

Nitrogen-Based Catalysts for the Electrochemical Reduction of CO₂ to CO

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S Supporting Information

ABSTRACT: The synthesis and application of carbon-supported, nitrogen-based organometallic silver catalysts for the reduction of CO₂ is studied using an electrochemical flow reactor. Their performance toward the selective formation of CO is similar to the performance achieved when using Ag as the catalyst, but comparatively at much lower silver loading. Faradaic efficiencies of the organometallic catalyst are higher than 90%, which are comparable to those of Ag. Furthermore, with the addition of an amine ligand to Ag/C, the partial current density for CO increases significantly, suggesting a possible co-catalyst mechanism. Additional improvements in activity and selectivity may be achieved as greater insight is obtained on the mechanism of CO₂ reduction and on how these complexes assemble on the carbon support.

The electrochemical reduction of CO₂ offers a potentially economically viable route to recycle CO₂, with the goal to reduce CO₂ emissions and to reduce our dependence on fossil fuels.¹ Specifically, CO₂ can be reduced to CO, an intermediate for the production of chemicals and fuels.² However, this “artificial photosynthesis” via an electrochemical process for CO₂ reduction is inhibited by the lack of catalysts for CO₂ reduction with (a) sufficiently low overpotentials to be energetically efficient^{1,3–5} and (b) high enough current densities to be profitable.^{1,6} While electron conversion efficiencies of greater than 50% can be obtained, this efficiency comes at the expense of very high overpotentials (~1.5 V).⁷ Consequently, more efficient and higher throughput catalysts are needed.^{3,7–9}

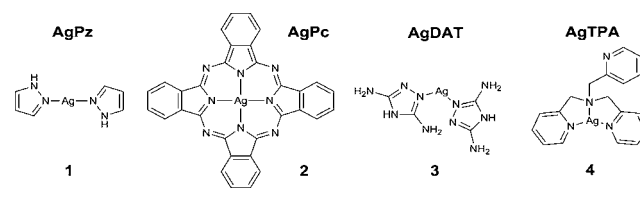
In prior work, four distinct classes of pure metal catalysts have been identified for CO₂ reduction. Those selective for carbon monoxide production include Ag, Au, and Zn. Those selective for formic acid production include Sn, Cd, and Ti. Those selective for hydrogen production include Pt, Ni, and Fe, and those selective to produce a wide range of hydrocarbons include Cu.^{4,10–13} Of these catalysts, we are most interested in studying those selective for CO production as they exhibit the highest energetic efficiencies.¹ Using one of the catalysts selective for CO, Ag, we previously demonstrated that the ionic liquid, EMIM BF₄, serves as a co-catalyst and reduces the onset potential for CO₂ production.³ Similarly, the presence of pyridinium in an electrolyte solution improves the selectivity for electrochemical reduction of CO₂ to methanol at low

overpotentials when using copper as the cathode catalyst.^{14–16} These studies indicate that N-based complexes can significantly assist the electrochemical reduction of CO₂ in terms of reducing the overpotential and increasing the product selectivity. Also, metallophthalocyanines have been shown to improve the catalytic activity of metal catalysts for CO₂ reduction.¹⁷

Here, we interrogate four N-based organometallic silver catalysts with the goal to reduce reaction overpotentials, improve reaction selectivity, and increase reaction rates for CO₂ reduction: (1) silver pyrazole supported on carbon (AgPz/C), (2) silver phthalocyanine supported on carbon (AgPc/C), (3) silver 3,5-diamino-1,2,4-triazole supported on carbon (AgDAT/C), and (4) silver tris[(2-pyridyl)methyl]amine supported on carbon (AgTPA/C). These catalysts were tested on a glassy-carbon electrode in a three-electrode cell, as well as on gas diffusion electrodes (GDE) (carbon paper) in a flow reactor, for their catalytic activity for CO₂ reduction. The Supporting Information (SI) provides details regarding catalyst synthesis.

Scheme 1 shows molecular structures for the catalysts tested here. The crystal structure of AgNO₃ complexed with pyrazole

Scheme 1. Proposed Structures for the N-Based Organometallic Silver Catalysts



is known.^{18,19} The structure of silver phthalocyanine is also known.²⁰ The complex formed when AgNO₃ is added to methyl-substituted TPA is mononuclear.²¹ However, we have not been able to obtain a crystal structure of the unsubstituted TPA ligand complexed with Ag₂SO₄. A structure for the complex formed from the DAT ligand and AgNO₃ has been reported, but the analogous sulfate salt is not known.²² The structural expectations for AgTPA and AgDAT are based on these literature precedents. The role of the carbon support on the resulting structure of these complexes is also unknown.

