 40% on copper.[7, 23, 35] Hanselman *et al.* hypothesized this disagreement may be a consequence of CO desorbing rather than reacting further on silver due to its unfavorable adsorption strength.[31] Hence, herein we probe the validity of the theory that silver can produce ethanol if the CO coverage on the surface is sufficiently high. To this end, we study CO reduction at elevated pressure as a means of increasing

surface coverage which enhances the likelihood of (intermolecular) reactions involving CO_{ads}. In line with DFT calculations we observe ethanol (whose formation is positively influenced by increasing the pressure) and no ethylene during CORR. Furthermore, ethylene glycol and n-propanol are also observed and found to exhibit an similar pressure dependency as ethanol, providing us with additional insight into carbon-carbon bond formation and the mechanistic aspects of C3 production.

2.2. Experimental

Experiments were carried out in three-compartment electrochemical cell inside an autoclave that could be pressurized up to $60 \ barg$, with the gaseous products leaving the cell analyzed by gas chromatography, and liquid products analyzed by NMR. The working electrode was a silver gas diffusion electrode (GDE) with a $1 \ cm^2$ exposed geometrical area. Alkaline conditions were employed as these promote C2 formation from CO on copper.[37–39] A Ag|AgCl|KCl (3M) reference was used as a reference electrode and potentials are reported on this scale unless denoted otherwise. Reported potentials are not IR-corrected because of the inherent inhomogeneity of the interfacial potential on a GDE, rendering the nominal reported potentials unrepresentative of the 'real' potential. As a figure of merit, the nominal IR-corrected potential of the most negative potential employed in this work ($-4.5 \ V$) was calculated to be ca. $-1 \ V$ vs. RHE (see supporting information; SI). A comprehensive description of the experimental setup can be found in the SI, including control experiments conducted in the absence of CO and in the absence of applied potential in the presence of CO to prove that the products we report are indeed the result of electrochemical CO reduction.

