Tuning Catalytic Selectivity at the Mesoscale via Interparticle Interactions

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ABSTRACT: The selectivity of heterogeneously catalyzed chemical reactions is well-known to be dependent on nanoscale determinants, such as surface atomic geometry and composition. However, principles to control the selectivity of nanoparticle (NP) catalysts by means of mesoscopic descriptors, such as the interparticle distance, have remained largely unexplored. We used well-defined copper catalysts to deconvolute the effect of NP size and distance on product selectivity during CO2 electroreduction. Corroborated by reaction-diffusion modeling, our results reveal that mesoscale phenomena such as interparticle reactant diffusion and readsorption of intermediates play a defining role in product selectivity. More importantly, this study uncovers general principles of tailoring NP activity and selectivity by carefully engineering size and distance. These principles provide guidance for the rational design of mesoscopic catalyst architectures in order to enhance the production of desired reaction products.

KEYWORDS: copper, nanoparticles, electrocatalysis, CO2 electroreduction, methane, CO

INTRODUCTION

The direct electrocatalytic reduction of CO2 to hydrocarbons is a highly promising pathway to high-value chemicals and fuels. If realized on an industrial scale, it would not only provide a chemical storage technology for renewable electricity ("Power-to-X" technologies), but the capture and reutilization of CO2 would mitigate the detrimental environmental consequences caused by rising atmospheric CO2 concentrations. Much attention has been focused on copper as a CO2 electroreduction catalyst, since it is the only metal that can convert CO2 to appreciable amounts of hydrocarbons. However, problems remain with high overpotentials, low current densities, and poor selectivity to desired products.1,2

In an effort to improve catalyst design, many recent theoretical3−7 and experimental8−12 studies have investigated the mechanism of CO2 reduction over different copper single-crystal electrodes, and also nanostructured copper catalysts,13−20 revealing highly interesting insights into the structure-sensitivity of this reaction. Since insights gained from studies on bulk single-crystal surfaces cannot fully explain reactivity and selectivity results from nanostructured catalysts, further work on model, highly controlled nanoscale systems is needed to uncover the unique reaction mechanism on these catalysts.

Investigations of nanostructured copper catalysts have focused on the effect of surface structure on the CO2 electroreduction reaction, particularly with respect to the change in binding energy of reactants and reaction intermediates on different surface sites.1,2 However, the effect of nanocatalyst structure on the reaction at the mesoscale, up to this point, has been overlooked. An important structural parameter of nanoscale catalysts is the interparticle (IP) distance, which can significantly affect mass transport during a reaction. Several studies have investigated mass transport effects in the oxygen reduction,21−28 CO oxidation,29−31 and alcohol oxidation32,33 reactions. However, further information is needed on transport phenomena for small, nanometer-sized electrocatalysts, which can account for both size and IP distance effects during multistep, multiproduct reactions.

CO2 electroreduction is a kinetically complex reaction that can produce CO, HCOOH, CH4, or C2H4; therefore, reactant mass transport and readsorption phenomena are expected to play a significant role in catalyst activity and selectivity. Here, we present a comprehensive analysis on how the IP distance and size of NP ensembles affect their catalytic product selectivity for the electrocatalytic reduction of CO2. Our analysis of reaction-diffusion processes at the mesoscale not only deconvolutes the individual roles of NP size and distance,
but, more importantly, uncovers previously unaddressed principles governing the catalysis of NP ensembles in general, and that of the electroreduction of CO$_2$ in particular. We propose the "IP distance" as a largely overlooked, yet important experimental mesoscopic descriptor for selectivity that provides a deeper mechanistic understanding, as well as predictive control of catalyst activity and selectivity in the conversion of CO$_2$ to hydrocarbons.

