Study on the structure vs activity of designed non-precious metal electrocatalysts for CO₂ conversion

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Abstract

The rising level of carbon dioxide (CO₂), mainly a consequence of human activities, it is leading to devastating consequences to our environment and has raised concerns to the public opinion. To face this issue, governments are working to reduce the level of CO₂ emissions, whilst the scientific community is focusing to implement the electrochemical conversion of the emitted CO₂ (CO₂RR) as source of added value chemicals. Due to the high stability of the CO₂ molecule, to make its conversion practical, the process requires a suitable electro-catalyst. With the aim to understand the mechanism toward specific CO₂RR product and thus increase selectivity, in this contribution, we have explored copper nanoparticles (Cu NPs), as one of the most promising catalyst for CO₂ conversion, and investigated the reactivity as a function of selected experimental parameters. The results were rationalized via theoretical investigation, also discussed in the paper, to understand the mechanism behind their activity but, most importantly, to relate structure to selectivity. The Cu NPs, prepared via an unconventional sol-gel process, were shown to be pure, with homogeneous size and morphology, and were tested toward CO₂RRs showing a total FE above 90%. The higher FE toward the production of C₂H₄ (up to 33% at an applied potential of -1.0 V) is one of the highest FE reported so far for Cu, without using expensive support. The final products were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Introduction

The severe consequences of greenhouse emission to the environment have made the public opinion aware of the importance to find alternative energy sources to the current fossil fuels. The main concerns are toward the high amount of carbon dioxide (CO₂) in the atmosphere. Alongside strategies aimed at reducing CO₂ emission, a complementary approach is its conversion into added value chemicals. In fact, CO₂ represents a virtually unlimited source of carbon that may be transformed into a variety of chemicals¹; these include methanol^{2,3}, methane⁴, formic acid⁵, formic acid ester⁶, formamides⁷, carbonic acid esters⁸, carbamic acid esters (urethanes)⁹, lactones¹⁰, and more, some of which are otherwise produced from fossil sources. However, the C=O bond energy (750 kJ mol⁻¹) is significantly higher than C–C (336 kJ mol⁻¹), C–O (327 kJ mol⁻¹), and C–H (411 kJ mol⁻¹), making it difficult to convert CO₂. Electrocatalysts are required to lower the energy cost of reducing CO₂. The efficiency of noble metal-based catalysts such as gold¹¹, silver¹² and palladium¹³ has been demonstrated but these metals are too scarce, making the process not economically feasible. In addition, the process is hardly selective, and many products are formed during the reduction process. To make the process practical, the attention has been focused on finding low-cost non-precious metals alternative, with high selectivity. Several metals have been explored so far including Ni¹⁴, Co¹⁵, Fe¹⁶, Ti¹⁷, Zn¹⁸, Sn¹⁹, Bi²⁰, Cu^{21,22}. Results showed that copper and copper-based materials are the most promising because, beside CO, other more interesting products can be obtained, including the conversion into hydrocarbons^{23,24,25}. As a further advantage, the Cu future supply is not a concern as it is estimated to exceed 5,000 MT (i.e. 200+ years of availability)²⁶.

Unfortunately, the overpotential needed by Cu electrocatalysts for CO₂ reduction is very high²⁷, while the selectivity is always a problem especially for the formation of C₂ products (namely C₂H₄ and C₂H₆). For instance, selective production of C₂H₄ and C₂H₆ have been achieved on nanoporous Cu film by controlling the morphology which attained a faradic efficiency of 38% and 46% at -1.7 V, respectively.²⁸ Despite this research proving the pore depth has an influence on the formation of C₂ products, a large overpotential was used, hence lowering the energy efficiency of the reduction process. For this reason, several research are now focusing in optimizing CO₂RR, to

make it practically but also economically feasible.

Strategies adopted to improve the catalytic activity of Cu include modification of the surface topology²⁹ (to increase the specific surface area and to create more reactive sites), metal doping^{30, 31} and alloying³² (to promote the adsorption/activation of CO₂ and to improve stability), and also nano-structuring^{33,34} (to expose a higher fraction of coordinative corner and edge unsaturated surface atoms). Recent research has also highlighted the superior performance of *amorphous* nanoparticles compared to *crystalline* nanoparticles in promoting the transformation of CO₂ to profitable formic acid and ethanol³⁵. Such an improvement in the catalytic performance has been ascribed to the higher electrochemical surface-active area compared with crystalline nanoparticles that may originate from the higher number of active sites generated from the structural heterogeneity on the amorphous surfaces. However, due to the complexity in structure and difficulties in feature engineering, few studies have been conducted on the catalytic performance of amorphous compounds.

