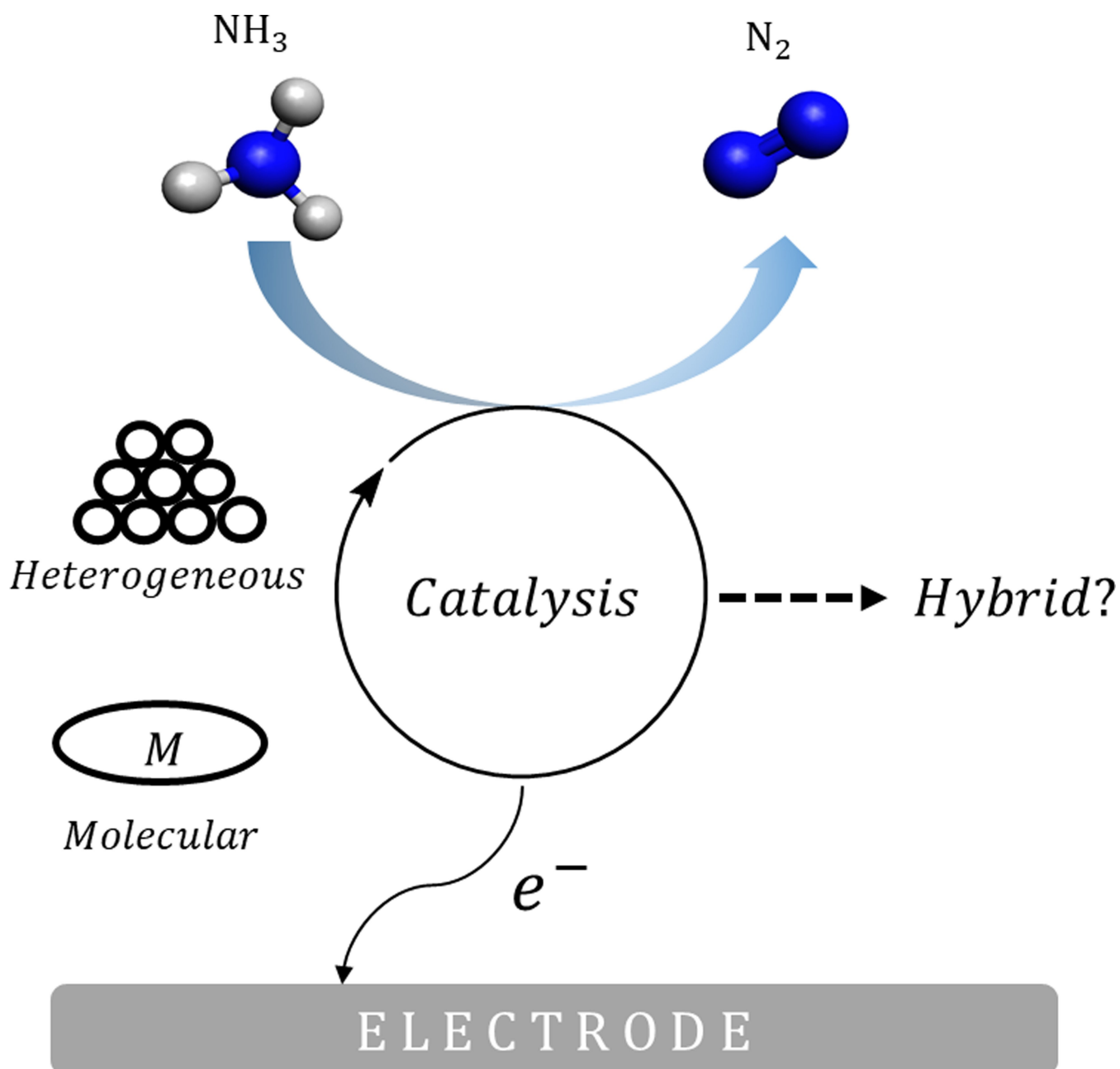


The Potential of Molecular Electrocatalysis for Ammonia-to-Dinitrogen Conversion

Nikolaos Kostopoulos,^{*[a]} Marc Robert,^[b, c] and Alina Sekretareva^[a]



Electrochemical ammonia oxidation reaction (eAOR) regains interest due to ammonia being an interesting alternative to hydrogen for fuel cell technologies. In the present review, we first discuss some of the most important findings on eAOR with solid catalysts, including mechanistic and feasibility aspects for practical implementation. We then examine the reports on

molecular catalysis of eAOR that have recently emerged. We finally discuss immobilization strategies of these molecular catalysts, and discuss intrinsic advantages of those strategies, so as to guide the design of efficient catalytic systems able to compete with heterogeneous, solid catalysts.

1. Introduction

The use of fossil fuels for energy production has greatly contributed to the development of society and the economy, but at the same time is detrimental to the earth's ecosystem. It has resulted in an excessive accumulation of carbon dioxide in the atmosphere. The latter is a greenhouse gas that contributes to global warming.

