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# Syngas Production with a Highly-Robust Nickel(II) Homogeneous Electrocatalyst in a Water-Containing System

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**ABSTRACT:** Syngas (CO and H<sub>2</sub>) is an essential raw material for producing various chemicals in industry. The reduction of CO<sub>2</sub> in a water-containing system can serve as a more sustainable pathway to obtain syngas than the transformation of fossil fuels, while the modulation of the H<sub>2</sub>/CO ratios is a challenge. Herein a nickel(II) tripodal complex is employed as a homogeneous electrocatalyst for CO<sub>2</sub> and H<sub>2</sub>O reduction. With this catalyst, selective CO formation with negligible H<sub>2</sub> evolution can be accomplished in the presence of 5.0 M H<sub>2</sub>O in *N*,*N'*-dimethylformamide (DMF). By further varying the applied potentials, the H<sub>2</sub>/CO ratio can be delicately tuned. The catalyst is appreciably robust with a high turn-over number of  $1.9 \times 10^6$ in 1 day operation with negligible deactivation, which can be attributed to the redox innocence of the used ligand. Based on the results of electrochemistry and DFT calculation, the catalytic mechanism is proposed.

**KEYWORDS:** *carbon dioxide reduction, water reduction, syngas, mononuclear nickel complex, electrocatalysis, high stability, redox innocence* 

#### **INTRODUCTION**

Synthetic gas (syngas), the mixture of carbon monoxide (CO) and hydrogen (H<sub>2</sub>), is a key chemical feedstock in the production of chemical products, such as methanol, dimethyl ether, acetic acid, etc.<sup>1-3</sup> Non-renewable fossil fuels, especially natural gas (mainly CH<sub>4</sub>) and coal, are the dominant sources of syngas production in current industry.<sup>2</sup> Carbon dioxide (CO<sub>2</sub>) is viewed as an abundant carbon source in preparation of value-added chemicals.<sup>4-5</sup> In particular, the utilization of solar energy or electricity to drive the reduction of both CO<sub>2</sub> and H<sub>2</sub>O to gain

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syngas can be a promising renewable pathway for chemical production. This process requires bi-functional catalysts to reduce both  $CO_2$  and  $H_2O$ . It should be mentioned that the design of efficient catalysts for  $CO_2$  reduction presents a challenge,<sup>6</sup> as the high thermodynamic stability of  $CO_2$  makes its activation and reduction energy-demanding.<sup>7-8</sup> Recently, metal complexes as molecular, homogeneous catalysts for  $CO_2$  reduction, have been considered as attractive candidates due to the following reasons:<sup>9-13</sup> (1) homogeneous catalysts have shown high activity, stability and selectivity for the certain reactions; (2) catalytic intermediates of homogeneous catalysts are relatively feasible to spectroscopic, crystallographic and theoretical characterization, enabling the verification of catalytic mechanisms; (3) homogeneous catalysts possess well-defined structures that can be deliberately optimized by synthetic methods; (4) immobilizing homogeneous catalysts on various substrates can be a promising method to prepare atomically dispersed heterogeneous catalysts with remarkably improved catalytic efficiency.

In terms of syngas production, the H<sub>2</sub>/CO ratio is a key factor for the synthesis of downstream products: syngas with 1:1 H<sub>2</sub>/CO ratio is needed in the hydroformylation to yield aldehyde<sup>14</sup> and the one with 2:1 is the required composition in Fischer-Tropsch hydrocarbon synthesis.<sup>1</sup> In modern technologies, the modulation of syngas composition relies on the additional water-gas shift reaction, which makes the entire process more costly.<sup>3</sup> The co-reduction of CO<sub>2</sub> and H<sub>2</sub>O to obtain adjustable H<sub>2</sub>/CO ratios may eliminate the requirement for intermediate adjustments in syngas composition, which, however, still remains a significant challenge. Besides the lethargic activation of CO<sub>2</sub>,<sup>8</sup> the reduction of H<sup>+</sup>/H<sub>2</sub>O to H<sub>2</sub> is thermodynamically favored in contrast to the CO<sub>2</sub>-to-CO conversion (-0.41 vs. -0.53 V vs. NHE at pH 7, Equations 1 and 2).<sup>6</sup> A significant

$$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O \qquad E^0 = -0.53 V$$
 (1)

$$2H^+ + 2e^- \rightarrow H_2$$
  $E^0 = -0.41 \text{ V}$  (2)

