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Hydrogen Storage

A Charge/Discharge Device for Chemical Hydrogen Storage and Generation**

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The storage and distribution of H_2 are crucial issues for the expected "hydrogen economy".[1] The groups of Beller,[2] as well as of Laurenczy,[3] reported the catalytic decomposition of formic acid using Ru–phosphine-based homogeneous catalysts. The results led to a breakthrough in chemical storage of H_2[4] and initiated intense research in this field by several groups.[5] Outstanding achievements of this research are the acceleration of formic acid decomposition by visible light,[6] as well as the recent discovery of iron-based homogeneous catalysts.[7]

The above procedures capitalize on the decomposition of HCO_2H to provide CO_2 and H_2. For carbon-neutral hydrogen storage, HCO_2H should be obtained from CO_2, that is, there should be a way to attain the equilibrium in Equation (1) from both sides.

$$HCO_2H \rightleftharpoons H_2 + CO_2 \qquad (1)$$

However, hydrogenation of CO_2 to HCO_2H is endergonic, and presently there are no efficient procedures for obtaining formic acid on this way.[8] To get meaningful conversions of a CO_2/H_2 feedstock, formic acid should be stabilized by the addition of suitable additives, such as organic amines or inorganic bases.

Some time ago we demonstrated that bicarbonate could be hydrogenated to formate in purely aqueous solution on the catalytic action of water-soluble Ru^{II}- and Rh^{I}-tertiary phosphine catalysts with no need for other bases.[9] We have also considered that catalytic decomposition of formate by the same catalysts might be the reason for incomplete ($<100\,\%$) final conversions of HCO_3^- to HCO_2^-.[10]

Very recently, decomposition of formate salts in dmf–water mixtures with a $[\{RuCl_2(benzene)_2\}_2]$ + dppm catalyst (dmf = *N*,*N'*-dimethylformamide; dppm = 1,2-bis(diphenylphosphino)methane) was suggested by Beller and co-workers as a viable route to hydrogen generation.[11] The resulting bicarbonate was isolated, and in a separate experiment it was hydrogenated back to formate with the same catalyst. These two reactions represent the two half-cycles of a chemical H_2 storage and generation process. Nevertheless, the question arises as to how these half-cycles can be coupled when no isolation of the intermediate formate or bicarbonate is possible.

The bicarbonate–formate equilibrium in aqueous solution [Eq. (2)] has already been considered by Sasson and co-workers for hydrogen storage and transportation.[12]

$$HCO_2^- + H_2O \rightleftharpoons HCO_3^- + H_2 \qquad (2)$$

This early work was based on the ability of the Pd/C heterogeneous catalyst both to decompose alkali metal formates[13] and to hydrogenate sodium bicarbonate[14] in aqueous solutions. A thorough analysis of the (hypothetical) procedure of storing hydrogen by means of formate salts supported the feasibility of such a process.[12]

An important aspect missing from the cited works on decomposition of formic acid or formate salts is, however, that construction of a practical hydrogen storage/discharge device critically depends on the position of the chemical equilibria in Equations (1) and (2). For entropy reasons, the equilibrium in Equation (1) is shifted largely to the side of products, and, while this is beneficial for generating H_2 even at high pressures, it does not allow the reverse reaction (charging of the hydrogen storage device) by simply raising the pressures of H_2 and CO_2. This is, however, not the case with Equation (2) as is demonstrated in the following.

In the course of our extensive studies on hydrogen transfer from aqueous formate to aldehydes with water-soluble Rh^{I}- and Ru^{II}-tertiary phosphine catalysts,[15] in some cases we observed signs of slow gas evolution, and this phenomenon was subjected to closer scrutiny.