Hydrogen is regarded as a promising candidate for cleaner energy production because it has higher gravimetric energy density compared to fossil fuels, and the product of its combustion is water. Therefore, hydrogen-fuelled devices (hydrogen fuel cells) have been a hotspot of research during the last decades.^[1]

Green hydrogen production technologies, such as photo- and electro- catalysis of water, are developing rapidly.^[1,2] However, the use of hydrogen technologies for power and heating applications suffers from several drawbacks. The H₂ molecule is characterized by high reactivity and low density,^[3] that leads to low volumetric energy density, difficulties regarding handling and storage,^[4] high leakage risks,^[5] and operational issues due to its high reactivity and diffusivity.^[6] Furthermore, its storage for long periods is more expensive than other alternative fuels.^[7]

Ammonia as a fuel has recently started to receive wide international attention because of several benefits compared to hydrogen. The commercial viability of ammonia as an energy carrier is supported by both its high volumetric and gravimetric energy density (108 kgH₂/m³ NH₃ at 20 °C/8.6 bar, and 17.8 wt% respectively).^[8] Furthermore, ammonia has a lower cost per unit of energy stored compared to hydrogen (0.54 \$/kg-H₂ vs

14.95 \$/kg-H₂)^[4] along with a well-established production and distribution infrastructure, and well-defined regulations. This is due to ammonia being manufactured and transported throughout the world for more than a century, with an already existing high-capacity infrastructure for liquefied ammonia, including pipelines, bunker shipping, and tank trucks.^[9]

Ammonia can be catalytically decomposed into carbon-free hydrogen,^[10] but it can also be used directly in electrochemical power generation devices such as fuel cells and combustion engines with zero carbon footprint. The electrochemical AOR is thermodynamically favored as compared to water electrolysis: the thermodynamically required potential for water splitting is 1.23 V, while NH₃ oxidation requires 0.06 V.^[11,12] However, due to kinetic limitations, ammonia-oxidation reaction requires a large overpotential, resulting in considerable efficiency loss.^[11,13,14] In order to address these kinetic limitations, scientists have made huge efforts in catalyst design, combining theoretical calculations and experiments.^[15–17] Furthermore, the poisoning of the electrocatalyst surface significantly lowers the durability and consequently also plays a central role in the design of efficient catalysts.

It is noteworthy that ammonia electro-oxidation reaction is not only central in ammonia-fed fuel cells,^[10,18,19] but it is also crucial for several other fields including wastewater remediation,^[20] onboard hydrogen production,^[21] and electrochemical sensors.^[22]

In this review, we discuss recent progress and perspectives of AOR catalyzed by molecular catalysts, after having presented some milestones and challenges of heterogeneous catalysts. Some excellent reviews on molecular ammonia oxidation have recently been published.^[23,24] Herein, we focus not only on the benefits of molecular AOR catalysts but also on how potential drawbacks towards practical use can be circumvented by immobilizing them at electrode surfaces. Furthermore, we dedicate the last session to paradigms for the implementation of molecular catalysts that have been uncovered for other catalytic reactions and could be transposed to AOR.

2. Heterogeneous catalysts

The potential of ammonia as a hydrogen fuel substitute was recognized as early as the beginning of the twentieth century.^[25] However, studies conducted at temperatures lower than 200 °C have revealed that ammonia oxidation on heterogeneous catalysts is less reversible compared to hydrogen, and thus it necessitates high overpotentials.^[26] The low thermal efficiency of AOR is still one of the factors that hinder the extended use of ammonia as a fuel.

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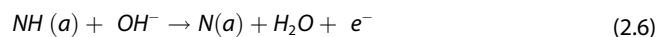
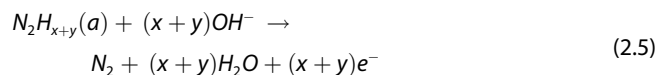
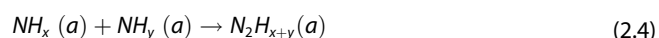
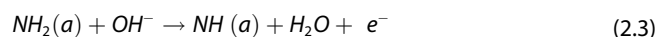
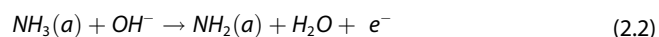
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In early works, Fe-based catalysts under high temperatures were mainly considered. Winter conducted the first experiments on ammonia oxidation over Fe catalysts in a flow system in 1931, studied the kinetics of the reaction and proposed a mechanism.^[27] The mechanism was further disputed by Temkin and Pyzhev, who pointed out that one of the steps in the proposed mechanism required activation energies exceeding those determined for the overall reaction. In their work, Temkin and Pyzhev derived kinetic equations allowing the investigation of the catalysts based on the assumption that nitrogen desorption from the surface is the rate-limiting step.^[28] Over the years, several mechanisms for heterogeneous ammonia oxidation have been proposed.^[13] As ammonia oxidation is sluggish in acidic media and on many electrode materials, mechanistic and kinetic investigations were mostly conducted in alkaline conditions on platinum electrodes. This resulted in two major mechanisms that are now widely accepted: the Oswin-Salomom (O–S) and Gerisher-Mauerer (G–M) mechanisms. According to the O–S mechanism, AOR occurs through the complete dehydrogenation of ammonia to adsorbed atomic hydrogen followed by dimerization (equations 1.1 to 1.5), with the second dehydrogenation step being rate-determining.



