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Efficient production of hydrogen from formic acid using a Covalent Triazine Framework supported molecular catalyst

A. V. Bavykina, M. G. Goesten,* F. Kapteijn, M. Makkee, and J. Gascon*[a]

A heterogeneous molecular catalyst based on $Ir^{III}Cp^*$ ($Cp^*=$ pentamethylcyclopentadienyl) attached to a covalent triazine framework (CTF) is reported. It catalyses the production of hydrogen from formic acid with initial turnover frequencies (TOFs) up to 27 000 h^{-1} and turnover numbers (TONs) of more than one million in continuous operation. The CTF support, with a Brunauer–Emmett–Teller (BET) surface area of 1800 $m^2 g^{-1}$, was constructed from an optimal 2:1 ratio of biphenyl and pyridine carbonitrile building blocks. Biphenyl building blocks induce mesoporosity and, therefore, facilitate diffusion of reactants and products whereas free pyridinic sites activate formic acid towards β-hydride elimination at the metal, rendering unprecedented rates in hydrogen production. The catalyst is air stable, produces CO-free hydrogen, and is fully recyclable. Hydrogen production rates of more than 60 $mol L^{-1} h^{-1}$ were obtained at high catalyst loadings of 16 wt% Ir, making it attractive towards process intensification.

The use of formic acid as a convenient material for hydrogen storage is increasingly gaining attention in the development of a hydrogen economy.[1,2] The main advantages of formic acid over proposed alternatives in the frame of a sustainable energy cycle include easy handling, refuelling and transportation,[3] price (600–1250$ per tonne), as well as the possibility of synthesising it through electrochemical reduction of CO_2 using water as hydrogen donor.[4]

Although the decomposition of formic acid to yield hydrogen and CO_2 is thermodynamically favourable ($HCO_2H \rightarrow H_2 + CO_2$, $\Delta G^\circ = -32.8$ kJ mol^{-1}), efficient H_2 release is only obtained with the use of a catalyst. The most active catalysts are homogeneous and transition-metal based for which impressive turnover frequencies (TOFs) have been documented[5,6] even for a base metal such as iron.[7–10]

The requirement of a heterogeneous catalytic system has been questioned,[11] yet the aim of developing an air-stable, solid catalyst that produces hydrogen seems justified as it would certainly present advantages in handling and recycling, two important parameters in device-based applications (for example, fuel cells). To date, the task of developing a heterogeneous catalyst that performs well in hydrogen production from formic acid has proven challenging. In comparison with homogeneous catalytic systems, suppression of the undesired dehydration reaction ($HCOOH \rightarrow H_2O + CO$)[12] remains an obstacle, and TOFs and corresponding rates per unit reactor volume are often low. Whereas the majority of these attempts focus on the use of nanoparticles,[13–17] promising reports involve the use of molecular catalysts.[18,19] Here, particular progress has come from the group of Laurenczy, who immobilised their homogeneous Ru-mTPPTS catalyst on various supports to develop a heterogeneous molecular catalyst.[20] As support, mesoporous silica worked best, with a maximum TOF of 2780 h^{-1} at 110 °C.[21] This work demonstrates the potential of 'heterogenised' molecular systems in catalysis.

Herein, we report a highly active, selective and air-stable molecular heterogeneous catalyst based on a covalent triazine framework (CTF),[22–24] a porous type of organic polymer synthesised from inexpensive feedstocks that had earlier been successfully applied to immobilise the molecular Periana catalyst for methane-to-methanol oxidation.[25] Here, $Ir^{III}Cp^*$ ($Cp^*=$ pentamethylcyclopentadienyl) is coordinated to a mesoporous CTF [Brunauer–Emmett–Teller (BET) surface area: 1800 $m^2 g^{-1}$] constructed using a 1:2 ratio of 2,6-pyridinedicarbonitrile and 4,4′-biphenyldicarbonitrile. The coordination was confirmed by X-ray photoelectron spectroscopy (XPS).[26–29] In a subsequent step, the counterion Cl^- was replaced by triflate, OTf^-, a weakly coordinating anion. This was performed in DMF, a solvent known for binding H–Cl[30] instead of the conventional method using AgCl, which would result in precipitation within the CTF pores. The obtained heterogeneous catalyst **1** (Scheme 1), is highly active for the production of hydrogen whilst being air stable and fully recyclable.

When dispersed in a 3 M formic acid solution of pH 1.5 at 80 °C, **1** instantaneously produces a large flow of gas, which was determined by GC analysis to be a CO-free CO_2/H_2 (1:1) mixture.

