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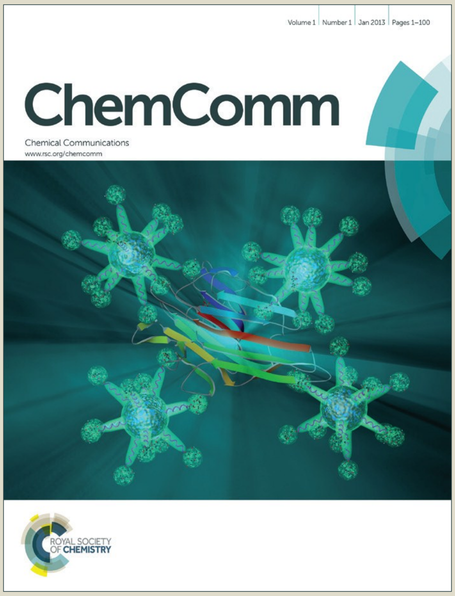

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Oxidation of Carbon Monoxide in Basic Solution Catalyzed by Nickel Cyano Carbonyls at Ambient Condition and the Prototype of a CO-Powered Alkaline Fuel Cell

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CO reduces nickel(2+) cyanides in basic solution to form tetrahedral $Ni^0(CN)(CO)_3^-$ or $Ni^0(CN)_2(CO)_2^{2-}$. Both nickel(0) complexes can be oxidized back to nickel(2+) cyanide/hydroxide so that they behave as CO oxidation catalysts in basic solution. A primitive fuel cell was constructed to demonstrate the feasibility of a CO-powered fuel cell.

Carbon monoxide (CO) is an energy carrier molecule. It contains almost the same amount of energy as hydrogen gas (H_2) volume-wise in gas phase.[1] Like H_2, the oxidation of CO at room temperature is kinetically impossible without a catalyst.[2] However, unlike H_2, which has been used widely in many fuel cells for better energy efficiency,[3] CO is still utilized mainly through combustion due to the lack of suitable CO oxidation catalysts. Catalytic oxidation of CO and construction of CO-powered fuel cells have always been an interesting topic to chemists in energy-related areas.[4] In the past, people have reported that gold nanoparticles and polyoxometalate can be used as CO oxidation catalysts and several prototype CO-powered fuels have been built based on those catalysts.[5] In this paper, we would like to report that the synthetic nickel cyano carbonyls can be used as CO oxidation catalysts in alkaline solution and to utilize this system to build a CO-powered alkaline flow-battery type fuel cell.

We are very interested in the carbonylation of first row transition metal cyanides. We recently reported that the reaction between cobalt(2+) salt and 4 equivalents of cyanide under 1 atmospheric CO in aqueous solution yielded $Co^I(CN)_2(CO)_3^-$ and $Co^{III}(CN)_6^{3-}$ through disproportionation.[6] We have now expanded our study to nickel systems. Unlike cobalt, the carbonylation of nickel(2+) salt in neutral aqueous solution with 1 to 3 equivalents of cyanide did not yield any CO-containing product. However, the carbonylation of nickel(2+) salt with 1 or 2 equivalents of cyanide in strong basic solution led to the quantitative formation of nickel(0) cyano carbonyls. The reduction of nickel(2+) to nickel(0) by CO in basic solution is not unprecedented: A. A. Blanchard reported early in the 1930s that nickel(2+) sulfide or cyanide can be reduced by CO to the very toxic $Ni(CO)_4$ in alkaline solution with low yield.[7] However, nickel cyano carbonyls were never isolated or suggested in his work. E. Peters described the oxidation of CO by Ni-amine complexes in aqueous solution and an M-COOH intermediate was suggested.[8]

In a typical experimental setup, 5mmol $NiCl_2 \cdot 6H_2O$, 5mmol NaCN and 50mmol NaOH were stirred in 50mL water under 1 atm CO at 25°C. CO was kept in a gas reservoir (**Figure S1** in supplementary information). The initially formed green precipitate was identified as nickel hydroxide by X-ray power diffraction. As the reaction progressed, the volume of CO decreased and the green color precipitate dissolved. After 36 hours, the reaction mixture became clear and colorless, and the gas absorption ceased. The gas in the reservoir was then checked by GCMS and it was still pure CO. The volume of CO consumed was 485mL (19.8mmol). The colorless solution was subsequently added to 150mL 0.05M $Ba(OH)_2$ solution under CO and white color precipitates ($BaCO_3$) formed immediately. The precipitate was filtered and washed with water and dried under vacuum overnight yielding a weight of 0.952 gram (4.83mmol). Addition of PPh_4Cl to the colorless reaction mixture followed by CH_2Cl_2 extraction led to the isolation of $(PPh_4)[Ni(CN)(CO)_3]$ as white solid in good yield.[6]

