Electrochemical Reduction of CO$_2$ using Supported Cu$_2$O Nanoparticles

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The oxidation state of Cu is reported to have a significant effect on its product selectivity during CO$_2$ electroreduction. For metallic Cu, it is widely accepted that CO and HCOOH are the main products formed at low overpotentials, while hydrocarbons (notably CH$_4$ and C$_2$H$_4$) become the dominant products at higher potentials [1,2]. However, a few groups have reported CH$_3$OH as a major product using pre-oxidized Cu electrodes [3] or supported Cu$_2$O nanoparticles [4]. It has also been reported that supported Cu$_2$O layers, although being reduced to Cu metal under CO$_2$ reduction conditions, result in a decreased overpotential for CO formation, relative to Cu metal [5].

In this study we examine the stability and product selectivity of CO$_2$ electroreduction using colloidally prepared Cu$_2$O nanoparticles [4]. The starting solution of aqueous CuCl$_2$ with polyethylene glycol (PEG) surfactant is reduced using L-ascorbic acid sodium (LAAS), aged for 6 hours, then rinsed with deionized water. The resulting slurry is mixed with a Nafion/ethanol solution, sonicated for 10 minutes, and dried onto Toray carbon paper. The CO$_2$ reduction experiments are performed using a two compartment cell with a Nafion membrane separator, a Pt wire counterelectrode, and Ag/AgCl reference electrode. The working electrolyte is aqueous 0.5M KHCO$_3$ that is bubbled continuously with CO$_2$. Product concentrations are determined using gas chromatography. Gas phase products (H$_2$, CO, CH$_4$, and C$_2$H$_4$) are sampled directly from the CO$_2$ purge gas leaving the reactor. Liquid products (mainly CH$_2$H$_5$OH) are measured by taking syringe samples of the electrolyte at 15 minute intervals.

The SEM images of freshly prepared electrodes show the cubic morphology expected for Cu$_2$O particles, as reported by Chang *et al*. [4]. X-ray diffraction measurements confirm that only peaks assigned to the Cu$_2$O phase are present (i.e., no peaks assignable to metallic Cu are observed). After being used for CO$_2$ reduction (i.e., 120 minutes at −1.745 V(SCE), the XRD measurements indicate that nearly all of the Cu$_2$O is reduced to Cu metal. The SEM images show the reduced electrode material retains the same cubic morphology as the starting Cu$_2$O nanoparticles, but the surface of the cubes become decorated with much smaller clusters.

The CO$_2$ reduction experiments are performed at a single potential, −1.745 V(SCE). This potential is selected to be well into the region for CH$_4$ and C$_2$H$_4$ formation on Cu electrodes [1,6]. For our supported Cu$_2$O nanoparticle electrodes at this potential, the largest CO$_2$ reduction product is C$_2$H$_4$, with a Faradaic efficiency of 34%. We also observe the formation of C$_2$H$_5$OH in parallel to C$_2$H$_4$, with a Faradaic efficiency of about 6%. In contrast, the formation rate of CH$_4$ is much lower, with a Faradaic efficiency of only 1%. (The largest overall product in these experiments is H$_2$, which we attribute to H$_2$O reduction on the incompletely covered carbon support. Control experiments using both unmodified and Nafion-treated carbon paper confirm very low activity for CO$_2$ reduction in the absence of Cu$_2$O nanoparticles on these supports.)

The most noticeable feature of the CO$_2$ reduction behavior using the supported Cu$_2$O nanaparticle electrodes appears to be the large C$_2$H$_4$/CH$_4$ product ratio. At our selected electrode potential of −1.75 V(SCE), Hori *et al*. [6] reported that CH$_4$ formation actually exceeded C$_2$H$_4$ formation by a factor of 2 on polycrystalline Cu. Using single crystal studies, the group later showed the C$_2$H$_4$/CH$_4$ ratio is sensitive to surface structure, with C$_2$H$_4$ formation being favored on higher index surfaces [7]. The highest ratio they reported (i.e., observed using the Cu(711) surface) was C$_2$H$_4$:CH$_4$ = 14:1, which approaches the value reported here. More recently, Schouten *et al*. [8] were able to resolve separate pathways for C$_2$H$_4$ and CH$_4$ formation on Cu(111) and Cu(100) surfaces, with the latter (somewhat) more open surface providing an independent, lower energy pathway for C$_2$H$_4$ formation.

Our present results support a model in which the Cu$_2$O particles are converted to metallic Cu during CO$_2$ reduction. The morphological evolution of the starting Cu$_2$O nanoparticles during this reduction leads to the formation of more highly dispersed Cu clusters on the surface of the converted particles. The dispersed Cu clusters are expected to contain a higher concentration of more open crystal faces and lower co-ordination surface atoms, which leads to the observation of a higher C$_2$H$_4$/CH$_4$ ratio, relative to low-index planar Cu surfaces. Additional work is underway to further characterize these dispersed Cu clusters, and to explore methods to improve their stability during prolonged electrochemical operation.

References

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