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Hydrogen Storage

CO_2-“Neutral” Hydrogen Storage Based on Bicarbonates and Formates**

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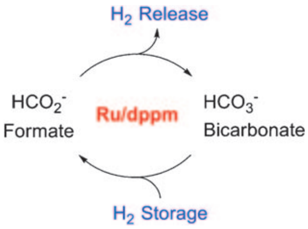
Hydrogen is considered to be an attractive candidate as a chemical “energy vector” for a sustainable energy technology.[1] The so-called hydrogen economy is based on the sustainable production of hydrogen without the release of stoichiometric amounts of carbon dioxide (CO_2).[2] For its realization, practical solutions for hydrogen storage, distribution, and usage are also required. The safe and practical storage of hydrogen in particular constitutes a yet insufficiently solved issue. Despite progress in the fields of physical hydrogen storage,[3] metal hydride technologies,[4] and hydrogen adsorption,[5] no general solution for hydrogen storage has yet been developed that meets industrial requirements (ambient conditions, high power-to-volume ratios).

In addition to methanol[6] and methane,[7] formic acid (FA) and formates have recently gained considerable interest for hydrogen generation.[8] These chemical compounds are nontoxic and stable with a hydrogen content of 4.4 wt% (FA) and 2.35 wt% (for $NaHCO_2/H_2O$). As formates are noncorrosive and nonirritating, they are also easy to handle.

In 2008, parallel to the work of Laurenczy and coworkers,[9] we demonstrated that hydrogen release from formic acid/amine adducts proceeds smoothly under mild conditions in the presence of ruthenium catalysts.[10] Since then, research groups led by Fukuzumi,[11] Wills,[12] Iglesia,[13] and others[14] have demonstrated the possibility of using various other homogeneous or heterogeneous catalysts for hydrogen release from formic acid. Although most catalysts are based on noble metals, recently it was shown that even iron complexes are suitable for this reaction.[15]

After several decades of research, the back reaction of this hydrogen generation—the catalytic reduction of carbon dioxide and carbonates—is still a challenging topic; many reviews have reflected the current research at their respective time.[16,17] Recently, we reported a ruthenium phosphine catalyst system[18] and an iron catalyst,[19] which facilitate the hydrogenation of bicarbonates without the use of additional CO_2. Clearly, the “real” use of formates as a hydrogen-storage material sets both the release and the uptake of hydrogen as prerequisites. In this context Himeda et al. were able to hydrogenate CO_2 under basic conditions and dehydrogenate formic acid under acidic conditions by applying the same catalysts at different pH.[20]

Ideally, the hydrogen carrier, CO_2, should be re-used and a closed carbon cycle should be achieved. Therefore, trapping carbon dioxide in the dehydrogenation process is fundamental. Unfortunately, this has not yet been achieved. Here, we describe for the first time the design of a reversible hydrogen-storage cycle based on the redox system bicarbonate/formate (Scheme 1).



Scheme 1. Hydrogen uptake and hydrogen release in the bicarbonate/formate system.

Our concept has the following advantages: Compared to carbon dioxide, solid bicarbonates are easy to handle and highly soluble in aqueous media (96 $g\,L^{-1}$ $NaHCO_3$ at 20 °C in H_2O). The resulting aqueous bicarbonate solution can be catalytically converted to a formate solution under much milder conditions than those required for reactions of methanol or methane. The nontoxic aqueous solution of formate is easily stored and transported. Finally, hydrogen can be released on demand in the presence of a suitable catalyst. Again, this hydrogen discharge can be performed at or below room temperature. Most importantly, after full conversion of the formate, the bicarbonate solution may be recharged with hydrogen to close the cycle. To the best of our knowledge, no catalyst system has yet been described that can facilitate both reaction pathways under basic conditions and also trap the CO_2 formed in the dehydrogenation.

At the start of this work we studied the hydrogenation activity of a catalyst system comprising $[\{RuCl_2(benzene)\}_2]$ and 1,2-bis(diphenylphosphino)methane (dppm) towards different formates. Here, we examined the hydrogenation of bicarbonates, carbonates, and carbon dioxide—H_2 uptake—under different conditions (Table 1). Basically, formates can be obtained by catalytic hydrogenation of a) carbonates and bicarbonates (often with additional CO_2 pressure) or b) CO_2 in the presence of inorganic bases. Obviously, method a is the

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Table 1: Catalytic hydrogenation of bicarbonates and carbonates as well as CO_2 and base in the presence of [{RuCl$_2$(benzene)}$_2$] and dppm.[a]