Stirring aqueous solutions of HCO_2Na with $[\{RuCl_2(m\text{tppms})_2\}_2]$ (**1**) (*m*tppms = sodium diphenylphosphinobenzene-3-sulfonate; **2**) in an atmospheric gas burette at 40–80 °C yielded substantial amounts of gas (Figure 1). GC analysis showed this gas to be H_2 and virtually free from CO (≤ 10 ppm), which is a prerequisite for use in present-day fuel cells. The turnover number (TON = mol reacted substrate (mol catalyst)$^{-1}$) achieved at 80 °C in 1 h was 120, and the maximum amount of the gas evolved corresponded to 47 % of the theoretical yield. Arrhenius analysis of the initial rate of gas evolution as a function of temperature resulted in an activation energy of formate decomposition of

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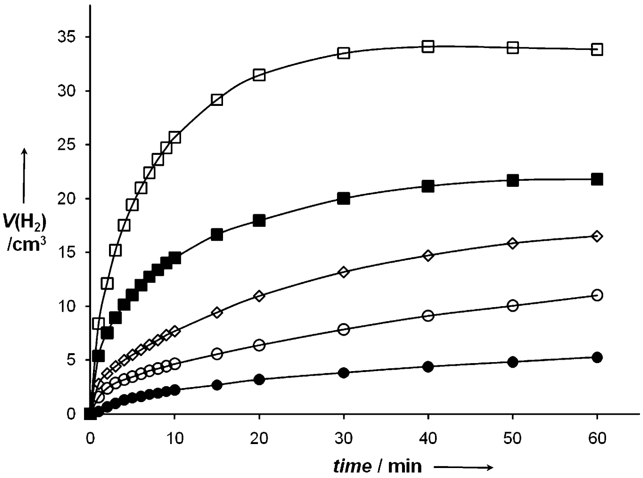

Figure 1. Hydrogen evolution from aqueous HCO_2Na solutions in a constant-pressure gas burette. Catalyst: **1** + **2**; [Ru] = 2 mM; [**2**] = 8 mM; [HCO_2Na] = 0.24 M; $V(H_2O)$ = 5.5 mL; P(total) = 1 bar, T = 40 (●), 50 (○), 60 (◇), 70 (■), 80 (□) °C.

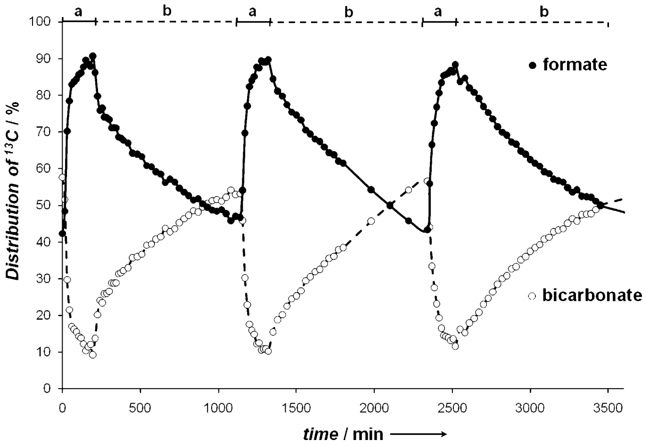

Figure 3. Relative amounts (%) of formate and bicarbonate during cycles of a) storage and b) generation of H_2 in a closed reactor. Catalyst: **1** + **2**; [Ru] = 10 mM; [**2**] = 42,5 mM, [$H^{13}CO_3Na$] = 0.257 M; $V(D_2O)$ = 2 mL; V(total) = 7 mL; T = 83 °C; a) $P(H_2)$ = 100 bar; b) $P(H_2$, initial) = 1 bar.

41 ± 2 kJ mol^{-1}, which is close to the value of 49 ± 2 kJ mol^{-1} determined by Blum and co-workers.[13]

Next we investigated the generation of H_2 in a glass pressure tube. At 80 °C the pressure inside the tube rose rapidly and levelled off at 6.2 bar (Figure 2), corresponding to 32 % conversion of formate to bicarbonate. Release of the pressure to 2 bar triggered further formate decomposition, but this time with a lower rate in accord with the lower concentration of HCO_2Na in the solution.

For a multiple-use hydrogen storage device, only closed vessels are appropriate which contain the storage chemical(s) and the catalyst and can be charged at elevated pressure and discharged (release H_2) at low pressure. The thermodynamic requirement for construction of such a device is that H_2 must be involved in an equilibrium sufficiently mobile in the expected pressure (and temperature) range. The above experiments demonstrated that the formate/bicarbonate equilibrium is well-suited for such a purpose; however, they also showed that there is a practical limit on the extent to which the hydrogen storage capacity of aqueous formate solutions can be utilized. These limits, as well as the reversibility of the hydrogen storage system are convincingly illustrated by the following measurements (Figure 3).