From the amount of $NiCl_2$, NaCN, CO used and the amount of $Ni^0(CN)(CO)_3^-$, $BaCO_3$ generated, the carbonylation of nickel(2+) with 1 equivalent of cyanide in alkaline solution can be expressed in **Reaction (1)**:

$$Ni^{2+} + CN^- + 4CO + 4OH^- \rightarrow Ni^0(CN)(CO)_3^- + CO_3^{2-} + 2H_2O \qquad \textbf{(1)}$$

Quantitative solution IR measurement showed that the formation of $Ni^0(CN)(CO)_3^-$ after the reaction mixture turned colorless is close to 100%. To ensure the purity of isolated $(PPh_4)[Ni^0(CN)(CO)_3]$, only 0.6 – 0.8 equivalents of PPh_4Cl were used in extraction.

$Ni^0(CN)(CO)_3^-$ can further react with 1 equivalent of CN^- to form $Ni^0(CN)_2(CO)_2^{2-}$ in either aqueous or CH_2Cl_2 solution through **Reaction (2)**:

$$Ni^0(CN)(CO)_3^- + CN^- \rightarrow Ni^0(CN)_2(CO)_2^{2-} + CO \qquad \textbf{(2)}$$

Both $Ni^0(CN)(CO)_3^-$ and $Ni^0(CN)_2(CO)_2^{2-}$ have been reported previously as reaction intermediates in the catalytic cycle of the phase-transfer-catalyzed carbonylation of allyl halides and other reactions and in theoretical computations.[9] They have been isolated as Et_4N^+ salts without structure identification.[9a-c] Here, we are able to provide a much more straightforward preparation and to determine the structures of both complexes crystallographically.

Both nickel complexes take tetrahedral geometry, thus, only one structural isomer is possible for either $Ni^0(CN)(CO)_3^-$ or $Ni^0(CN)_2(CO)_2^{2-}$. The ORTEP drawings of both anions are shown in **Figure 1**. Selected bond distances and angles are shown in **Table 1**.

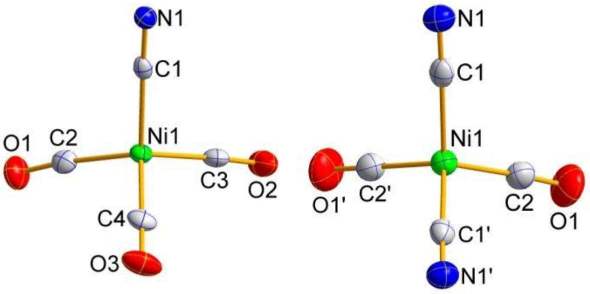

Figure 1: ORTEP drawings of $Ni^0(CN)(CO)_3^-$ or $Ni^0(CN)_2(CO)_2^{2-}$ anions at 50% probability level. $Ni(CN)_2(CO)_2^{2-}$ has crystallographic C_{2v} symmetry.

Table 1: Selected bond distances and angles for $Ni^0(CN)(CO)_3^-$ and $Ni^0(CN)_2(CO)_2^{2-}$.

Bond length (Å)		Bond angle (°)	
$Ni^0(CN)(CO)_3^-$			
Ni1-C1	1.942(2)	C1-Ni1-C2	111.84(9)
Ni1-C2	1.794(2)	C1-Ni1-C3	108.44(9)
Ni1-C3	1.795(2)	C1-Ni1-C4	105.95(9)
Ni1-C4	1.795(2)	C2-Ni1-C3	111.26(10)
		C2-Ni1-C4	108.70(10)
		C3-Ni1-C4	110.53(10)
$Ni^0(CN)_2(CO)_2^{2-}$			
Ni1-C1	1.955(2)	C1-Ni1-C2	112.99(9)
Ni1-C2	1.759(2)	C1-Ni1-C1'	105.12(11)
		C1-Ni1-C2'	107.82(9)
		C2-Ni1-C2'	110.08(12)

* The primed atoms are generated by the symmetry operation (-x+1, y, -z+0.5).