2.3. Results and discussion

Absolute formation rates of CORR-related products obtained for CO reduction in $0.5 \ M$ KOH on a silver GDE at various potentials are depicted in Figures 2.1a, b and c, for reactant (carbon monoxide) pressures ranging between 10 and $60 \ barg$. Investigated reaction times were between 2.6 and $73 \ hours$, with more positive potentials necessitating longer times to guarantee a minimum of charge had passed. The CORR products depicted in Figure 2.1 are minority species, with hydrogen and formate (Figures A.3a and b, respectively) being the main products. As we study the carbon-carbon bond formation mechanism on silver, we will disregard H_2 and HCOO$^-$ as neither is the result of CO reduction or contains a C-C bond. However, to briefly address the possible origin of formate (being in equal oxidation state as CO), we refer the reader to literature wherein formate is proposed to form through a solution phase reaction between CO and hydroxide, which may occur in this work given the high electrolyte alkalinity and elevated carbon monoxide pressures.[40–42]
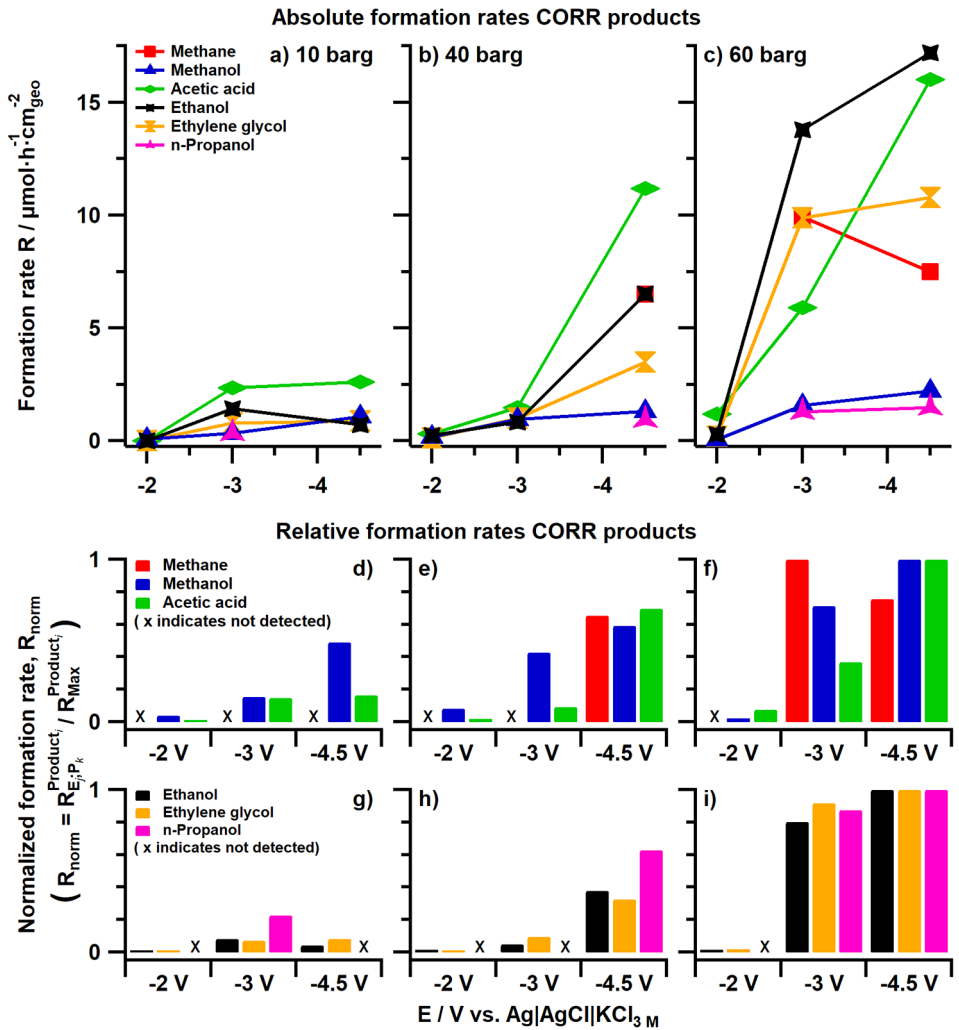
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Figure 2.1: Color-coded formation rates for CORR products (methane: red, methanol: blue, acetic acid: green, ethanol: black, ethylene glycol: orange, n-propanol: pink) plotted as a function of applied potential (non-IR corrected) for three different reactant pressures; $10\ barg$ (a,d & g), $40\ barg$ (b, e & h) and $60\ barg$ (c, f & i) expressed in absolute rates (a, b & c) and relative rates (d, g & e, h & f, i). All axes in a given row are of equal magnitude. Not detected products are marked by an 'x' in the subfigures depicting relative rates.

Specifically, the CORR-related products (Figure 2.1) comprise a product with carboxylic acid functionality (acetic acid, green), the simplest hydrocarbon (methane, red) and four compounds with alcohol functionality (methanol, ethylene glycol, ethanol and n-propanol; blue, orange, black and purple, respectively). Notably, ethylene, which is very commonly observed on copper electrodes[3], was not observed. The predominance of oxygenates (excluding methane) agrees with the DFT predictions of Hanselman *et al.*, who computed silver to be a poor catalyst for breaking C-O bonds.[31] Unconventionally, formation rates rather than partial current densities are depicted in Figure 2.1. This approach allows for directly comparing molar product rations, which is valuable from a mechanistic point of view considering certain reaction pathways yielding C2 species (e.g., Cannizzaro disproportionation[43]) would result in equimolar concentrations of particular types of products. Partial current densities are provided in Figures A.4 (for CORR products) and A.5 (for hydrogen), whilst the overall current response of the system is depicted in Figure A.6. Faradaic efficiencies are given in Table A.1.

Pressure and potential dependencies for these CORR products can be determined from Figures 2.1a, b and c. Overall, formation rates increase when either the overpotential or CO pressure is increased, although formation rates at $10 \ barg/-3 \ V$ and methane formation at $60 \ barg/-3 \ V$ are exceptions. However, because the products' formation rates overlap to a considerable degree, these figures can only provide us with general trends. To better distinguish individual trends, each product has been normalized to its highest observed formation rate and is depicted on a per-pressure-basis in Figures 2.1d, e and f (for methane, methanol and acetic acid) and Figures 2.1g, h and i (for ethanol, ethylene glycol and n-propanol) for $10, 40$ and $60 \ barg$ from left to right, respectively. The first group (methane, methanol and acetic acid) comprises products weakly correlating to pressure, potential and one another whereas the second group (ethanol, ethylene glycol and n-propanol) is comprised of products that show fairly straightforward trends that are shared between them.

