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A [NiFe]hydrogenase model that catalyses the release of hydrogen from formic acid†

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We report the decomposition of formic acid to hydrogen and carbon dioxide, catalysed by a NiRu complex originally developed as a [NiFe]hydrogenase model. This is the first example of H_2 evolution, catalysed by a [NiFe]hydrogenase model, which does not require additional energy.

An enzyme complex, formate hydrogen lyase (FHL, Fig. 1),[1] catalyses H_2 evolution from HCOOH (eqn (1)). This complex is constructed from a formate dehydrogenase (FDH),[2] which catalyses the extraction of protons and electrons from HCOOH (eqn (2)), and a [NiFe]hydrogenase ([NiFe]H_2ase),[3] which recombines those protons and electrons into H_2 (eqn (3)). It should be noted that this latter process is the reverse of the usual role of [NiFe]H_2ase in natural organisms.[3]

$$\mathrm{HCOOH} \overset{\mathrm{FHL}}{\rightleftharpoons} \mathrm{CO_2} + \mathrm{H_2} \quad (1)$$

$$\mathrm{HCOOH} \overset{\mathrm{FDH}}{\rightleftharpoons} \mathrm{CO_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \quad (2)$$

$$2\mathrm{H^+} + 2\mathrm{e^-} \overset{\mathrm{[NiFe]H_2ase}}{\rightleftharpoons} \mathrm{H_2} \quad (3)$$

Two [NiFe]H_2ase model complexes have been reported so far, a NiFe catalyst by Rauchfuss *et al.* that requires additional electrical energy[4] and a $NiFe_2$ catalyst by Schröder *et al.* that requires additional light energy.[5] Since we have developed a successful [NiFe]H_2ase model catalyst,[6] we felt that it would be a good candidate for a FHL model system, which proved to be the case.[7]

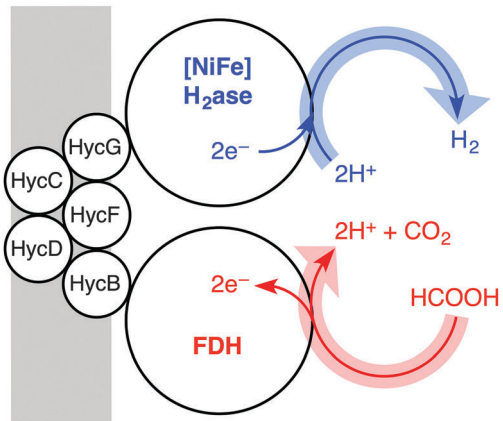

Fig. 1 A structure of formate hydrogen lyase (FHL) constructed from a [NiFe]hydrogenase ([NiFe]H_2ase) and a formate dehydrogenase (FDH). The HycB, C, D, F and G polypeptides are membrane-integral electron transfer components. The gray-shaded component is the membrane. (Adapted from ref. 1*a*).

Here, we report the first catalyst that is capable of both heterolytically splitting dihydrogen into protons and electrons and decomposing formic acid into CO_2 and H_2. Furthermore, this catalyst needs no additional energy to achieve useful rates.

A μ-hydrido $Ni^{II}Ru^{II}$ complex, $[Ni^{II}L(H_2O)(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)](NO_3)$ {[**2**](NO$_3$), L = *N*,*N*′-dimethyl-3,7-diazanonane-1,9-dithiolato}, reacts with one equivalent of HCOONa in water to produce a (μ-hydrido)(formato) $Ni^{II}Ru^{II}$ complex, $[Ni^{II}L(HCOO)(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)]$ (**1**), which was followed by UV-vis spectroscopy (Fig. S1, ESI†). The H_2O ligand was replaced with $HCOO^-$, which is coordinated to the Ni centre as an axial ligand. The structure of **1** has been unequivocally determined by X-ray analysis (Fig. 2) as well as positive- and negative-ion electrospray ionization mass spectrometry (ESI-MS) (Fig. S2 and S3, ESI†) and IR spectroscopy (Fig. S4, ESI†).