preference of H<sub>2</sub> evolution over CO production in water-containing systems makes the H<sub>2</sub>/CO ratio less controllable. To overcome this problem, the catalyst kinetically favoring the reduction of CO<sub>2</sub> over H<sup>+</sup>/H<sub>2</sub>O should be designed. Moreover, although selective CO<sub>2</sub> reduction to CO with homogeneous catalysts have been reported,<sup>15-19</sup> effective strategies and systems to easily control the H<sub>2</sub>/CO ratio are still limited.<sup>20</sup> Kubiak and co-workers<sup>21</sup> constructed a system to produce syngas by combining a homogeneous  $CO_2$ -reduction catalyst,  $Re(bpy)(CO)_3Cl$  (bpy = 2,2'-bipyridine), with an illuminated p-Si that acted as a photoelectrochemical heterogeneous H<sub>2</sub>O-reduction catalyst. Based on the remarkable catalytic activity of the rhenium complex toward CO<sub>2</sub>-to-CO conversion, the addition of water increased H<sub>2</sub> evolution and thus modulated the H<sub>2</sub>/CO ratio. Meyer et al<sup>22</sup> used a ruthenium complex,  $[Ru(tpv)(Mebim-pv)(H_2O)](PF_6)_2$  (tpv  $= 2.2^{\circ}:6^{\circ}.2^{\circ}$ -terpyridine; Mebim-py = 3-methyl-1-pyridyl-benzimidazol-2-ylidene), as a homogeneous CO<sub>2</sub>/H<sub>2</sub>O-reduction electrocatalyst for syngas production. The H<sub>2</sub>/CO ratios were regulated by varying the applied potentials and pH values. Obviously, simple and low-cost catalytic systems for syngas production with controllable H<sub>2</sub>/CO ratio are much desired. Additionally, the longevity of those reported homogeneous catalysts for CO<sub>2</sub>/H<sub>2</sub>O-reduction are not satisfactory, which usually suffers from CO-poisoning,<sup>23</sup> catalyst polymerization<sup>24-25</sup> or ligand hydrogenation/decomposition,<sup>7,26-27</sup> causing low turn-over numbers (TONs) and thus restricting their further applications.

To address the above issues, a nickel(II) tripodal complex,  $[Ni^{II}(Me_3NTB)(CH_3CN)_2](BF_4)_2$  (1; Me<sub>3</sub>NTB = tris(*N*-methylbenzimidazol-2-ylmethyl)amine, Figure 1), was prepared as a

homogeneous electrocatalyst for  $CO_2$ -to-CO conversion in DMF/H<sub>2</sub>O electrolyte. During electrocatalysis, the ratio of H<sub>2</sub> and CO in the products can be effectively controlled by adding appropriate amounts of water or varying applied potentials in the system. Benefitting from the redox innocence of Me<sub>3</sub>NTB ligand, **1** can function as a highly robust catalyst for CO<sub>2</sub>-to-CO conversion with a high TON.



Figure 1. (a) The schematic structure of 1. (b) The crystallographic structure of 1. Hydrogen atoms, counter anions and guest solvents were omitted, probability = 30%.

#### **RESULTS AND DISCUSSION**

Synthesis and Structure. 1 was obtained as violet crystals from a CH<sub>3</sub>CN solution of Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and Me<sub>3</sub>NTB. The result of X-ray structural analysis reveals that the structure of 1 contains a  $[Ni^{II}(Me_3NTB)(CH_3CN)_2]^{2+}$  cation, two BF<sub>4</sub><sup>-</sup> counter anions and three guest acetonitrile molecules (Table S1). As shown in Figure 1, the nickel(II) center is six-coordinated to four N atoms from the tripodal ligand and two N atoms from two CH<sub>3</sub>CN molecules, forming a slightly distorted octahedral geometry. Dissolved in DMF solution, 1 remains a mononuclear structure based on the result of electro-spray ionization mass spectrometry (ESI-MS, Figure S1). The UV-Vis spectrum of 1 in DMF solution exhibits a characteristic band at ca. 600 nm (Figure

S2), which can be assigned to the *d*-*d* transition of  $Ni^{II}$ . This absorbance remained unchanged in the presence of water after 1 day of aging, showing the high stability of **1** in the solution.

**Cyclic Voltammetry under Argon.** Initially, the redox property of **1** was investigated by cyclic voltammetry in anhydrous DMF in the presence of 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate (TBAPF<sub>6</sub>) at a glassy-carbon (GC) disc electrode (1 mm diameter) in absence of proton source. Unless otherwise stated, all potentials were footnoted as versus normal hydrogen electrode (vs NHE). The cyclic voltammogram (CV) of **1** under argon featured two reduction peaks at -1.33 and -1.63 V, respectively (Figure 2). The two peaks are assigned as metal-centered Ni<sup>11/1</sup> and Ni<sup>1/0</sup> reduction, respectively, as the Me<sub>3</sub>NTB ligand cannot be reduced at the same conditions (Figure S3, Equations 3 and 4). According to the Randles-Sevcik analysis at the quasi-reversible Ni<sup>11/1</sup> couple at  $E_{1/2} = -1.29$  V (*ca.* 80 mV peak-to-peak separation), **1** is freely diffusing in solution with a diffusion coefficient of  $D = 1.2 \times 10^{-6}$  cm<sup>2</sup>/s (see SI and Figure S4 for details).<sup>28</sup>



**Figure 2.** CVs scanned at potentials from 0 to (a) -1.5 V and (b) -1.8 V with 1.0 mM **1** in a 0.1 M TBAPF<sub>6</sub> DMF solution under 1 atm argon (black) and  $CO_2$  (violet) at a scan rate of 100 mV/s.

$$[Ni^{1}(Me_{3}NTB)]^{+} + e^{-} \rightarrow [Ni^{0}(Me_{3}NTB)] \qquad E_{p} = -1.63 \text{ V} \quad (4)$$