The catalyst could be recycled for at least four times under standard reaction conditions (80 °C) without any loss of catalytic activity.[26] During recycling, the catalyst was filtered and stored under ambient conditions, only requiring an oxygen-free environment during its synthesis. XPS also indicates that the oxidation state of Ir remained +3 between runs whereas elemental analysis indicated that Ir leaching was negligible.

At a loading of 0.2 wt% and at 80 °C, the catalyst reached an initial TOF of 27 000 h^{-1}, by far the highest reported for any

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[a] A. V. Bavykina, M. G. Goesten, Prof. F. Kapteijn, Prof. M. Makkee, Prof. J. Gascon
Catalysis Engineering–ChemE
Delft University of Technology
Julianalaan 136, 2628BL, Delft (The Netherlands)
E-mail: m.g.goesten@tudelft.nl
j.gascon@tudelft.nl

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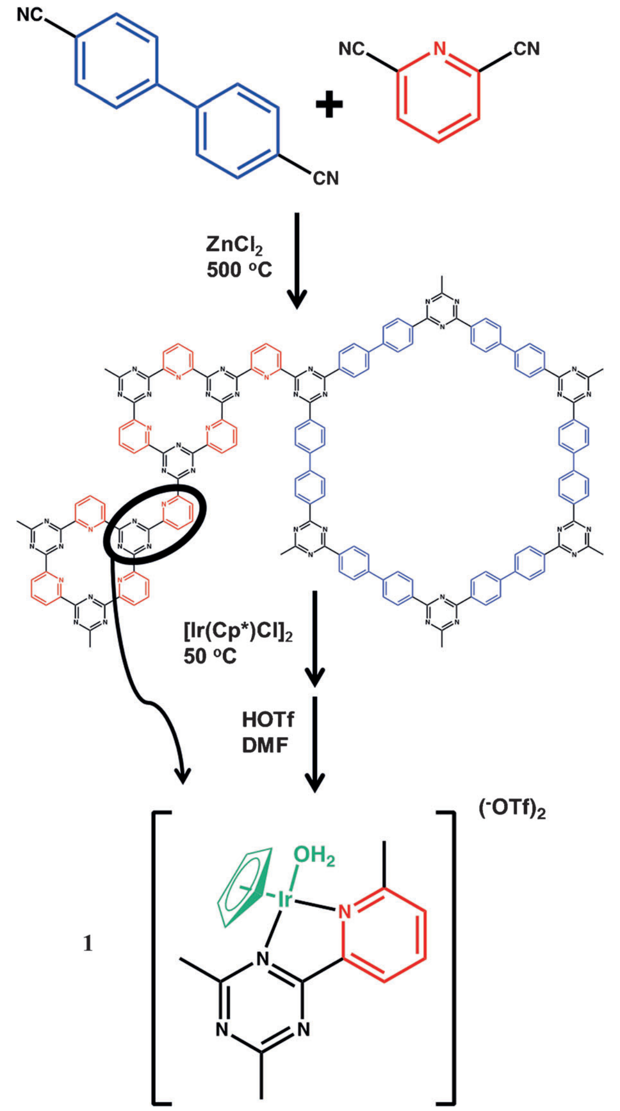


Scheme 1. Synthesis of the CTF through triazination, with corresponding attachment of IrCp*(H$_2$O) and counterion exchange. The methyl groups of Cp* are omitted for the sake of clarity. The CTFs are depicted schematically, and no long-range order was observed using X-ray diffraction (XRD).

heterogeneous catalytic system to date for this reaction (Table 1). At 30 °C and a loading of 16 wt%, the catalyst remained active at an initial TOF of 1350 h^{-1} and even at 0 °C the catalyst still displayed an initial TOF of 70 h^{-1}.

