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COMMUNICATION

Nickel Dimethyl Glyoximato Complex to Form Nickel Based Nanoparticles for Electrocatalytic H₂ Production

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Stéphanie Cherdo,^a Sanae El Ghachtouli,^a Marie Sircoglou,^{a*} François Brisset,^a Maylis Orio^b and Ally Aukauloo^{a,c*}Received 00th January 2012,
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We report on the electrochemical alteration of a nickel(II) bis-glyoximato complex into nickel-based nanoparticles at a glassy carbon electrode under acid reducing conditions. These particles show electrocatalytic activity towards hydrogen production at +410 mV compared to the bare glassy carbon electrode. Mechanistic insights are discussed based on DFT calculations.

A pressing contemporary issue is to develop new ways for the production of a clean source of energy.¹ Among different alternatives, hydrogen is expected to play a key role in our future energetic mix.² To date there are still several technological concerns to overcome to set an economy based on H₂. However, a sustainable and cheap way to produce H₂ remains the main challenge on the agenda.³ Molecular chemists are devoting a considerable effort to design and prepare abundant first row transition metal complexes that can potentially share the catalytic activity of platinum.⁴⁻⁶ An increasing number of molecular systems for hydrogen evolution reaction (HER) based on iron, cobalt and nickel complexes have been reported with interesting catalytic activities.⁷⁻¹⁵ However, a major concern with the molecular catalysts is that they are plagued by the inevitable limited turnover number.¹⁶ This arguably raised questions on the weak features in the design of the molecular catalysts and on the intimate nature of the catalytic species.¹⁷ An often-disregarded pathway is the chemical alteration of the initial molecular complex leading to the real catalytic species. Previously, Aukauloo and coll. reported on the electrocatalytic activity of cobalt tris-glyoximato complexes for the HER. However, there were concerns on the catalytic aspects of these coordinatively saturated cobalt complexes.⁸ An electrochemical investigation by Saveant and coll. has shown that the cobalt tris-glyoximato complexes were acting as precatalysts.¹⁸ More interestingly, we have evidenced that an open coordination sphere pyridine-oxime cobalt complex under acid reducing medium was also generating cobalt-based particles that were catalytically active towards hydrogen production.¹⁹ A first trend that emerges from a comparative study on the source of metal

ion tends to support the fact that the nature of the initial complex is necessary for the formation of these catalytic particulates. Nickel-based complexes are also under focus for the HER. Dubois and coll. have developed a series of nickel complexes with amino phosphine ligands that have remarkable electrocatalytic properties towards the HER.^{20,21} Artero and coll. have reported on nickel imine oximate complexes as efficient molecular catalysts for the HER.²² In a recent article, Roberts and coll. reported on the electrodeposition of Ni-S film at the surface of a glassy carbon electrode from a solution of nickel bis(benzenedithiolate) in acidic conditions.²³ They also emphasised that the formation of such catalytic material depends on the molecular precursor. In this study, we have been interested in re-investigating the electrochemical behaviour of the [Ni(DMGBF₂)₂] (DMG = dimethylglyoxime), a complex that we previously described as a poor molecular catalyst for the reduction of protons.²⁴ We found that the [Ni(DMGBF₂)₂] complex lead to the formation of nickel-based nanoparticles at the surface of a graphite carbon electrode under acid reducing conditions. The chemically modified electrode shows remarkable activity for the HER in an aqueous solution at pH 7. Controlled experiments indicate that the use of the starting molecular complex is necessary for the formation of the electroactive nickel particles.

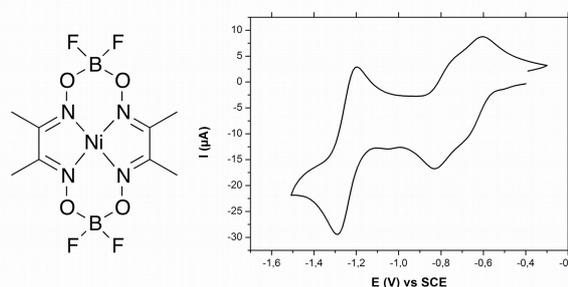


Fig. 1 Cyclic voltammogram (CV) in DMF (0.1 M TBAPF₆, $\nu = 0.1$ V/s) of [Ni(DMGBF₂)₂] complex (2mM) at a glassy carbon electrode

The synthesis of complex $[\text{Ni}(\text{DMGBF}_2)_2]$ was realised following literature procedures. The electrochemical behaviour of this complex was studied in dimethylformamide for solubility reason. The cyclic voltammogram (CV) of $[\text{Ni}(\text{DMGBF}_2)_2]$ is depicted in Fig. 1. As we can observe, the first reduction wave consists of a twin redox processes at around -0.8 V vs. SCE while the second wave at -1.25 V with a $\Delta(E_{\text{pa}}-E_{\text{pc}})$ of 60 mV indicates a reversible one electron process. We explain the splitting of the first reduction wave by the existence of a dimer $[\text{Ni}(\text{DMGBF}_2)_2]_2$ in solution (Fig. S1 and Scheme S1). Previous studies mentioned the formation of a metal-metal bond for such nickel *vic*-dioximes complexes both in solution and solid state.^{25,26}