Cyclic Voltammetry under CO<sub>2</sub>. Subsequently, the cyclic voltammetry of 1 under 1 atm CO<sub>2</sub> in an anhydrous DMF solution were recorded. As shown in Figure 2a, the CV of 1 displayed that the Ni<sup>II/I</sup> redox couple became irreversible and the reduction peak shifted positively by ca. 80 mV (at -1.25 V), followed by a sharp increase of the current that peaked at -1.60 V. The positive shift of the Ni<sup>II/I</sup> reduction suggests the binding of  $CO_2$  to the Ni<sup>I</sup> species of **1** (Equation 5).<sup>23</sup> The irreversibility and current increase may result from a rapid, irreversible chemical step following the binding of CO<sub>2</sub>, most probably catalytic CO<sub>2</sub> reduction,<sup>23</sup> which was clarified by controlled-potential electrolysis (CPE, see below) experiments.

$$[Ni^{T}(Me_{3}NTB)]^{+} + CO_{2} \rightarrow [Ni(CO_{2})(Me_{3}NTB)]^{+}$$
(5)

 $[NI (Me_3NIB)]^+ + CO_2 \rightarrow [NI(CO_2)(Me_3NIB)]^+$ (5) The catalytic CO<sub>2</sub> reduction reaction is first order in the concentration of catalyst ([1]), as a linear relationship by plotting catalytic currents ( $i_{cat}$ ) at -1.60 V versus [1] (Figure S5). Additionally, plotting  $i_{cat}$  versus the square root of  $[CO_2]$  revealed a linear relationship (Figure S6a), showing that the catalytic reaction is also first order in  $[CO_2]$ . The reaction constant of  $CO_2$ binding  $(K_{CO2})$  can be calculated following the Equation (6).

$$\Delta E_{\rm CO_2} = \frac{RT}{nF} \ln\{1 + [\rm CO_2]K_{\rm CO_2}\}$$
(6)

Equation (6) illustrates an  $E_{\rm R}C_{\rm cat}$  mechanism, where electron transfer and onward/backward reactions are substantially fast and  $K_{CO2}$  is relatively large.<sup>29</sup> Although in our case the reverse reaction of CO<sub>2</sub> binding is slow due to the absence of Ni<sup>II/I</sup> oxidation wave under CO<sub>2</sub> atmosphere (Figure 2), this equation can still be applied here to estimate the  $K_{CO2}$  according to the work of Sampson et al.<sup>30</sup> Since the observed shift in potential of the cathodic peak ( $\Delta E_{CO2}$ ) at low [CO<sub>2</sub>] is a linear function of ln[CO<sub>2</sub>] with a slope (22.4) near 26 mV/decade (Figure S7), a

 $K_{CO2}$  of *ca.* 350 M<sup>-1</sup> can be tentatively estimated according to the Equation 6.<sup>23,29-30</sup> This value is considerably higher than those well-defined electrocatalysts for CO<sub>2</sub> reduction, such as  $[Ni(cyclam)]^{2+}$  (6 M<sup>-1</sup>; cyclam = 1,4,8,11-tetraazacyclotetradecane)<sup>23</sup> and  $[Mn(mesbpy)(CO)_3]^+$ (46±10 M<sup>-1</sup>; mesbpy = 6,6'-dimesityl-2,2'-bipyridine),<sup>30</sup> demonstrating a high affinity of the catalyst to CO<sub>2</sub>. This result also infers its high selectivity toward CO<sub>2</sub> reduction rather than hydrogen evolution. The facile CO<sub>2</sub>-binding is attributable to the open site of Me<sub>3</sub>NTB ligand platform. In addition, the strong basicity of methylated benzimidazole N-donors<sup>31</sup> offers substantial electron density to the Ni<sup>1</sup> center and also facilitates the binding of CO<sub>2</sub> at the carbon atom.

**Cyclic Voltammetry with Proton Addition.** It can be noticed that, under CO<sub>2</sub> and dry condition, the catalytic current at the Ni<sup>II/I</sup> reduction wave (-1.25 V) was not significant and a more drastic current appeared at potentials more negative than -1.50 V (Figure 2), indicating that the catalytic reduction reaction following the CO<sub>2</sub> binding is slow. Based on our previous findings<sup>32</sup> and other reports,<sup>33-34</sup> the slow catalytic reduction reaction may be ascribed to the fact that the cleavage of the C-O bond in the [Ni-CO<sub>2</sub>]<sup>+</sup> adduct is unfavorable without proton source. Thus we were intended to add water as a proton source in the system of **1** to improve its performance.<sup>23,33,35</sup> Along with the addition of water, the CV of **1** under argon showed that both of the peak potentials of Ni<sup>II/I</sup> and Ni<sup>I/0</sup> reduction remained unchanged, which demonstrates that no proton-dependent transfer was involved in the two redox processes.<sup>23</sup> However, their currents would increase along with increasing [H<sub>2</sub>O] (Figure 3a). In particular, the peak current at Ni<sup>I/0</sup> increased dramatically at [H<sub>2</sub>O]  $\geq$  7.0 M. The increase in current suggests that the Ni<sup>0</sup> species of **1** can reduce protons to evolve hydrogen from water (Equation 7).