This finding significantly increases the interest in the tailored synthesis of Cu nanoparticles with fine control over the degree of crystallinity, alongside size and porosity. The synthetic methodology to prepare Cu nanoparticles is, therefore, of critical importance to maximize catalytic activity and selectivity toward a specific product. It is surprising that not much attention has been devoted to optimizing such a key step. Cu nanoparticles have been prepared for different applications, using selected pathways, e.g. via microwave³⁶ or electron beam irradiation³⁷, bio-synthesis³⁸ and laser ablation³⁹. Since Cu is easily aggregated and oxidized, many researchers synthesize Cu nanoparticles capped with polymers, such as PVP (poly vinyl pyrrolidone) and gelatin^{40,41}. However, polymers cannot be decomposed easily so the remaining polymers might affect catalytic performances. Alternatively, surfactants can be used for this process since they decompose more easily than polymers because of their lower molecular masses. Other researchers used strong reducing agents, such as hydrazine and sodium borohydride, to synthesize Cu nanoparticles with surfactants, such as CTAB (cetyl trimethyl ammonium bromide), SDS (sodium dodecyl sulfate), thiol and carboxylic acid^{42,43}. However, hydrazine is extremely toxic and dangerous, and sodium borohydride will produce impurities, such as boron and sodium salts, which are difficult to remove by solvent washing. Kim et al. managed to synthesize

monodispersed copper nanoparticles without the use of strong reducing agents by using thermal decomposition of Cu-oleate complex, which was prepared by the reaction of CuCl₂ with aqueous sodium oleate. However, this method required very low pressure (0.3 torr)⁴⁴.

The present contribution introduces an alternative, easy to use, and green (non-toxic) synthetic methodology for phase-pure, monodispersed Cu particles with different crystallinity. A sol-gel based procedure called urea glass route⁴⁵ was tailored for the first time for the preparation of pure copper particles.

The as-prepared particles were tested for the electrochemical CO₂ reduction reaction (CO₂RR) and showed ability towards the formation of highly valuable ethylene rather than CO and CH₄ production, already at -1.0 V applied potential (vs RHE), with the catalyst not undergoing conversion, thus showing high stability. These catalytic findings were rationalized by density functional calculations of the processes controlling the adsorption and mechanism of CO₂ formation.

Methods

Figure 1. From left to right, solutions of Cu-Urea in ethanol with different urea-metal ratio (R); corresponding products after solvent evaporation and heat treatment under N₂ flow at 350°C.

Synthesis of Cu Nanoparticles

Cu nanoparticles were synthesized by modification of a typical urea glass route methodology⁴⁵. Copper(II) nitrate hydrate (CAS Number 13778-31-9, 99.999% trace metals basis) and urea (CAS 57-13-6, ACS, Reag. Ph Eur) were purchased from Sigma-Aldrich, Inc. Samples with different urea/Cu salt molar ratio (R) were prepared to investigate the influence of the urea amount over nanoparticles crystallinity and/or size. In a standard synthesis, copper nitrate and suitable amount of urea (depending on the final R) were dissolved in ethanol to form a homogeneous solution (figure 1.A).

The solution was stirred for 24 hours and the mixture then transferred into a crucible and the solvent was let to evaporate. The resulting product was a blue fused phase (figure 1.B). This “fused” phase was heat treated under nitrogen flow up to 350°C. This temperature was found to be ideal to achieve phase pure particles. Lower temperatures lead to a mixture of metallic copper and copper oxides (see figure SI.1), while samples treated at higher temperature are a mixture of different products (data not shown). After cooling down to room temperature, a brown powder was obtained (figure 1.C).

