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■ Catalysis

Pyrolysis of Deep Eutectic Solvents for the Preparation of Supported Copper Electrocatalysts

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Electrochemical CO_2 reduction on Cu-based catalysts can form a variety of products including hydrocarbons, alcohols and formate, besides carbon monoxide and hydrogen. Compared to other electroactive metals, copper has a rather low cost and low toxicity.

We have developed a novel method for catalyst preparation using deep eutectic solvents (DES), where the pyrolysis of a metal-containing DES leads to a material consisting of a metal embedded in a carbon support rich in oxygen and nitrogen functional groups (CNO). We focus on the preparation of copper-based materials as catalysts for the electrochemical CO_2 reduction. Depending on the nature of DES, the properties of the carbon support can be changed. The electrochemical activity of the materials was correlated with the preparation parameters such as variation of DESs, copper precursor and/or pyrolysis temperature. These Cu/CNO copper catalysts showed formate formation rates up to 85.5 $\mu mol\,h^{-1}\,cm^{-2}$ at 1.5 V $vs.$ Ag/AgCl.

1. Introduction

Formate is widely used in the feed industry, grass silage, leather tanning and anti-icing.[1] The worldwide production of formic acid amounts to 620 $kt\,a^{-1}$ in 2012 and its demand is likely to increase steadily when considering applications such as fuel cells or hydrogen carrier.[1] The hydrolysis of methyl formate is currently the worldwide dominant process route to formate.[2] Thus, the electrochemical production of formate from renewable energy, CO_2 and water is an environmentally friendly alternative compared to the existing commercial production routes. Furthermore, the electrochemical route contributes to the reduction of greenhouse gas emissions via carbon-capture and usage.[3] Principally, the electrochemical reduction of CO_2 offers an option for CO_2 utilization as building block for synthesis of value-added chemicals and avoids further CO_2-emissions by using renewable energy. In addition, such processes provide a method for intermittent energy storage in energy-dense and portable chemicals.[4] Both aspects reduce our dependence on fossil energy sources, especially crude oil, and offers a way to substitute petrochemicals.[4b] The electro-catalytic route for CO_2 conversion in aqueous media is a promising method, because it can be performed at ambient pressure and temperature, using low-cost catalysts.[5] However, the efficiency of this process depends strongly on the activity and selectivity of the catalyst material, which should bind and activate CO_2 at lower overpotentials, enabling the CO_2 conversion and suppressing H_2 evolution.[4a,6] A low-cost catalyst operating at high current densities and lower overpotentials would improve the commercial viability of the whole process.[4c,7]

Regarding product selectivity, Pb, Hg, Tl, In, Sn, Cd and Bi electrodes lead mainly to formate,[7a,8] while Au, Ag, Zn, Pd and Ga electrodes produce mainly CO. Ni, Fe, Pt and Ti electrodes have a rather low overpotential for hydrogen evolution and lead mostly to H_2.[4a,8] Compared to the other catalyst materials, copper is the only metal that can convert CO_2 to a mixture of products, including alcohols, hydrocarbons, formate and CO at ambient pressure and temperature.[4a,6c, 8–9] An extra advantage of copper as a catalyst, besides its low toxicity, is the rather low cost (~5900 \$/t, 02/04/2019) compared to catalysts that produce mainly formate from CO_2 such as tin (~20000 \$/t) and indium (~340000 \$/t).[10]

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In this work, we report a new preparation method for copper materials on a carbon support (Cu/CNO). The Cu/CNO materials were applied as catalysts for the electrochemical production of formate from CO_2. A facile single step preparation method involving the pyrolysis from deep eutectic solvents (DES) was used.[11] A great advantage over conventionally used impregnation methods is that the loading of the catalyst support is not determined by the adsorption behavior of the metal compounds on the support surface. Thus, different copper precursors or even bimetallic mixtures can be used as starting materials and loaded in desired amounts on the DES-based supporting material. The choice of DES and preparation temperature influence the properties of the CNO support and therefore, the activity of the electrocatalysts. The preparation procedure may improve the activity of the obtained copper catalysts due to a better stabilization of the copper on the support and *in situ* building of an active copper modification. Spatial proximity of CO_2 binding domains (amines)[12] or basic surface properties on the support and the active sites of the catalyst should favour product formation.