In the G–M mechanism, it is proposed that dimeric intermediate species N_2H_{x+y} is formed, which is further electro-oxidized to N_2 (equations 2.1 to 2.6):



The design of AOR heterogeneous catalysts, like that of other energy-related reactions, is largely guided by theoretical studies that combine first principle calculations and microkinetic analysis. We would like to highlight two recent works in which extensive theoretical investigations were conducted and reactivity descriptors were proposed to guide the design of ammonia oxidation catalysts. The Mavrikakis group conducted a thorough investigation of AOR activity trends on (100) facets of eight transition metals: Au, Ag, Cu, Pt, Pd, Ni, Ir, and Rh.^[29] The authors suggested the free energy of adsorbed nitrogen as a reactivity descriptor, which agrees with the earlier kinetic model proposed by Temkin and Pyzhev based on experimental observations. Notably, the proposed descriptor could be applied also for other facets as demonstrated for (111) surfaces. Except for Pt(100) and Cu(111), the rate-limiting step is the formation of an N–N bond, and the process is more favorable via the G–M mechanism than the O–S mechanism. The activity of Pt(100) and Cu(111) is limited by proton-electron transfer steps. Pt(100) has been found to be the most active surface, followed by Ir (100), which is consistent with experimental findings. Later,^[30] a similar study by Yang et al. for AOR on low index facets of transition metals: Ag, Au, Cu, Ir, Pd, Pt, Rh and Ru and their alloys found the same trend in metal facets



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activity, with Pt being the most active surface, followed by Pd (Figure 1). The authors included in their study O-related intermediates (O^* and OH^*), which were not considered by the Mavrikakis group but have been shown to activate NH_3 .^[30,31] The O binding energy was considered as an additional independent descriptor for catalytic performance in terms of N_2 selectivity. Cu (100) and Rh (111) were found to have the highest selectivity. Overall, optimizing N binding energy to moderate ranges of -5 to -4 eV in conjunction with strengthening oxygen binding resulted in increasing N_2 selectivity. Additionally, the authors identified Pt–Rh alloys as potential superior AOR catalysts with high selectivity towards N_2 , which was confirmed experimentally.^[31,32]