Preparation of Electrocatalysts

5 mg of the synthesized Cu particles were dispersed in a mixed aqueous solution of 750 μ L deionized water, 200 μ L ethanol and 50 μ L Nafion solution (CAS 31175-20-9, Sigma-Aldrich). The mixture suspension was ultrasonicated to obtain a homogeneous ink. Polished graphite discs ($\varnothing$ =10 mm, Ted Pella) served as substrates for all the catalysts. They were polished to a mirror-like finish using SiC paper (grit 1200, Struers) followed by diamond slurries (Diapro 9 and 3 μ m Struers). The Cu particle ink was then drop cast on the graphite with a loading of 325 μ g/cm². The catalyst was dried under a heat lamp and used for the electrochemical reactions.

Electrochemical Setup

Identification and quantification of the CO₂ reduction products was achieved using a custom-built gastight Teflon electrochemical cell based on the design of Kuhl et al.²³

(Figure 2) where the counter electrode is a graphite rod. Details of the experimental procedure are reported in the SI.

Figure 2. Schematic diagram of the electrochemical cell used for CO₂ electro-reduction (WE: Working Electrode).

Computational Details

We have used density functional theory (DFT) calculations to rationalize the experimentally observed distribution of products from the CO₂ reduction reaction on Cu. All calculations were conducted with the Vienna Ab initio Simulation Package (VASP) using the following computational settings: Perdew–Burke–Ernzerhof (PBE) exchange correlation functional with the Grimme’s-D3 dispersion correction; plane-wave (PW) basis set within the framework of the projector augmented wave method with a PW cutoff of 450 eV; Monkhorst-Pack k -point samplings of (5×5×1). We have computed the adsorption of the CO₂ and the experimentally observed molecules on the low index Cu (100), (110), and (111) surfaces. These surfaces were represented by 3×3 (for C1 molecules) or 4×4 (for C2 molecules) slab models with four Cu layers and a vacuum of 15 Å. The adsorption energy, E_{ads} , of a species on the Cu surface or cluster was computed according to the expression $E_{ads} = E_{surf+mol} - (E_{surf} + E_{mol})$, where $E_{surf+mol}$ is the total energy of the adsorbate-substrate system, E_{surf} is the energy of the slab, and E_{mol} is the energy of the isolated CO₂ molecule. Transition states (TS) were determined using the nudge elastic band method in VASP.

Result Discussion

Structural characterization

Phase attribution of as-prepared samples was achieved by XRD investigation. Figure 3 shows the samples prepared with two different urea/Cu salt molar ratio (R) and treated at 350 °C. In both cases, the expected crystal structure of pure metallic (cubic) Cu is achieved and no other crystalline phase is observed, including carbon (expected peak at 26°), a typical side product when urea is used. A closer look at the patterns shows that the peaks of the prepared Cu samples at 43° (111) and 50° (200), regardless of the R value, are slightly shifted to higher angles compared to the expected pattern, indicating a slightly contracted structure, possibly due to the nano-sized nature of the material. The effect on R is more pronounced on the peak broadness (FWHM), which increases going from $R=3$ to $R=7$, indicating either smaller sizes or a lower degree of crystallinity in the sample prepared with $R=7$ (i.e. using higher urea/Cu salt ratio). We can speculate that an excess of urea, which implies

Figure 3. XRD patterns of Cu samples prepared with different Urea/Cu molar ratio and treated at 350°C. The expected pattern for pure Cu° (ICDD 96-950-0217) is also reported (dashed vertical lines) for comparison.

the formation of a larger amount of N-rich matrix (where the matrix is the result of the urea polymerization process REF) that “contrast” nanoparticles coalescence and growth. However, further studies are in progress to confirm this point.

Results from the X-rays study are reported in Table 1.

Table 1. Results from the X-rays study on the prepared samples.

Sample Name	R (Urea/Metal)	FWHM 2 θ	Diameter (nm)	Phase attribution by XRD
Cu R3	3	0.08	112	Cu (ICCD 96-500-0217)
Cu R7	7	0.09	99	

To have information on the morphology of the particles and general homogeneity, a SEM study was performed. A SEM image of sample prepared with R=3 and R=7 and treated at 350 °C is reported in Figure 4. From this figure it can be observed that for R=3 sample, small spheroidal nanoparticles are interconnected forming a rather homogeneous network, while for R=7 a higher homogeneity and smaller particles

Figure 4. SEM images of A) CuU3, B) CuU7 synthesized at 350°C.

dimension (99 nm) can be observed (compared to R=3; 112nm). This is in line with what observed from XRD where the pattern for sample prepared by R=7 showed broader peaks (i.e. smaller sizes or lower degrees of crystallinity) compared to sample prepared with R=3.