2. Results and Discussion

2.1. Catalyst preparation and characterization

The influence of the different parameters on the activity of the 96 prepared copper catalysts was investigated by cyclic voltammetry (CV) and chronoamperometry (CA) in argon and CO_2 saturated 0.5 M $KHCO_3$ electrolyte (Table 1). The comparison of current densities in CO_2 and Ar saturated electrolytes gives a hint of the material activity, although this method is not conclusive and chemical analysis is needed. Those with the highest current densities in CO_2 and the highest difference compared to Argon saturated solutions were chosen for chemical analysis (Table S2, Supporting Information). Based on these data and a methodical comparison of the preparation parameter, 19 catalysts (Table 1, marked in   ) were used for CO_2 reduction with chemical analysis of the products.

The properties of the different Cu/CNO catalysts and the different supporting materials were investigated by XRD and SEM, which respectively provide information on the resulting crystal structure, the distribution and morphology of copper after the pyrolysis. All catalysts show XRD reflexes attributed to metallic copper and the materials prepared from the DES based on CF, UG and UGF show additionally reflexes related to

copper(I) and copper(II) oxides (Figure S1, Supporting Information). The influence of the metal precursor and pyrolysis temperature was compared exemplarily by changing the pyrolysis temperature and keeping the DES and metal precursor constant (Figure S2, Supporting Information) and keeping the DES and pyrolysis temperature constant and changing the metal precursor (Figure S3, Supporting information). Thereby, all XRD measurements show only reflexes from metallic copper and no influence from the metal precursor or pyrolysis temperature on the oxidation state of the metal was found. SEM images (Figure S4, Supporting Information) show that the choice of the deep eutectic solvent also influences the particle size. UG-based DES (Figure S4e) formed a fine powder, whereas DES based on CV led to larger particles (Figure S4b). It is also noticeable that the pyrolysis of the DF-based DES (Figure S4c) resulted in a mixture of a fine powder and large particles, while the other DES showed more homogeneous particle sizes. Elemental mapping measurements with an EDX detector (Figure S5, Supporting Information), verified a good distribution of copper on the surface of the catalyst particles with exception of the DL based material (Figure S5d), in which only copper spots on DES support can be found. This can be explained by the large polymeric structure of lignin, which may not lead to a completely homogeneous DES and thus to an inhomogeneous distribution of the metal in the DES.

Besides the comparison of catalyst particle sizes by SEM, the metal crystallite size was estimated by XRD (Equation 1, experimental section in the Supporting Information).[13] According to Reskes group,[14] the size of copper nanoparticles influences strongly the activity and selectivity of the electrochemical CO_2 reduction. Smaller nanoparticles (< 5 nm) increase the catalytic activity, but suppress the selectivity towards hydrocarbon production. Thus, investigations of the copper crystallite sizes in the prepared Cu/CNO catalysts may clarify the catalytic activity. The calculation of the crystallite dimension in one direction using the (200) plane is sufficient due to the cubic crystallographic system of copper. By applying the Scherrer equation, crystallite sizes in a range of 33.8 and 68.2 nm were calculated (Figure 1 and Table S3, Supporting Information). According to Figure 1, the copper precursor and pyrolysis temperature (Figure 1b and c, respectively) have less influence on the crystallite size than the choice of DES. Crystal size variations between 33.8 nm and 52.3 nm were measured for materials prepared by different DES using the same copper precursor and pyrolysis temperature (Figure 1a). It is known

Table 1. Overview of the catalysts prepared with different DESs, copper precursors and pyrolysis temperatures: $\sqrt{}$ – investigated with product analysis, ♦ – CV and CA measurements for pre-characterization; – – coating on a current collector was not possible.

DES	Copper precursor and pyrolysis temperature [°C]															
	CuNP				CuO				CuAc				Cu$_2$O			
	425	450	475	500	425	450	475	500	425	450	475	500	425	450	475	500
CF	♦	$\sqrt{}$	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦
CV	$\sqrt{}$	$\sqrt{}$	$\sqrt{}$	$\sqrt{}$	$\sqrt{}$	$\sqrt{}$	$\sqrt{}$	$\sqrt{}$	$\sqrt{}$	♦	♦	♦	$\sqrt{}$	♦	♦	♦
DF	♦	$\sqrt{}$	♦	♦	–	–	–	–	–	–	♦	♦	♦	♦	♦	♦
DL	♦	$\sqrt{}$	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦
UG	$\sqrt{}$	$\sqrt{}$	$\sqrt{}$	$\sqrt{}$	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦
UGF	♦	$\sqrt{}$	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦	♦