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We tested the catalytic activity of the synthesized catalysts relative to that of ca. 70 nm diameter Ag nanoparticles (Ag) and 60 wt% Ag (>100 nm diameter) on C (Ag/C) using a flow reactor operated as reported previously.^{3,23} CO and H₂ are the major products, consistent with the results reported in the literature.^{10,24} Based on GC analysis, no products other than CO and H₂ were generated in any of our experiments. Figure 1a shows the partial current density for CO production as a

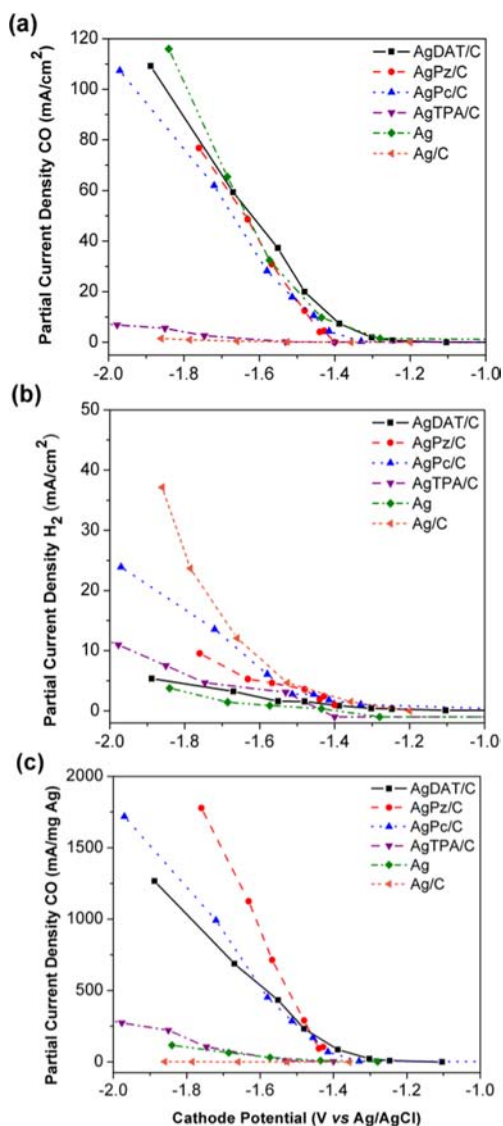


Figure 1. Partial current densities vs cathode potential for (a) CO and (b) H₂ relative to the electrode area, and for (c) CO relative to the cathode silver loading. Data collected at room temperature and ambient pressure; electrolyte, 1 M KOH; catalyst loading, 1 mg/cm²; CO₂ stream, 7 sccm.

function of applied cathode potential with the four cathode catalysts and two Ag catalysts (Ag) and (Ag/C), all at a loading of 1 mg/cm² in the electrochemical flow reactor operated with 1 M KOH as the electrolyte under ambient conditions. Comparable performance was observed with Ag nanoparticles as the cathode catalyst relative to three of the synthesized cathode catalysts, AgDAT/C, AgPz/C, and AgPc/C. Specifically, the partial current density for CO observed with the AgDAT/C, AgPz/C, AgPc/C, and Ag catalysts was approx-

imately 95 mA/cm² at a cathode potential of -1.8 V vs Ag/AgCl. Similar values have been reported for a Teflon-backed Ag GDE (10 cm²), demonstrating current densities of approximately 50 mA/cm² (20 °C) and 80 mA/cm² (80 °C) at approximately -1.7 V vs Ag/AgCl.²⁴ While these four catalysts had comparable performance for CO formation, one of the Ag complex materials, AgTPA/C, and the Ag/C catalyst showed poor kinetics for CO production as seen in Figure 1a. Corresponding partial current densities for H₂ from the six materials (Figure 1b) show that H₂ production is significantly higher when Ag/C is used as the catalyst as compared to the other catalysts.

The advantage of the organometallic catalysts lies in their low mass fraction of silver. Remarkably, the organometallic catalysts exhibit similar performance for the formation of CO compared to the Ag catalyst (Figure 1a), but this performance is achieved at much lower total silver loading (Figure 1c). Specifically, the partial current density for CO production relative to the Ag loading is more than an order-of-magnitude higher when AgDAT, AgPz, or AgPc instead of Ag is used as the cathode catalyst.

Cyclic voltammetry (CV) measurements show that the Ag, AgDAT, AgPz, and AgPc catalysts exhibit a decrease in the onset potential and an increase in the current density in the presence of CO₂ as compared to when Ar is the reactant gas (see Figure S1 in the SI), behavior that confirms the observations from the flow reactor. The Ag/C and AgTPA materials, however, exhibit no change in either the onset potential or current density in the presence of CO₂ instead of Ar. These results suggest that both Ag/C and Ag/TPA are less active for CO₂ reduction relative to the other four materials examined.