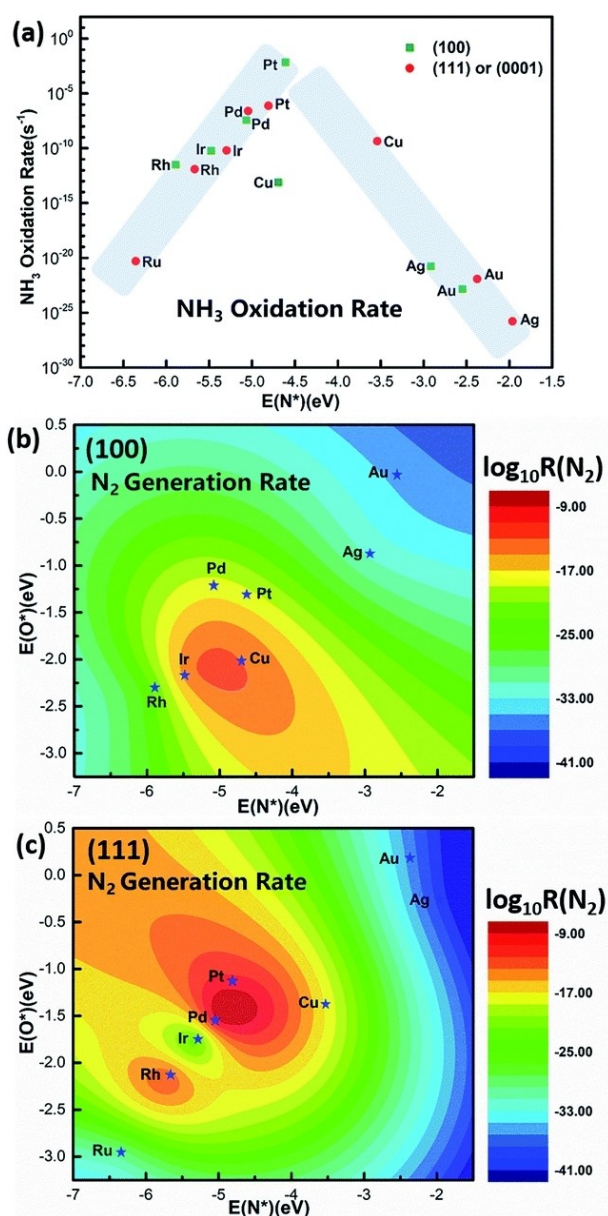


Figure 1. (a) The relation between NH_3 oxidation rates and the binding energy of Nitrogen atom (b and v) and 3D representations of the relation between N_2 generation rates and the binding energies of N and O atoms at low-index facets (b and c). Reproduced from ref.^[30] Copyright (2012), with permission from the Royal Society of Chemistry.

Experimental results confirm theoretically predicted trends in AOR catalytic activity. To date, Pt-group metals are the most active and well-studied heterogeneous catalysts for AOR. They are also the only catalysts commercially used in ammonia fuel cell technologies. In low-temperature ammonia fuel cells ($100^\circ C$) that are particularly appealing for commercial applications, only Pt and Ir are sufficiently catalytically active. However, at these temperatures, the catalysts are deactivated by the irreversible adsorption of intermediates of the reaction.^[33] Combining the catalytic material with a plasmonic light-absorbing material has the potential to locally increase the surface temperature of the catalyst, which might result in improved catalyst stability. Indeed, Jain's group reported a bimetallic catalyst made of Pt and Au, with Pt particles acting as an AOR catalyst and Au as a light-absorbing material.^[34] The authors observed increased activity under irradiation which was attributed to the participation of hot carriers in the reaction, but they did not look into the effects of temperature on catalyst deactivation.

Non-noble metals such as Ni, Cu, Co, and Fe are being actively scrutinized as AOR catalysts to overcome the problems of high cost and rapid deactivation of Pt group metals.^[35] Ni-based catalysts, particularly NiOOH, are currently one of the most widely studied non-noble heterogeneous AOR catalysts due to their superior stability when compared to Pt-group metals. Based on first principle calculations, the onset potential for Ni is predicted to be 0.33 V vs. RHE, compared to 0.28 V vs. RHE for Pt.^[36] Overpotentials measured experimentally, on the other hand, are much higher, being well above 1 V.^[37] This has been attributed to significant differences in activity demonstrated by various facets^[38] or differences in the AOR mechanism when compared to Pt.^[39] The large overpotentials observed with non-noble metals is one of their main drawbacks that can hinder their practical use.

Substantial efforts have been devoted to the development of eAOR solid catalysts that would meet the requirements for practical applications. However, despite decades of research, high overpotential and fast deactivation still hamper the ultimate goal of a robust and highly active eAOR catalyst. The Pt-based electrocatalysts are viewed as promising candidates for eAOR because of their low overpotential and high selectivity for N_2 , even though they have a crucial limitation upon poisoning by N adatoms ($*NO$, $*NO_x$, and $*N$). Such poisoning of Pt catalysts imposes a challenge to commercial technologies that require a robust, long-term operation, and adds up to their high cost.^[37] The use of molecular catalysts, and in particular of metal complexes, may contribute to tackling such issues. For instance, the use of appropriate supporting ligands can enable the usage of non-noble metals that could even outperform noble metal homologs (vide infra).

3. Homogeneous catalysts

Molecular catalysis of N_2 reduction to NH_3 has been at the center of numerous studies during the last few decades.^[40] Those studies have led to a thorough mechanistic under-

standing of N₂ reduction by a large spectrum of transition metal complexes. This catalytic process is also being explored both by bio-electrocatalytic^[41] and bio-inspired systems.^[42]

Despite electrocatalytic AOR by heterogeneous catalysts being studied since the end of the 19th century, the first example of molecular electrochemical AOR was only reported some four years ago. Smith et al. reported the catalysis of the electrochemical AOR by a Ru complex containing pyridine ligands, namely the [(trpy)(bpy)Ru^{II}(NH₃)](PF₆)₂ (Figure 2, top left),^[43] that led to the oxidation of ammonia to nitrogen in bulk electrolysis performed under an inert atmosphere in THF solutions. The authors of that study were inspired by the work of Meyer et al., who reported, in 1981, the stoichiometric oxidation of coordinated ammonia to nitrate by the same complex.^[44]

Since 2019, a handful of reports have focused on the molecular electrochemical AOR (Table 1).

