Electroreduction of Carbon Dioxide to Hydrocarbons Using Bimetallic Cu–Pd Catalysts with Different Mixing Patterns

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Supporting Information

ABSTRACT: Electrochemical conversion of CO2 holds promise for utilization of CO2 as a carbon feedstock and for storage of intermittent renewable energy. Presently Cu is the only metallic electrocatalyst known to reduce CO2 to appreciable amounts of hydrocarbons, but often a wide range of products such as CO, HCOO−, and H2 are formed as well. Better catalysts that exhibit high activity and especially high selectivity for specific products are needed. Here a range of bimetallic Cu–Pd catalysts with ordered, disordered, and phase-separated atomic arrangements (Cuat:Pdat = 1:1), as well as two additional disordered arrangements (Cu3Pd and CuPd3 with Cuat:Pdat = 3:1 and 1:3), are studied to determine key factors needed to achieve high selectivity for C1 or C2 chemicals in CO2 reduction. When compared with the disordered and phase-separated CuPd catalysts, the ordered CuPd catalyst exhibits the highest selectivity for C1 products (>80%). The phase-separated CuPd and Cu3Pd achieve higher selectivity (60%) for C2 chemicals than CuPd3 and ordered CuPd, which suggests that the probability of dimerization of C1 intermediates is higher on surfaces with neighboring Cu atoms. Based on surface valence band spectra, geometric effects rather than electronic effects seem to be key in determining the selectivity of bimetallic Cu–Pd catalysts. These results imply that selectivities to different products can be tuned by geometric arrangements. This insight may benefit the design of catalytic surfaces that further improve activity and selectivity for CO2 reduction.

Atmospheric CO2 levels recently have reached 400 ppm and are expected to continue to rise. This increase in CO2 levels has been associated with undesirable climate effects such as global warming, rising sea levels, and more erratic weather patterns. A variety of strategies (e.g., switching to renewable energy sources, enhancing the energy efficiency of buildings and cars, and capturing carbon from point sources) needs to be pursued to reduce CO2 emissions and, thereby, curb the increase in atmospheric CO2 levels. Another promising strategy to help address the issue of high atmospheric CO2 levels is the electrochemical reduction of CO2 to useful intermediates or fuels such as formic acid, carbon monoxide, hydrocarbons, and alcohols. This process can be driven by the vast amounts of intermittent excess electricity that are becoming available with the rapid increase in the number of solar and wind power plants.

Although the electroreduction of CO2 to value-added products has promise, the high overpotential of this reaction and low activity of the currently known catalysts still hamper this process from becoming close to commercialization. Cu is the only catalyst known to electrochemically convert CO2 to hydrocarbons and/or oxygenates at considerably high Faradaic efficiency (FE), but it also produces other products such as CO, HCOO−, and H2 at fairly high FEs. Intensive research efforts, both experimental (nanostructured Cu catalyst, oxide-derived Cu catalyst, etc.) and theoretical (key intermediates, different reaction pathways, etc.), have focused on improving the overpotential and selectivity of Cu catalysts for the electroreduction of CO2 to a specific product. However, the observed Faradaic efficiencies for both C1 and C2 chemicals are typically below 40%. Norskov et al. suggested developing bimetallic Cu-based catalysts to break the scaling relationship and stabilize the reaction intermediate to lower the overpotential. Recently, experimentalists have started to develop various Cu-based bimetallic catalysts such as Au–Cu nanoparticles, polymer-supported CuPd nanolalloys, and Au@Cu core@shell nanoparticles for CO2 reduction. However, most of these studies only focused on improving the selectivities for C1 products. Also, these reports only studied the effect of composition (ratio of two metals). To date the lack of bimetallic catalysts with well-defined arrangement of respective metal atoms has prevented study of the effect of structure (different mixing patterns of two elements) on product distribution. Here, we pursue a major challenge, the synthesis and characterization of bimetallic catalysts with well-defined elemental arrangements, specifically bimetallic Cu–Pd catalysts with different elemental arrangements (ordered, disordered, phase-separated, Figure 1a) and different atomic ratios (1:3 to 3:1) to study the effect of structure and composition on catalyst activity and selectivity for CO2 reduction. Possible active sites for the production of C2...
The absence of the characteristic peak of the ordered B2 structure around $2 \theta = 30^\circ$ ((001) plane) suggests that the Cu and Pd atoms form a disordered structure in this sample. XRD data also reveal that the sample we will refer to as phase-separated is composed of three separate phases: fcc-type Cu, Cu$_2$O, and fcc-type Pd (Figure S1c).

