CellPress

Chem Catalysis
Previews

Electrocatalytic hydrogenation of nitriles: A step toward electrification of amine production

Ricardo Mathison[1] and Miguel A. Modestino[1,*]

In this issue of *Chem Catalysis*, Zhang et al. describe a method to electrochemically hydrogenate nitriles to primary amines on nanostructured copper electrocatalysts. Through the implementation of CO_2-saturated electrolytes, the primary amines are reversibly converted to carbamic acids or carbamates, which prevents their condensation into secondary or tertiary amines.

As the world progressively moves toward its commitment of carbon neutrality by mid-century, the focus is starting to shift to decarbonize the industrial manufacturing sector. Industrial processes account for ~33% of the global greenhouse gas (GHG) emissions, and practical approaches to decarbonize them are largely nonexistent.[1] Chemical manufacturing accounts for 30% of the energy-derived industrial emissions in the US,[2] which primarily arise from thermochemical processes powered by fossil-fuel-derived heat. One promising route to decarbonize chemical manufacturing involves the electrification of organic chemical processes via organic electrosynthesis powered by carbon-neutral electricity.[3] Electrosynthetic manufacturing methods would also open new routes to operate chemical reactors at milder temperatures and pressures, avoid stoichiometric oxidants and reducing agents, reduce separation requirements, and also enable distributed chemical manufacturing approaches where products are manufactured close to the source of their feedstocks or their utilization sites.[4] Although the interest in organic electrosynthesis has rapidly expanded, there remains a gap between new synthesis methods developed in chemistry labs and engineering approaches to enhance their performance and scalability. Motivated by this need, the interest in reaction engineering and catalysis research applied to electroorganic reactions has increased, leading to advances that could lead to the deployment of electrochemical manufacturing processes of petrochemical products.[5]

As a recent example, in this issue of *Chem Catalysis* Zhang et al. recently reported a room-temperature, selective electrocatalytic process for the production of primary amines via the electrohydrogenation of nitriles.[6] Primary amines are important building blocks used broadly in the chemical industry for the production of polymers, consumer products, agrochemicals, and pharmaceuticals. In their work, the authors find that the reduction of alkyl nitriles, such as acetonitrile (MeCN), requires a favored adsorption of nitrile (CN) groups on the catalyst surface in order to suppress undesired parasitic cathodic reactions (e.g., hydrogen evolution reaction). In this study, favorable adsorption of the CN groups is achieved on a nanostructured oxide-derived Cu catalyst, where the hydrogenation of MeCN proceeds at cathodic potentials of −0.7 V in a CO_2-saturated $KHCO_3$ aqueous solution, resulting in ethylamine ($EtNH_2$) as the main product. These conditions led to an overall selectivity of 99% and a faradaic efficiency (FE) of 94%. Contrarily, when the reaction is carried in an Argon-saturated electrolyte, a mixture of the primary, secondary, and tertiary amines is produced. The authors hypothesize that CO_2 dissolved in the electrolyte reacts reversibly with the primary amines and results in the formation of carbamic acid or carbamates, which prevents their condensation into secondary or tertiary amines. Although the identified reaction conditions for MeCN electrohydrogenation are similar to those used in CO_2 reduction reaction (CO_2RR), the observed product distribution is drastically different. This discrepancy is attributed to the large concentration of water used, which results in low concentration of CO_2 in the electrolyte and weakens the CO_2RR.

Although the MeCN reduction selectivity was not affected significantly by changes in reactant concentration or potential, the electrocatalytic material implemented had strong effects on the product distribution. Cu and Ni were the only electrocatalysts capable of producing $EtNH_2$ thanks to their strong interactions with CN groups, whereas Au, Ag, Pt, and Pd promoted the hydrogen evolution reaction (HER). The authors also explored the influence of transport effects on reaction selectivity. Although water concentration was roughly 100 times larger than that of MeCN, the HER process is suppressed by the presence of MeCN when its concentration is >0.5 M. Cyclic voltammetry (CV) was used to better understand the mechanism of the reaction. Under Ar-saturated electrolytes, the CV exhibited characteristic features of the accumulation of imine intermediates. Such features were not observed under the presence of CO_2, suggesting that CO_2 plays a role in supporting the fast hydrogenation of these imines to primary amines.