Figure 2 demonstrates that AgDAT, AgPz, and AgPc also exhibit significantly higher Faradaic efficiencies for CO

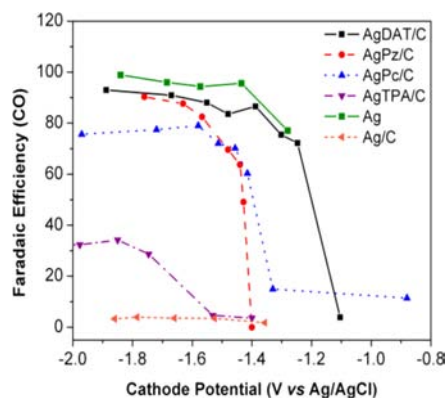


Figure 2. Faradaic efficiency vs cathode potential for the four synthesized catalysts, as well as for Ag and Ag/C.

production relative to AgTPA and Ag/C. Details on the Faradaic efficiency calculation can be found in the SI. Of the organometallic catalysts, the highest Faradaic efficiency (>90%) was achieved using AgDAT/C at cathode potentials below -1.5 V vs Ag/AgCl. Again, similar values have been reported for a Teflon-backed Ag GDE (10 cm²), where Faradaic efficiencies were >90% at potentials below -1.4 V vs Ag/AgCl, albeit with much higher Ag loadings.²⁴

N-containing compounds may act as a co-catalyst in the electrochemical reduction of CO₂ even when introduced as a neat material.³ We were wondering whether the N-containing

ligands examined here might also enhance CO production on a less active material. To examine the co-catalytic efficacy of these ligands, DAT was added to the Ag/C catalyst solution and sonicated before being hand-painted on a Sigracet 35BC electrode. Specifically, DAT was added to the Ag/C catalysts solution such that the DAT to Ag/C ratio was 30 to 100 on a per mass basis. Figure 3 compares the performance of the Ag/C

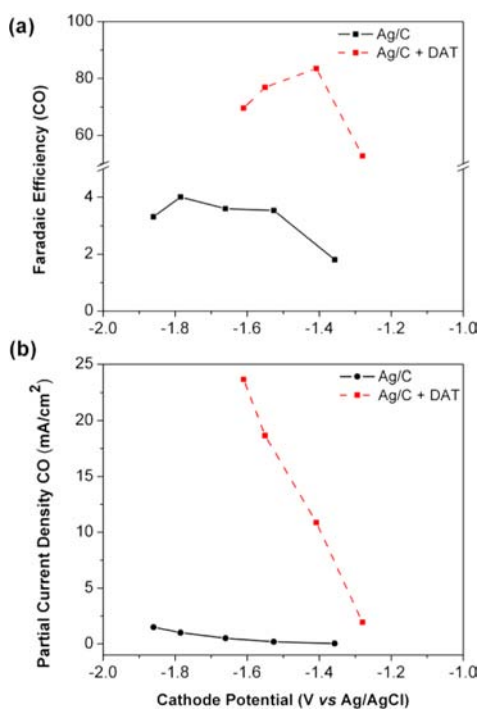


Figure 3. (a) Faradaic efficiency and (b) partial current density as obtained in a flow cell for CO production with a Ag/C electrode as compared to a Ag/C electrode to which DAT was added before hand-painting the catalyst on the Sigracet 35BC electrode.

catalyst to that where the Ag/C catalyst is combined with DAT. The addition of DAT to the catalyst improved the selectivity of the material for CO production as opposed to H₂ by a factor of 20. Control experiments in the absence of Ag (Figure S2 shown in the SI) indicate that the increase in activity upon the addition of DAT cannot be attributed to the presence of DAT alone.

The observation that addition of DAT to the bare Ag surface enhances the Faradaic efficiency for CO production suggests that these nitrogen frameworks may play a critical role as co-catalysts even when not in an organometallic complex. The presence of N-containing compounds in electrolyte solution has previously been shown to influence both product selectivity and kinetics for the electrochemical reduction of CO₂ to CO using a Ag electrode.³ Three of the four N-based organometallic complexes we reported here as catalysts for the electrochemical reduction of CO₂ to CO drastically increase the partial current densities for CO compared to the state-of-the-art Ag catalyst when comparing the catalysts' performances with respect to the Ag loading.

This effect could have a number of possible origins. First, DAT and other ligands possibly could alter the shape and/or size of the Ag particles. Addition of DAT could cause surface and or particle reconstruction, as has been observed in other contexts.²⁵ The complexes themselves may be reduced at the negative potentials utilized here, leading to particles exhibiting the ostensibly special properties. Second, the N-containing

ligands may act as cocatalysts, by, for example, coordinating to the Ag surface and facilitating electron transfer. Of course other mechanisms are possible. Finally, we note that not all of the N-containing species introduced to the carbon surface exhibit the catalytic effect. The AgTPA, in particular, was less active. While the availability of Ag in these materials should not be much different than that found for DAT or the Pc complexes, other features of this ligand may make it less suitable.

A major obstacle to the broader application of the electrochemical reduction of CO₂ lies in simultaneously achieving high current densities and energetic efficiencies.¹ Here, we demonstrated a major step toward improving both the Faradaic efficiencies and current densities of the electrochemical reduction of CO₂ to CO on a Ag cathode. The work reported here suggests that further exploration of the effect of nitrogen-enhanced Ag catalysis on the electrochemical conversion of CO₂ to CO may lead to further improvement of cathode performance. Specifically, further investigation is needed regarding the state of the catalysts before and after reaction operation.

■ ASSOCIATED CONTENT

📄 Supporting Information

Catalyst and electrode preparation, cell assembly, testing procedures, and three-electrode cell cyclic voltammetry. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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📝 Notes

The authors declare no competing financial interest.

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