The behavior of these latter three higher alcohols yields important insights into the C-C formation mechanism since they all exhibit very similar trends: at the lowest applied pressure and potential ($10 \ barg, -2 \ V$) they are just barely detectable. Then, as the potential is decreased ($-3 \ V$) their formation rates go through a maximum and subsequently slightly decrease again for higher overpotentials ($-4.5 \ V$). Increasing the CO pressure from 10 to $40 \ barg$ results in this maximum disappearing, with observed relative formation rates increasing rapidly as higher overpotentials are applied. However, this potential dependency becomes weaker as the pressure is increased further, with more moderate increases of ca. $5 - 25\%$ observed between successively more negative potentials at CO pressures of $60 \ barg$.

Exhibiting such strong similarities in their potential and pressure dependency indicates commonalities in their formation mechanism, separate from the pathway via which methanol and acetic acid form (to be discussed later). The absence of ethylene (which cannot be explained by insufficient hydrogen coverage, considering the still high rate of H_2 formation) in concert with the comparable behavior of ethanol and n-propanol is especially interesting. Namely, this observation makes

it unlikely that the coupling of CO and ethylene ("hydroformylation") is responsible for the formation of C3 products on silver, as hypothesized to occur on copper by Ren *et al.*[44] Instead, acetaldehyde, being both reactive and difficult to detect via standard NMR techniques (especially in alkaline media)[45], is known to only reduce to ethanol and not ethylene (on copper).[46, 47] Its high reactivity would facilitate further reduction rather than desorption. This possibility would agree with recent work by Xu *et al.* who showed that propanol is formed on copper via the coupling between CO and a surface-bound methylcarbonyl, an intermediate which is one hydrogen short of acetaldehyde.[46] This latter observation agrees well with DFT calculations conducted by Hanselman *et al.*, who propose ethanol formation takes place via a surface-bound acetaldehyde species.[31]

The fact that both ethylene glycol and ethanol are observed and exhibit similar behavior proves that silver is capable of breaking one of the C-O bonds in a molecule comprised of two carbon atoms containing two C-O bonds. However, the absence of ethylene shows that silver is indeed a poor catalyst for breaking the final C-O bond, as predicted by DFT calculations. From these observations, our results suggest that an oxygenated intermediate, probably surface-bound methylcarbonyl (as proposed by Hanselman *et al.* and Xu *et al.*)[31, 46] is involved in the formation of ethanol, as well as in the coupling with adsorbed CO to lead to the formation of n-propanol (through propanal).

Additional insights regarding C-C coupling on silver can be derived from the behavior of the other 'group' of products (methane, methanol and acetic acid) whose trends with regards to potential, pressure and one another are more inconsistent. Of these, the methane 'trends' disagree with all other observed CORR products. The most notable observation that can reasonably be made is that it is more prevalent at increased CO pressures and more cathodic potentials. More important are methanol and acetic acid, as they exhibit some similarities although their correlation is much weaker than the previously discussed alcohols. Comparing these products, we find that methanol generally exhibits higher relative formation rates than acetic acid at lower overpotentials, and for all investigated potentials in the case of $10 \ barg$ of CO pressure. However, when the pressure is increased (from 10 to 40 or $60 \ barg$), relative acetic acid formation rates start to become very similar to those of methanol formation for the most cathodic potentials investigated ($-4.5 \ V$). This results from the fact that methanol formation rates are relatively invariant with potential and pressure, whereas acetic acid is strongly influenced by both of these parameters. (This observation that acetic acid formation remains strongly potential dependent also at increased pressures is what makes its behavior different from the previously discussed 'alcohol group' as they exhibit much weaker relative increases in formation rate with potential at $60 \ barg$ of CO).

