Adaptive framework CO_2 catalysis

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Enzymes use adaptive catalytic pocket to accelerate catalysis. Recently published in *Nature Catalysis*, Zhong and coworkers have translated this functionality into a MOF with a Cu-Ni active site in which the Cu-Ni distance changes to stabilize intermediates along the CO_2 to CH_4 pathway and give rise to exceptional catalytic selectivity.

The development of adaptive catalysts is a long-standing challenge and point of interest in the fields of chemistry, materials, and energy science. Synthetic catalysts are often limited by scaling relations, in which the intermediate-catalyst binding energies scale with respect to one another along a liner relationship.[1] This often caps the catalyst efficiency at a certain level as the optimal point for certain reactions lies off of this line. Enzymes have long been studied as a blueprint for catalyst design, and in contrast to conventional inorganic catalysts, they feature an adaptive catalytic pocket that adapts to stabilize key reaction intermediates through interactions with amino acid residues within its hydrophobic interior.[2] These features are a source for inspiration for the development of CO_2 reduction catalysts that aim to use light and/or renewable electricity to generate carbon-based products as alternatives to fossil fuels.[3,4] CO_2 can be reduced to a wide array of possible species, and, thus, rationally steering the reaction pathway toward a particular one is key to attaining a selective catalytic system.

Just published in *Nature Catalysis*, Zhong et al. have translated the adaptability commonly found in enzymes into a synthetic metal-organic framework (MOF) catalyst.[5] In their system, the Zr-oxo nodes within MOF-808 were first functionalized with ethylenediaminetetraacetic acid (EDTA) flexible tethers, which then chelated Cu and Ni ions to

generate dual metal site pairs (DMSPs) and the MOF-808-CuNi final material. *Ab initio* molecular dynamics (AIMD) modeling of the DMSPs elucidated their flexible nature in which the distances between the Cu and Ni readily change.

After characterization with electron microscopy and X-ray absorbance spectroscopy to prove the existence of the DMSPs, MOF-808-CuNi was evaluated as a catalyst within a photochemical CO_2 reduction system with an acetonitrile-water mixed solvent. When combined with a Ru-based photosensitizer and triethanolamine sacrificial reagent, MOF-808-CuNi converted CO_2 to CH_4 under simulated solar illumination with a remarkable selectivity of 97.5% Figure 1. This selectivity was much higher than for MOF-808-Cu (88.7%), MOF-808-Ni (18.8%), or their physical mixture (36.6%). Similarly superior CH_4 selectivity was seen when CO or HCOOH were used in place of CO_2, indicating that the DMSPs can readily adapt to a host of C_1 species. Electron spin resonance indicated that Cu(I) and Ni(I) serve as the active sites for the reaction. In parallel, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to detect several intermediates formed during the reaction, including *CO_2 *CO, *OCH_3 and *CH_3. Theoretical modeling revealed a plausible reaction pathway for CO_2 to CH_4 conversion, and the sum of the theoretical and experimental results point to the adap-

tive nature of the DMSPs as the driving factor behind the high CH_4 selectivity of the system. The distance between the Cu and Ni can fluctuate between 4 and 5 Å, and this distance changes in response to the intermediate adsorbed to stabilize. Further, the fluctuating Cu-Ni distance likely results in the system passing through a configuration which minimizes the energy barrier to the next catalytic step, accelerating the reaction process.

In all, the work presented is certainly an interesting demonstration of a powerful concept in catalysis that has rarely been demonstrated in synthetic systems. It would certainly be worthwhile to see if this can be translated over to other catalytic reactions. For example, can the reaction be run in reverse to oxidize CH_4 to CH_3OH through judicious selection of photosensitizer and sacrificial reagent? Can N-based intermediates be stabilized to convert N_2 to NH_3? Does the same adaptive flexibility and catalytic efficacy remain if other transition metal sites are chelated within the MOF (e.g., Zn, Co, Fe…)? Finally, while the selective nature of the reaction is exceptionally impressive, the quantum efficiency at 420 nm was only 2.31%. This certainly has to be improved upon before the system approaches economic practicality, along with finding a suitable oxidation half reaction (ideally water oxidation) instead of TEOA oxidation.

In parallel, it would be interesting to translate this concept into an electrocatalytic setting in which an applied voltage is used to drive the reaction. Would the DMSPs within the MOFs function similarly in a CO_2 reduction electrolyzer? Which key aspects are necessary: do the DMSPs need to be