CO₂ reduction reaction

The Cu particles were tested for CO₂RR at different applied potential versus RHE (Table 2). Interesting, the major products on both catalysts was neither CO nor HCOO⁻ but C₂H₄ (alongside H₂, from the competitive RHE reaction). The observed FE for ethylene

(C₂H₄) is up to 33% for an applied potential of –1.0 V, one of the highest values reported in literature so far for pure Cu particles (Table 3). Moreover, the FE of C₂H₄ at –1.0 V is almost seven times higher than CH₄. In comparison, the FE(C₂H₄) / FE(CH₄) ≈ 1 on polycrystalline copper²³. This is an important result because the CO₂ conversion to ethylene is a highly profitable process: C₂H₄ is a feedstock for many various products and represents the most important organic chemical by tonnage manufactured. In comparison, natural gas market prices put constraints on the methane market price⁴⁶. From **Table 2**, we can also observe that regardless of the catalyst used (R=3 or R=7), the more negative is the applied potential, the lower is the FE of CO and HCOO[–], while the FE for CH₄ increases. No trend is observed for C₂H₄, ethanol and n-propanol, with Ethanol displaying the highest FE for an applied potential of –1.0 V.

Table 2. Faradaic efficiencies (FE) of CO₂ reduction reaction under different applied potentials.

Cu R=3									
E (V vs RHE)	j _{total} (mA/cm ²)	FE (H ₂)	FE (CO)	FE (HCOO [–])	FE (CH ₄)	FE (C ₂ H ₄)	FE (EtOH)	FE (PrOH)	Total FE
-0.9	-5.1	45.0	6.3	8.0	0.4	18.9	4.1	3.5	89.6
-1.0	-9.3	33.0	1.4	5.0	4.9	32.6	9.2	3.7	92.9
-1.1	-22.6	40.0	0.7	1.4	18.4	25.4	7.4	1.0	95.8
Cu R=7									
E (V vs RHE)	j _{total} (mA/cm ²)	FE (H ₂)	FE (CO)	FE (HCOO [–])	FE (CH ₄)	FE (C ₂ H ₄)	FE (EtOH)	FE (PrOH)	Total FE
-0.9	-3.6	56.8	8.9	5.4	N.D*	12.0	3.8	2.1	91.4
-1.0	-6.5	32.4	3.9	4.6	5.8	29.8	7.2	3.1	90.7
-1.1	-16.4	54.9	1.0	1.7	13.2	17.9	6.1	0.9	96.9

*N.D. = not detected. EtOH = Ethanol, PrOH = *n*-Propanol.

To rationalize the preferential conversion CO₂ to molecular hydrogen and ethylene, we have computed the adsorption of H₂O and CO₂ on the Cu (100), (110), and (111) surfaces and of the molecules resulting from their reduction reaction: H₂, CO, HCOO⁻, CH₄, C₂H₄, EtOH, and PrOH (Table 4). The H₂O and CO₂ molecules have similar binding strength with values adsorption energies (E_{ads}) between -0.44 eV and -0.65 eV, depending on the surface considered. However, H₂ has an adsorption energy of approximately -0.1 eV, which corresponds to a significantly weaker surface binding than *COOH and *CO, the first two intermediates in the CO₂RR reaction pathway⁴⁷. Therefore, H₂ desorbs more easily than COOH and CO, leading to the observed high FE of H₂ (Table 2) due to the competitive hydrogen evolution reaction ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$).

Table 3: Comparison of the Faradaic efficiency (FA) of ethylene on Cu nano-catalysts used for CO₂RR reported in literature.