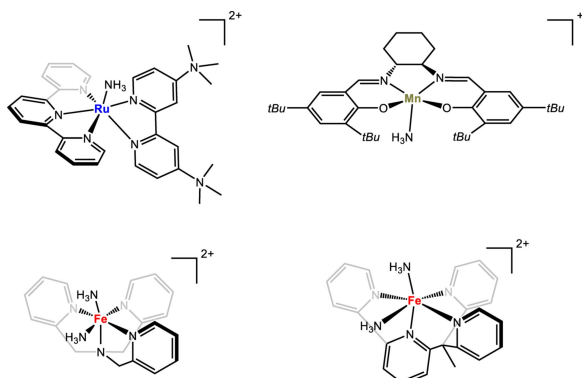


Figure 2. Structures of some molecular AOR catalysts of Smith (top, left, no.9 of Table 1), Nishibayashi (top, right, no.4 of Table 1), and Peters (bottom, left no 8 and right no. 7 of Table 1).

Table 1 summarizes the main studies reporting molecular complexes as homogeneous catalysts of the electrochemical oxidation of ammonia to nitrogen, and some of the main characteristics of each reaction system, namely the electrolysis potential, the solvent, the electrode material, as well as the Faradaic efficiency (FE) and turnover numbers. The overpotential is also included in the table as information, however, we need to note that a straightforward comparison of all the studies is not possible, since the used solvents differ.

The work of Peters et al. constitutes an important milestone in the field. The first report was published in 2019, presenting a mononuclear Fe ion supported in a tris(2-pyridylmethyl)amine ligand (Figure 2, bottom, left).^[51] The complex catalyzes the electrochemical ammonia oxidation in acetonitrile at 1.40 V vs SCE with a Turnover Number (TON) of 16 and a Faradaic efficiency reaching 80%. In 2021, the same group reported another Fe polypyridyl complex with a more rigid ligand, that led to a higher TON, reaching 100, improved selectivity and lower overpotential (Figure 2, bottom right).^[50] During the same year, Llobet et al. reported a tetradentate Ru complex that was able to catalyze the AOR in acetonitrile, nevertheless, without better metrics as compared to previous reports. More importantly, they showed that the complex was able to catalyze the reaction in water, but with a relatively low selectivity (FE = 35%).^[49] The same year, Nishibayashi reported that a Mn salen-type complex (Figure 2, top right) also catalyzed that reaction in THF with high FE (above 95%), however at the expense of low stability (low TON).^[48]

Several additional works reporting the electrochemical catalysis of AOR by organometallic complexes are worth mentioning. Very recently, Berry et al reported a bimetallic Ru catalyst,^[47] Wang et al. a Fe pentamethylcyclopentadienyl catalyst,^[46] and Warren et al. reported a Cu β -diketiminato

Table 1. Main examples of molecular complexes that catalyze the electrochemical ammonia oxidation to nitrogen, in solution.

No.	Group, and metal	Potential, and solvent	Electrolysis time	FE	TON	TOF (h ⁻¹), turnover frequency (TON/t)
1	Warren et al. ^[45] Cu complex	-0.4 V vs SCE, acetonitrile	26.5 h	< 84% (for shorter exp.)	8.2	0.3
2	Wang et al. ^[46] Fe complex	-0.18 V vs SCE, THF	8 h	73.9%	4.4	0.55
3	Berry et al. ^[47] Bimetallic Ru complex	-0.4 V vs SCE, acetonitrile	3x30 min	52%	5	3.33
4	Nishibayashi et al. ^[48] Mn Complex	0.46 V vs SCE, acetonitrile	18 h	96%	6.6	0.37
5	Llobet et al. ^[49] Ru complex	1.155 V vs SCE, water	17 h	35-40%	Less than 1	-
6	Llobet et al. ^[49] Ru complex	1.155 V vs SCE, acetonitrile	11 h	74%	7.5	0.68
7	Peters et al. ^[50] Fe complex	1.23 V vs SCE, acetonitrile	24 h	87%	93	3.87
8	Peters et al. ^[51] Fe complex	1.48 V vs SCE, acetonitrile	18 h	80%	16	0.88
9	Smith 2019 ^[43] Ru complex	0.49 V vs SCE, THF	3 h	86%	2	0.66

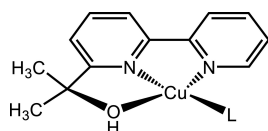


Figure 3. Chemical structure of the Cu-based catalyst reported by Brudvig for electrochemical AOR in water.^[54]

catalyst.^[45] These studies provide important mechanistic insights into the catalytic reaction, focusing on coordination chemistry aspects. The main advantage of this group of catalysts is the remarkably low overpotential needed for the reaction to occur, as compared to previous reports (Table 1).

As far as the mechanism of the reaction is concerned, two possible pathways of the N–N bond formation step have been proposed.^[24] The first involves the nucleophilic attack of ammonia on nitrogenous (amido, imido, or nitride) species.^[43,46,48–52] The second pathway involves a bimetallic coupling, i.e., reaction between two nitrogenous species.^[45,53] To date, mechanistic investigations in the molecular eAOR are based on theoretical computations and/or experiments in homogeneous conditions that do not involve electrochemistry. In the work of some of us, reporting on the eAOR catalyzed by a Mn porphyrin (manuscript under preparation), we provide for the first time experimental electrochemical evidence for a dimerization pathway. A Mn-nitrido was detected during operando UV-vis spectroelectrochemistry, isolated, and was further shown, upon preparative scale electrolysis in the absence of NH₃, to give N₂.