The strong pressure dependency of acetic acid suggest that CO is involved in its formation. Furthermore, the fact that this dependency persists even at elevated reactant pressures, signifies that the C-C coupling step for its formation has a significant barrier. Additionally, the (weak) correlation observed between methanol and acetic acid can be interpreted as them sharing a common intermediate. Hence we speculate there may exist a pathway where CO couples with a methanol-like moiety
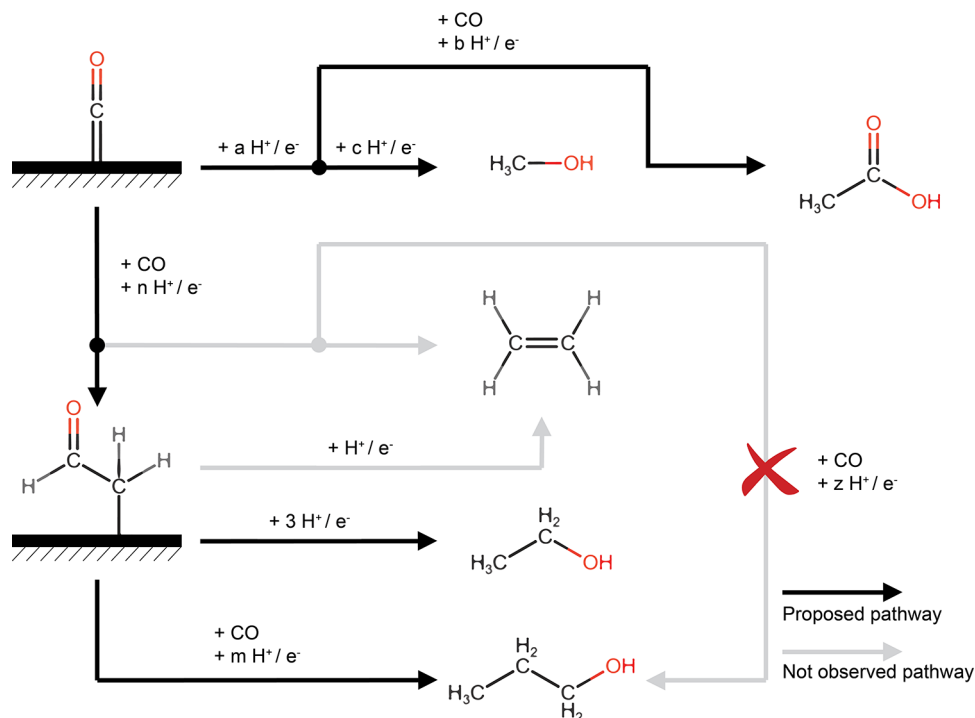
Figure 2.2: Proposed mechanistic pathway based on literature and the products (and their trend similarities) observed in this study.

to form acetic acid. Some plausibility for this hypothesis can be derived from the existence of a rhodium-catalyzed industrial process for acetic acid synthesis involving the carbonylation of methanol called the Monsanto process.[48, 49] However, we emphasize that the most important observation from Figure 2.1 is that the pathway for the formation of acetic acid differs from the pathway via which ethanol, ethylene glycol and n-propanol are formed.

2.4. Conclusions

In summary, high-pressure CO electroreduction experiments reveal that silver is capable of further reducing carbon monoxide if the CO surface coverage is sufficiently high, with the total production rates of C2+ CORR products (ethanol, ethylene glycol and propanol) increasing as the pressure is increased. Contrary to one literature report[22], ethylene formation was not observed in this work. The fact that silver is capable of reducing CO to ethanol but not to ethylene is in agreement with DFT calculations.[31]

The comparable potential and pressure dependence of the formation of ethanol, n-propanol and ethylene glycol indicates a commonality in their formation pathways. An oxygenated surface species is likely to be the shared intermediate be-

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tween ethanol and n-propanol, and this species is likely to be one hydrogen short of acetaldehyde, as suggested by Hanselman *et al.* and Xu *et al.*[31, 46] We propose it is the coupling of this species with adsorbed CO that is responsible for the formation of propanal, which is then further reduced to n-propanol, as opposed to a reaction between a surface bound ethylene molecule with carbon monoxide (Figure 2.2).