Traces of methanol (<0.08 mmol) were found to be present in the liquid phase after full conversion, a product from the formic acid disproportionation reaction (transfer hydrogenation of formic acid using formic acid as hydrogen donor), a reaction recently also reported for [Ir^{III}Cp*(H$_2$O)(bpy)] (bpy = 2,2′-bipyridine).[31]

When an experiment with fully deuterated formic acid, DCOOD, was followed in situ by means of mass spectroscopy, the molar flow ratios H$_2$/HD/D$_2$ were found to be 195:46:1. The surprisingly large value for H$_2$ suggests a protonic hydride and very efficient exchange of the type Ir–D⇄Ir–H, which had been observed by Ogo et al. before for [Ir^{III}Cp*(bpy)H] at low pH values.[32]

Table 1. Catalytic performance of **1** in production of H$_2$ from formic acid.[a]

Catalyst	Conditions loading [wt%]	T [°C]	$c_{\text{formic acid}}$ [mol L−1]	Time to 99% conversion [min]	Initial TOF [h^{-1}]
1	16	0	3	3600[b]	70
1	16	30	3	1100	1350
1[c]	16	80	3	<20	3960
1	16	80	0.5	<5	2000
1	16	80	12	160	7900
1	2	80	3	70	21300
1	0.2	80	3	120[d]	27000
2[e]	2.7	80	3	120[d]	4020

[a] Standard conditions, unless specified differently: 30 mL 3 M formic acid solution, 300 mg catalyst, 80 °C, pH 1.5; wt% refers to the metal loading on the CTF. [b] Max. conversion 65%. [c] The initial TOF on the fourth recycle was 3930 h^{-1}. [d] Max. conversion 65%. [e] **2** is the Ruthenium(II)-based equivalent of **1**, using the benzene (η_6-C$_6$H$_6$) ligand instead of Cp*.

After reaction, a typical Ir–H stretching at 2050 cm^{-1} was identified performing diffuse reflectance infrared spectroscopy (DRIFTS) on the spent catalyst.[33]

As indicated in Table 1, a less expensive catalytic system can be obtained by attaching Ru^{II}(η_6-C$_6$H$_6$), **2**, to CTF instead of Ir^{III}Cp*, but the corresponding catalytic activity is lower.

It is reasonable to assume that for loadings lower than 0.2 wt% even higher TOFs can be obtained, but this goes at the cost of net productivity per unit reactor volume (or per mass of catalyst). Although the value of the TOF as parameter for catalytic efficiency should certainly not be underestimated, the highest TOFs are usually obtained for very low concentrations of active sites per unit mass of catalyst, which translates to very large reactor dimensions to obtain reasonable total production. Since intensification of hydrogen production is clearly vital for device-based applications, we investigated the effect of catalyst metal loading, formic acid concentration and reactor temperature on (molar) hydrogen production rate per unit volume. The results are shown in Figure 1. Although TOF values decrease for high loadings (Table 1), the trend in Figure 1 indicates that intensifying the hydrogen production through higher metal loadings and formic acid concentrations can be an attractive option. This is an important asset, for homogeneous systems frequently suffer from dramatic drops in performance and/or catalyst deactivation upon increase of catalyst concentration.[34]

To test its suitability for device-based application, the catalyst's durability was tested in continuous mode, in which a highly concentrated formic acid solution (88 wt%) was fed to a glass reactor initially containing a 30 mL 3 M formic acid solution at 80 °C. The H$_2$/CO$_2$ production was measured by a volumetric flowmeter a in fashion similar to the experimental procedure reported by Beller et al.[8] At termination of this experiment, a turnover number (TON) of 1 060 000 was obtained, which demonstrates the durability of the catalyst.

Scheme 2 displays a plausible molecular pathway for the system, which consists of the three steps that have been shown to govern this particular type of catalysis: 1) formic acid deprotonation, 2) β-hydride elimination under decarboxylation and 3) hydrogen evolution.