Brudvig et al. have reported a novel copper complex (Figure 3) [Cu(bipyalk)]⁺, a homogeneous electrocatalyst that catalyzes ammonia oxidation to nitrate and nitrite in water with a total Faradaic efficiency of 93.8%.^[54] The authors underline the high selectivity of the catalyst towards NO₃[−] in aqueous media compared to Cu(NH₃)₄ (FE 65.3% and 28.5% for NO₃[−] and NO₂[−] respectively, versus 30.5% and 69.1% for the Cu(NH₃)₄) while they experimentally show that their complex is not electrodeposited.

As far as the six-electron ammonia oxidation is concerned, all the above-mentioned studies, reporting on different catalysts for electrochemical AOR, present original findings with significant insights into this chemistry. They constitute a first step towards the rational design of new molecular catalytic systems. Crucial requirements for molecular catalysts include the use of non-noble, abundant metals, and green and simple (few steps) synthetic procedures. In this respect, the catalysts proposed by Peters and Nishibayashi (see Figure 2) are particularly interesting.

Furthermore, in order to benefit from molecular electrocatalysts at their full potential in relevant operative conditions for lab-scale devices, there is a need to focus on the immobilization of such catalysts, as we explain in the next sections.

4. Immobilization strategies for AOR molecular electrocatalysts

Homogeneous catalyst systems, where catalyst molecules freely diffuse and perform the reaction in a solution or a suspension, typically suffer from drawbacks, such as tedious catalyst recovery and product separation. Nonetheless, they can achieve high efficiencies and low overpotentials, which can be further enhanced thanks to their well-defined structures. In addition, the availability of numerous spectroscopic techniques facilitates the fundamental understanding of the catalytic processes. At the same time, their drawbacks can be in principle alleviated, using the approach of immobilizing them on electrode surfaces. In this approach, catalysts can be employed under conditions where they might not be soluble or stable for homogeneous catalysis. Furthermore, they can be separated more easily from the reaction products, while much less catalyst is needed since it is localized at the electrode surface. In addition to these general issues, immobilizing molecular catalysts for ammonia oxidation can partly address the problems of stability at oxidizing potentials, selectivity (of AOR vs Water Oxidation reaction, WOR), and slow kinetics.

Currently, there is only one report related to the heterogenization of an AOR molecular catalyst. Llobet et al. have described the ammonia oxidation activity of a ruthenium catalyst, namely the oligomer {[Ru^{II}(bda-κ-N₂O₂)(4,4'-bpy)]₁₀(4,4'-bpy)}, Rubda-10, where bda is [2,2'-bipyridine]-6,6' dicarboxylate and 4,4'-bpy is 4,4'-bipyridine, anchored at a graphitic surface throughout CH-π cation interactions (Figure 4).^[55] A Faradaic efficiency close to 100%, and a turnover of 7500 (for an hour) were obtained. Electrolysis in a basic aqueous solution (pH 9.7), gave a turnover number of 1990 (20 min duration). The turnover number far exceeds the ones of the non-supported-homogeneous systems, as expected due to the much lower catalyst concentration. The high turnover numbers and the fact that the reaction can take place in water are important milestones in the field.

In this section, we will highlight immobilization that can be applied to AOR molecular catalysts, using graphite and metal oxide materials which are the most viable electrode materials for practical applications. It is noteworthy that in the field of enzymatic catalysis, there has been significant development in immobilization strategies, which have been shown to enhance the performance of biocatalysts.^[56] Many of these strategies can be adapted for the attachment of molecular catalysts as well.^[57,58]

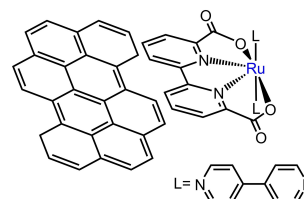


Figure 4. Schematic view of a molecular site of the immobilized Ru catalysts on graphite.^[55]

A straightforward way to immobilize molecular catalysts is through physisorption onto the supporting electrode. In such cases, molecular catalysts are often modified with aromatic groups, such as pyrene, to facilitate interaction with the graphite component through π - π stacking. Pyrene anchoring of Ru-based WOCs was reported.^[59,60] The immobilization of the catalyst resulted in an exceptionally stable anode for water oxidation, exhibiting a turnover number of over a million without any observable degradation. In another example, the immobilization of a diruthenium complex based on the bis(bipyridyl)pyrazolate (bbp-) ligand scaffold demonstrated that the number of pyrene anchoring groups used affects the positioning of the active site relative to the surface, thereby controlling the accessibility of the substrate.^[61] Copper-based molecular water oxidation catalysts with tetraamide ligands were immobilized via pyrene moiety and it was shown that π - π stacking with the electrode support induces π -delocalization, leading to a decrease in overpotential and an increase in catalytic activity.^[62] As far as AOR is concerned, the pyrene immobilization strategy can enhance the stability of the catalysts and also provide a means to improve selectivity by limiting water access to the active sites. This has been previously achieved in heterogeneous AOR catalysis, by anchoring catalysts to the gas diffusion electrode and exposing them to ammonia vapor.^[63]