**RESULTS AND DISCUSSION**

The inverse micelle encapsulation technique allows for the synthesis of highly ordered NP arrays with a controlled, uniform size and tunable IP spacing. In this study, three different Cu NP sizes with various IP distances were synthesized using this method. Further details are given in the Supporting Information. Figure 1 shows atomic force microscopy (AFM) images of 4.7 nm Cu NPs dip-coated multiple times onto SiO$_2$/Si(111) acquired after ligand removal: (a) 1 coat and (b) 5 coats, corresponding to IP distances of 53 and 24 nm, respectively. (c) Linear sweep voltammogram at 5 mV/s in CO$_2$-saturated 0.1 M KHCO$_3$ on 4.7 nm Cu NP samples with different average IP distances (24, 31, and 53 nm) supported on glassy carbon.

![Figure 1. Characterization of Cu NPs with varied IP distances. Atomic force microscopy (AFM) images of 4.7 nm Cu NPs dip-coated multiple times onto SiO$_2$/Si(111) acquired after ligand removal: (a) 1 coat and (b) 5 coats, corresponding to IP distances of 53 and 24 nm, respectively. (c) Linear sweep voltammogram at 5 mV/s in CO$_2$-saturated 0.1 M KHCO$_3$ on 4.7 nm Cu NP samples with different average IP distances (24, 31, and 53 nm) supported on glassy carbon.](image)

AFM images and corresponding histograms are shown in Figure S1 in the Supporting Information.

To characterize the catalytic activity of these NPs as a function of the IP distance, the NPs were deposited on glassy carbon plates and used as working electrodes during CO$_2$ electroreduction. Linear sweep voltammetry (LSV) voltammograms were measured up to a potential of $E = -1.12$ V vs RHE in 0.1 M KHCO$_3$. The electrolyte was saturated with CO$_2$ and kept well mixed by bubbling CO$_2$ at a constant flow of 30 mL/min through the bottom of the cell. LSV measurements on the 4.7 nm NPs with various IP distances are shown in Figure 1c. Additional LSV data for all samples are provided in Figure S2 in the Supporting Information. The stability of the NPs during the reaction was confirmed by measuring AFM on HOPG and SiO$_2$/Si(111) supported NPs after the electrochemical measurements (Figures S3 and S4 in the Supporting Information). The AFM measurements confirmed that no sintering, loss of material, or change in IP distance occurred during the reaction.

To investigate changes in selectivity with IP distance, reaction products were sampled using gas chromatography (GC) after 10 min of reaction at $E = -1.12$ V vs RHE, and Faradaic selectivity was calculated as described in the Supporting Information. The changes in Faradaic selectivity with IP distance for catalysts with three different sizes are shown in Figure 2. A change in Faradaic selectivity, as a function of IP distance, is observed for the 1.5 and 4.7 nm NPs (Figures 2a and 2b), while a much smaller variation is detected for the largest (7.4 nm) NPs (Figure 2c). Interestingly, the 1.5 nm particles showed a different trend in selectivity from the 4.7 nm particles. To confirm the trend for the smallest NPs, the Faradaic selectivity for a similarly sized NP (1.9 nm) with an IP distance of 27 nm is also plotted in Figure 2a.

The complex trends observed in the Faradaic selectivities indicate that the activity and selectivity of NP catalysts for the CO$_2$ electroreduction reaction cannot be understood solely in terms of NP size and its effect on the binding strength of reactants. In addition to these nanoscale phenomena, mesoscale processes such as mass transport through diffusion, the readsorption of reaction intermediates on a given NP or, if spaced closely enough, on neighboring NPs should be considered.

The first mesoscale transport process that we will consider is the diffusion of reactants to the NP surface. Under our experimental conditions, the CO$_2$ bubbles fed into the reaction cell lead to a forced convection in the electrolyte and a uniform reactant concentration in the bulk of the electrolyte. However, very close to the electrode surface, the electrolyte may be considered stationary, and the diffusion process is the only pathway for mass transfer through this region. Mass-transfer transport phenomena within the diffusion layer determine how the reactants diffuse toward the NPs, as well as how the reaction products leave the NPs and enter the bulk of the electrolyte. Limitations in mass transfer are expected to hinder the reaction rate (e.g., current density).