$Ni^0(CN)(CO)_3^-$ has C_{3v} molecular symmetry and $Ni^0(CN)_2(CO)_2^{2-}$ has C_{2v} molecular symmetry; thus, two CO stretching vibrations are allowed in IR spectra for each complex. The IR spectra of both complexes in CH_2Cl_2 solution are shown in **Figure 2**. The absorption at 1966cm^{-1}, 2049cm^{-1} in $Ni^0(CN)(CO)_3^-$ and the absorption at 1866cm^{-1}, 1942cm^{-1} in $Ni^0(CN)_2(CO)_2^{2-}$ are assigned to CO stretches. The small absorption at 2098cm^{-1} in $Ni^0(CN)(CO)_3^-$ and 2063cm^{-1} in $Ni^0(CN)_2(CO)_2^{2-}$ are assigned to CN stretches. The red shift of both CO and CN stretching frequencies when CO is substituted by CN^- agree with the trend shown in $Fe^{II}(CN)_3(CO)_3^-/Fe^{II}(CN)_4(CO)_2^{2-}/Fe^{II}(CN)_5(CO)_3^-$, $Fe(CN)(CO)_4^-/Fe(CN)_2(CO)_3^{2-}$ and $Co^I(CN)_2(CO)_3^-/Co^I(CN)_3(CO)_2^{2-}$ series.[7,10]

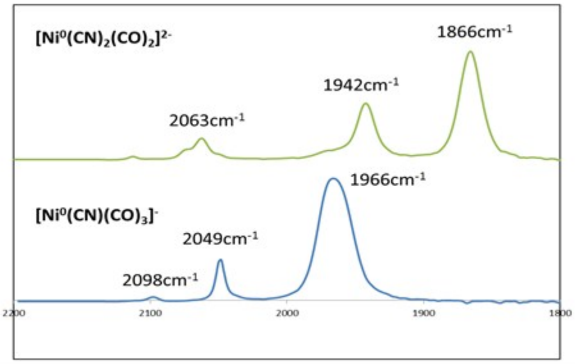

Figure 2: IR spectra of $Ni^0(CN)(CO)_3^-$ or $Ni^0(CN)_2(CO)_2^{2-}$ from 1800 – 2200cm^{-1} in CH_2Cl_2 solution.

Both $Ni^0(CN)(CO)_3^-$ and $Ni^0(CN)_2(CO)_2^{2-}$ are air-sensitive and light sensitive. They can easily be oxidized by oxygen or other oxidants in solution and in solid form. Cyclic voltammetry measurements of $Ni^0(CN)(CO)_3^-$ were performed in basic aqueous solution, an irreversible oxidation was observed at -200mV vs Ag/AgCl reference electrode (**Figure S2** in supplementary information). When quantitative amounts of O_2 gas were injected to $Ni^0(CN)(CO)_3^-$ or $Ni^0(CN)_2(CO)_2^{2-}$ solution in CH_2Cl_2 or water, the nickel complexes were destroyed and green color precipitate appeared. The identity of the green precipitate was not determined. However, once the green precipitate was mixed with hydroxide solution and kept stirring under CO, they quantitatively converted back to $Ni^0(CN)(CO)_3^-$ or $Ni^0(CN)_2(CO)_2^{2-}$. We assume that the green precipitates are nickel cyanide/nickel hydroxide and the oxidations of $Ni^0(CN)(CO)_3^-$ or $Ni^0(CN)_2(CO)_2^{2-}$ by oxygen gas can be expressed as **Reaction (3)** and **(4)**:

$$Ni^0(CN)(CO)_3^- + \tfrac{1}{2}O_2 + H_2O \rightarrow Ni^{2+} + CN^- + 3CO + 2OH^- \qquad (3)$$

$$Ni^0(CN)_2(CO)_2^{2-} + \tfrac{1}{2}O_2 + H_2O \rightarrow Ni^{2+} + 2CN^- + 2CO + 2OH^- \qquad (4)$$

Combining the formation of $Ni^0(CN)(CO)_3^-$ and $Ni^0(CN)_2(CO)_2^{2-}$ in **Reaction (1)** and **(2)** and the oxidation of both complexes in **(3)** and **(4)**, the net reaction becomes:

$$CO + \tfrac{1}{2}O_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O \qquad (5)$$

Reaction (5) is the oxidation of CO at room temperature and atmospheric pressure in alkaline solution catalyzed by nickel cyano carbonyls.

To test our hypothesis, we injected O_2 gas to the solution of 5mM $Ni^0(CN)(CO)_3^-$ in 200mL 1M NaOH under 1000mL CO gas at 1 atmospheric pressure and recorded the total gas volume change at 25°C. The volumes of O_2 injected ranged from 20 – 200mL. The total volume of CO and O_2 mixture started to decrease immediately after O_2 was added. When the gas volume decrease stopped, the gas mixture sample was checked by GCMS and it was found that the peak of O_2 (m/z = 32) vanished completely, showing O_2 was totally consumed. This reaction was repeated 10 times using the same $Ni^0(CN)(CO)_3^-$/NaOH solution. In each case, the total volume decrease was 3 times the volume of O_2 injected (with 5% error margin). In total, 600mL (24.5mmol) O_2 was injected and the total volume decrease was 1800mL. Finally, the reaction mixture was added to 1.5L 0.05M $Ba(OH)_2$ and white precipitates ($BaCO_3$) formed immediately. The $BaCO_3$ formed was filtered, washed thoroughly and dried in vacuum to a weight of 9.670g (49mmol). The volume of O_2, CO used and the amount of $BaCO_3$ obtained agreed well with the catalytic oxidation described in **Reaction (5)**.