If the CO coverage is sufficiently high, as can be achieved by increasing CO pressure, the product spectrum of silver starts to resemble that of copper under CO2RR conditions.[9] However, the formation rates for CORR products on silver are orders of magnitude lower than what is observed on copper, making detecting minority products beyond the scope of this work. The main difference between the two systems seems twofold. Firstly, due to the rather unfavorable adsorption energy of CO, silver has the propensity for desorbing CO rather than reducing it further, even though thermodynamically speaking it is capable of doing so. Secondly, due to silver being a poor catalyst for breaking C-O bonds[31], no ethylene (nor ethane) formation is observed although the rest of the products observed compare favorably with copper-catalyzed CO(2) reduction.

References

[1] Y. Hori. *Electrochemical CO2 Reduction on Metal Electrodes*, book section 3, pages 89–189. Springer New York, New York, NY, 2008.

[2] Qi Lu, Jonathan Rosen, and Feng Jiao. Nanostructured metallic electrocatalysts for carbon dioxide reduction. *ChemCatChem*, 7(1):38–47, 2015.

[3] Stephanie Nitopi, Erlend Bertheussen, Soren B. Scott, Xinyan Liu, Albert K. Engstfeld, Sebastian Horch, Brian Seger, Ifan E. L. Stephens, Karen Chan, Christopher Hahn, Jens K. Nørskov, Thomas F. Jaramillo, and Ib Chorkendorff. Progress and perspectives of electrochemical CO2 reduction on copper in aqueous electrolyte. *Chemical Reviews*, 119(12):7610–7672, 2019.

[4] Jinli Qiao, Yuyu Liu, Feng Hong, and Jiujun Zhang. A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. *Chemical Society Reviews*, 43(2):631–675, 2014.

[5] Cao-Thang Dinh, Thomas Burdyny, Md Golam Kibria, Ali Seifitokaldani, Christine M. Gabardo, F. Pelayo García de Arquer, Amirreza Kiani, Jonathan P. Edwards, Phil De Luna, Oleksandr S. Bushuyev, Chengqin Zou, Rafael Quintero-Bermudez, Yuanjie Pang, David Sinton, and Edward H. Sargent. CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science*, 360(6390):783–787, 2018.

[6] F. Sloan Roberts, Kendra P. Kuhl, and Anders Nilsson. High selectivity for ethylene from carbon dioxide reduction over copper nanocube electrocatalysts. *Angewandte Chemie*, 127(17):5268–5271, 2015.

[7] Christina W. Li, Jim Ciston, and Matthew W. Kanan. Electroreduction of carbon monoxide to liquid fuel on oxide-derived nanocrystalline copper. *Nature*, 508(7497):504–507, 2014.

[8] Yuanjie Pang, Jun Li, Ziyun Wang, Chih-Shan Tan, Pei-Lun Hsieh, Tao-Tao Zhuang, Zhi-Qin Liang, Chengqin Zou, Xue Wang, Phil De Luna, Jonathan P. Edwards, Yi Xu, Fengwang Li, Cao-Thang Dinh, Miao Zhong, Yuanhao Lou, Dan Wu, Lih-Juann Chen, Edward H. Sargent, and David Sinton. Efficient electrocatalytic conversion of carbon monoxide to propanol using fragmented copper. *Nature Catalysis*, 2(3):251–258, 2019.

[9] Kendra P. Kuhl, Etosha R. Cave, David N. Abram, and Thomas F. Jaramillo. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy & Environmental Science*, 5(5):7050–7059, 2012.

[10] Sonja A. Francis, Jesus M. Velazquez, Ivonne M. Ferrer, Daniel A. Torelli, Dan Guevarra, Matthew T. McDowell, Ke Sun, Xinghao Zhou, Fadl H. Saadi, Jimmy John, Matthias H. Richter, Forrest P. Hyler, Kimberly M. Papadantonakis, Bruce S. Brunschwig, and Nathan S. Lewis. Reduction of aqueous CO2 to 1-propanol at MoS2 electrodes. *Chemistry of Materials*, 30(15):4902–4908, 2018.