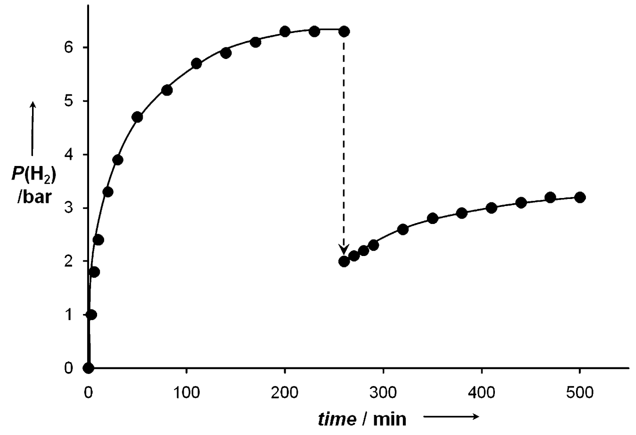

Figure 2. Changes of hydrogen pressure during catalytic decomposition of HCO_2Na in a closed reactor. Catalyst: **1** + **2**; [Ru] = 2 mM; [**2**] = 8 mM; [HCO_2Na] = 2.50 M; $V(H_2O)$ = 10 mL; V(total) = 80 mL; T = 80 °C. The dashed arrows represents the release of pressure to 2 bar, which triggered further formate decomposition.

In a medium pressure sapphire NMR tube, an aqueous solution of $H^{13}CO_3Na$ was pressurized with 100 bar H_2 at a temperature of 83 °C in the presence of **1** and the reaction was followed by recording ^{13}C NMR spectra of the solution. In 200 min, 90 % of $H^{13}CO_3Na$ was hydrogenated to $H^{13}CO_2Na$. At this point H_2 was released against ambient pressure and after closing the tube the reaction mixture was left to equilibrate at 83 °C, leading to decomposition of formate. The hydrogenation/decomposition cycle was repeated twice more, keeping the reaction mixture under H_2 pressure at 83 °C for altogether 2.5 days; this experiment also shows the chemical stability of the system. Importantly, decomposition of formate slowed down around 40–50 % conversions, so approximately half of the nominal H_2 storage capacity of aqueous formate solutions could be utilized.

In conclusion, we have constructed for the first time a simple, truly rechargable hydrogen storage device based on the hydrogenation of bicarbonate and decomposition of formate in aqueous solution with the same catalyst, [{$RuCl_2$(*m*tppms)$_2$}$_2$] + *m*tppms, in both directions without the need of isolating either the formate or bicarbonate to start a new cycle. Note that no organic solvent was applied. The reaction mixture showed excellent stability upon prolonged use, and the results encourage further research into the practical applications of this and similar hydrogenation–dehydrogenation equilibria for storage of hydrogen.

Experimental Section

Monosulfonated triphenylphosphine (**2**) and [{$RuCl_2$(*m*tppms)$_2$}$_2$] (**1**) were prepared by published procedures.[16]

Details of hydrogenation of $NaHCO_3$ in water have been published.[9] For H_2 generation, solid $NaHCO_2$, **1**, and **2** were placed into the reactor (a jacketed flask connected to a thermostated gas burette or a home-made glass pressure tube), which was carefully deoxygenated and filled with H_2 or with Ar. Reactions were initiated by adding H_2O (amounts are found in the figure captions) and were followed by recording the increase of total gas volume or that of pressure. Gases were analyzed on a Shimadzu GC2010 gas chromatograph using a Varian Plot, Molsieve 5 A, 30 m × 0.32 mm column at 65 °C with He as carrier gas and a thermal conductivity detector at 70 °C.

Reactions in a 10 mm medium-pressure sapphire NMR tube were run as described in reference [9]. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker DRX 400 NMR spectrometer and referenced to DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid sodium salt) and phosphoric acid, respectively.

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