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Ni<sup>0</sup>(Me<sub>3</sub>NTB) + 2H<sup>+</sup> → [Ni<sup>II</sup>(Me<sub>3</sub>NTB)]<sup>2+</sup> + H<sub>2</sub> (7) When CO<sub>2</sub> was introduced into this water-containing catalytic system, the peak position of the catalytic wave (at 1.60 V in anhydrous DMF) was positively shifted (Figure 3b). The shift of the catalytic peak ( $\Delta E$ ) reached to a maximum of ca. 0.23 V with [H<sub>2</sub>O] ≥ 8.0 M, and the current at Ni<sup>II/I</sup> peak (-1.25 V) was also enhanced substantially. Similar positive shifts were found in the CVs of **1** upon the addition of two other Brønsted acids, 2,2,2-trifluoroethanol (TFE) and phenol (Figure S8). These observations demonstrate that the addition of protons thermodynamically facilitates the CO<sub>2</sub> reduction process and thus lowers the catalytic potential. This facilitation is likely to undergo a concerted proton-coupled electron transfer (PCET) involving a protonation on the Ni-CO<sub>2</sub> adduct to activate the formation of product (Equation 8).<sup>23,33</sup> The above findings indicate that, assisted by the water addition, the catalytic reduction of CO<sub>2</sub> would be thermodynamically favored via a protonation pathway.

$$[Ni^{1}(Me_{3}NTB)]^{+} + H_{2}O + CO_{2} + e^{-} \rightarrow [Ni(COOH)(Me_{3}NTB)]^{+} + OH^{-}$$
(8)



Figure 3. CVs of 1.0 mM 1 in a 0.1 M TBAPF<sub>6</sub> DMF solution under 1 atm (a) argon and (b) CO<sub>2</sub> in the presence of water ([H<sub>2</sub>O] =  $0 \sim 11.0$  M), scan rate = 100 mV/s.



Scheme 1. Proposed mechanism of CO<sub>2</sub>-to-CO conversion catalyzed by 1.

**Proposed Mechanism.** Based on some reported studies<sup>32,36</sup> and the experimental results, including the fact that the main product of catalytic CO<sub>2</sub> reduction with **1** is CO (see below), a catalytic mechanism of **1** can be tentatively proposed as Scheme 1, which is further clarified by DFT calculations. At the beginning, the Ni<sup>1</sup> species is generated by one-electron reduction of **1**, followed by the dissociation of acetonitrile molecules and then binding with CO<sub>2</sub> to form a  $[Ni-CO_2]^+$  species. The Ni<sup>II</sup>/Ni<sup>I</sup> reduction potential was estimated as -1.27 V, close to the experimental value (-1.33 V). Next, the weak Brønsted acid (i.e. water) protonates the Ni-CO<sub>2</sub> intermediate to yield a Ni-COOH species, and thus facilitates the cleavage of its C-OH bond to produce CO.<sup>33,37</sup> The calculation reveals that the energy barrier of Ni-CO<sub>2</sub> formation (TS 1; 7.7 kcal/mol) is lower than that of CO-cleavage step (TS 2; 8.9 kcal/mol). This result indicates that the CO-cleavage process is the rate-determining step rather than the CO<sub>2</sub>-binding process, which, as mentioned before, can be attributed to the high affinity of the Ni<sup>I</sup> intermediate with CO<sub>2</sub>.

**Modulation of Product Selectivity.** To determine the composition of CO<sub>2</sub> reduction product, CPE experiments were carried out with 1.0 mM **1** in a DMF solution with different concentrations of water at -1.24 V in a one-room cell. As shown in Table 1 (Entry 1), after CPE for 6 h in an 'anhydrous' DMF, the Faradaic efficiency of **1** for CO production [denoted as F(CO)] was determined as ~82%. With increasing water (3.0 ~ 11.0 M), the F(CO) values can be improved to above 90%, concomitant with decreasing amounts of H<sub>2</sub>. With 5 M H<sub>2</sub>O in DMF, the F(CO) reached the highest value (~ 96%) (Entry 6 in Table 1). These results show that the CO selectivity and the F(CO) of **1** can be readily improved by the addition of water into this system.

**Table 1.** Electrocatalytic reduction of CO<sub>2</sub> by 1.<sup>a</sup>

Entry	$[H_2O](M)$	<i>Q</i> (C)	<i>n</i> (CO) (µmol)	$n(\mathrm{H}_2) \ (\mu \mathrm{mol})$	CO selectivity	<i>F</i> (CO) (%)
1	0	$3.1 \pm 0.2$	$13.2 \pm 0.4$	$2.51 \pm 0.21$	84	82
2	1.0	$3.2 \pm 0.2$	$13.9\pm0.4$	$1.63 \pm 0.11$	90	84
3	2.0	$3.0\pm0.3$	$13.8\pm0.5$	$1.12 \pm 0.21$	92	89
4	3.0	$3.6 \pm 0.3$	$16.8\pm0.6$	$0.70\pm0.05$	96	90
5	4.0	$4.3\pm0.2$	$20.5\pm0.4$	$0.81\pm0.10$	96	92
6	5.0	$4.4\pm0.3$	$21.8\pm0.8$	$0.70\pm0.08$	98	96
7	6.0	$4.8\pm0.5$	$22.8\pm0.7$	$1.27 \pm 0.15$	95	92
8	8.0	$5.3\pm0.3$	$24.8\pm1.2$	$2.04\pm0.32$	93	90
9	11.0	$5.6 \pm 0.6$	$25.3 \pm 1.7$	$2.07\pm0.24$	92	88
10 <sup>b</sup>	0	$2.2 \pm 0.4$	$9.2 \pm 0.5$	$1.70\pm0.20$	84	81
11 <sup>b</sup>	5.0	$3.8 \pm 0.5$	$18.7\pm1.0$	$0.83\pm0.10$	96	95
12 <sup>c</sup>	0	$3.2 \pm 0.3$	$8.0 \pm 0.8$	$0.20\pm0.05$	98	48