Spectroelectrochemical studies were performed to investigate on the locus of addition of the electrons. As we reported previously, addition of the first electron for the parent complex $[\text{Ni}(\text{DPGBF}_2)_2]$ (DPG = diphenylglyoxime) results in the formation of intense bands in the near IR region together with noticeable changes in the UV-Visible region. In the case of the $[\text{Ni}(\text{DMGBF}_2)_2]$ complex, the uptake of the first electron leads to the formation of a broad band with the I_{max} peaking at 895 nm, together with the formation of three other bands at 505, 425 and 300 nm (Fig. S2-a). These bands are typical for the formation of metal-radical species.²⁷⁻²⁹ Interestingly, we note that the intense low energy transition band at 895 nm shifts to 825 nm near the end of the electrolysis (Fig. S2-b). We attribute this to the release of the mononuclear radical species from the dimer in solution. This is further confirmed by TDDFT calculations, which adequately reproduce the energy of the key features of the experimental electronic absorption spectrum and provide the assignment of its salient features (Fig. S7, Table S2). The low-energy band arises from metal-to-ligand charge transfer (MLCT) since the donor orbital (β -HOMO) is mainly metal-centered while the acceptor orbital (β -LUMO) is ligand-based, essentially distributed over the oximate and the diiminic fragments. Poising the potential at -1.5 V vs. SCE lead to the disappearance of the band at 825 nm with the concomitant formation of a band absorbing at 520 nm (Fig. S2-c). The presence of isobestic points for the above reduction processes and the regain of the original absorption spectra after re-oxidation (Fig. S2-d) are supportive for reversible electron transfer processes. Confirmation of the locus of addition of the first electron to generate a metal radical species, comes from the EPR spectrum of an electrolysed solution of the initial Ni(II) complex indicating a narrow signal at $g = 2.00$ (Fig S3).²⁹ These findings are supported by DFT calculations performed on the one electron reduced species (see SI). In particular, the computed spin density for the monoreduced $[\text{Ni}(\text{DMGBF}_2)_2]^-$ is mainly distributed over the ligand skeleton with a minor contribution from the metal centre (Table S3, Fig. S11). These data are thus supportive for a ligand-based reduction process.

The CV of $[\text{Ni}(\text{DMGBF}_2)_2]$ in DMF is strongly modified upon addition of increasing amounts of perchloric acid. The current density increases at the potential of the first reduction wave reaching a maximum for (i_p/i_0-1) of *ca.* 4. Scanning at more negative potentials upon addition of acid reveals the formation of a new wave peaking at around -1.05 V vs. SCE (Fig. 2).

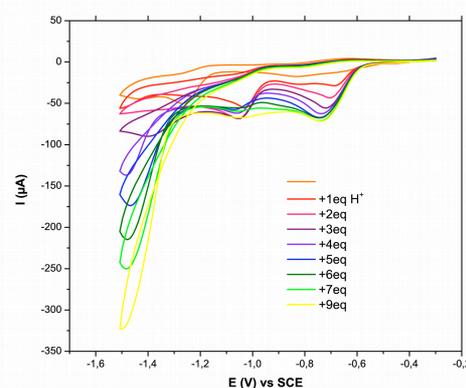


Fig. 2 CV in DMF (0.1 M NaClO₄, $v = 0.1$ V/s) at a glassy carbon electrode of $[\text{Ni}(\text{DMGBF}_2)_2]$ complex (2mM) upon addition of HClO₄

This electrochemical behaviour upon addition of acid lead us to investigate more on the fate of the nickel complex upon electrolysis in the presence of acid. It is to be noted that similar electrochemical responses were observed for different cobalt-based oximes complexes in presence of acid.^{18,19,30} A controlled potential electrolysis of a solution of $[\text{Ni}(\text{DMGBF}_2)_2]$ at around -0.8 V vs. SCE indicated the consumption of four electrons and four protons (Fig. S4) while no H₂ was detected. We assigned this uptake to the reduction of the four imino groups on the periphery of the macrocyclic ligand.^{31,32} In this study, we have made no attempt to isolate such a reduced species. However, to gain more insight on the locus of addition of the successive protons following the electrochemical reduction processes, we have conducted DFT calculations. For this purpose, we have considered three putative sites for the addition of the first proton on the monoreduced $[\text{Ni}(\text{DMGBF}_2)_2]^-$, the metal centre, one carbon atom and one nitrogen atom of the iminic fragment (Fig. 3).