Entry	Reagent	Product	$p_{H_2/CO}$ [bar][b]	Yield [%][c]	TON
1	$NaHCO_3$	$NaHCO_2$	50/0	35	807
2	$KHCO_3$	$KHCO_2$	50/0	23	531
3	NH_4HCO_3	NH_4HCO_2	50/0	20	461
4[d]	**$NaHCO_3$**	**$NaHCO_2$**	**80/0**	**96**	**1108**
5[e]	$NaHCO_3$	$NaHCO_2$	80/0	16	320
6	$NaHCO_3$	$NaHCO_2$	50/30	75	1731
7	Na_2CO_3	$NaHCO_2$	50/30	45	1038
8	$KHCO_3$	$KHCO_2$	50/30	69	1592
9	LiOH	$LiHCO_2$	50/30	76	1754
10	NaOH	$NaHCO_2$	50/30	38	877
11	KOH	$KHCO_2$	50/30	68	1569
12	$Ca(OH)_2$	$Ca(HCO_2)_2$	50/30	48	1108
13	$Mg(OH)_2$	$Mg(HCO_2)_2$	50/30	39	900

[a] Reaction conditions: 5.2 μmol [{RuCl$_2$(benzene)}$_2$], 20.8 μmol dppm (Ru/P = 1:4), 24 mmol reagent, 25 mL distilled H_2O, 5 mL THF, 2 h reaction time, 70 °C. [b] Pressure at room temperature. [c] Yield based on ^{1}H NMR analysis using THF as an internal standard. [d] 10.4 μmol catalyst and 4 equiv dppm, 20 h reaction time. [e] 5.0 μmol [{RuCl$_2$(benzene)}$_2$], 30.0 μmol dppm (Ru/P = 1:6), 20 mmol $NaHCO_3$, 5 mL H_2O, 25 mL THF, RT, 24 h reaction time.

most convenient process, since only H_2 is needed; however, higher yields are generally obtained when both CO_2 and H_2 are added.

Several formate salts were obtained in moderate yields after a reaction time of 2 h at low temperature (70 °C) in the presence of 125 ppm of the Ru catalyst. When pure H_2 was used for the hydrogenation of sodium or potassium bicarbonate, yields of 35 % (TON: 807) and 23 % (TON: 531) were obtained, respectively (Table 1, entries 1 and 2). Similarly, ammonium bicarbonate was converted in 20 % yield and moderate activity (TON: 461; Table 1, entry 3). However, when 80 bar of H_2 was applied, almost full conversion of $NaHCO_3$ and an excellent yield (96 %) of $NaHCO_2$ were possible with a TON of 1108 (Table 1, entry 4). Notably, reasonable activity was observed even at room temperature (Table 1, entry 5). These results highlight $NaHCO_3$ as the most suitable candidate for H_2 storage since addition of H_2 is sufficient to recover the formate with high yield. Nevertheless, in the presence of additional CO_2 the conversion and activity were higher after 2 h than in the reaction with only 50 bar H_2 (yield: 75 %, TON: 1731; Table 1, entries 1 and 6). Interestingly, using sodium carbonate instead of sodium bicarbonate in the presence of carbon dioxide resulted in a significant decrease of activity and conversion (Table 1, entries 6 and 7). The use of carbon dioxide along with inorganic bases such as calcium, lithium, and magnesium hydroxide also led to good yields and catalyst activities. The highest conversions and activities were observed when LiOH or KOH were used (Table 1, entries 9 and 11). Therefore the base strength is not the predominant factor. We also observed significant conversion of CO_2 in the presence of $Ca(OH)_2$ and $Mg(OH)_2$ (Table 1, entries 12 and 13).

Next, we investigated the selective dehydrogenation—H_2 release—of different formates. We used the same in situ system comprising the Ru precursor (5.0 μmol) and dppm at 60 °C. The evolved gases were quantitatively and qualitatively analyzed using automatic gas burettes and GC in a setup described elsewhere.[14a] Besides hydrogen, argon, and to a minimal extent CO_2, no other gas was detected (CO < 1 ppm). Since the formation of hydrogen from formates requires additional protons, we used an excess of water (11-fold excess of H_2O). In water the liberation of hydrogen causes a shift of the pH to more basic media. Consequently, the formed CO_2 is captured in the basic solution as bicarbonate, which precipitates during the reaction. Selected results of this set of experiments are given in Table 2.

