

Efficient storage of hydrogen fuel in formic acid using an active iron-based catalytic system

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Hydrogen is one of the most important reactants in the chemical industry. It plays key role in the future renewable energy¹. It is one of the environment-friendly fuels used in modern days. If hydrogen is combusted in the engine or fuel cell, only water emerges as exhaust. However, generation of hydrogen and its storage in a safe and reversible manner remain challenging to researchers. Hydrogen is used as clean transportation fuel on a large scale. However, flammability of hydrogen can cause a safety hazard. It can be stored with solid absorbent materials such as palladium under pressure, which further adds unwanted weight to vehicles. This storage problem of hydrogen can be overcome using more stable chemical compounds with high hydrogen content. Most of these compounds are liquid at room temperature. Small organic compounds like alcohol (such as methanol) or formic acid (HCOOH) can be used for storage of hydrogen due to easy delivery and release of hydrogen. The release of hydrogen is known as dehydrogenation and the reaction is



However, dehydrogenation from HCOOH does not occur spontaneously and suitable catalysts are required for this process. Expensive, low-abundant noble metals such as rhodium, iridium, ruthenium and platinum are used for dehydrogenation in HCOOH^{2,3}. In addition, various iron-based enzymes catalyse the formation and oxidation of hydrogen in many organisms present in nature. A class of metalloenzymes such as hydrogenases, whose active sites contain the earth-abundant first-row transition metals such as iron or nickel, efficiently metabolize hydrogen as an energy source in many organisms. For example, the enzyme formate dehydrogenase (FDH_H) in bacteria *Escherichia coli* catalyses the oxidation of formate ion to carbon dioxide. Natural hydrogenases binding iron or iron–nickel centres catalyse the formation of hydrogen with turnover frequencies (speed of the catalyst cycles) of $\sim 10^3$

to $10^4/\text{s}$ at 30°C, which exceeds the currently known industrial hydrogenation/dehydrogenation catalysts⁴. Besides the [Fe–Fe]- and [FeNi]-metalloenzymes, the [Fe]-hydrogenase is known to facilitate the oxidation of an organic hydride donor to give metal hydride, which can subsequently react with protons to yield hydrogen⁵.

In recent times, various efforts have been made to mimic the structure and function of active sites of hydrogenases. Recently, Boddien *et al.*⁶ from the University of Rostock, Germany and EPFL, Switzerland, have successfully introduced a new molecular iron complex which can catalyse hydrogen from formic acid both at high rates and for many catalytic cycles. They took a new approach by screening first-row transition-metal catalysts for the decomposition of formic acid using different metal precursors and ligands in a combinatorial approach. The catalyst was formed by mixing 0.005 mol% of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and tris[(2-diphenylphosphino)ethyl]phosphine [$\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$, PP_3] to a solution of formic acid in propylene carbonate without any further additives or highly advanced reaction set-up. The catalyst exhibits high turnover number (the number of times the catalyst molecule performs the reaction before it decomposes) of up to 10^5 and a high turnover frequency of nearly $10^4/\text{h}$. It also illustrates high selectivity for hydrogen formation, whereas the competing pathway of the decomposition of formic acid to carbon monoxide and water is negligible.

The catalyst consists of an iron cation which is permanently coordinated by phosphorus centres of a tetradentate phosphine ligand. The remaining two coordination sites of the iron (II) (Fe^{II}) centre are occupied by HCOOH substrate and/or product-derived species during the catalytic cycle. The catalyst can be formed *in situ* from $[\text{Fe}(\text{BF}_4)_2]$ and the PP_3 ligand under reaction conditions, or can be added to the reaction mixture in a presynthesized form as $[\text{FeH}(\text{PP}_3)]^+$.

Boddien *et al.*⁶ carried out *in situ* nuclear magnetic resonance spectroscopy,

kinetic studies and density functional theory calculations to explain possible reaction mechanisms. In the first type of catalytic cycle, the Fe-hydride combines with a proton from HCOOH to form hydrogen. The formate (HCOO^-) anion remains coordinated to the Fe centre and undergoes β -hydride elimination. The subsequent release of CO_2 reforms $[\text{FeH}(\text{PP}_3)]^+$. In the second type of catalytic cycle, formate anion coordinates to $[\text{FeH}(\text{PP}_3)]^+$ to form neutral $[\text{FeH}(\text{HCO}_2)(\text{PP}_3)]$ species. The Fe centre remains exclusively in the formal +2 oxidation state during both the catalytic cycles. It resembles the Fe^{II} centre in the active site of hydrogen activating [Fe] hydrogenase.

Formic acid must be produced in large quantities in environment-friendly processes to fully utilize it as an efficient hydrogen material. Formic acid can be considered as solar fuel when it is obtained from biomass fermentation and processing. At present, more than 90% of hydrogen is produced either from oil by steam reforming or from coal by coal gasification. The direct conversion of solar energy to hydrogen either from biomass or by a photochemical reaction would provide an alternative option. It is expected that the catalyst introduced by Boddien *et al.*⁶ will find its place in connection with solar hydrogen generation.

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