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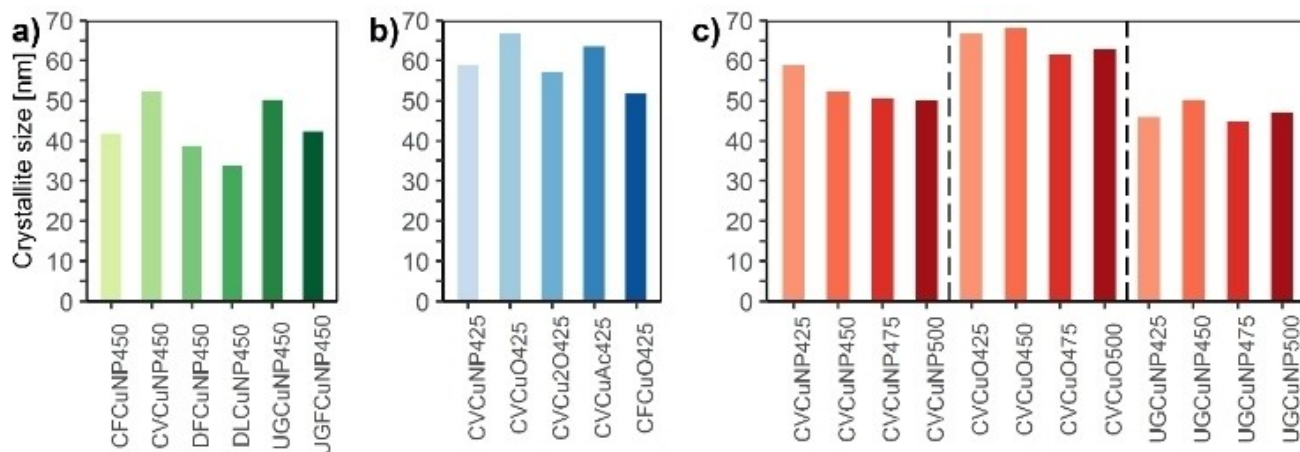European Chemical
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Figure 1. Crystallite sizes of the different copper catalysts determined by XRD: a) influence of the different DES in different shades of green, b) influence of the copper precursor in different shades of blue and c) influence of the pyrolysis temperature on the copper crystallite size in different shades of red (the higher the temperature, the darker the red).

from literature[15] that DES can fulfil multiple roles in directing chemistry at the nanoscale such as acting as supramolecular templates and stabilizing reagents for nanoparticles. Moreover, DES components may modulate nucleation and growth mechanisms and thus, dictate growth along defined directions.[15] After structural and optical characterization of the Cu/CNO catalysts, the properties of the supporting material CNO were investigated. Figure S6 (Supporting Information) compares the elemental composition of the CNO support prepared by different DES before and after pyrolysis at 440 °C, which are determined by stoichiometric calculations and CHNS/O elemental analysis. The amount of nitrogen after pyrolysis shows an obvious increase or decrease up to 12 wt%, while the carbon ratio increases distinctly and the amounts of oxygen, hydrogen and chloride decrease. The urea-based mixtures (UG, UGF) show the highest nitrogen content followed by the N,N'-dimethylurea (DF, DL) and choline chloride-based (CF, CV) materials. Thus, the amount of nitrogen is mainly defined by the choice of starting materials. Moreover, we can assume, based on comparison of X-ray photoelectron spectroscopy (XPS) and elemental analysis that the nitrogen content on the upper surface with a depth up to 10 nm and in the bulk material is in a same range. Comparing the XPS and elemental analysis results of a palladium catalyst based on a urea - fructose DES in a former study, 22.6 wt% and 19.6 wt% of nitrogen were measured, respectively.[11] Thus, the amounts of nitrogen on the upper surface tend to be slightly higher than in the bulk material, but the amounts of nitrogen are comparable. Due to the Lewis acidic properties of CO_2, the basic functional groups on the surface of the materials should be beneficial for the activity of the materials in electrochemical CO_2 reduction. Thus, a high amount of basic groups is expected to have a positive effect on CO_2 adsorption and therefore on the CO_2 electrolysis. To compare the binding capacities and the influence of the basic surface groups with a commercial activated carbon sample, the amounts of functional groups on