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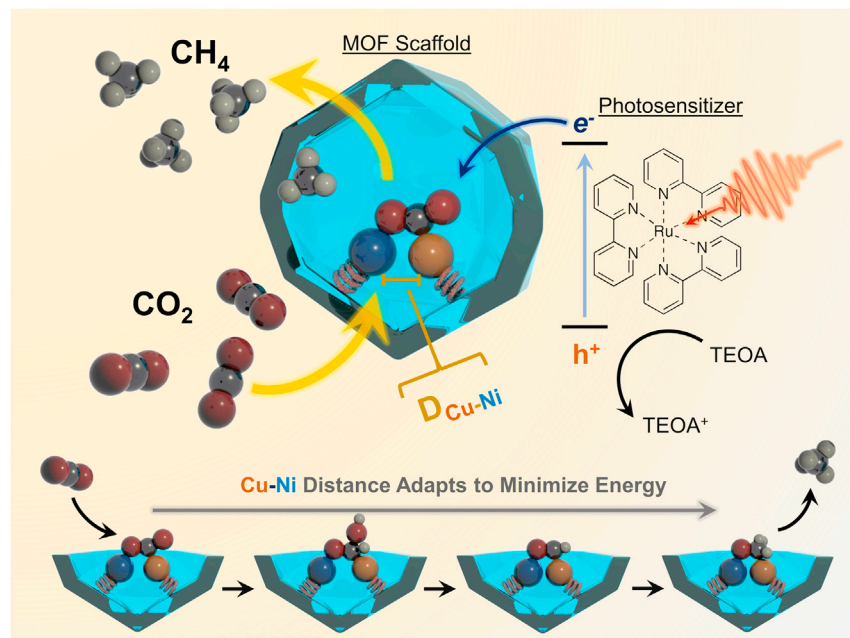
Figure 1. Photocatalytic CO$_2$ to CH$_4$ reduction scheme in which the Cu-Ni DMSPs modulate the Cu distance to stabilize key reaction intermediates en route to CH$_4$ generation

grafted within a MOF, or will a similar chelation strategy suffice if EDTA was grafted on the surface of any heterogeneous scaffold? Extending beyond catalysis, one can imagine that adaptive flexibility within such MOFs can find uses in membranes, gas storage, and sensing, further underlining the power of this concept.

While the complexity of the MOF-808-CuNi system still pales in comparison to that found in enzymes, the demonstration of active site adaptability places MOF-808-CuNi in a growing list of dynamic MOFs[6–9] and is an exciting concept worth pursuing in the drive to develop increasingly effective catalysts.

1. Medford, A.J., Vojvodic, A., Hummelshøj, J.S., Voss, J., Abild-Pedersen, F., Studt, F., Bligaard, T., Nilsson, A., and Nørskov, J.K. (2015). From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis. J. Catal. *328*, 36–42. https://doi.org/10.1016/j.jcat.2014.12.033.

2. Hansen, H.A., Varley, J.B., Peterson, A.A., and Nørskov, J.K. (2013). Understanding Trends in the Electrocatalytic Activity of Metals and Enzymes for CO2 Reduction to CO. J. Phys. Chem. Lett. *4*, 388–392. https://doi.org/10.1021/jz3021155.

3. Li, J., Zhang, Y., and Kornienko, N. (2020). Heterogeneous electrocatalytic reduction of CO2 promoted by secondary coordination sphere effects. New J. Chem. *44*, 4246–4252. https://doi.org/10.1039/C9NJ05892C.

4. Wagner, A., Sahm, C.D., and Reisner, E. (2020). Towards molecular understanding of local chemical environment effects in electro- and photocatalytic CO2 reduction. Nat. Catal. *3*, 775–786. https://doi.org/10.1038/s41929-020-00512-x.

5. Li, J., Huang, H., Xue, W., Sun, K., Song, X., Wu, C., Nie, L., Li, Y., Liu, C., Pan, Y., et al. (2021). Self-adaptive dual-metal-site pairs in metal-organic frameworks for selective CO2 photoreduction to CH4. Nat. Catal. *4*, 719–729. https://doi.org/10.1038/s41929-021-00665-3.

6. Heidary, N., Morency, M., Chartrand, D., Ly, K.H., Iftimie, R., and Kornienko, N. (2020). Electrochemically Triggered Dynamics within a Hybrid Metal-Organic Electrocatalyst. J. Am. Chem. Soc. *142*, 12382–12393. https://doi.org/10.1021/jacs.0c04758.

7. McDonald, T.M., Mason, J.A., Kong, X., Bloch, E.D., Gygi, D., Dani, A., Crocellà, V., Giordanino, F., Odoh, S.O., Drisdell, W.S., et al. (2015). Cooperative insertion of CO2 in diamine-appended metal-organic frameworks. Nature *519*, 303–308. https://doi.org/10.1038/nature14327.

8. Yang, Y., Li, L., Lin, R.-B., Ye, Y., Yao, Z., Yang, L., Xiang, F., Chen, S., Zhang, Z., Xiang, S., and Chen, B. (2021). Ethylene/ethane separation in a stable hydrogen-bonded organic framework through a gating mechanism. Nat. Chem. https://doi.org/10.1038/s41557-021-00740-z.

9. Ehrling, S., Reynolds, E.M., Bon, V., Senkovska, I., Gorelik, T.E., Evans, J.D., Rauche, M., Mendt, M., Weiss, M.S., Pöppl, A., et al. (2021). Adaptive response of a metal-organic framework through reversible disorder-disorder transitions. Nat. Chem. *13*, 568–574. https://doi.org/10.1038/s41557-021-00684-4.