<sup>a</sup> CPE experiments were operated with 1.0 mM **1** in a 0.1 M TBAPF<sub>6</sub> DMF solution at  $E_{cat} =$  -1.24 V for 6 h in a one-room cell. <sup>b</sup> A carbon rod was used as the counter electrode instead of the Pt wire. <sup>c</sup> CH<sub>3</sub>CN was employed as the solvent instead of DMF.

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Several experiments were operated to verify the origins of the significant hydrogen evolution at anhydrous conditions. The results are included in Table 1. First, no significant changes were observed when a carbon rod was used as the counter electrode. Especially, the results in Entry 10 indicate that the replacement of counter electrode could not suppress the hydrogen evolution in the absence of water. These results infer that the contamination of Pt ions from the Pt anode<sup>38,39</sup> is less likely to induce the hydrogen evolution. Then, we used CH<sub>3</sub>CN instead of DMF as the electrolyte. As shown in Entry 12, the Faradaic efficiency and yield of CO production were relatively low in contrast to those in the case with DMF. Such differences induced by solvents were also reported.<sup>18</sup> We tentatively attribute it to the stronger coordination ability of CH<sub>3</sub>CN, which hinders the substrate (CO<sub>2</sub>) from binding to the metal catalytic center and subsequent catalysis. Importantly, negligible hydrogen was evolved with CH<sub>3</sub>CN as the solvent, suggesting that the presence of DMF is an origin of significant hydrogen evolution under anhydrous conditions.

With the above results, we speculate that the DMF might be oxidatively decomposed at the Pt electrode in the one-room cell. Such oxidative degradation at the Pt anode may generate proton source and facilitate the hydrogen evolution. However, due to the competition of water oxidation, the degradation of the water-containing electrolyte is much slighter. That is one of the reasons why the CO selectivity was enhanced along with adding water. To confirm this speculation, we utilized a Nafion membrane to isolate the cathode and anode, followed by the CPE experiments at different concentrations of water. This set-up can avoid the contamination of degraded electrolyte at the cathode. As summarized in Table S2, different from those in the one-room cell, the results from the two-room cell reveal that the hydrogen evolution became increasingly significant in the CPE along with increasing water. More importantly, it can be found that little

hydrogen was detected during the CPE in dry DMF, achieving a CO selectivity of 99%. These results support that the oxidation degradation of electrolyte at the anode is a dominant origin of significant hydrogen evolution in dry DMF, which can be avoided by using a two-room cell. At present, we consider that one of the decomposition pathways is to generate formate, and the corresponding dimethylamine<sup>40</sup> (susceptible to further oxidation). However, the decomposition of DMF is complicated and the detailed identification of the products is still on the progress. On the other side, the *F*(CO) values still revealed an improvement along with the addition of water. This observation can be attributed to the facilitation of the PCET-involved catalysis by water addition (Equation 8).

In both types of electrolytic cells, although a relatively large amount of water (approximately 20% volume ratio) was added in the DMF system, the hydrogen evolution was not significant, with CO-selectivity values over 89%. The F(CO) values were even enhanced by adding appropriate amounts of water. Based on our experimental observations and the results from Savéant et al,<sup>41</sup> a feasible interpretation of the factors favorable to CO formation against H<sub>2</sub> evolution in the presence of water can be described as follows. First, the high  $K_{CO2}$  of Ni<sup>1</sup> species of 1 indicates its higher intrinsic affinity for CO<sub>2</sub>, indicating that CO<sub>2</sub> is the more advantageous substrate than H<sup>+</sup> in this catalytic reaction. Second, the thermodynamic barrier for CO production by 1 is readily lowered by the addition of water, as observed in the CVs along with water addition, where the Ni<sup>1</sup>-involved catalytic wave was positively shifted due to the participation of PCET (Figure 3 and Equation 8). We consider this factor readily improves the F(CO) along with the water addition. Third, the reaction that converts CO<sub>2</sub> and H<sub>2</sub>O into HCO<sub>3</sub><sup>-</sup> and H<sup>+</sup>, is thermodynamically difficult with an equilibrium of approximately  $10^{-6}$ ,<sup>37</sup> leading to a much

lower concentration of  $H^+$  than  $CO_2$  in DMF/H<sub>2</sub>O system. In all, the above factors favor the  $CO_2$ -to-CO pathway and restrict the H<sub>2</sub>-evolution one, resulting in the high CO selectivity in the presence of water.