the surface of the pyrolysis products and on the surface of a commercially available sample were investigated. Boehm titrations of the supporting material without copper loading showed that the DES-based carbon materials are rich in acidic and basic oxygen-containing functional groups (Figure 2 and Table S4, Supporting Information). Commercially available activated carbon showed a total amount of 1094 μmol g^{-1} functional groups on the surface, while some of the DES-based materials provided evidently higher values with overall amounts of functional groups from 888 μmol g^{-1} (CF) to 2091 μmol g^{-1} (UG). Actually, the amount of functional groups may be even higher due to limitations of the Boehm method.

Porosity of the materials can reduce the surface accessible by the solvent and only acidic and basic surface groups are detected.[16] Examples of oxygen-containing acidic functional groups are carboxylates, lactones, phenols and ketones, where-
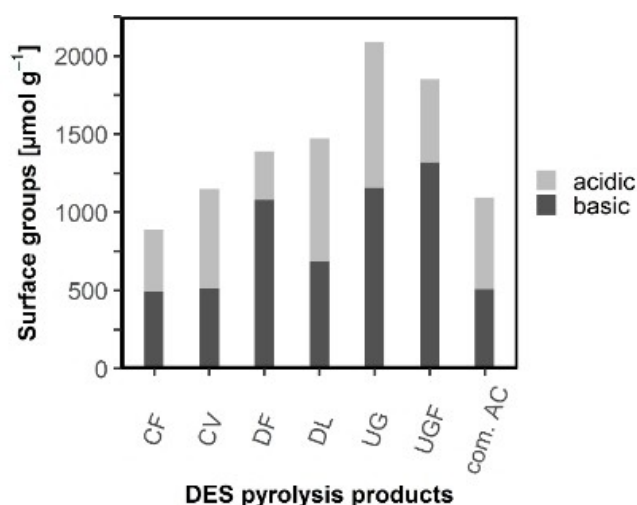

Figure 2. Characterization of the supporting material using Boehm titrations.

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as pyrenes and chromenes can be assigned to basic groups.[17] It was found that the hydrogen bond acceptor in the DES primarily influences the amount of surface groups on the pyrolyzed materials. The urea-based DES UG and UGF exhibit the highest amount of functional groups, followed by the N,N'-dimethylurea (DF, DL) and the choline chloride-based (CF, CV) mixtures. Apart from a commercial sample of activated carbon, only the DES DL and CV show more acidic than basic surface groups, while all other mixtures show more basic than acidic functional groups.

Comparing Boehm titration with CHNS/O elemental analysis confirms the trend. Urea-based materials show the highest nitrogen content and result in a higher amount of basic surface groups compared to choline chloride-based supports with comparable low nitrogen contents and the lowest amounts of basic surface groups. The pyrolysis of the nitrogen-containing mixtures under inert conditions promotes the formation of amine groups, which is supposed to improve the CO_2 adsorption.[12] Therefore, higher nitrogen contents in the support should also increase the amount of adsorbed CO_2, when the N-containing starting materials form amines during the pyrolysis.

Thus, the capacity of CO_2 binding was investigated using CO_2 adsorption experiments of two differently prepared materials, a nitrogen-rich (UG) and a nitrogen-poor (CV) DES support and a commercial sample of activated carbon (Table S5, Supporting Information). Usually, adsorption measurements with CO_2 are performed to determine the amount and volume of micropores in solid materials by the Dubinin-Radushkevich equation,[18] but in our case the amount of overall adsorbed carbon dioxide on the support was of interest. Contrary to the theory, the nitrogen-poor and comparably less basic CV material adsorbs almost twice the amount of carbon dioxide (3.96 mL g^{-1} at a relative pressure of 0.03) as the nitrogen-rich and significantly more basic UG support (2.60 mL g^{-1} at a relative pressure of 0.03). The commercially available sample, which shows less basic functional groups and a low nitrogen content (about 6.5 wt%) as well, adsorbs

9.38 mL g^{-1} carbon dioxide at a relative pressure of 0.03. This shows the same tendency as the DES CV that higher amounts of carbon dioxide are adsorbed with less basic and N-containing groups. Thus, it was ascertained that there is no influence of basic surface groups and high nitrogen contents on the CO_2 binding capacities of the supporting material. One explanation is that nitrogen is not present as amine and therefore has no influence on the CO_2 binding capacity. However, the question remains, which parameter promotes the adsorption of CO_2 on the surface of the catalyst materials. Since the preparation of the catalysts with various deep eutectic solvents provides different particle morphologies (Figure S4, Supporting Information) and functional groups on the surface of the materials (Figure 2), it is possible that the different surface structures influence the adsorption of carbon dioxide. The larger particle sizes of the material prepared from the DES CV lead to a higher CO_2 adsorption.