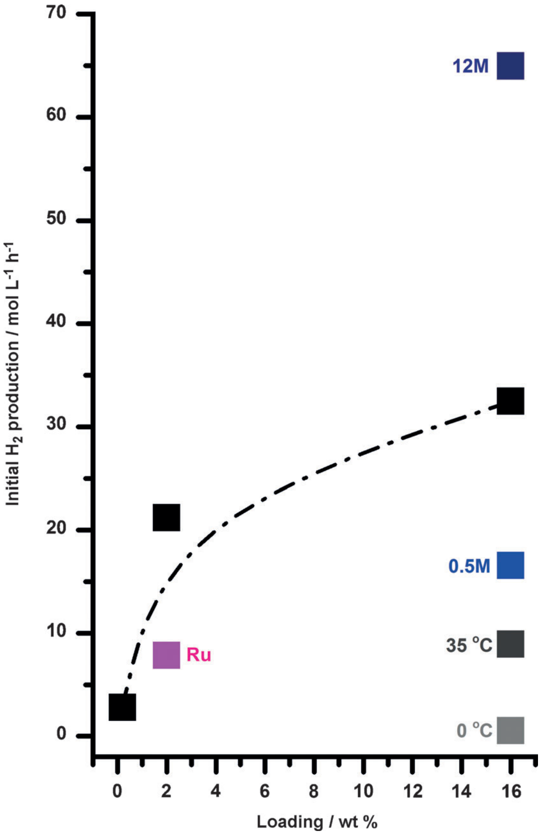
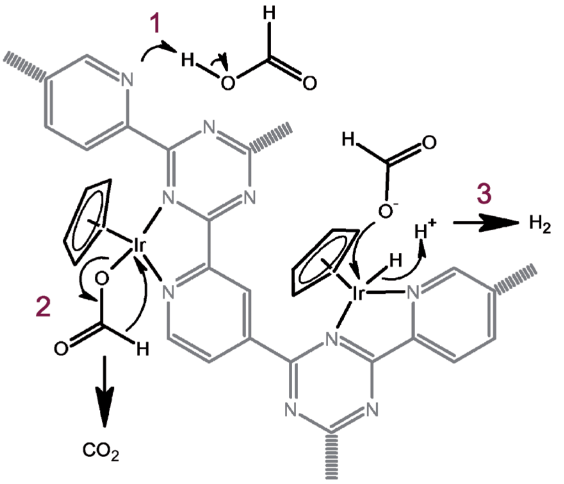


Figure 1. Performance of **1** at various metal loadings in initial net production rate of H_2 per unit liquid volume. Standard conditions, unless differently specified: 3 M formic acid solution, 80 °C, pH 1.5. $[Ru^{II}(\eta_6\text{-}C_6H_6)] = \mathbf{2}$ (see text). In all experiments, reactions were carried out in a 30 mL glass flask with 300 mg of solid catalyst.



Scheme 2. Simplified scheme displaying the catalytic cycle within the CTF polymer backbone (sketched grey). Methyl groups of the Cp* ligand and coordination of the labile aqua ligand are not depicted. 1) formic acid activation, 2) β-hydride elimination, 3) hydrogen release.

Of these three steps, (2) has been shown to be rate-limiting for a very similar system ($[Rh^{III}Cp^*(bpy)(H_2O)][SO_4]$),[35] but also for an iron phosphine system $[P(CH_2CH_2PPh_2)_3FeH]^+$.[36] Evidence for (2) to proceed starting from coordinated formato was proposed for similar systems,[33] which is herein further supported by elemental analysis indicating that weakly coordinating OTf^- is washed out during the recycling of the catalyst, pointing at formate/formato replacing triflate as charge-balancing anion within the scaffold.

For (2) to occur, formic acid must be deprotonated, which only occurs under relatively basic conditions ($pK_{a_{HCOOH}} = 3.77$) in which Ir hydride species are too stable for efficient hydrogen production and thus impede step (3).[35] It is for this reason that many catalysts for hydrogen production operate in tandem with an additional base.[3] The catalyst in this study operates efficiently without any auxiliary base, which we link to the presence of the free pyridinic sites that provide inherent basicity within the CTF matrix (see step 1 in Scheme 2).[37] Indeed, formic acid is well known to have strong hydrogen-bond interactions with pyridine, which facilitates the abstraction of protons.[38] It is noteworthy that this CTF is a co-polymer and that the ratio between the building blocks in Scheme 1 can be tailored to yield an optimum between inherent basicity (by 2,6-pyridinedicarbonitrile) and reactant diffusion (by mesopore-inducing 4,4′-biphenyldicarbonitrile building blocks). The respective 1:2 ratio between the building blocks reported in this work provides an ideal match between basic functionality and mesoporosity.

Finally, it must be emphasised that we expect further improvement in TOFs and overall H_2 productivity in this system to come from reactor engineering improvements in which mass transfer and catalyst dispersion are optimised, as well as the removal of water from the formic acid feed in continuous H_2 production. For now, this Ir/CTF catalyst sets a new standard for hydrogen production from formic acid using heterogeneous catalysts. The catalyst allows straightforward handling and recycling under ambient conditions and provides flexibility for process intensification in a broad temperature range.

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Keywords: covalent triazine frameworks · formic acid · heterogeneous catalysis · hydrogen production · iridium

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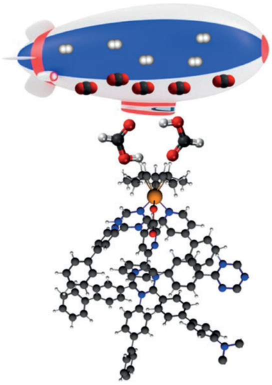

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