To further investigate the factors that influence the product selectivity of 1, we also conducted CPE measurements in DMF/H<sub>2</sub>O solution ([H<sub>2</sub>O] = 5.0 M) at varying potentials (-1.19  $\sim$  -1.49 V). The results shown in Table 2 illustrate that when the reduction potential was varied from -1.19 to -1.24 V, the CO yield and selectivity were improved. From -1.24 to -1.49 V, the CO yield was also enhanced, however, more hydrogen was evolved and the selectivity of CO formation markedly decreased. Further negatively increasing the potential to -1.44 and -1.49 V, substantial amounts of syngas products with H<sub>2</sub>/CO ratio of 1:1 and 2:1 could be generated, respectively (Entry 4 and 5 in Table 2). This can be attributed to the fact that these applied potentials are increasingly closer to the Ni<sup>1/0</sup> reduction, as observed in previous CVs (Figure 3). The formed Ni<sup>0</sup> species possesses stronger affinity to H<sub>2</sub>O over CO<sub>2</sub> and tends to proceed the reduction of  $H_2O$  to  $H_2$  (Equation 7), leading to the syngas production with higher  $H_2/CO$  ratios. Therefore, by controlling the applied potentials in the system with 1, the ratio of the products of electrocatalytic CO<sub>2</sub> reduction and H<sub>2</sub>O reduction can be tuned. To the best of our knowledge, this is the first catalytic system that can produce syngas with tunable compositions with a molecular catalyst based on earth-abundant elements.

Entry	$F_{(M)}$	<i>Q</i> (C)	n(CO)	$n(H_2)$	H.:CO	<i>F</i> (CO) (%)	$F(H_2)$ (%)
	$L_{cat}(\mathbf{v})$		(µmol)	(µmol)	112.00		
1	-1.19	$2.2 \pm 0.1$	$10.0\pm0.2$	$1.02 \pm 0.04$	1:9	88	8.9
2	-1.24	$4.4\pm0.3$	$21.3\pm0.8$	$0.72\pm0.08$	1:50	96	3.2
3	-1.34	$6.6\pm0.4$	$29.3\pm0.8$	$3.82\pm0.10$	1:9	86	11
4	-1.44	$6.9\pm0.3$	$14.8\pm0.4$	$14.5\pm0.2$	1:1	41	41
5	-1.49	$7.3\pm0.4$	$10.1\pm0.7$	$20.4\pm0.5$	2:1	27	54

**Table 2**. Electrocatalytic reduction of  $CO_2$  by 1 at -1.19 ~ -1.49 V.<sup>a</sup>

<sup>a</sup> CPE experiments were operated with 1.0 mM 1 in a 0.1 M TBAPF<sub>6</sub> DMF solution in the presence of  $5.0 \text{ M H}_2\text{O}$  for 6 h.

After CPE experiments at  $-1.19 \sim -1.49$  V with 1 for 6 h, besides CO and H<sub>2</sub>, no formaldehyde and oxalate but a trace amount of formate ( $\sim 1 \mu mol$ ) was detected by capillary electrophoresis. We noticed that a similar amount of formate was also discovered in the electrolyte after the CPE experiment without 1. Thus, the formation of the formate is attributable to the decomposition of DMF rather than 1. In the meantime, during all CPE experiments in the absence of 1, no CO but the aforementioned formate and certain amounts of hydrogen can be detected. These results further demonstrate that the CO generation originates from the CO<sub>2</sub> reduction by 1.

**Investigation of Catalyst Robustness.** The stability of **1** was initially checked by cyclic voltammetry before and after CPE. It can be seen that a small current enhancement was obtained after the CPE at anhydrous conditions in the one-room cell, while no significant change took place by using the two-room cell (Figure S9a). These observations further indicate that additional proton source was generated in the one-room cell and enhanced the catalytic current, which could be prevented by the use of two-room cell. More importantly, the two reduction waves are still well-defined in both cases, demonstrating the high robustness of **1** during electrocatalytic

CO<sub>2</sub> reduction. Moreover, with the addition of 5 M H<sub>2</sub>O, negligible changes were observed in the CVs (Figure S9b) and the characteristic *d-d* transition band in the UV-Vis spectra (Figure S10) before and after CPE in the one-room cell for 6 h. These results further indicate that the addition of water can diminish the DMF decomposition and that **1** is stable during electrocatalysis. Also, the results of <sup>13</sup>C labeling experiment demonstrate that the dominant CO product originates from CO<sub>2</sub> rather than the decomposition of **1** or the organic electrolyte (Figure S11). Furthermore, no nickel residue was found on the surface of working electrocatalysis of **1**.<sup>42</sup> We also conducted the energy dispersive X-ray spectroscopy (EDX, Figure S12), which clearly demonstrates that no nickel-based heterogeneous catalyst is involved in electrocatalysis of **1**.<sup>42</sup> We also conducted the EDX measurements on the working electrode after CPE, which further demonstrates the high stability of **1** during CPE process.

