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► **To cite this version:**

Cyrille Costentin. Hybrid catalyst to the rescue. *Nature Synthesis*, 2023, 2 (12), pp.1134-1135.
10.1038/s44160-023-00391-7 . hal-04682415

HAL Id: hal-04682415

<https://hal.science/hal-04682415v1>

Submitted on 30 Aug 2024

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Electrocatalysis

Hybrid catalyst to the rescue

Cyrille Costentin

Univ Grenoble Alpes, CNRS, DCM, 38000 Grenoble, France

cyrille.costentin@univ-grenoble-alpes.fr

twitter: @costentin

A hybrid carbon nanotube/molecular catalyst achieves highly selective electrochemical conversion of CO to methanol via mechanistic-guided optimizations.

Electrochemical reduction of CO₂ is an attractive pathway for the sustainable production of fuels and commodity chemicals. However, the reaction pathway is complex, with many roads, various destinations and high mountains to climb. Catalysis is therefore required to selectively reach a targeted product (such as carbon monoxide, formic acid, methanol, methane, ethylene, ethanol or acetic acid) in an efficient manner (at high current density and low overpotential). Although the electrochemical conversion of CO₂-to-CO is well-established using either electrocatalysts (such as gold or silver) or molecular catalysts, going beyond CO selectively is still challenging. One interesting strategy which has emerged for methanol production consists of a domino process where CO₂ is first converted to CO, and then CO is converted to methanol. In that regard, cobalt phthalocyanine molecules deposited on carbon nanotubes (CNT) are promising catalysts because, starting from CO, they lead exclusively to methanol as the carbonated product, although the faradaic efficiency is limited to ca. 40% due to concurrent hydrogen production.^{1,2} Improving the methanol yield and the current density is therefore necessary to elevate this transformation to a level required for practical applications.

Now, writing in *Nature Synthesis*, Wang and co-workers report a mechanism-guided selective CO-to-methanol electroreduction catalyzed by a hybrid CNT/molecular catalyst. The optimized catalyst achieves a remarkable 84% faradaic efficiency with a partial current density of 20 mA cm⁻² at -0.98 V vs. reversible hydrogen electrode (RHE).³ A previously

developed, hybrid material electrocatalyst¹ was used and systematic kinetic studies were performed, allowing for the rational design of the experimental conditions, increasing faradaic efficiency and current density. The hybrid electrocatalyst material consists of amine-substituted cobalt phthalocyanine (Pc) molecules supported on carbon nanotubes (CoPc-NH₂/CNT) and deposited on a carbon paper support. As an initial improvement compared to previous studies, the carbon support was modified by coating it with a microporous layer which consisted of carbon particles and fluoropolymers. This modification is intended to increase the limiting diffusion current for CO reduction. The physical effect appears modest as the limiting current density at high overpotential is ca. 15 mA cm⁻² whereas it is ca. 8 mA cm⁻² on the carbon paper. However, an increase of the faradaic efficiency for methanol is observed, reaching 66%. Importantly, it is shown that, at low overpotential, partial current densities for methanol production are free from mass transport contributions, allowing for mechanistic investigation.

A systematic analysis of Tafel plots indicates that the rate determining step for CO-to-methanol conversion involves a proton transfer coupled with an electron transfer (PCET) as attested by the pH-dependence of the overpotential at a given current density vs. standard hydrogen electrode (SHE) and a H₂O/D₂O kinetic isotopic effect. Additionally, it is shown that the major proton donor is H₂O with only a partial contribution from HCO₃⁻ and H₂PO₄⁻/HPO₄²⁻ if the latter couple is used as a buffer. From this kinetic analysis, Wang and co-workers conclude that 0.1 M KHCO₃ is the optimal electrolyte for CO-to-methanol conversion using the CoPc-NH₂/CNT hybrid catalyst. The fractional reaction orders for HCO₃⁻ and H₂PO₄⁻ emphasize the complexity of the role of the electrolyte for proton-coupled electron transfer reactions in aqueous solutions where the pathway of interest is in competition with hydrogen evolution.^{4,5} Finally, the reaction order with respect to CO was determined to be close to one at -1.35 V vs. SHE for CO partial pressures between 0.01 atm and 1 atm. This suggests a low coverage of the catalyst by CO at 1 atm and that enhanced methanol production could be obtained at higher CO pressure. Using a two compartment electrochemical cell and a pressure of 10 atm CO, a remarkable 84% faradaic yield for methanol was obtained in 0.1 M KHCO₃ at -0.98 V vs. RHE with a partial current density of 23.5 mA cm⁻².