2.2. Electrochemical CO_2 Reduction

The optimum copper loading in the carbon support and the optimum catalyst material loading immobilized on an electrode surface were investigated by comparing their current densities in a CO_2 saturated electrolyte (more details shown in Figure S7, Supporting Information). All measurements are performed against an Ag/AgCl reference electrode. The highest investigated copper loading of 50 wt% shows the highest current density and a catalyst loading of 5 mg cm^{-2} on the electrode led to a stable and high current density, thus, the following measurements were all performed with 5 mg cm^{-2} of a 50 wt% Cu/CNO.

The electrochemical activity of catalysts containing 50 wt% Cu and prepared from six different DES were investigated by linear sweep voltammetry (LSV). The first runs of the LSV were compared regarding the effect of the DES, the copper precursors and the pyrolysis temperature on the current densities and onset potentials (Figure 3). Since the materials were not stabilized before recording the LSV, the materials
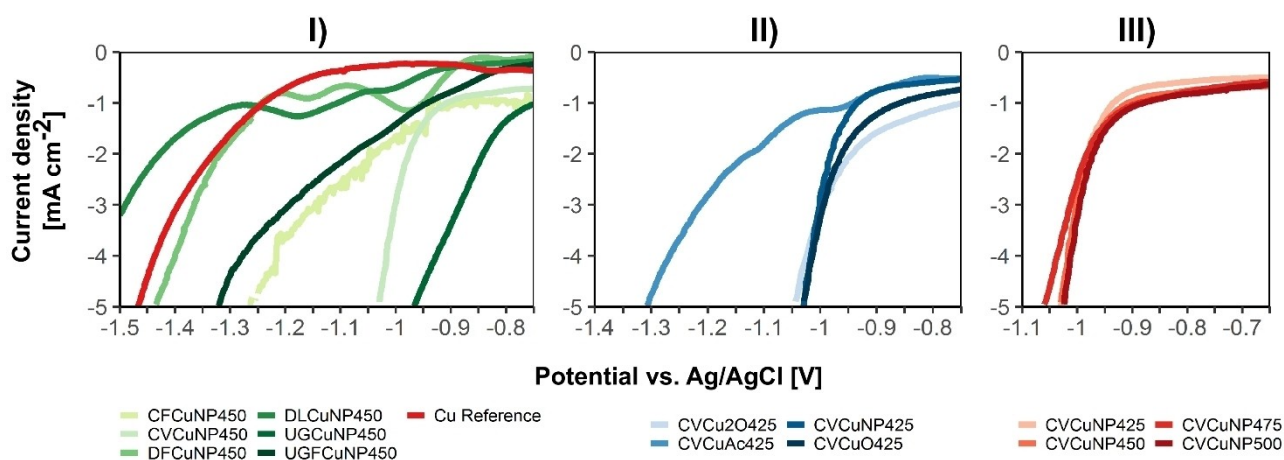
Figure 3. LSV of Cu/CNO catalysts in 0.5 M KHCO$_3$ solution saturated with CO_2 at 50 mV s^{-1} scan rate. In the preparation of the catalysts, different parameters were varied: **I**) the nature of the DES; **II**) the copper; **III**) the pyrolysis temperatures.

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prepared by different DES (Figure 3-I) contain oxides, which can influence the reduction of the materials as well. Figures S8 to S10 in the Supporting Information show the LSV from Figure 3 in a wider current and potential range.