---

[1] Department of Chemical and Biomolecular Engineering, New York University, Brooklyn, NY 11201, USA

*Correspondence: modestino@nyu.edu

https://doi.org/10.1016/j.checat.2021.06.003

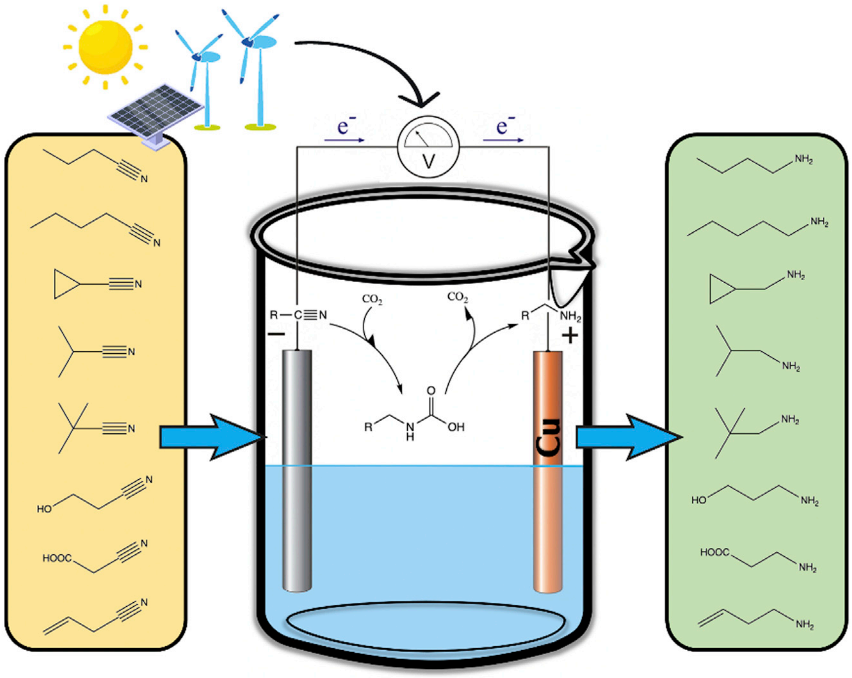

Figure 1. Electrochemical hydrogenation of nitriles to primary amines on Cu electrocatalysts can enable the integration of renewable electricity into chemical manufacturing

Zhang et al. demonstrated the selective hydrogenation of various aliphatic nitriles as depicted in this image (adapted from Zhang et al.[6]).

These observations were further supported by *in situ* Raman spectroscopy that suggested that under CO_2-saturated electrolytes, imine intermediates are more rapidly reduced.

Experimental results were complemented by density functional theory (DFT) calculations that confirmed that the active catalytic species in this reaction are reduced metallic Cu species where MeCN is adsorbed through N-end bonding. Based on the success obtained in the MeCN reduction reaction, the authors implemented similar reaction conditions for the electrohydrogenation of various aliphatic nitriles (shown in Figure 1), all of which showed improved selectivity and FE with the presence of CO_2. These results demonstrate the generality of the electrohydrogenation methodology, including for the production of valuable biomolecules (e.g., β-alanine via the reduction of 2-cyanoacetic acid). When studying different chemical substrates, the authors found that larger chain lengths or steric hindrance lowered the FE toward primary amines due to the decline in the adsorption of the nitrile. Furthermore, the solubility of nitriles plays an important role in the FE of the reaction underscoring the importance of mass transport in controlling product distribution.

Hydrogenation of nitriles to primary amines is rapidly becoming a topic of broad interest. Recently, Xia et al. reported a similar study on MeCN electrohydrogenation in flow reactors.[7] Similar to Zhang et al.'s work, the authors found that Cu electrocatalysts exhibit an exceptional preference toward nitrile adsorption, and this resulted in a remarkable FE (96%) toward the ethylamine at cathodic potentials of −0.29 V. The authors also compared Cu catalyst with other metals, finding that Ni and Pd are viable options for this reaction, although at lower efficiencies. Furthermore, Pt, Sn, In, and Bi presented a clear preference for the HER. These results were also supported by DFT calculations that confirmed the binding affinity of reaction intermediates in the Cu surface, possibly leading to the exceptional selectivity when compared with other metals. Although the report by Zhang et al. demonstrated the electrohydrogenation of aliphatic nitriles in batch mode at moderate currents, Xia et al. implemented a flow reactor that can mitigate the anticipated mass-transport limitations and also led to significantly higher current densities (i.e., up to 1000 mA cm^{-2}).

The catalyst, electrolyte, and reactor design guidelines presented by these acetonitrile electrohydrogenation studies can help improve the performance of electrochemical processes for the production of other industrially relevant primary amines such as the hexamethalinediamine[8] or 6-aminocapronitrile,[9] which are precursors to nylon-66 and nylon-6, respectively, and are produced via adiponitrile hydrogenation. As more research groups start to explore electrochemical engineering approaches to organic electrosynthesis, the progress toward the deployment of large-scale sustainable chemical manufacturing processes will accelerate. The work of Zhang et al. demonstrates the importance of understanding the interactions between electrolyte species, chemical substrates, and electrocatalyst interfaces and also shows that the balance of these interactions can promote high-performing reactions. As we move toward scalable processes, it will be increasingly important to understand these interactions under conditions relevant to practical chemical production (e.g., in high current density and/or continuous operation, in membrane-separated reactors) where enhancing mass-transport rates of reactants and electrolyte species is required to achieve high throughput, energy efficiency, and selectivity.[10]

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of the National Science Foundation and NYU Tandon School of Engineering through M.A.M.'s startup fund. This material is based upon work supported by the National Science Foundation under grant no. 1943972.