[11] Yilin Hu, Chi Chung Lee, and Markus W. Ribbe. Extending the carbon chain: Hydrocarbon formation catalyzed by vanadium/molybdenum nitrogenases. *Science*, 333(6043):753–755, 2011.

[12] Kazuki Tanifuji, Nathaniel Sickerman, Chi Chung Lee, Takayuki Nagasawa, Ko-suke Miyazaki, Yasuhiro Ohki, Kazuyuki Tatsumi, Yilin Hu, and Markus W. Ribbe. Structure and reactivity of an asymmetric synthetic mimic of nitro-genase cofactor. *Angewandte Chemie*, 128(50):15862–15865, 2016.

[13] R. Kortlever, I. Peters, C. Balemans, R. Kas, Y. Kwon, G. Mul, and M. T. M. Koper. Palladium-gold catalyst for the electrochemical reduction of CO2 to C1-C5 hydrocarbons. *Chemical Communications*, 52(67):10229–10232, 2016.

[14] Yanming Liu, Shuo Chen, Xie Quan, and Hongtao Yu. Efficient electrochem-ical reduction of carbon dioxide to acetate on nitrogen-doped nanodiamond. *Journal of the American Chemical Society*, 137(36):11631–11636, 2015.

[15] Yanming Liu, Yujing Zhang, Kai Cheng, Xie Quan, Xinfei Fan, Yan Su, Shuo Chen, Huimin Zhao, Yaobin Zhang, Hongtao Yu, and Michael R. Hoffmann. Selective electrochemical reduction of carbon dioxide to ethanol on a boron- and nitrogen-Co-doped nanodiamond. *Angewandte Chemie International Edi-tion*, 56(49):15607–15611, 2017.

[16] Jingjie Wu, Sichao Ma, Jing Sun, Jake I. Gold, ChandraSekhar Tiwary, By-oungsu Kim, Lingyang Zhu, Nitin Chopra, Ihab N. Odeh, Robert Vajtai, Aaron Z. Yu, Raymond Luo, Jun Lou, Guqiao Ding, Paul J. A. Kenis, and Pulickel M. Ajayan. A metal-free electrocatalyst for carbon dioxide reduction to multi-carbon hydrocarbons and oxygenates. *Nature Communications*, 7:13869, 2016.

[17] Agustín F. Pérez-Cadenas, Cornelia H. Ros, Sergio Morales-Torres, María Pérez-Cadenas, Patricia J. Kooyman, Carlos Moreno-Castilla, and Freek Kapteijn. Metal-doped carbon xerogels for the electro-catalytic conversion of CO2 to hydrocarbons. *Carbon*, 56:324–331, 2013.

[18] Kotaro Ogura, Kenichi Mine, Jun Yano, and Hideaki Sugihara. Electrocatalytic generation of C2 and C3 compounds from carbon dioxide on a cobalt complex-immobilized dual-film electrode. *Journal of the Chemical Society, Chemical Communications*, (1):20–21, 1993.

[19] Jun Tamura, Akihiko Ono, Yoshitsune Sugano, Chingchun Huang, Hideyuki Nishizawa, and Satoshi Mikoshiba. Electrochemical reduction of CO2 to ethy-lene glycol on imidazolium ion-terminated self-assembly monolayer-modified Au electrodes in an aqueous solution. *Physical Chemistry Chemical Physics*, 17(39):26072–26078, 2015.

[20] Daniel A. Torelli, Sonja A. Francis, J. Chance Crompton, Alnald Javier, Jonathan R. Thompson, Bruce S. Brunschwig, Manuel P. Soriaga, and Nathan S. Lewis. Nickel–gallium-catalyzed electrochemical reduction of CO2

to highly reduced products at low overpotentials. *ACS Catalysis*, 6(3):2100–2104, 2016.

[21] Karin U. D. Calvinho, Anders B. Laursen, Kyra M. K. Yap, Timothy A. Goetjen, Shinjae Hwang, Nagarajan Murali, Bryan Mejia-Sosa, Alexander Lubarski, Krishani M. Teeluck, Eugene S. Hall, Eric Garfunkel, Martha Greenblatt, and G. Charles Dismukes. Selective CO2 reduction to C3 and C4 oxyhydrocarbons on nickel phosphides at overpotentials as low as 10 mV. *Energy & Environmental Science*, 2018.

