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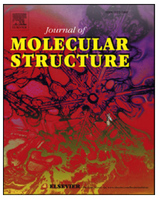

Effect of molecular structure of the N, N′-bis(2-hydroxy-1-naphthaldehyde)-1,3-phenylenediimine ligand on the electrocatalytic properties of its Ni(II) complex for reduction of CO_2

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The electrocatalytic activity of N, N′-bis(2-hydroxy-1-naphthaldehyde)-1,3-phenylenediimine, NMPD, and its Ni(II) complex in reduction of CO_2 was studied in an N, N′–dimethylformamide, DMF, solvent by cyclic voltammetry and chronoamperometry methods. According to the cyclic voltammetry studies, the potential of CO_2 reduction was −1.40 V and −1.18 V versus Ag/AgCl/KCl (sat'd) in the presence of the NMPD ligand and its Ni(II) complex respectively. In this way, the overpotential of CO_2 reduction was reduced for about 700 mV and 920 mV in the presence of NMPD and its Ni(II) complex respectively. However, in the presence of NMPD, a higher increase was observed in the catalytic current of CO_2 reduction with respect to the Ni(II) complex. By chronoamperometry, the homogeneous catalytic rate constant, *k*, for the electron transfer between the NMPD ligand and CO_2 as well as the Ni(II) complex and CO_2 was found to be $24.90 \pm 0.98\ M^{-1}\ s^{-1}$ and $0.71 \pm 0.05\ M^{-1}\ s^{-1}$ respectively. The diffusion coefficients, D, of the NMPD ligand and the Ni(II) complex in the DMF solvent were also determined as $9.8 \times 10^{-6}\ cm^2\ s^{-1}$ and $8.9 \times 10^{-6}\ cm^2\ s^{-1}$ respectively. Considering the results and also the molecular structure of the ligand, the electrocatalytic behavior of these compounds toward CO_2 reduction are discussed in detail.

1. Introduction

Electrochemical activation of carbon dioxide, CO_2, mediated by homogeneous catalysis has been a major issue during recent years. This is due to the high thermodynamic stability of this molecule that makes it difficult to be used in synthesis of organic compounds [1,2] despite the fact that it is the most abundant low-cost carbon source on the earth. Furthermore, some of unique properties of CO_2, like being a single-electron acceptor, pose a challenge to chemists to study its chemistry and the other fundamental issues in this field [3]. There are numerous ways for CO_2 activation [4,5]. Among them, electrochemical reduction is one of the most common techniques to this purpose [6–11]. In direct reduction, at the surface of ordinary electrodes, CO_2 is reduced at high overpotentials [12]. Therefore, different electron transfer mediators have been used to reduce the overpotential of CO_2 reduction and, thus, overcome the problem [3,6–9,13–20]. Redox mediators are compounds which are reduced in less negative potentials respect to CO_2 and then can be regenerated by electron transfer to CO_2. Hence, they decrease the overpotential of CO_2 reduction by an electrocatalytic mechanism (E_rC_i' or E_iC_i' mechanism) [34]. In this way, CO_2 is reduced indirectly by electron transfer from the catalyst to CO_2 [6,21]. The result of this process turns out to be a decrease of the CO_2 reduction overpotential and an increase of the electrocatalytic current. As it seems, indeed, studying the electrocatalytic activity of new electron transfer mediators is useful, more than ever, to decrease the overpotential of CO_2 reduction and to increase the catalytic current.

In this regard, the present paper reports the electrocatalytic activity of a Schiff base (N, N′-bis(2-hydroxy-1-naphthaldehyde)-1,3-phenylenediimine, NMPD) and its Ni(II) complex for CO_2 reduction. According to voltammetric responses, the electrocatalytic reduction of CO_2 is both ligand-based and metal-based. Also, the electrocatalytic behavior of the free ligand toward CO_2 reduction is better than that observed for the central metal of the Ni(II) complex or the coordinated ligand.

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2. Experimental section

N, N′-bis(2-hydroxy-1-naphthaldehyde)-1,3-phenylenediimine, NMPD, (see Scheme 1 for structure), and its Ni(II) complex were prepared according to the instructions reported in the literature [22,23]. N,N′-dimethylformamide (DMF), tetrabutylammonium perchlorate (TBAP) and other reagents were of analytical grades and were purchased from Merck Company and used without any further purification. Carbon dioxide (CO_2) and Argon (Ar) had a purity of 99.995%. Prior to every experiment, the solution was bubbled with Ar gas for 20 min. Chronoamperometry and cyclic voltammetry were performed using an EG&G PARSTAT 2273 equipped with a Power Suite software in a conventional three-electrode electrochemical cell. A glassy carbon electrode (GCE) with 2 mm diameter, a Pt wire, and an Ag/AgCl/KCl (sat'd) electrode were used as the working electrode, the counter electrode, and the reference electrode respectively.