High-resolution transmission electron microscope (HR-TEM) measurements showed that three CuPd alloys indeed have different morphologies and particle sizes (Figure 1c–e): the ordered sample consists of interconnected crystalline features with a particle size of ~50 nm; the disordered sample consists of uniform spheres with a particle size of ~5 nm; the phase-separated sample consists of two aggregates with distinct morphologies: (1) spherical particles ~50 nm in size and (2) an interconnected structure with smaller particles ~20 nm in size.

We also examined the chemical microstructure of these three different CuPd alloys using a scanning transmission electron microscope combined with EDS (STEM-EDS) to yield high-angle annular dark-field STEM (HAADF-STEM) images and STEM-EDS maps of the alloys (Figure 1f–k). Similar morphologies as shown in the HR-TEM images were evident from the HAADF-STEM images; however, clear differences in the elemental distributions were observed. The EDS mapping of the ordered sample (Figure 1i) shows that Cu (red) and Pd (green) atoms are homogeneously distributed, forming an ordered intermetallic structure. We could not find large domains composed of only Cu or Pd throughout the disordered alloy particles (Figure 1j). XRD data indicate that this sample has a solid-solution type alloy structure that contains small domains of Cu atoms due to its disordered character (Figure 1a). In contrast, the EDS mapping of the phase-separated sample exhibits separate phases of Cu and Pd elements; within each phase, most of the neighboring sites are from the same element (Figure 1k). In summary, these STEM-EDS results are in good agreement with the XRD results; we successfully obtained ordered, disordered, and phase-separated mixing patterns in the samples.

X-ray photoemission spectroscopy (XPS) results combined with Auger spectra (Figure S2) show that different valence states of Cu exist on the surface of the different bimetallic Cu−Pd samples due to the differences in their elemental arrangement. Note, however, that the initial amount of Cu oxides on the surface does not affect the product distribution significantly in the electroreduction of CO$_2$, as previously reported.19

To evaluate activities of catalysts for CO$_2$ reduction, each bimetallic Cu−Pd catalyst was deposited onto a gas diffusion layer to form a gas diffusion electrode (GDE), which was assembled in a flow reactor that we reported previously.19 The electrolysis was performed in a 1 M KOH electrolyte in potentiostatic mode under ambient conditions. Gas- and liquid-phase products were analyzed by gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy, respectively. Figure S3 shows the single electrode polarization curves of the ordered, disordered, and phase-separated samples with Table S2 summarizing total current densities (CDs) using different potentials. The phase-separated sample achieves the highest total CD of 370 mA cm$^{-2}$, while the ordered sample has the lowest total CD, indicating that the phase-separated sample exhibits the highest overall production rate among these three samples.