Initial kinetics of this nickel cyano carbonyl catalyzed CO oxidation was studied. A typical reaction setup was: 5.9mM $Ni^0(CN)(CO)_3^-$, 1.0M NaOH, 17mL H_2O, 4.4mL O_2 and 58.3mL CO at 25°C (**Figure S3** in supplementary information). The volume changes were recorded over a 12-hour period. It showed that the catalytic oxidation of CO is first-order with respect to O_2 partial pressure with a rate constant k = 0.0038min^{-1}. (The plot of logarithm of O_2 partial pressure vs. time is given in **Figure S4** in supplementary information.)

Reaction (5) has inspired us to build a CO-powered fuel cell. A primitive fuel cell setup is shown in **Figure S5** in supplementary information. CO was kept over a 1M NaOH solution containing 5mM $NiCl_2$ and 5mM NaCN in the anode chamber. NaClO (6%) in 1M NaOH solution was used as an oxidant. An agar gel containing 1M NaCl was used as a salt bridge. Platinum net or copper wires were used as electrodes. The measured voltage from this primitive fuel cell was 1.1V and current was 3.2mA at room temperature.

Alternatively, we have tested a flow battery type fuel cell.[11] 5mM nickel cyano carbonyls generated *in situ* was used as the reductant and NaClO (6%) was used as the oxidant to build a cell using the same salt bridge described above. The voltage and current obtained were 1.1V and 5.5mA, respectively. In this flow battery design, the nickel(0) cyano carbonyls generated in the carbonylation flask were transferred to the anode to produce electricity and the nickel(2+) products generated after battery discharge were transferred back to the carbonylation flask to regenerate the reductant. Even though the discharge current from our primitive fuel cell was very low, it still showed nickel cyano carbonyls catalyzed CO-powered fuel cell is a real possibility. We are currently actively investigating the details of this fuel cell to improve its performance.

Conclusions

We have discovered a straightforward method to prepare nickel cyano carbonyls and demonstrated that a CO-powered fuel cell can be developed using these nickel cyano carbonyls as catalysts in alkaline solution.

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Notes and references

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† **Preparation of $PPh_4[Ni^0(CN)(CO)_3]\cdot 0.25CH_2Cl_2$:** To a green solution of $NiCl_2\cdot 6H_2O$ (238 mg, 1.00 mmol) in 30 mL H_2O under 1 atm CO, a solution of NaCN (49 mg, 1.0 mmol) and NaOH (800mg, 20mmol, excess) in 10 mL H_2O was added. The mixture was stirred under CO for 24 hours to give a clear colourless solution. A solution of PPh_4Cl (263 mg, 0.70 mmol) in 30 mL CH_2Cl_2 was added to the colourless aqueous solution and stirred under 1 atm CO for another hour. The CH_2Cl_2 layer was collected under 1 atm CO, dried under vacuum to afford 313 mg (59% yield) $PPh_4[Ni^0(CN)(CO)_3]$ as off-white solid. Elemental analysis calculated for $NiC_{28.25}H_{20.5}NO_3PCl_{0.5}$: C 64.10%, N 2.65%, H 3.90%; found: C 64.11%, N 2.58%, H 4.15%.
Preparation of $(PPh_4)_2[Ni^0(CN)_2(CO)_2]$: To a colourless solution of $PPh_4[Ni^0(CN)(CO)_3]\cdot 0.3CH_2Cl_2$ (120 mg, 0.23 mmol) in 5 mL CH_2Cl_2, a solution of PPh_4CN[12] (83 mg, 0.23 mmol) in 2 mL CH_2Cl_2 was added and the resulting solution was stirred for 2 hours. 20 mL hexane was added to the reaction mixture and pale green crystalline material was precipitated. The light green crystalline material was filtered and rinsed three times by 3 mL hexane and dried in vacuo to afford 105 mg (55% yield) $(PPh_4)_2[Ni^0(CN)_2(CO)_2]$ as light green powder.

Electronic Supplementary Information (ESI) available: [experimental details, crystallization, X-ray diffraction and cyclic voltagram of $Ni^0(CN)(CO)_3^-$]. See DOI: 10.1039/c000000x/

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