Composition	Support	Electrolyte	Potential (V)	FE (%) C ₂ H ₄	Ref
Cu NPs	Graphite	0.1 M KHCO ₃	-1.0 V vs. RHE	~ 33	This paper
Cu film	-	1 M KHCO ₃	-0.5 V vs. RHE	40	⁴⁸
Cu porous	Template Al ₂ O ₃	0.1 M KHCO ₃	N/R	38	²⁸
Cu NPs	Carbon	0.5 M KHCO ₃	-1.1 V vs. RHE	6.3	⁴⁹
Cu NPs	SWCNTs	0.1 M KHCO ₃	0.9 V vs. RHE	41	118 our table
Cu NPS	MoS ₂	0.1 M KHCO ₃	-1.4 V vs SCE	2	121 our table
Cu NPs	-	0.1 M KHCO ₃	-1.8 V vs Ag/AgCl	44	⁵⁰
Cu NP ensemble	Carbon	0.1 M KHCO ₃	-0.86 V vs. RHE	33.2	²²
Cu nanocrystals (44 nm)	Carbon	0.1 M KHCO ₃	-1.1 V vs. RHE	41	⁵¹
Cu nanocubes	-	10 M KOH	-0.8 V vs. RHE	60	⁵²

(70 nm)					
Cu NPs	-	0.1 M KHCO ₃	-1.11 V vs. RHE	41.1	53
Prism shaped Cu	-	0.1 M KHCO ₃	-1.16 V vs. RHE	~29	54
Twinned Cu nanowire	Carbon	0.1 M KHCO ₃	-1.0 V vs. RHE	<5	25
Cu NPs	Vulcan Carbon	0.1 M KHCO ₃	-2.2 V vs. RHE	~42	55
Cu NPs dispersed carbon aerogels	Carbon	0.1 M KHCO ₃	-0.6 V vs. RHE	15.83	21
Star Decahedron-Cu NPs	-	0.1 M KHCO ₃	-0.99 V vs. RHE	52.43 ±2.72	56
Commercial Cu NPs	-	0.1 M KHCO ₃	-1.01 V vs. RHE	37.08 ±6.87	56

Figure 4. The energy profiles for the competitive reaction pathways for C₂H₄ (Path-1) and CH₄ (Path-2) formation on the Cu(111) surface.

For the other CO₂RR products, ethylene is the most stable species on the copper surfaces because of the ability of the H₂C=CH₂ molecule to form π bonding interactions with the copper surface, which CH₄, and other Csp³ hybridized molecules (EtOH, PrOH) are unable to form (Figure SI.4 in ESI). Calculation of two competitive energy pathways for the formation of CH₄ and C₂H₄ starting from the *CH₂ intermediate on the Cu(111)

surface (Figure 4) shows that the CH₂-to-CH₃ reaction has an activation barrier of 0.19 eV (path-2), while the dimerization of *CH₂ to form C₂H₄ has an activation energy of 0.19 eV (path-1). Moreover, the reaction energy (enthalpy) for C₂H₄ (−1.81 eV) is more exergonic than CH₄ (−1.09 eV). Hence, these results suggest that both thermodynamic and kinetic factors contribute to the higher FE of C₂H₄ compared to CH₄. The reaction pathway on the Cu(100) surface gave slightly different energetics (Figure SI.5 in ESI), but still provides similar conclusions.

Table 4: Adsorption energies on Cu surfaces. Values in eV.

Cu	(1 0 0)	(1 1 0)	(1 1 1)
H ₂ O	-0.54	-0.65	-0.44
H ₂	-0.13	-0.11	-0.13
CO ₂	-0.60	-0.61	-0.58
CO	-1.08	-1.50	-1.22
COOH	-2.57	-3.75	-1.72
CH ₄	-0.23	-0.22	-0.28
C ₂ H ₄	-0.85	-1.02	-0.69
EtOH	-0.50	-0.45	-0.48
PrOH	-0.60	-0.51	-0.57

Conclusion

Cu particles phase pure and with homogeneous morphology were synthesized for the first time by a sol-gel process called urea-glass-route. The particles were tested toward CO₂RRs showing a total FE above 90%. The higher FE toward the production of C₂H₄ with a faradaic efficiency up to 33% at an applied potential of -1.0 V, one of the highest FE reported so far, without using expensive support. Interesting, the FE_{CO} and FE_{HCOO} decrease, when a more negative potential is applied, while for production of methane, a more negative applied potential (-1.1V versus RHE) was proved to be the most suitable.

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