Almost all tested catalysts show higher current densities compared to a bare copper sheet, with exception of the DES based on lignin (DL). The different preparation parameters also influenced the onset potential for the parallel occurring reactions: CO_2 and water reduction. The overpotential is defined as difference between the standard equilibrium potential and the onset potential for a given reaction.[4c] Materials synthesized from six different DES (Figure 3-I), all with copper nanoparticles (CuNP) and with a pyrolysis temperature of 450 °C, showed remarkable differences in current densities and onset potentials. The DES UG (−0.8 V) and CV (−0.95 V) exhibit a more positive onset potential compared to a bare copper sheet (−1.2 V). The DES CF (−0.95 V) and UGF (−0.85 V) show similar behavior, both have significantly more positive onset potentials than copper. However, comparing CF and UGF with UG and CV, the current density is considerably lower. In a distinct fashion, the DES DL and DF show more negative onset potentials compared to the copper and rather low current densities.

The pyrolysis temperature and the copper precursor effects were investigated on materials prepared from the DES CV, firstly by varying the copper source at 425 °C and later by varying the temperature using CuNP as copper source. Considering LSV of catalysts prepared from different copper precursors shown in Figure 3-II, the onset potential becomes more positive compared to copper and increase from −1.2 V to about −0.95 V for CuNP, CuO and Cu_2O, and -1.05 V for copper acetate.

Comparing the effect of the pyrolysis temperature in the LSV in Figure 3-III, the onset potentials of the materials synthesized from 425 °C to 500 °C (−0.95 V) also show an onset potential considerably more positive than copper.

According to Hori,[9c] since hydrogen evolution takes place simultaneously with the CO_2 reduction, the analysis of current densities in CO_2 saturated solutions without chemical analysis and quantification of the eventual products is not reliable. Thus, chemical analysis of the gas and liquid phase for the CO_2 reduction on the catalyst CVCuNP450 were carried out at different applied potentials, from −1.3 V to −2.1 V (more details shown in Figure S11 and Table S6, Supporting Information). The applied potentials were chosen based on the onset potentials obtained in the LSV. Hence, the catalyst was immobilized in a gas diffusion layer (GDL) and chemical analysis was performed at potentials more negative than −1 V. GDLs allow a better supply of CO_2 to the catalyst, which otherwise would be limited by the CO_2 solubility in the electrolyte, and consequently higher current densities for CO_2 reduction can be achieved.[19] Formate is solely produced in liquid phase at −1.5 V (Figure S11, Supporting Information) and thus, the selectivity towards formate production is higher at this potential, whereas at more negative potentials ethanol and n-propanol were produced as well. Thus, this potential is used for all further experiments.

Reproducibility investigations show rather similar formate concentrations (more details shown in Table S7, Supporting Information).

The catalysts showing the highest current densities in CO_2 saturated solutions in the pre-characterization (Table 1), thus considered as the most active, were investigated on GDLs at a constant potential (−1.5 V) for two hours. Figure 4 shows the measured current densities with the corresponding Faraday efficiencies and formation rates of formate. The catalysts were grouped according to the nature of the DES (I), the copper source (II) and the pyrolysis temperature (III).