Table 2: Hydrogen generation from formates with the Ru/dppm in situ catalyst.[a]

Entry	Formate	V_{H_2} (3 h) [mL]	TON (3 h)	Initial TOF [h^{-1}]	Vol % CO_2
1	$LiHCO_2$	490	2000[c]	2923	33.7
2	**$NaHCO_2$**	**490**	**2000[c]**	**2592**	**8.3**
3[b]	**$NaHCO_2$**	**218**	**889**	**377**	**0.8**
4[d]	$NaHCO_2$	14	56	19	0.06
5	$KHCO_2$	299	1222	234	0.9
6	NH_4HCO_2	23	93	126	27.9
7	$Mg(HCO_2)_2$	337	1377	420	34.5
8	$Ca(HCO_2)_2$	486	1985	770	34.2

[a] Reaction conditions: 5.0 μmol [{RuCl$_2$(benzene)}$_2$], 30 μmol dppm (Ru/P = 1:6), 20 mmol formate, 20 mL DMF, 5 mL H_2O, 60 °C; gas volumes determined using automatic gas burettes and analyzed by GC; TON = $n(H_2)/n(Ru)$, for the determination of the initial TOF the conversion was kept below 20 %. [b] Reaction temperature 40 °C, 14 h reaction time. [c] Full conversion. [d] THF as solvent, 25 °C.

To our delight full conversion and selective dehydrogenation (CO < 1 ppm) was observed in all cases. The highest activity (initial TOF: 2923 h^{-1}) was observed when lithium formate served as the starting material (Table 2, entry 1). However, in this case the CO_2 content of the gas mixture was relatively high. Notably, comparable activity but significant lower CO_2 content was observed in the case of $NaHCO_2$ and $KHCO_2$ (Table 2, entries 2 and 5). Interestingly, the reaction rate drops significantly when the the reaction temperature is lowered from 60 °C (TOF: 2592 h^{-1}) to 25 °C (TOF: 19 h^{-1}). However, at low temperatures all CO_2 could be collected (Table 2, entries 2–4). Ammonium formate was converted with comparable low activity and high CO_2 content (Table 2, entry 6). In the reactions of $Mg(HCO_2)_2$ and $Ca(HCO_2)_2$ hydrogen was liberated with good activities of 420 h^{-1} and 770 h^{-1}, respectively (Table 2, entries 6 and 7). However, CO_2 was not trapped effectively during the reaction. Nevertheless, when $NaHCO_2$ was used, 100 % conversion was reached at 40 °C with a relatively low loss of CO_2 (< 1 %). A representative gas evolution curve along with a plot of the H_2 content of the gas mixture is given in Figure 1.

Our investigations indicate that $NaHCO_2$ is a suitable hydrogen-storage material since only H_2 is needed for the transformation. Both the starting material (sodium bicarbonate) and the product (sodium formate) are nontoxic and noncorrosive solids and easy to handle. High yields can be observed for both reactions under mild conditions including excellent conversion of CO_2 to bicarbonate during the release of hydrogen (Table 1, entry 4 and Table 2, entry 3). Notably,

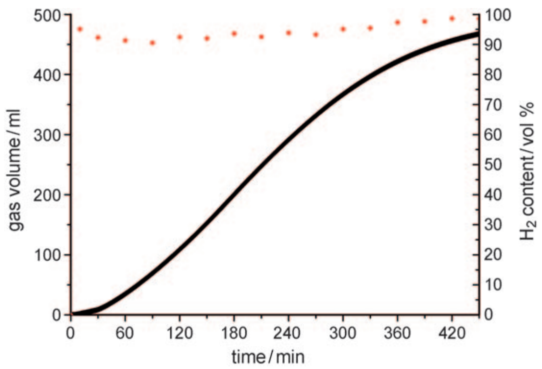
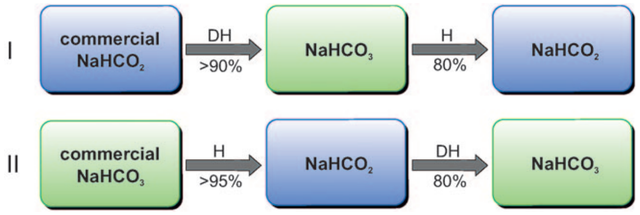


Figure 1. Hydrogen evolution curve and plot of H_2 content (red dots) at 40 °C from $NaHCO_2/H_2O$ mixture using 10 μmol [{$RuCl_2$(benzene)}$_2$]/6 equiv dppm in 20 mL DMF and 5 mL H_2O.

in contrast to all previously reported work with formic acid or formic acid/amine adducts, we have achieved a fully closed carbon cycle for the first time. This is far from trivial because of the exigency of CO_2 capture for a closed cycle!