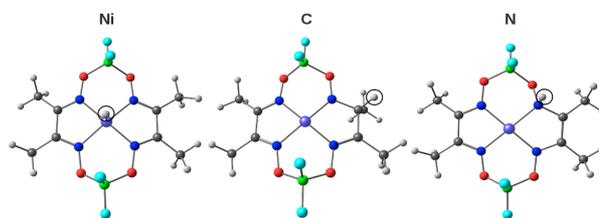


Fig. 3 DFT-optimized structures for the protonated $[\text{Ni}(\text{DMGBF}_2)_2]^-$

Our results clearly pinpoint that the carbon of an iminic group is the preferential locus. The calculated free energies for the three forms predict the carbon-directed protonation to be lower in energy by 8.0 and 36.4 kcal.mol⁻¹ than the nitrogen and metal ones, respectively (Table S4). The successive addition of the three electrons and protons were also investigated (Figs. S12-S14) and the theoretical data further support that the preferential locus for multiple protonation are the carbon atoms of the iminic groups. Again, the calculated free energies show that the most stable species is the one with four protonated carbon centres (Tables S5-S7). Based on these studies, we can reasonably assign the reduction wave that appears at around -1.05 V vs SCE to the additional reduction of the four-electron and four-proton reduced species. In order to further

investigate on the fate of these reduced intermediates in presence of acid, we have performed an electrolysis experiment poisoning the potential at -0.8 V vs. SCE for 16 hours. The resulting electrode was then washed and characterised by the Scanning Electron Microscopy (SEM). An image of the surface of the chemically modified electrode is shown Fig. 4 and depicts the presence of nickel-based nanoparticles with a size distribution ranging from 80 to 300 nm. Energy Dispersive Spectroscopy was used to qualitatively analyse the chemical composition of these particles and reveals mainly the presence of nickel.

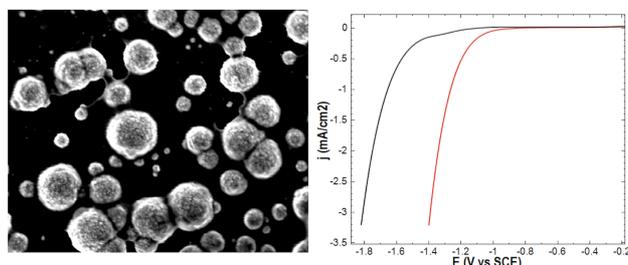


Fig. 4 Left: SEM image of the particles deposited onto a 1 cm^2 glassy carbon surface after the 16h electrolysis of a solution of $[\text{Ni}(\text{DMGBF}_2)_2]$ in DMF (2 mM, NaClO_4 : 0.1 M, HClO_4 : 18 mM, -0.8 V vs SCE); Right: CV at a 0.07 cm^2 glassy carbon electrode in water (0.1 M KPi pH 7, NaClO_4 : 0.1M, 0.1 V/s): black: bare electrode; red: electrode modified after 20 min electrolysis.

A chemically modified electrode with these nanoparticles was prepared, rinsed and transferred under inert conditions to an aqueous solution buffered at pH 7 with a phosphate buffer. This electrode was used as the working electrode for the reduction of protons. A current density of 2 mA/cm^2 was observed at a potential of 410 mV more positive than the bare glassy carbon (Fig. 4 right). It is to be noted that the electrocatalytic properties of nickel particles for HER have been recently reported in different experimental conditions.^{33,34} Further work will aim in a more thorough study on the nature and fate of these catalytic particles after electrocatalytic runs.

Conclusions

In this study, we show for the first time that a molecular complex, formerly described as a modest catalyst for the HER in organic medium, is actually electrochemically modified under acid reducing conditions to form highly active nickel-based nanoparticles for HER at pH 7. Both DFT calculations and experimental data support that the first $4e^-/4\text{H}^+$ are used for the reduction of the iminic groups. The resulting species is further subjected to electro-chemical alteration at the surface of the electrode leading to the formation of nickel nanoparticles. Such an electro-chemical activation pathway of the nickel bis-glyoximate complex clearly evidenced the crucial role of the ligand in the process for the nanoparticles deposit at the surface of the electrode.

Notes and references

^a Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR-CNRS 8182, Université Paris-Sud XI, F-91405 Orsay, France.

^b Laboratoire de Spectrochimie Infrarouge et Raman, UMR-CNRS 8516,

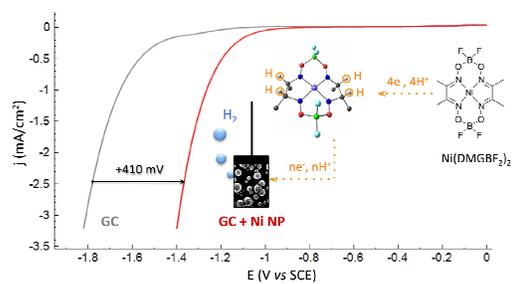
Université Lille 1, F-59655 Villeneuve d'Ascq Cedex, France

^c CEA, iBiTec-S, Service de Bioénergétique, Biologie Structurale et Mécanismes (SB2SM), F-91191 Gif-sur-Yvette, France.

† Electronic Supplementary Information (ESI) available.

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Mechanistic insights on the electrochemical alteration of Ni^{II}(DMGBF₂)₂ into Ni-based nanoparticles showing electrocatalytic HER activity are provided based on experimental and theoretical studies