3. Results and discussion

3.1. Cyclic voltammetric studies

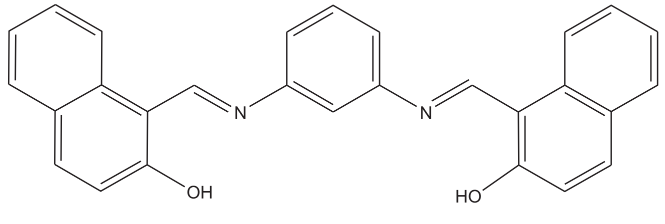
Voltammogram (a) of Fig. 1 shows the voltammetric response of GCE in a DMF solution containing 0.1 M TBAP saturated with CO_2 in the potential range of −0.7 to −2.1 V. As it can be seen, CO_2 begins to reduce at a potential of about −2.1 V versus the Ag/AgCl/KCl (sat'd) reference electrode. Fig. 1 shows the voltammograms of a 1.0 mM Ni(II) complex and a free ligand of NMPD, in a DMF solution containing 0.1 M TBAP, in the absence and the presence of CO_2 at a GCE and in the potential range of −0.60 V to −1.80 V. The voltammograms of (b) and (c) are related to the Ni(II) complex and its corresponding ligand respectively. The voltammogram of the complex (Fig. 1 and Fig. S1, voltammogram b) consists of a redox couple ($E_{pc.}/E_{pa.}$: −1.18/-1.10) with a formal potential of −1.14 V (peaks I/III) and one cathodic peak at the potential of −1.50 V (peak II), while the voltammogram of the NMPD ligand (Fig. 1 and Fig. S1, voltammogram c) only consists of one cathodic peak at the potential of −1.42 V. A comparison of voltammograms (b) and (c) shows that the redox couple of (I/III) is related to the reduction/oxidation process of the central metal (reaction (1)).

$$\text{Ni(II) complex} + e^- \rightleftarrows \text{Ni(I) complex} \tag{1}$$

Cathodic peak (II) of voltammogram (b) is almost located in the same position of the reduction peak of NMPD (voltammogram c). Then, cathodic peak (II) is attributed to the reduction of the ligand in the Ni(II) complex. Reduction peak (II) in voltammogram (b) and the reduction peak of the ligand in voltammogram (c) are related to the reduction of the ligand imine bond and the formation of its radical anion as shown in reaction (2) [24,25].

$$\text{NMPD} + e^- \rightleftarrows \text{NMPD}^{\bullet-} \tag{2}$$

Voltammogram (d) of Fig. 1 is related to the Ni(II) complex solution in the presence of CO_2. As it can be seen, in the presence of CO_2, the currents of cathodic peaks (I) and (II) increase to some extent, the potential of cathodic peak (II) shifts to less negative values, and anodic peak (III) disappears. By comparison of voltammograms (a) and (d), it can be distinguished that the overpotential of CO_2 reduction is reduced for about 920 mV in the presence of Ni(II) complex. The increase of the cathodic current of peak (I) and the disappearance of anodic peak current (III) are most likely related to the electrocatalytic activity of the complex for CO_2 reduction. This catalytic effect corresponds to an electron transfer from the reduced form of the complex, Ni(I) complex, to CO_2 and formation of $CO_2^{\bullet-}$ as well as regeneration of Ni(II) complex (reactions (1) and (3)).



Scheme 1. Chemical structure of N, N′-bis(2-hydroxy-1-naphthaldehyde)-1,3-phenylenediimine, NMPD.

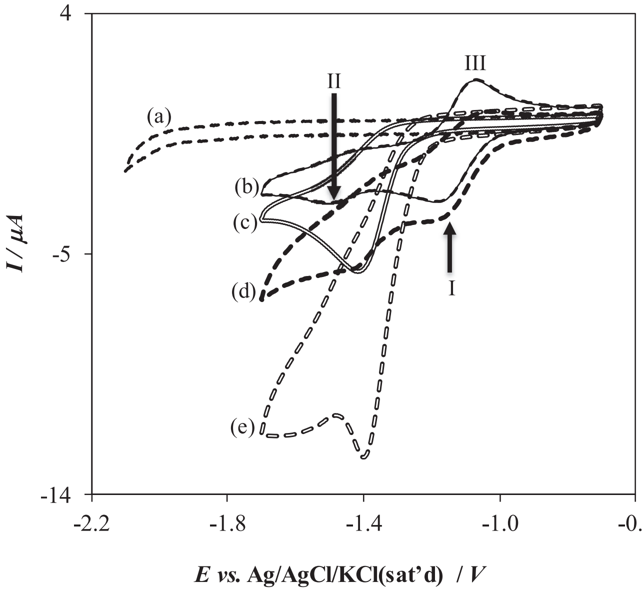


Fig. 1. Cyclic voltammograms of a glassy carbon electrode in a DMF solution containing 0.1 M TBAP as the supporting electrolyte (a) after bubbling of CO_2, (b) after addition of 0.5 mM Ni(II) complex, and (c) after addition of 0.5 mM NMPD. (d) as (b) in the presence of CO_2 and (e) as (c) in the presence of CO_2. Potential scan rate: 100 mV s^{-1}.

$$\text{Ni(I) complex} + CO_2 \rightarrow \text{Ni(II) complex} + CO_2^{\bullet-} \tag{3}$$

To confirm reaction (3) and the role of the central metal in the catalytic activity of the Ni(II) complex for CO_2 reduction, the potential was scanned in the potential range of −0.80 to −1.40 (Fig. 2). As noted, the central metal ion of the Ni(II) complex can only be reduced in this potential range. Voltammograms (a) and (b) of Fig. 2 correspond to the solution of the Ni(II) complex in the absence and the presence of CO_2 respectively. A comparison of voltammograms of (a) and (b) of this figure indicates that the reduction of CO_2 is due to electrocatalytic activity of the central metal of the complex. In other words, the increase of cathodic peak current (I) and the disappearance of anodic peak current (III) in the presence of CO_2 (Fig. 1, voltammogram d or Fig. 2, voltammogram b) is as a result of the electrocatalytic activity of the central metal for CO_2 reduction.

Not so much increase in the catalytic peak current of the central metal in the presence of CO_2 can be indicative of the fact that the electron transfer kinetic from the reduced form of the central metal in the complex (Ni(I) complex) to CO_2 (reaction (3)) is slow. In the Ni(II) complex, Ni(II) ion is coordinated to the NMPD ligand through the nitrogen of imine bonds and hydroxyl groups [26,27]. From the structural point of view, NMPD is a fully conjugated planar π-acceptor ligand, and, therefore, it is expected that the electrons