CO_2 reduction on the DES-based catalysts provide formate concentrations between 7.8 mM and 34.2 mM, corresponding to formation rates between 19.5 µmol h^{-1} cm^{-2} and 85.5 µmol h^{-1} cm^{-2} (more details shown in Table S8, Supporting Information). The nature of the DES strongly influences the catalyst activity, as already indicated by the LSV, with variations of the formation rate between 19.5 µmol h^{-1} cm^{-2} (UG) and 56.0 µmol h^{-1} cm^{-2} (CF) (Figure 4-Ib). Regarding the effect of the copper precursor in Figure 4-IIe, the copper nanoparticles and copper(II) oxide result in higher formation rates (78.25 µmol h^{-1} cm^{-2}, 82.0 µmol h^{-1} cm^{-2} and 85.5 µmol h^{-1} cm^{-2}, respectively), compared to copper(I) oxide and copper acetate (55.75 µmol h^{-1} cm^{-2} and 58.5 µmol h^{-1} cm^{-2}, respectively). The pyrolysis temperature shown in Figure 4-IIIh has a considerable effect on the catalyst activity, since the highest formation rates of formate were obtained with samples prepared at 425 °C, with exception of the UG-based DES, which shows negligible fluctuations of formation rates for the investigated pyrolysis temperatures (425 °C, 450 °C, 475 °C and 500 °C). These results confirm the importance of product analysis in electrochemical measurements. Both, the influence of the copper precursor and the different pyrolysis temperatures show clear deviations from the LSV. According to LSV, Cu_2O should perform as well as CuNP and CuO, and all different pyrolysis temperatures should similarly affect the activity. A summary of all results show clear trends, which preparation parameters have the greatest influences. Choline chloride based catalysts (CV and CF) prepared with copper nanoparticles or copper(II) oxide at a pyrolysis temperature of 425 °C showed the highest formate formation rates, while urea based materials revealed the lowest. Comparing these best-performing catalysts and their material properties show that a lower amount of acidic and basic functional groups on the surface of the materials, in the range of commercially available activated carbon (Figure 2), has a positive effect on the activity of the catalysts in electrochemical CO_2 reduction. In addition, a comparable low nitrogen content, which can be observed in both CC-based materials (Figure S6, Supporting Information), a larger crystallite size of copper (51.8 nm, 58.8 nm and 66.7 nm for CFCuO425, CVCuO425 and CVCuNO425, respectively) and a DES with a higher CO_2 binding capacity (Table S5, Supporting Information) are also advantageous for the catalyst activity. The following correlations between the highest (CV-based materials) and lowest (UG-based materials) catalyst activities and the material properties can be observed. Materials prepared with CV and UG DES
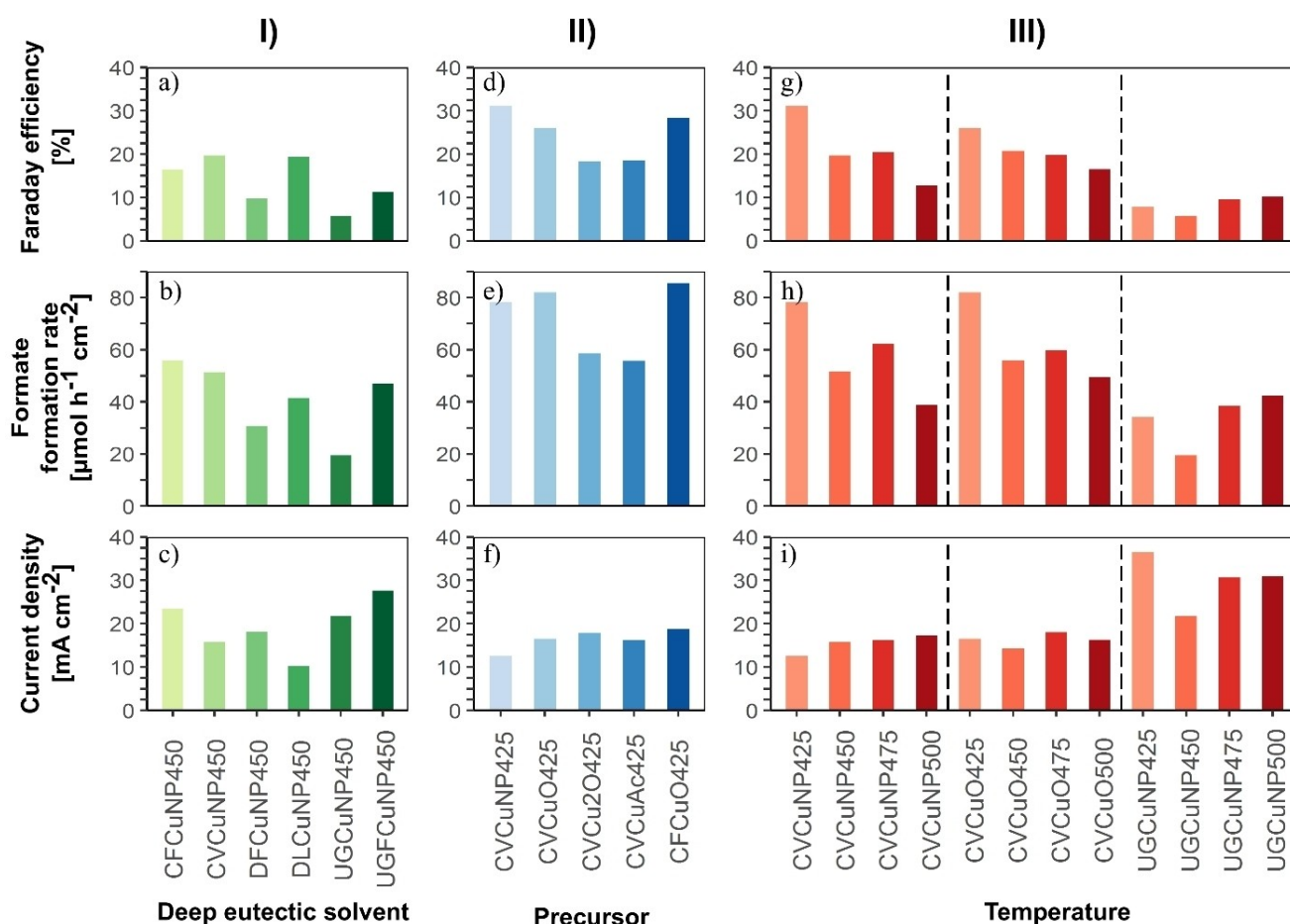
Figure 4. Overview of formate Faraday efficiency, formation rate and current density on catalyst prepared varying the following parameters: I) nature of DES, II) copper precursor and III) pyrolysis temperature.