Figure 2a–2d show Faradaic efficiencies (FEs) as a function of cathode potential for each of the major products using the ordered, disordered, and phase-separated CuPd samples. At cathode potentials more positive than −0.3 V$_{RHE}$, the CO FE is
The higher CH4 FE observed for the disordered sample may be due to the ordered structure, Cu intermediate with the oxygen atom partially adsorbed on the Pd. The ordered CuPd catalyst, with the latter converting adsorbed CO to C2 chemicals more easily than the phase-separated catalyst. The ordered CuPd converts adsorbed CO to C2 products, we suspect that the catalyst structure with dominant neighboring Cu atoms. The CH4 FEs for both Cu3Pd and CuPd3 are lower than that for the disordered CuPd, probably due to the lower amount of Cu–Pd intermetallic sites within these two samples compared to the disordered CuPd. The disordered CuPd, Cu3Pd, and CuPd3 have different FEs for C2 chemicals despite their similar morphology. The fact that the phase-separated CuPd achieves the highest total current density (Cu-1 data from prior work under the same condition), and Pd nanoparticles, are provided in Figure 3. As the concentration of Cu increases from 0.16 to 0.31, the FE for CH4 decreases, while the FE for C2C2H4 increases. Theoretical studies indicate that the formation of CH4 and C2 chemicals proceeds through different reaction pathways as proposed previously.

To study the effect of composition on catalyst activity and selectivity, we prepared two samples with different Cu:Pd ratios for the disordered structure: Cu3Pd (Cuat:Pdat = 3:1) and CuPd3 (Cuat:Pdat = 1:3). The HR-TEM data (Figure S4) show that the morphologies of Cu3Pd and CuPd3 resemble the disordered CuPd sample. The crystalline structure of Cu3Pd is similar to that of the disordered CuPd sample, with some shoulder peaks around 35°–40° indicating the existence of oxides, while the crystalline structure of CuPd resembles that of fcc-type Pd (Figure S5).

Next, we performed electrochemical characterization: The FEs for various products using these two samples, as well as the disordered CuPd sample, Cu nanoparticles (Cu-1 data from prior work under the same condition), and Pd nanoparticles, are provided in Figure 3. As the concentration of Cu increases from

Figure 2. Faradaic efficiencies for (a) CO; (b) CH4; (c) C2H4; (d) C2H5OH for bimetallic Cu–Pd catalysts with different mixing patterns: ordered, disordered, and phase-separated.

Figure 3. Faradaic efficiencies for (a) CO; (b) CH4; (c) C2H4; (d) C2H5OH for catalysts with different Cu:Pd ratios: Cu, Cu3Pd, CuPd, CuPd3, and Pd.
separated samples, as well as Cu and Pd nanoparticles, were collected. The d-band centers of these samples relative to the Fermi level are plotted in Figure 4. According to Hammer and Norskov, \(^{(2)}\) for different transition metals, a lower d-band position (relative to the Fermi level) leads to weaker binding between the intermediate and the catalyst surface due to the occupancy of antibonding states. Phase separated CuPd has the lowest lying d-band center, while Cu nanoparticles have the highest lying d-band center (Figure 4), which indicates that the phase separated CuPd should have the weakest binding, while Cu nanoparticles should have the strongest binding with CO. However, since phase separated CuPd and Cu nanoparticles have similar catalytic selectivity and activity, geometric/structural effects probably play a more important role rather than electronic effects to determine catalytic selectivity and activity among various alloy samples in this study. Specifically, we suspect that the different mixing patterns of Cu and Pd atoms in various samples cause different orientations of the intermediate on the surface, therefore leading to different selectivities. In homogeneous catalysis, the orientation of intermediates toward the active site affects reaction activity. \(^{(2)}\) Here, we suspect similar effects occur on the alloys with different mixing patterns.

In summary, through the synthesis and characterization of bimetallic Cu–Pd catalysts with different elemental mixing patterns and compositions, we demonstrate that mixing patterns of the components play an important role in determining each catalyst’s activity and selectivity. The sample that features neighboring Cu atoms (phase-separated) favors production of C2 products, while the sample that features the alternating Cu–Pd arrangement favors the production of CH₄. This finding provides insight for the design of even better Cu-based alloy catalysts for the conversion of CO₂ to desired products. Maintaining the neighboring Cu sites while alloying with other transition metal atoms seems to be important. Computational studies on determining the actual number of Cu atoms within the active site for the production of C₂ chemicals would be desired in the future.

**REFERENCES**