Another physisorption approach consists of mixing molecular catalysts with carbon porous materials, such as carbon nanotubes or carbon powder, in an organic solvent. The resulting suspension is dropcasted on electrode surfaces. This approach has been used in electrochemical Oxygen Reduction Reaction (ORR) with transition metal macrocycles,^[64] and has been also developed for CO₂ reduction (CO₂RR) with metal macrocycles.^[65]

Covalent attachment is another frequently employed technique for immobilizing catalysts. The surface of graphite can be modified with functional groups, which then enable the catalyst to be coupled to these groups using click chemistry or other coupling reactions. The functionalization of the graphite surface can be achieved through direct electrochemical oxidation,^[66] resulting in the generation of oxygen-containing groups on the surface. Alternatively, aryl diazonium ions can be electrochemi-

cally reduced to form radicals that spontaneously attach to the graphitic surface.^[67]

The introduced moieties can act as coordinating ligands directly to the metal center or can serve as a linker between the electrode functional groups and the catalysts. For metal oxide surfaces, moieties containing oxygen, such as carboxylates and phosphonates, are introduced either as ligands themselves or as substituents linked to the molecular complex.^[57]

Although not yet reported for the immobilization of molecular catalysts, ion-selective ammonia membranes^[68,69] and molecular imprinted polymers^[70] are known and can be utilized for the entrapment of anodic oxidation catalysts, thereby improving catalyst selectivity.

Furthermore, similar to molecular biocatalysts, molecular complexes can be entrapped within a polymer matrix.^[71,72] The polymer matrix allows for control over the immobilization environment, stabilizes the catalyst, and potentially improves selectivity. For instance, Ruff et al. demonstrated that oxygen-sensitive molecular catalysts can be effectively shielded from ambient oxygen by entrapping the catalyst within an O₂-reducing redox polymer matrix.^[71] Meyer's group reported stabilization of a Ru-based water oxidation catalyst attached to the ITO surface via vinyltrimethoxysilane by reductive electropolymerization of the vinyl-derivatized complex.^[61]

5. Molecular catalysts tested under application relevant conditions

In this section, we would like to discuss two emblematic examples of catalytic systems based on molecular catalysts, that were compared to solid ones, in application relevant conditions. The first concerns CO₂, and the second O₂ reduction.

In 2019, Berlinguette, Robert, et al.^[73] reported the electrochemical reduction of CO₂ to CO by a molecular catalyst, namely cobalt phthalocyanine, in a flow cell (Figure 5). Their custom-designed cell consisted of a hydrophobic carbon paper cathode; that is porous; in which the molecular catalyst was drop-casted as a dispersion containing carbon powder and Nafion. Nafion is a binder, i.e., a polymer contributing to the

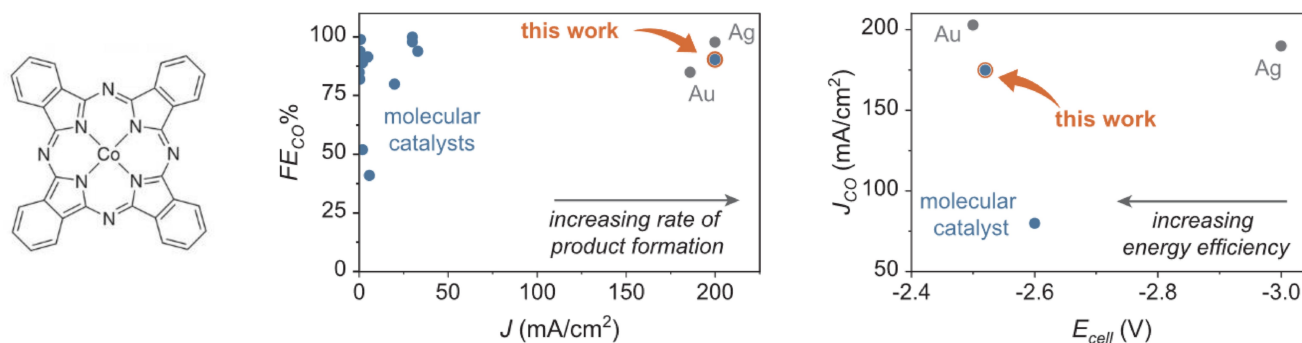


Figure 5. A molecular CO₂RR catalyst used in a flow cell, reported by Robert, Berlinguette et al. Left: Structure of the Cobalt phthalocyanine that was used as the catalyst. Middle: FE_{CO} as a function of the current density, J . Right: CO partial current density, J_{CO} , as a function of overall cell voltage, E_{cell} , for the high-performing molecular Co catalyst (and the state-of-the-art heterogeneous Au and Ag catalysts (grey)). The data for CoPc featured in this study are indicated in orange. Reproduced from ref.^[99] Copyright (2019), with permission from The American Association for the Advancement of Science.