[22] Abhijit Dutta, Carina Elisabeth Morstein, Motiar Rahaman, Alena Cedeño López, and Peter Broekmann. Beyond copper in CO2 electrolysis: Effective hydrocarbon production on silver-nanofoam catalysts. *ACS Catalysis*, 8(9):8357–8368, 2018.

[23] Toru Hatsukade, Kendra P. Kuhl, Etosha R. Cave, David N. Abram, and Thomas F. Jaramillo. Insights into the electrocatalytic reduction of CO2 on metallic silver surfaces. *Physical Chemistry Chemical Physics*, 16(27):13814–13819, 2014.

[24] Akihiko Kudo, Shinji Nakagawa, Akira Tsuneto, and Tadayoshi Sakata. Electrochemical reduction of high pressure CO2 on Ni electrodes. *Journal of The Electrochemical Society*, 140(6):1541–1545, 1993.

[25] Yansong Zhou and Boon Siang Yeo. Formation of C–C bonds during electrocatalytic CO2 reduction on non-copper electrodes. *Journal of Materials Chemistry A*, 8(44):23162–23186, 2020.

[26] Kayode Adesina Adegoke, Rhoda Oyeladun Adegoke, Asiata Omotayo Ibrahim, Samson Ademola Adegoke, and Olugbenga Solomon Bello. Electrocatalytic conversion of CO2 to hydrocarbon and alcohol products: Realities and prospects of Cu-based materials. *Sustainable Materials and Technologies*, 25:e00200, 2020.

[27] Haochen Zhang, Jing Li, Mu-Jeng Cheng, and Qi Lu. CO electroreduction: Current development and understanding of Cu-based catalysts. *ACS Catalysis*, 9(1):49–65, 2019.

[28] Qiang Zhang, Shuihui Tao, Jun Du, Anbang He, Yong Yang, and Changyuan Tao. A cold plasma-activated in situ AgCo surface alloy for enhancing the electroreduction of CO2 to ethanol. *Journal of Materials Chemistry A*, 8(17):8410–8420, 2020.

[29] Yao Zheng, Anthony Vasileff, Xianlong Zhou, Yan Jiao, Mietek Jaroniec, and Shi-Zhang Qiao. Understanding the roadmap for electrochemical reduction of CO2 to multi-carbon oxygenates and hydrocarbons on copper-based catalysts. *Journal of the American Chemical Society*, 141(19):7646–7659, 2019.

[30] Qun Fan, Mingli Zhang, Mingwen Jia, Shizhen Liu, Jieshan Qiu, and Zhenyu Sun. Electrochemical CO2 reduction to C2+ species: Heterogeneous electrocatalysts, reaction pathways, and optimization strategies. *Materials Today Energy*, 10:280–301, 2018.

[31] Selwyn Hanselman, Marc T. M. Koper, and Federico Calle-Vallejo. Computational comparison of late transition metal (100) surfaces for the electrocatalytic reduction of CO to C2 species. *ACS Energy Letters*, 3(5):1062–1067, 2018.

[32] Isis Ledezma-Yanez, Elena Pérez Gallent, Marc T. M. Koper, and Federico Calle-Vallejo. Structure-sensitive electroreduction of acetaldehyde to ethanol on copper and its mechanistic implications for CO and CO2 reduction. *Catalysis Today*, 262:90–94, 2016.

[33] Jinmo Kim, Woong Choi, Joon Woo Park, Cheonghee Kim, Minjun Kim, and Hyunjoon Song. Branched copper oxide nanoparticles induce highly selective ethylene production by electrochemical carbon dioxide reduction. *Journal of the American Chemical Society*, 141(17):6986–6994, 2019.

[34] Hemma Mistry, Ana Sofia Varela, Cecile S. Bonifacio, Ioannis Zegkinoglou, Ilya Sinev, Yong-Wook Choi, Kim Kisslinger, Eric A. Stach, Judith C. Yang, Peter Strasser, and Beatriz Roldan Cuenya. Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene. *Nature Communications*, 7:12123, 2016.