showed both a copper crystallite size of ~50 nm, but a quite distinct electrochemical activity. CV led to considerably higher formation rates of formate compared to UG-based materials. Therefore, the copper crystallite size cannot be correlated with the activity of the catalysts.

The choline chloride-based supports with comparable low nitrogen contents and the lowest amounts of acidic and basic surface groups adsorb against expectations a higher amount of carbon dioxide compared to the UG-based material with the highest nitrogen content and the highest amount of functional surface groups (Figure 2 and Figure S6, Table S5, Supporting Information). Nevertheless, a clear correlation of CO_2 adsorption and the product formation can be observed. The CV material, which adsorb more CO_2, result in higher product amounts compared to materials with lower CO_2 adsorption (UG). This indicates that the carbon support influences the reaction in the copper active sites by increasing the CO_2 adsorption and thus, the CO_2 supply on the electrode surface.

Overall, the formate formation rates of the best-performing catalysts can be further optimized by improving the electrochemical CO_2 reduction process, such as electrode preparation (catalyst loading, binder and procedure),[20] type and concentration of supporting electrolytes as well as the CO_2 gas flow

and the GDL properties.[21] Changing the electrochemical cell type can also greatly improve the activity. However, the aim of all these investigations was the development of a novel type of copper catalysts based on deep eutectic solvents. Therefore, the setup was not varied. Optimization of the electrochemical setup with the best-performing catalysts is on-going. Nevertheless, the achieved formation rates for formate show already good results compared to formation rates of copper catalysts selected as examples in recent literature[22] and can be further increased by optimization of the electrochemical setup. Tin catalysts exhibit about threefold higher rates for formate compared to the Cu/CNO catalyst.[23] Nevertheless, the facile method for the catalyst preparation and the low cost of starting materials offer additional benefits for this method based on the pyrolysis of DES.

3. Conclusion

The reported protocol demonstrates a novel and facile preparation method for copper supported on carbon material rich in oxygen and nitrogen groups through the pyrolysis of deep eutectic solvents. These copper/carbonaceous materials could be used as electrocatalysts for CO_2 reduction to formate,

resulting in good formation rates compared to exemplarily chosen formation rates using copper catalysts in recent literature. Several parameters such as copper loading in the carbon support, material loading on the electrode, as well as the nature of the DES, copper precursors and influence of pyrolysis temperatures were investigated. The catalysts prepared led to the production of formate in yields up to 85.5 µmol h^{-1} cm^{-2} as the only liquid product from CO_2 reduction at -1.5 V *vs.* Ag/AgCl. In summary, choline chloride-based materials (CV and CF) prepared with copper nanoparticles or copper(II) oxide at a pyrolysis temperature of 425 °C showed the highest formation rates. We conclude that the different preparation parameters significantly affect the catalysts activity and correlation of the catalyst activity and their material properties showed clear tendencies. A lower amount of functional groups on the surface of the materials, a lower nitrogen content, larger crystallite sizes of copper and materials with a higher CO_2 binding capacity are advantageous for the catalyst activity.

Supporting Information Summary

Supporting information includes the experimental section and tables/ figures with additional information. XRD, SEM, elemental analysis and Boehm titration results are shown as well as chronoamperometry measurements for determination of the optimum copper loading and catalyst loading on the electrodes, LSV investigations in a broader range, potential screening results, reproducibility experiments and a complete overview of the product amounts.

Conflict of Interest

The authors declare no conflict of interest.

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