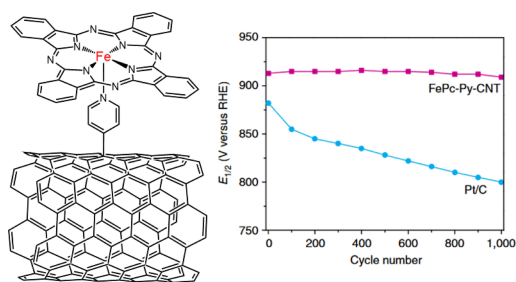


Figure 6. ORR catalyst reported by Cao et al. Left: Representation of a catalytic site of the Fe phthalocyanine – carbon nanotubes hybrid. Right: Comparison of the durability of the material with a commercially available ORR catalyst based on Pt. Reproduced from ref.^[74] Copyright (2013), with permission from Springer Nature.

integrity of the constructed electrode, and to the tuning of its physical properties such as proton conductivity.

The authors showed that the electrocatalyst can produce CO with >95% selectivity at current densities of 150 mA/cm² in their flow cell, and a maximum partial current density for CO production (J_{CO}) of 175 mA/cm² with an overall two-electrode cell voltage (E_{cell}) close to 2.5 V. This value is 0.4 V lower (or a 4% gain in energy efficiency) relative to that reported for a silver solid-state CO₂ catalyst at a similar CO partial current density. The authors underlined that the best technology known until 2019 could produce CO with a Faradaic efficiency (FE) of >90% at 200 mA/cm² for 1000 hours, which in practice remains inadequate for commercially relevant use.

In 2013, Cao et al. reported an electrocatalytic hybrid material that consisted of Fe phthalocyanine with an axial ligand anchored on single-walled carbon nanotubes (Figure 6).^[74] The catalysts showed higher electrocatalytic activity for oxygen reduction than the state-of-the-art Pt/C catalyst as well as good durability during cycling in alkaline media. Furthermore, the FePc–Py–CNTs composite retained 92% of the initial current density at 0.9 V versus RHE after 1,000 cycles, compared with the 30% retained for the commercial Pt/C catalyst. In addition, the authors used FePc–Py–CNTs composite as a cathode catalyst to evaluate its performance in Zn-air batteries under realistic conditions that illustrated the potential of their material.

Those two studies can constitute paradigmatic examples for the development of catalytic systems for eAOR based on molecular catalysts. In particular, we would like to highlight the following points: (i) in both examples, the catalyst was a macrocycle complex bearing a non-noble metal. It was shown that they were highly active, selective, and robust. Such catalysts have not yet been applied to eAOR (ii) The catalysts were immobilized on an electrode, supported on a carbonaceous material, in the first case carbon powder, and in the second carbon nanotubes. Those examples show the path for effective immobilization methods. (iii) The catalytic efficiency and robustness were compared with highly active heterogeneous catalysts. This constitutes a good practice for evaluating the potential of such molecular catalytic supported systems.

6. Summary and Outlook

Electrochemical ammonia oxidation has recently received renewed, intense attention because ammonia has several benefits compared to hydrogen, making it a promising fuel for fuel cell technologies. Research focusing on the development of eAOR has led to important findings. However, Pt-based electrocatalysts are still seen as the most promising candidates for eAOR, despite their cost, scarcity, and limitations due to poisoning issues.

During the past four years, a handful of metal complexes have been discovered as catalysts for eAOR with promising results. Even though homogeneous molecular catalysts have several benefits, they suffer from a series of drawbacks that impede them from being competitive with heterogeneous catalysts. However, immobilizing molecular catalysts for various electrocatalytic reactions (e.g. CO₂ reduction to CO) on electrode surfaces has been shown to be a promising methodology for pushing molecular catalysts to their full potential. Recent implementation of diverse immobilization methods may equally be beneficial for eAOR molecular catalysis.

Furthermore, it has been recently shown that catalytic systems based on non-noble metal molecular catalysts can reach very high activities and robustness (O₂ and CO₂ reduction), making them competitive with solid, heterogeneous catalysts. Electrochemical AOR with molecular catalysts is an emerging field that will undoubtedly benefit from these methodologies for the design of the next generation of catalytic electrodes.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: ammonia oxidation · electrocatalysis · molecular catalysis · earth abundant metals · renewable fuel

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