Finally, in two different sets of proof-of-principle experiments we demonstrated that the same ruthenium catalyst system can be used in consecutive hydrogenation/dehydrogenation sequences (Scheme 2). In the first set of experiments (sequence I) commercially available sodium formate was dehydrogenated in the presence of the Ru/dppm catalyst at room temperature (> 90 % conversion). After simple removal of all solvents, the obtained powder was used in a hydrogenation reaction under pressure giving back sodium formate with 80 % yield in 20 h. Remarkably, no additional catalyst was required for the hydrogenation experiment. In a second set of experiments we started with commercially bicarbonate (sequence II in Scheme 2). After hydrogenation to sodium formate with 95 % yield, the product was reverted back to hydrogen and sodium bicarbonate with 80 % yield. Again, no additional catalyst was applied in the second step.



Scheme 2. Reversible hydrogen storage with a bicarbonate/formate system: Catalytic hydrogenation of bicarbonate and hydrogen release from formate with the same Ru/dppm in situ catalyst. Reaction conditions: dehydrogenation (DH): 40 mL DMF, 10 mL H_2O, 30 °C, 24–48 h; hydrogenation (H): 20 mL H_2O, 10 mL THF, 80 bar H_2, 24 h; sequence I: 71 μmol [{$RuCl_2$(benzene)}$_2$], 0.43 mmol dppm, 39.6 mmol $NaHCO_2$; sequence II: 10.4 μmol [{$RuCl_2$(benzene)}$_2$], 41.6 μmol dppm, 23.8 mmol $NaHCO_3$.

In conclusion, we have presented a ruthenium-based catalyst system for the selective hydrogenation of bicarbonates and the selective dehydrogenation of formates. Hydrogenation of $NaHCO_3$ to sodium formate was performed in 96 % yield at 70 °C in water/THF without additional CO_2. Dehydrogenation of sodium formate was achieved with high conversion (> 90 %) under ambient temperature (30 °C). It was demonstrated for the first time that the two reactions can be coupled leading to a closed carbon cycle for hydrogen storage. In contrast to our previous studies on the dehydrogenation of formic acid/amine adducts this process is amine-free.

Experimental Section

All reagents were purchased from a commercial supplier (Aldrich) and used without further purification. Solvents were degassed and distilled prior to use. Methods for quantification of gases as well as determination of conversions and yield were published elsewhere.[14a]

Hydrogen generation from formates: A thermostatically controlled reaction vessel was purged with argon six times to remove any other gases. The respective formate (20 mmol) was introduced as a powder together with degassed water (5 mL) and DMF (20 mL). After addition of dppm (30.0 μmol) the solution was heated to the desired temperature. After equilibration of the reaction mixture for 15 min [{$RuCl_2$(benzene)}$_2$] (5.0 μmol) was added in a Teflon crucible and gas evolution started. The evolved gases were collected with an automatic gas burette. After each reaction a GC sample was taken. At the end of the reaction period aqueous HCl was slowly added to the reaction mixture in order to determine the amount of bicarbonate present (indirectly based on the amount of CO_2 formed). CO_2 formation was confirmed by a second GC measurement. The deviation of measured gas volumes for two reactions was typically 1–15 %.

Hydrogenation of bicarbonates or carbonates and CO_2 in the presence of inorganic base: [{$RuCl_2$(benzene)}$_2$] (2.6 mg, 5.2 μmol) and dppm (8.0 mg, 21 μmol) were dissolved under argon in a solution of distilled water (25 mL), 24 mmol bicarbonate, carbonate, or base and THF (5 mL, to increase solubility of the catalyst). The mixture was transferred to a stirred (400 rpm) autoclave (100 mL) and deoxygenated with argon. H_2 (in some cases additional CO_2) was introduced to the autoclave at room temperature, and the reaction mixture was heated at 70 °C. After 2 h, the autoclave was cooled with ice water and the pressure was slowly released. All solvents were removed under reduced pressure, and the formate content in the resulting yellowish white solid was measured by ^1H NMR spectroscopy with D_2O as the solvent and THF as the internal standard with a relaxation delay (D_1) of 20 s. The deviation of determined yields for two reactions was typically 1–10 %.

Proof of principle of hydrogen storage: The formation of sodium bicarbonate or selective hydrogen generation from formates was carried out according to the procedures above. After the reactions all solvents were removed under reduced pressure and the recovered solid was stored under an inert gas atmosphere. No additional catalyst was needed for the next hydrogenation or dehydrogenation step.

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