DECLARATION OF INTERESTS

M.A.M. is a co-founder of and has financial interests in Sunthetics Inc., a company operating on the sustainable chemical manufacturing space. M.A.M. is also listed as an inventor on a related U.S. Provisional Patent Application No. 63/023,173.

1. Rissman, J., Bataille, C., Masanet, E., Aden, N., Morrow, W.R., Zhou, N., Elliott, N., Dell, R., Heeren, N., Huckestein, B., et al. (2020). Technologies and policies to decarbonize global industry: Review and assessment of mitigation drivers through 2070. Appl. Energy *266*, 114848.
2. DOE, U.S. (2015). Bandwidth Study on Energy Use and Potential Energy Saving Opportunities in U.S. Chemical Manufacturing. https://www.energy.gov/sites/prod/files/2015/08/f26/chemical_bandwidth_report.pdf.
3. Schiffer, Z.J., and Manthiram, K. (2017). Electrification and Decarbonization of the Chemical Industry. Joule *1*, 10–14.
4. Biddinger, E.J., and Modestino, M.A. (2020). Electro-organic Syntheses for Green Chemical Manufacturing. Electrochem. Soc. Interface *29*, 43–47.
5. De Luna, P., Hahn, C., Higgins, D., Jaffer, S.A., Jaramillo, T.F., and Sargent, E.H. (2019). What would it take for renewably powered electrosynthesis to displace petrochemical processes? Science *364*, eaav3506.
6. Zhang, D., Chen, J., Hao, Z., Jiao, L., Ge, Q., Fu, W.-F., and Lv, X.-J. (2021). Highly efficient electrochemical hydrogenation of acetonitrile to ethylamine for primary amine synthesis and promising hydrogen storage. Chem Catalysis *1*, 393–406.
7. Xia, R., Tian, D., Kattel, S., Hasa, B., Shin, H., Ma, X., Chen, J.G., and Jiao, F. (2021). Electrochemical reduction of acetonitrile to ethylamine. Nat. Commun. *12*, 1949.
8. Blanco, D.E., Dookhith, A.Z., and Modestino, M.A. (2020). Controlling Selectivity in the Electrocatalytic Hydrogenation of Adiponitrile through Electrolyte Design. ACS Sustain. Chem.& Eng. *8*, 9027–9034.
9. Song, Y., and Pintauro, P.N. (1991). The electrochemical synthesis of aminonitriles I. H-cell studies with adiponitrile and azelanitrile. J. Appl. Electrochem. *21*, 21–27.
10. Blanco, D.E., and Modestino, M.A. (2019). Organic Electrosynthesis for Sustainable Chemical Manufacturing. Trends in Chemistry *1*, 8–10.

The search for intermediates formed during water-oxidation catalysis

Rosalie K. Hocking[1,*]

The development of new methods to explore catalysts under conditions of operation is critical for materials innovation. In this issue of *Chem Catalysis*, Pushkar and co-workers investigate the photosystem II analog cubane compound $[Co_4O_4Py_4\ Ac_4]$ (Py= pyridine and Ac= CH_3COO^-) under conditions of water-oxidation catalysis at low pH.

Since people first began to appreciate photosynthesis, we have tried to understand it.[1] The reasons for this are clear: if we could mimic water oxidation, we would have a clean way to reduce atmospheric carbon dioxide and manufacture key commodity products in the process.

Similarly, if we could understand engineered "man-made" materials such as metal-oxides thin-film water-oxidation catalysts, we could understand how they work and improve their selectivity and durability. However, there are still many unanswered questions about how these processes work. Although we know the basic structure of photosystem II (PSII), there are still key questions about the processes that precede O-O bond formation.[2] The same is true with our benchmark electrocatalysts made from thin films of metal-oxides—the most active of which are observed to be both disordered and nanostructured.[3–5]

From an analytical perspective, two significant challenges limit our ability to characterize materials in their "functional, active" states, which are key for materials innovation. Historically analytical techniques work best at two extremes. They work well for molecular materials, as seen in Figure 1, top left. For molecular materials, spectroscopy is more straightforward than for clusters. This means transitions, whether magnetic or electronic, can be fully assigned, and materials can be understood well.[6] As clusters get bigger, transitions overlap and interact with each other, making assignments complex. At the other extreme shown in Figure 1, at right we have crystalline materials; when the material is a single crystal, we generally know its structure unambiguously. Unfortunately, the

---

[1] Department of Chemistry and Biotechnology and Centre for Translational Atomaterials, Swinburne University of Technology, Hawthorn, Melbourne, VIC 3122, Australia

*Correspondence: rhocking@swin.edu.au

https://doi.org/10.1016/j.checat.2021.06.004