In order to understand how mass-transfer effects may contribute to the electrocatalytic activity of our NPs, calculations were carried out to elucidate the changes in the CO$_2$ reaction rate, because of the diffusion processes. Finite-element calculations were used to solve Poisson’s equation and to obtain the spatial distribution of CO$_2$ at the NP surface. The diffusive flux of reactants, which is linearly proportional to the concentration gradient, was calculated following Fick’s first law.
It was assumed that the CO₂ concentration is constant outside the Nernst layer and that the CO₂ that reaches the NP surface reacts very quickly, resulting in zero CO₂ concentration at the NP surface. These two criteria were applied as the boundary conditions for the diffusion equations. Figure 3a shows calculation results for 7.4 nm NPs with an IP distance of 36 nm. The surface of the upper hemisphere of the NPs provides a higher contribution to the reaction, since the electrolyte in contact with the bottom hemisphere of the NP has a lower concentration of the reactants (depleted red color region). Figure 3b shows the normalized CO₂ flux to the surface of NPs with different sizes (d = 1.5, 4.7, and 7.4 nm) and IP distance. For a given NP size, Figure 3b shows that the normalized CO₂ flux is higher for NP arrangements with large IP distance and reaches a plateau for IP/d values larger than ∼10. The latter represents a threshold value above which the NPs can be considered as single NPs on an infinite support. However, for smaller IP distances, NPs can affect neighboring particles by depleting their reactant concentrations. This phenomenon is observed as an overlap in the diffusion profile that limits the available reactant concentration on the NP surface and reduces the normalized CO₂ flux, which leads to a decrease in the current density of the CO₂ reduction reaction (Figure 3b).

In Figure 3b, it is clear that the CO₂ flux saturates at a higher value for smaller NPs. However, the calculated reactant flux cannot be directly correlated to the current density, since the real number of electrons involved in the reaction per CO₂ molecule consumed is strongly dependent on the reaction products. Therefore, a large increase in the current density is expected when the selectivity shifts from CO and H₂ toward ethylene and methane. However, in cases where the selectivity remains almost constant, such as for our largest (7.4 nm) NPs, the electroreduction current will be proportional to the reactant flux. Figure 3c shows the experimental current density at −1.1 V vs RHE for the 7.4 nm NPs, as a function of the IP/d ratio, which shows good agreement with the trend in reactant flux obtained from theory in Figure 3b. The current density toward H₂ evolution will be similarly governed by the diffusion of H⁺ to the NP surface. As shown in Figure S5 in the Supporting Information, partial current densities toward CO₂ reduction and H₂ evolution both increase with increasing IP/d ratio for the 7.4 nm Cu NPs.

Figure 3b shows that above an IP/d ratio of ∼10, the reactant flux to the NP surface reaches a plateau and is not strongly affected by further increasing the IP distance for each NP size. Therefore, it is reasonable to assume that, in the large IP distance regime, the NPs are sufficiently far away from each other that only the NP size influences the selectivity, not the IP distance. In order to see this size effect, the Faradaic selectivity was plotted as a function of NP size only for samples with the largest IP distances (see Figure 4). In addition to these three sizes, measurements of 1.9 and 2.3 nm NPs with large IP/d ratios (14 and 10, respectively) were added to confirm the trends for the smallest NPs. As expected, the readsorption and
further reduction of reaction intermediates, such as CO, is limited by the decreased availability of neighboring particles, resulting in higher selectivity toward reaction intermediates for these samples. The H₂ and CO production do not vary for large NPs (4.7 and 7.4 nm), while there is a significant increase in CO and a suppression in H₂ production for the smallest NPs (Figure 4a). The suppression of H₂ may be assigned to CO poisoning (blockage of active surface sites by CO) that has been reported in the past for very small NPs with enhanced CO binding energy. Smaller NPs may have enhanced binding to reactants and intermediates due to low coordinated sites at the surface or altered electronic properties, such as the increase in the work function expected with decreasing NP size. In addition, the adsorbed CO will weaken the binding strength of the H⁺, H₂ evolution intermediate on Cu, which further suppresses H₂ production.36