[35] Xiaofeng Feng, Kaili Jiang, Shoushan Fan, and Matthew W. Kanan. A direct grain-boundary-activity correlation for CO electroreduction on Cu nanoparticles. *ACS Central Science*, 2(3):169–174, 2016.

[36] Lei Wang, Stephanie A. Nitopi, Erlend Bertheussen, Marat Orazov, Carlos G. Morales-Guio, Xinyan Liu, Drew C. Higgins, Karen Chan, Jens K. Nørskov, Christopher Hahn, and Thomas F. Jaramillo. Electrochemical carbon monoxide reduction on polycrystalline copper: Effects of potential, pressure, and ph on selectivity toward multicarbon and oxygenated products. *ACS Catalysis*, 8(8):7445–7454, 2018.

[37] Federico Calle-Vallejo and Marc T. M. Koper. Theoretical considerations on the electroreduction of CO to C2 species on Cu(100) electrodes. *Angewandte Chemie International Edition*, 52(28):7282–7285, 2013.

[38] N. S. Romero Cuellar, K. Wiesner-Fleischer, M. Fleischer, A. Rucki, and O. Hinrichsen. Advantages of CO over CO2 as reactant for electrochemical reduction to ethylene, ethanol and n-propanol on gas diffusion electrodes at high current densities. *Electrochimica Acta*, 307:164–175, 2019.

[39] Klaas Jan P. Schouten, Zisheng Qin, Elena Pérez Gallent, and Marc T.M. Koper. Two pathways for the formation of ethylene in CO reduction on single-crystal copper electrodes. *Journal of the American Chemical Society*, 134(24):9864–9867, 2012.

[40] Maitland C. Boswell and J. V. Dickson. The action of sodium hydroxide on carbon monoxide, sodium formate and sodium oxalate. *Journal of the American Chemical Society*, 40(12):1779–1786, 1918.

[41] J. Hietala, A. Vuori, P. Johnsson, I. Pollari, W. Reutemann, and H. Kieczka. *Formic Acid*, pages 1–22. 2011.

[42] Susan Topham, Alexis Bazzanella, Sebastian Schiebahn, Sebastian Luhr, Li Zhao, and Alexander Otto. *Carbon Monoxide*. 2001.

[43] Yuvraj Y. Birdja and Marc T. M. Koper. The importance of cannizzaro-type reactions during electrocatalytic reduction of carbon dioxide. *Journal of the American Chemical Society*, 139(5):2030–2034, 2017.

[44] Dan Ren, Nian Tee Wong, Albertus Denny Handoko, Yun Huang, and Boon Siang Yeo. Mechanistic insights into the enhanced activity and stability of agglomerated Cu nanocrystals for the electrochemical reduction of carbon dioxide to n-propanol. *Journal of Physical Chemistry Letters*, 7(1):20–24, 2016.

[45] Erlend Bertheussen, Arnau Verdaguer-Casadevall, Davide Ravasio, Joseph H. Montoya, Daniel B. Trimarco, Claudie Roy, Sebastian Meier, Jürgen Wendland, Jens K. Nørskov, Ifan E. L. Stephens, and Ib Chorkendorff. Acetaldehyde as an intermediate in the electroreduction of carbon monoxide to ethanol on oxide-derived copper. *Angewandte Chemie International Edition*, 55(4):1450–1454, 2016.

[46] Xiaoxia Chang, Arnav Malkani, Xuan Yang, and Bingjun Xu. Mechanistic insights into electroreductive C–C coupling between CO and acetaldehyde into multicarbon products. *Journal of the American Chemical Society*, 142(6):2975–2983, 2020.

[47] Bernhard Schmid, Christian Reller, Sebastian Neubauer, Maximilian Fleischer, Romano Dorta, and Guenter Schmid. Reactivity of copper electrodes towards functional groups and small molecules in the context of CO2 electroreductions. *Catalysts*, 7(5):161, 2017.

[48] F. E. Paulik and J. F. Roth. Novel catalysts for the low-pressure carbonylation of methanol to acetic acid. *Chemical Communications*, (24):1578a–1578a, 1968.

[49] James F. Roth. The production of acetic acid. *Platinum metals review*, 19(1):12–14, 1975.