To further check the stability of **1**, the CPE experiment by **1** was elongated up to 24 h. The result shows that a relatively stable current density ( $j = 0.12 \text{ mA/cm}^2$ , Figure S14) was obtained along with an accumulated charge of 22.2 C during a 24 h CPE. As shown in Figure 4, 104.6  $\mu$ mol of CO was detected, corresponding to a Faradaic efficiency of 91 ± 5%, concomitant with a trace amount of H<sub>2</sub> (~2%) and formate (~1%). Based on the number of catalyst molecules in the catalytic system, a total turn-over number (TON) value of 10.4 is calculated. This value, however, is considered as a lowered estimate, as only a small fraction of catalyst molecules that interact with the electrode are contributing to catalysis.<sup>43</sup> Therefore, we applied Equation (2) to calculate the intrinsic catalytic rate ( $k_{cat} = 757.3 \text{ s}^{-1}$ ) of **1** based on the number of catalyst

molecules in the diffusion layer of the cathode.<sup>44</sup> In Equation 9, [1] is the concentration of 1 (1.0 mM), E is the applied potential in CPE



**Figure 4.** Chronocoulometric plot (purple line and black pentagon) and the yields of CO (black star) and H<sub>2</sub> (black circle) obtained in a 24 h CPE at -1.24 V in DMF solution at a GC plate (1.5  $\text{cm}^2$ ) in the presence of 1.0 mM **1**, 0.1 M TBAPF<sub>6</sub> and 5.0 M H<sub>2</sub>O under 1 atm CO<sub>2</sub>.

$$j = \frac{[1]D^{\frac{1}{2}}(2k_{\text{cat}})^{\frac{1}{2}}F}{1 + \exp[\frac{F}{RT}(E - E_{\text{cat}})]}$$
(9)

$$TOF = \frac{k_{cat}}{1 + \exp[\frac{F}{RT}(E - E_{cat})]}$$
(10)

$$TON = \frac{k_{cat}}{1 + \exp[\frac{F}{RT}(E - E_{cat})]} \times t$$
(11)

(-1.24 V),  $E_{cat}$  is the standard potential for catalysis (namely the potential of Ni<sup>II/I</sup> reduction at -1.33 V), *T* is the environmental temperature (298.15 K), and *j* is the averaged electrolytic current density (0.12 mA/cm<sup>2</sup>). Since the catalytic current remained stable during 24 h electrolysis, a TOF of 22.1 s<sup>-1</sup> and a remarkable TON of  $1.9 \times 10^6$  could be calculated based on

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Equations 10 and  $11.^{45}$  To date, among the reported nickel electrocatalysts for CO<sub>2</sub>-to-CO conversion,  $[Ni(cyclam)]^{2+46}$  and its derivatives<sup>47-49</sup> are a type of well-known efficient catalysts at mercury-based electrodes, which, however, beyond the scope of homogeneous catalysis.<sup>50</sup> Herein, featuring high values of TON and Faradaic efficiency for CO production, the catalytic performance of **1** is competent to those pioneering mononuclear nickel-based homogeneous electrocatalysts toward CO<sub>2</sub>-to-CO conversion (Table S2).<sup>26,50-51</sup> These results demonstrate that **1** is a highly selective and stable catalyst for electrocatalytic CO<sub>2</sub>-to-CO conversion. Furthermore, by controlling the applied potentials, the syngas with diverse ratio of H<sub>2</sub>/CO could be produced, which further makes **1** outstanding among reported nickel-based homogeneous electrocatalysts.

To reveal the high robustness of 1, a nickel tripodal complex of [Ni(NTB)(CH<sub>3</sub>CN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (2; NTB = tris((1H-benzo[*d*]imidazol-2-yl)methyl)amine, Figure 5) with similar structure to 1 was designed and synthesized. The CV (Figure S15a) and CPE results (Table 3) indicate that 2 can also be used as an electrocatalyst for CO<sub>2</sub>-to-CO conversion in DMF. However, 2 was unstable during the electrocatalytic process, as indicated by its low overall Faradaic efficiencies (< 60%, Table 3), decreased catalytic current (Figure S16) and Ni-based residues on the used working electrodes (Figure S17) after CPE at -1.24 V for 6 h. The instability could be attributed to its redox-active NTB ligand, as verified by the CV of NTB ligand, where a large irreversible reduction wave appeared at potentials more negative than -1.2 V (Figure S18). In contrast, Me<sub>3</sub>NTB cannot be reduced at potentials less negative than -1.8 V in DMF (Figure S18). The redox inertness of Me<sub>3</sub>NTB is due to the methyl groups on the imidazole fragments.<sup>52</sup> This finding was further supported by the parallel experiments on other Ni(II) complexes with redox-active pyridyl<sup>53</sup> fragments (Figure 5). Although they were found to be effective in

electrocatalytic  $CO_2$  reduction (Figure S15), all of them would decompose during electrocatalysis (Table 3). On the basis of the above results, it can be concluded that the high stability of **1** during catalysis is due to its redox-innocent ligand. This observation is presently limited in nickel-based catalysts for  $CO_2$  reduction, which, however, should be instructive in the design of more efficient and robust molecular catalysts for electrochemical  $CO_2$  reduction in future.



**Figure 5.** Investigated Ni(II) complexes (1-5) for electrocatalytic CO<sub>2</sub> reduction in DMF. TPA = tris(2-pyridylmethyl)amine; MEP = N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-1,2-diamino-ethane; MCP = N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-1,2-diaminocyclohexane.