Because of the large IP distances considered here, the readsorption of reaction intermediate species originating from one NP onto a neighboring NP is unlikely. Therefore, self-readsorption processes are likely the only pathways leading to hydrocarbon production. This explains why the C₂H₄ production pathway, where the largest number of reaction steps is involved, is low for all NP sizes (Figure 4b). Also, since the probability of intermediate self-readsorption is proportional to the NP size (α d³), an increase in the CH₄ production rate is expected with increasing NP size, in excellent agreement with our experimental data.

For larger copper coverages, the IP distance may be small enough to allow the diffusive transfer of reaction intermediates between neighboring NPs. Therefore, in addition to the NP size, the IP distance should also be taken into account in order to understand the selectivity trends. The Faradaic selectivity for the smallest IP distances of each NP size is shown in Figure 5.
significantly higher hydrocarbon production, which consumes the CO intermediate.

Despite the fact that the electrolyte used in this study (CO₂/HKCO₃) is known to have a buffer effect, the increased hydrocarbon production is expected to result in a local increase in the electrolyte pH. Considering that the number of H⁺ species consumed to make hydrocarbon products is large, and that the normalized current densities on NPs are much higher than those on Cu foils, the buffer characteristic of the electrolyte may not be sufficient to counteract the rise in local pH at the surface of the NPs. Furthermore, an increase in local electrolyte pH would directly suppress the hydrogen evolution reaction by shifting its reversible potential more cathodically. Our experimental results in Figure 5 show a decrease in H₂ production at high Cu coverage where the hydrocarbon selectivity is highest, possibly due to local increases in pH near the NP surface.

It is clear from this work, using NP samples with controlled interparticle distances, that diffusion and adsorption phenomena are critical processes during CO₂ electroreduction. However, to gain further insight into these phenomena, further studies of the effect of CO₂ mass transport to the electrode surface would need to be performed. While the experiments conducted here were done under a constant flow of CO₂ in a well-mixed solution, it is difficult to quantify and control the transport of CO₂ to the catalyst. A possible method to allow this is to use a flow cell configuration in which the CO₂ saturated electrolyte is flowed in a thin layer over the catalysts at a controllable rate. Other opportunities for further investigation include getting a better understanding of the catalyst morphology during the reaction and finding alternative methods to quantify the electrochemically active surface area. For the latter, Pb underpotential deposition might be used.

CONCLUSIONS

In summary, we have demonstrated that exceptional control over the catalytic selectivity of Cu NPs of different size during the CO₂ electroreduction reaction can be achieved through variation of the IP distance. Through the synthesis and electrochemical characterization of Cu NPs with highly controlled size and spacing, we gained insight into mesoscale transport phenomena such as diffusion of reactants to the catalyst surface and adsorption of intermediate species. These results were further corroborated by theoretical calculations. Small IP distances are required to allow the adsorption and subsequent reduction of the CO intermediate to hydrocarbons. Larger NP sizes also allow the adsorption of reaction intermediates onto the same NP for further reaction, while small NPs may be affected by the poisoning of active sites by CO.

This study highlights previously unaddressed aspects in our understanding of product selectivity through the exploration of mesoscale transport processes and mesoscopic descriptors, while building on current knowledge of nanoscale structure-reactivity correlations. But more generally, this work uncovers catalyst design principles of fundamental importance for many heterogeneous catalyzed chemical processes with multiple products occurring on the surface of NP ensembles. Such design principles can aid in improved chemical product selectivity and yields for energy and environmental needs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b02202.

Experimental methods including details on sample preparation, electrochemical measurements, NP characterization, and diffusion calculations (PDF)

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Notes

The authors declare no competing financial interest.

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