Hydrogen Storage

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A Viable Hydrogen-Storage System Based On Selective Formic Acid Decomposition with a Ruthenium Catalyst**

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Hydrogen represents an important alternative energy feedstock for both environmental and economic reasons, and when combined with fuel-cell technology, very efficient energy conversion can be achieved.[1] Although the advantages of hydrogen over fossil fuels are numerous, the actual use of hydrogen as a transportation fuel is limited mainly because of storage and delivery problems. Conventional hydrogen-storage methods, such as high-pressure gas containers and cryogenic liquid/gas containers, have weight and safety issues.[2] Consequently, a great deal of research is being undertaken to develop new materials, such as metal hydrides[2,3] and carbon nanostructures,[4] that store hydrogen efficiently, although no entirely satisfactory options have been found so far. Formic acid containing 4.4 wt % of hydrogen, as well as its conjugate base, formate salt, are well known sources of hydrogen[5–7] and have previously been reported as potential hydrogen-storage material.[8] Formic acid has the advantage over other substrates that only gaseous products are formed (H_2/CO_2), hence preventing the accumulation of by-products, which is a limitation for mobile applications. However, until now potential applications have been limited by catalyst regeneration requirements, by harsh reaction conditions, and by poor selectivity. We present herein an efficient, completely selective, and robust system for hydrogen production from formic acid using water-soluble homogeneous catalysts.[9]

Decomposition of formic acid was carried out in aqueous solution using hydrophilic ruthenium-based catalysts, generated from the highly water-soluble ligand *meta*-trisulfonated triphenylphosphine (TPPTS) with either $[Ru(H_2O)_6]^{2+}$ or, more conveniently, commercially available $RuCl_3$.

The catalysts were activated prior to use by reaction with sodium formate and formic acid and the catalytic decomposition of formic acid performed under a wide range of pressures and temperatures. The generated H_2/CO_2 pressure was typically between 1 and 220 bar, but no inhibition of catalytic activity was observed up to a pressure of 750 bar (see the Supporting Information for details). The rate of formic acid decomposition increased with temperature, and at all temperatures a conversion of 90–95 % can be achieved (Figure 1). The total conversion does not reach 100 % because the formate salt added for the activation of the catalyst is not converted; however, all the formic acid is consumed.[10] In addition, the catalyst was stable up to 170 °C and remained active after one year in solution.

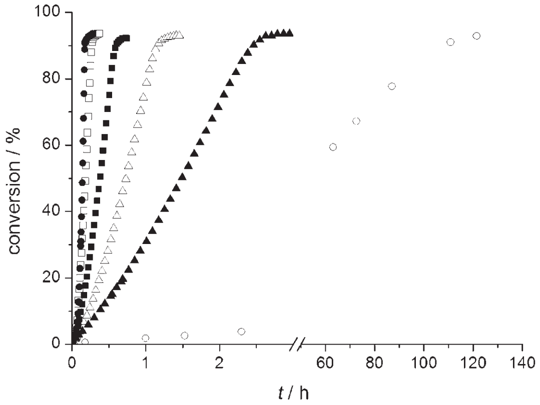

Figure 1. Effect of temperature on the decomposition of formic acid in a closed (batch) system: 25 °C (○) (125 mM Ru), 70 °C (▲), 80 °C (△), 90 °C (■), 100 °C (□), 120 °C (●) (22 mM Ru); $[Ru(H_2O)_6](tos)_2$, 2 equiv TPPTS, 4 M HCOOH/HCOONa (9:1), 2.5 mL H_2O/D_2O (1:1); addition of 0.38 mL HCOOH for recycling.

The thermal decomposition of formic acid into CO and H_2O, which depends on the temperature and the formic acid concentration, becomes nonnegligible at elevated temperatures.[11] No traces of CO, which is known to poison some fuel cells,[12] could be detected by FTIR spectroscopy (detection limit of 3 ppm) in a sample of gases generated by using this catalyst system at 100 °C (see the Supporting Information), because of the rapidity of the reaction and, hence, the short residence time of formic acid at this temperature.

A continuous system was developed in which formic acid (98–100 %) was added under pressure into a 50 mL reactor containing 12 mL of catalyst solution. The gases generated were released at a rate that maintained a constant pressure inside the reactor. The performance of the optimized catalytic system (125 mM Ru) obtained at two different temperatures under continuous conditions are given in Table 1. Although only the results for $[Ru(H_2O)_6](tos)_2$ (tos = toluene-4-sulfonate) are given, $RuCl_3$ also led to successful continuous hydrogen production.