Table 3. Electrocatalytic reduction of CO<sub>2</sub> by Ni complexes.<sup>a</sup>

Entry	Catalysts	Ecat	<b>Q</b> (C)	n(CO)	F(CO)	<i>n</i> (H <sub>2</sub> )	<i>F</i> (H <sub>2</sub> )	Deposit

		(V)		(µmol)	(%)	(µmol)	(%)	
1	1	-1.24	3.1 ± 0.2	$13.2 \pm 0.4$	82	$2.51 \pm 0.21$	16	No
2 <sup>b</sup>	1	-1.24	$4.4\pm0.3$	$21.8\pm0.8$	96	$0.70\pm0.08$	3.1	No
3	2	-1.24	$4.3\pm0.6$	$10.5 \pm 1.5$	47	$2.40\pm0.30$	11	Yes
4	3	-1.24	$4.9\pm0.3$	$14.1\pm0.7$	56	$2.71\pm0.20$	11	Yes
5	4	-1.55	$5.0 \pm 0.5$	$4.9\pm0.4$	19	$1.49\pm0.10$	5.7	Yes
6	5	-1.55	$3.5 \pm 0.3$	$7.6 \pm 0.9$	42	$3.10\pm0.40$	17	Yes

<sup>a</sup> CPE experiments were operated with 1.0 mM catalyst in a 0.1 M TBAPF<sub>6</sub> DMF solution for 6 h. The generated amount of formate after each entry of CPE was less than 0.1  $\mu$ mol. <sup>b</sup> CPE was conducted in the presence of 5.0 M H<sub>2</sub>O.

### CONCLUSION

In conclusion, we have prepared a nickel(II) tripodal complex which can be utilized as a homogeneous electrocatalyst for syngas production in a water-containing medium. It has been found that both adding water and varying the applied potential can well tune the composition of evolved syngas. Moreover, this catalyst can be operated with high stability that is contributed by its robust ligand. Its earth-abundance and synthetic ease are also notable. We believe that this study can open an avenue for the development of excellent catalysts and shed light on the control of product composition in  $CO_2$  reduction reaction.

#### **EXPERIMENTAL SECTION**

**Materials.** Me<sub>3</sub>NTB,<sup>54</sup> NTB,<sup>55</sup> nickel complexes (2,<sup>56</sup> 3,<sup>57</sup> 4<sup>58</sup> and 5<sup>59</sup>) were synthesized according to the literature methods. TBAPF<sub>6</sub> (99%+, J&K) was dried under vacuum overnight

with  $P_2O_5$ .  $CO_2$  (99.999%), argon (99.999%), <sup>13</sup> $CO_2$  (99%), DMF (99.8%, water < 0.005%, J&K), CH<sub>3</sub>CN (99.8%, water < 0.005%, J&K), Milli-Q ultrapure water and other chemicals are commercially available and used without further purification. Electrodes and other electrochemical accessories were all purchased from GaussUnion Co., Ltd.

**Characterization.** X-ray single crystal diffraction data for **1** were obtained on an Agilent Technologies Gemini A Ultra system at -123 °C, with Cu/*K* $\alpha$  radiation ( $\lambda$  = 1.54178 Å). Electrochemical measurements were performed using a CHI 760E electrochemical workstation. All potentials were referenced against Ag/AgNO<sub>3</sub> reference electrode (0.10 M), and converted to NHE by adding 0.60 V to the measured potentials. Unless otherwise stated, all potentials were footnoted as vs NHE. Gas composition was analyzed on an Agilent 7820A gas chromatography equipped with a thermal conductivity detector and a TDX-01 packed column. The gas products of <sup>13</sup>CO<sub>2</sub> isotopic experiment were checked by an Agilent 7890 GC-MS. The liquid products of the reaction system were analyzed by capillary electrophoresis. UV-Vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. EDX spectra were collected on a field emission scanning electron microscopes (FEI, Quanta 400 or Quanta EFG 250). All the calculations were carried out with Gaussian 09 program.<sup>60</sup> All the structures were optimized at the BP86<sup>61</sup>/BSI level of theory (BSI designated the basis set combination of SDD<sup>62</sup> for Ni atom and 6-31g(d) for non-metal atoms).

Synthesis of 1.  $Ni(BF_4)_2 \cdot 6H_2O$  (0.34 g, 1.0 mmol) and  $Me_3NTB$  (0.45 g, 1.0 mmol) were dissolved in 10 mL CH<sub>3</sub>CN to form a clear violet solution. Violet crystals (84% yield),  $1 \cdot (CH_3CN)_3$  (formulated based on the crystal structure), were isolated from slow diffusion of

ether into the CH<sub>3</sub>CN solution in 2 d. After drying under vacuum, violet powder of **1** would be obtained. Calcd for  $C_{31}H_{36}B_2F_8N_9Ni$  (1): C 48.55, H 4.73, N 16.44%; found: C 48.65, H 4.60, N 16.45%.

# ASSOCIATED CONTENT

Supporting Information.

Supplementary experimental detail, additional figures and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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# **Table of Contents Graphic**

# Syngas Production with a Highly-Robust Nickel(II) Homogeneous Electrocatalyst in a Water-Containing System

# Jia-Wei Wang, Hai-Hua Huang, Jia-Kai Sun, Di-Chang Zhong, \* and Tong-Bu Lu\*

A highly efficient and robust nickel(II) tripodal complex was developed as a molecular electrocatalyst for  $CO_2$ -to-CO conversion and syngas production in aqueous-organic media. The diverse syngas with different H<sub>2</sub>/CO ratio can be readily modulated by controlling of the applied potentials.