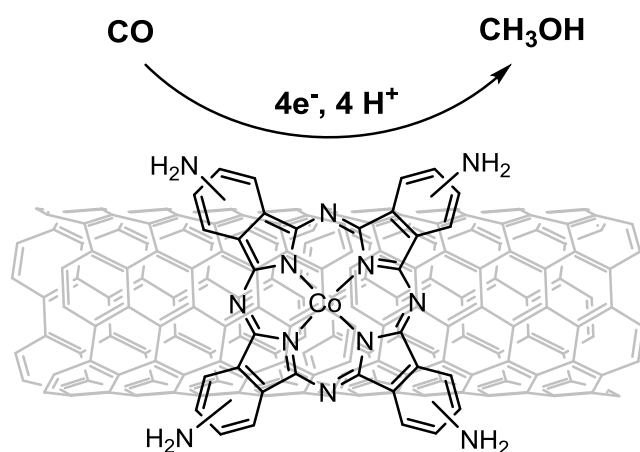
The strategy used by Wang and co-workers to optimize the CO-to-methanol electroconversion, based on mechanistic guidance (mostly centred on the role of the electrolyte), is an interesting approach. The findings of fractional and non-uniform reaction

orders for proton donors reveals the complexity of hybrid catalysts, especially considering that the same research group has previously shown that similar cobalt phthalocyanines are inefficient homogeneous molecular catalysts.⁶ This has stimulated further investigation of the role of the support and more specifically CNT in such hybrid catalysts.⁷ Interestingly, Liu, Robert, Hung and co-workers recently reported in *Nature Communications* the *in-situ* spectroscopic probing of intrinsic features of a similar hybrid catalyst (CoPc/CNT) in electrochemical CO and CO₂ reduction to methanol.⁸ Their strategy differs as they gain insights into the process via detection of intermediates compared to the proposal of a kinetic-based (reaction order) mechanism reported by Wang and co-workers..

Comparison of the studies raises questions, likely to be investigated in future research. A CO-intermediate is observed by *in operando* techniques (X-ray absorption spectroscopy, Fourier-transform infrared spectroscopy), whereas low CO coverage is expected from the kinetic studies of Wang and co-workers. It seems contradictory that a CO-intermediate accumulates after the rate determining step. Additional studies, including kinetic models, would be needed to resolve this apparent contradiction. Importantly, DFT calculations and Raman spectroscopy data reported by Liu, Robert, Hung and co-workers⁸ advocate a protonation at the phthalocyanine ring prior to catalysis that could be consistent with the PCET rate determining state revealed by Wang and co-workers.³ Altogether, this shows that gaining a coherent picture of the behaviour of hybrid catalysts is a complex task and it requires the consideration of not only the molecular catalyst (cobalt phthalocyanines) but also the effect of the support (CNT) and the role of the electrolyte.

Competing interests

The author declares no competing interests.



Kinetic studies lead to optimized conditions

⇒ **High selectivity (> 80% FE)**

Figure. CO to CH₃OH electroconversion catalyzed by hybrid cobalt phthalocyanine/carbon nanotube (CoPc-NH₂/CNT) catalyst. Kinetic studies allowed to define optimized conditions (high CO pressure, 0.1 M KHCO₃, -0.98 V vs RHE) to get high selectivity (> 80 % faradaic yield).

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