The purity of hydrogen obtained with this catalytic system makes it suitable for all types of fuel cells, and, since a constant pressure of hydrogen is produced, it can be used directly in combustion or electric engines, thus avoiding

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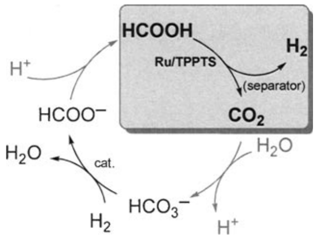
Table 1: Formic acid consumption rates, hydrogen production rates, and turnover frequencies (TOF) of the continuous system.[a]

T [°C]	HCOOH input [$mL^{-1}\,min^{-1}$]	H_2 outflow [$mL^{-1}\,min^{-1}$]	TOF [h^{-1}]
100	0.21 ± 0.01	140 ± 10	230 ± 5
120	0.42 ± 0.01	290 ± 10	460 ± 24

[a] 50 mL reactor, 12 mL initial solution of HCOOH/HCOONa (9:1, 4 M), $[Ru(H_2O)_6](tos)_2$ (125 mM), TPPTS (250 mM).

technical problems due to pressure drops that occur with high-pressure cylinders. H_2 and CO_2 can easily be separated if desired. Furthermore, prior to the hydrogen consumption process, the gas pressure can be used advantageously to generate energy in a similar manner to that of a compressed air engine.[13]

Formic acid is prepared commercially from carbon monoxide and also as by-product in the synthesis of other chemicals.[14] Numerous studies have demonstrated formic acid production from carbon dioxide,[15] either electrochemically[16] or in aqueous[10,17] or supercritical phases,[18] which require bicarbonate instead of CO_2 or addition of a base. Hence, a "green" CO_2 cycle could be achieved by separation of the CO_2 generated[19] and its conversion into formic acid using hydrogen from a stationary source (Scheme 1). In the case of mobile applications, CO_2 could be captured elsewhere to reform the formic acid in an economic way and ensure no net CO_2 production. However, none of the CO_2 reduction processes re-forming formic acid are commercial yet, mainly because of problems associated with the basic conditions required.



Scheme 1. CO_2 cycle proposed as a hydrogen-storage system. In the case of electrochemical formation of formic acid, the intermediates HCO_3^- and $HCOO^-$ are not characteristic.

The homogeneous catalytic decomposition of formic acid in aqueous solution presented herein provides an efficient in situ method for hydrogen production that operates over a wide range of pressures, under mild conditions, and at a controllable rate. Previous limitations to the application of formic acid as hydrogen-storage material, notably catalyst deactivation and the formation of side products, have been overcome.

Experimental Section

$Ru(H_2O)_6](tos)_2$ was prepared according to a literature method.[20] All other chemicals are commercial products and were used as received. Manipulation of $[Ru(H_2O)_6](tos)_2$ prior to activation was carried out under inert atmosphere by using Schlenk and glovebox techniques. NMR spectra were recorded on Brucker Avance DRX 400 MHz spectrometer and IR spectra on a Perkin–Elmer Spectrum GX FTIR spectrometer with a gas cell (path length 10 cm).

Kinetic measurements at variable temperature were performed in 10 mm medium pressure sapphire NMR tubes.[21] $[Ru(H_2O)_6](tos)_2$ (0.056 mmol, 31 mg) was dissolved in a formic acid/sodium formate (9:1, 4 M) aqueous solution (2.5 mL, 1:1 D_2O/H_2O) containing TPPTS (0.112 mmol, 63.9 mg). The active species were formed by heating the tube at 90 °C in an electric heating jacket. Recycling of the catalyst was performed at different temperatures, without protection against oxygen/air, by cooling the tube to room temperature, depressurization, and addition of formic acid (10 mmol, 0.38 mL). The reaction was followed by monitoring the pressure and by ^1H NMR spectroscopy.

For continuous hydrogen production, a 50 mL Parr autoclave with a modified output valve allowing control of the gas outflow, was connected to a high-pressure pump and to a gas flow meter. An initial aqueous solution of HCOOH/HCOONa (9:1, 4 M, 12 mL) was placed in the autoclave containing $[Ru(H_2O)_6](tos)_2$ or $RuCl_3{\cdot}x\,H_2O$, and 2 equivalents of TPPTS, and the autoclave was heated externally (activation period). Once the initial amount of formic acid was converted, formic acid (98–100 %) was added continuously, and the gases released at a rate that maintained a desired pressure inside the autoclave.

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