A brown crystal of **1** was obtained from its aqueous solution. The framework of **1** is based around a NiS_2Ru butterfly core with a bridging hydride (Fig. 2). The Ni atom adopts distorted

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† Electronic supplementary information (ESI) available: Experimental details and Fig. S1–S4. CCDC 1016741. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc05911e

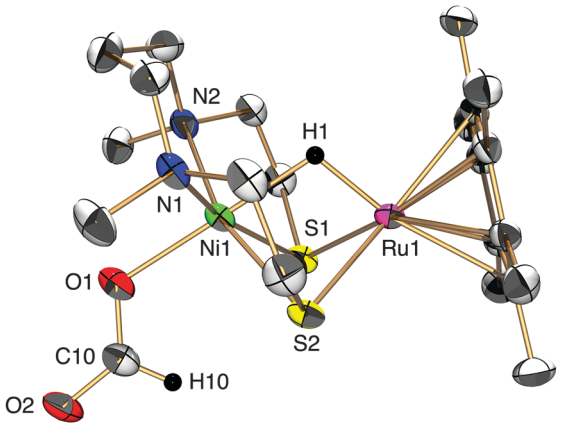

Fig. 2 An ORTEP drawing of **1** with ellipsoids at 50% probability. The solvents (H_2O) and hydrogen atoms of ligands L (*N*,*N*′-dimethyl-3,7-diazanonane-1,9-dithiolato) and C_6Me_6 are omitted for clarity. Selected interatomic distances (*l*/Å) and angles (ϕ/°): Ni1–H1 = 1.88(6), Ru1–H1 = 1.61(6), Ni1···Ru1 = 2.7780(11), Ni1–S1 = 2.3676(19), Ni1–S2 = 2.3818(19), Ni1–O1 = 2.060(5), Ni1–N1 = 2.125(6), Ni1–N2 = 2.120(6), Ru1–S1 = 2.4084(17), Ru1–S2 = 2.3939(17), Ni1–S1–Ru1 = 71.13(5), and Ni1–S2–Ru1 = 71.14(5).

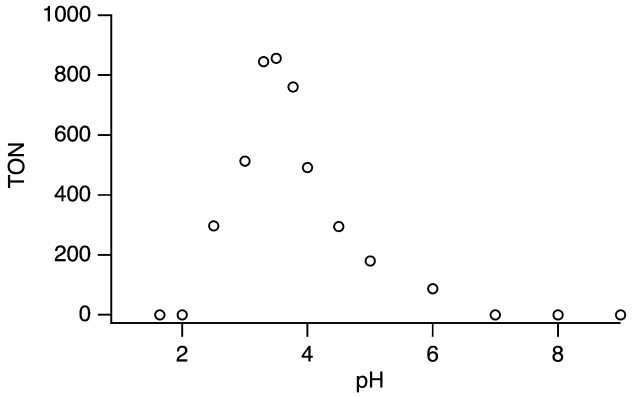

Fig. 3 pH-dependent H_2 evolution catalysed by **2** (7.3 nmol) with HCOONa (146 μmol) in water (510 μL) for 1 h at 60 °C. The maximum turnover number (TON) is 857 at pH 3.5.

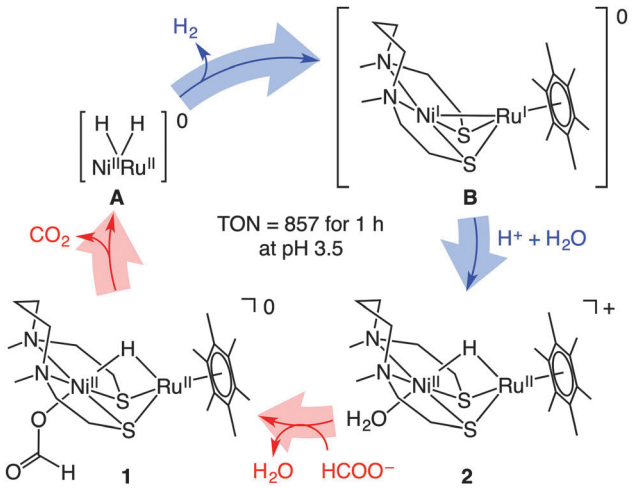

Fig. 4 A proposed mechanism for H_2 evolution from HCOOH catalysed by NiRu complexes in acidic media.

octahedral coordination that consists of the hydrido and formato ligands at the axial site and the N_2S_2 donor ligand at the equatorial site. The Ni–S–Ru angles are 71.13(5)° and 71.14(5)°, which are comparable to those of the μ-hydrido $Ni^{II}Ru^{II}$ complex **2** {70.7(3)° and 70.4(2)°}.[6] The Ni···Ru distance of 2.7780(11) Å is also comparable to that of **2** {2.739(3) Å}.

A positive-ion ESI mass spectrum of **1** exhibits a prominent signal at *m*/*z* 543.2 {relative intensity (*I*) = 100% in the range *m*/*z* 200–2000} (Fig. S2, ESI†). The signal has a characteristic isotopic distribution that matches well with the calculated isotopic distribution for $[\mathbf{1} - HCOO]^+$, which shifts to *m*/*z* 544.2 by the use of $[Ni^{II}L(DCOO)(\mu\text{-}D)Ru^{II}(\eta^6\text{-}C_6Me_6)]$ (double D-labelled **1**). A negative-ion ESI mass spectrum of **1** shows a $HCOO^-$ adduct, which displays a prominent signal at *m*/*z* 633.2 (*I* = 100% in the range *m*/*z* 200–2000) (Fig. S3, ESI†), whose characteristic isotopic distribution matches well with the calculated isotopic distribution for $[\mathbf{1} + HCOO]^-$. The signal shifts to *m*/*z* 636.3 by using double D-labelled **1**. An IR spectrum of **1** shows isotope-sensitive bands at 1349, 1760 and 2649 cm^{-1}, which shift to 1329, 1248 and 2114 cm^{-1}, respectively, after isotopic substitution of H by D in the hydrido and formato positions (Fig. S4, ESI†).

The (μ-hydrido)(formato) $Ni^{II}Ru^{II}$ complex **1** catalysed H_2 and CO_2 evolution from HCOOH in acidic media (pH 2.5–6.0). H_2 and CO_2 gases were detected by GC. Fig. 3 shows a pH-dependent profile of turnover numbers (TONs, mol of H_2 evolved/mol of catalyst) of the H_2 evolution from HCOOH for 1 h at 60 °C. The rate of H_2 evolution examined in this study shows a maximum around pH 3.5. The pH dependence should be explained by a protonation process of a proposed low-valent species **B** (see Fig. 4) and by the stability of the complex, *i.e.*, the species is decomposed to unidentified mononuclear species below pH 3.0. It was confirmed that the reaction of **2** with H_2 and CO_2 in H_2O in the range of pH 2.0–9.0 at room temperature did not afford **1**.

A proposed mechanism for H_2 evolution from HCOOH catalysed by **1** is shown in Fig. 4. The μ-hydrido $Ni^{II}Ru^{II}$ complex **2** reacts with $HCOO^-$ to form the (μ-hydrido)-(formato) $Ni^{II}Ru^{II}$ complex **1**. Liberation of CO_2 from **1** affords a dihydrido intermediate **A** and then reductive elimination of H_2 from **A** yields the low-valent species **B**. The species **B** reduces H^+ to reform **2**. This reaction mechanism is the same as the H_2 activation mechanism by **2** except that HCOOH is used instead of H_2.[8]

In conclusion, we have achieved H_2 evolution from HCOOH catalysed by a NiRu complex without any need for additional energy input. Furthermore, we have structurally defined the reaction intermediate of the (μ-hydrido)(formato) $Ni^{II}Ru^{II}$ complex during catalytic H_2 evolution.

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