

Hydrogen Storage in Formic Acid – Amine Adducts

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Abstract: Formic acid, containing 4.4 wt% of hydrogen, is a non-toxic liquid at ambient temperature and therefore an ideal candidate as potential hydrogen storage material. Formic acid can be generated *via* catalytic hydrogenation of CO₂ or bicarbonate in the presence of an amine with suitable ruthenium catalysts. In addition selective dehydrogenation of formic acid amine adducts can be carried out at ambient temperatures with either ruthenium phosphine catalyst systems as well as iron-based catalysts. In detail we obtained with the [RuCl₂(benzene)]₂/dppe catalyst system a remarkable TON of 260,000 at room temperature. Moreover applying Fe₃(CO)₁₂ together with tribenzylphosphine and 2,2':6',2''-terpyridine under visible light irradiation a TON of 1266 was obtained, which is the highest activity known to date for selective dehydrogenation of formic acid applying non-precious metal catalysts.

Keywords: Catalysis · Formic acid · Hydrogen generation · Hydrogen storage

Introduction

Due to an ever-increasing population and rampant energy demand a sufficient and benign supply of energy is a prerequisite for a stable global living standard.^[1] Among the various known energy carriers, hydrogen is foreseen to be the ultimate clean energy vector of the future. So far, hydrogen production *via* steam reforming and coal gasification is based to >95% on limited fossil resources such as gas, coal and oil. On a mid to long term basis, there is an increasing demand for alternative technologies to generate hydrogen in a more sustainable manner.^[2] However, the development of a hydrogen economy suffers from some major barriers, which have to be overcome in the near future. One of the major obstacles to use hydrogen for en-

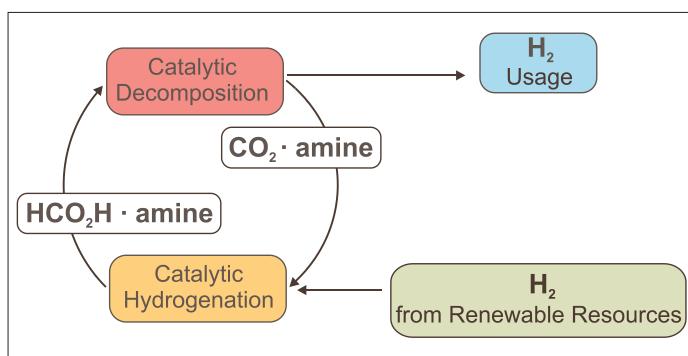


Fig. 1. Hydrogen storage *via* carbon dioxide–formic acid conversion.

ergy applications is the efficient and safe storage and handling of hydrogen.^[3]

Beside the classical hydrogen storage technologies,^[4] like pressurized and liquefied H₂, recently chemical hydrides especially formic acid (4.4 wt% hydrogen) have received increasing attention.^[5] HCO₂H (FA) is one of the major products formed in biomass processing such as fermentation, pyrolysis and supercritical reactions and can undergo selective decomposition to hydrogen and carbon dioxide only in the presence of a catalyst.^[6] In addition, a sustainable and reversible energy storage cycle can be envisioned by storage of hydrogen in formic acid and release from it (Fig. 1). Here, carbon dioxide is converted to formic acid or formate derivatives either electrochemically or by catalytic hydrogenation. The resulting products are liquids or solids at ambient conditions, and can thus be handled, stored, and transported easily.^[7]

In conclusion formic acid has some interesting features, which make it suitable

for a portable energy device: i) it is a liquid (~8–100 °C) at ambient conditions, ii) it has comparably low toxicity, iii) it can be easily and fully recovered by *e.g.* catalytic hydrogenation of CO₂, iv) hydrogen can be evolved at a wide temperature range (0–120 °C) with superior quality (<1 ppm CO) if suitable catalysts are used.

Our approach considering hydrogen storage *via* FA is the usage of convenient catalysts mainly based on ruthenium to decompose formic acid in the presence of different amines and further hydrogenate CO₂ to recover formic acid. These formic acid amine adducts, which are also known as trialkylammonium formates are well known as hydrogen donors in transfer-hydrogenation reactions, in particular triethylammonium formate (TEAF, 5HCO₂H/2NEt₃).^[8,9] Despite some observations of hydrogen generation from formic acid^[10] amine adducts and research in the field of CO₂ hydrogenation with various amines,^[11] the potential for hydrogen storage *via* formic acid amine adducts at ambient conditions

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(0–100 °C, 1–100 bar) has never been investigated in detail to explore the potential as hydrogen storage material.

Hydrogen Storage via FA Using Ruthenium Catalysts

Recently, our group and the group of Laurency independently demonstrated that hydrogen generation is possible at relatively mild conditions using ruthenium phosphine complexes.^[12] We identified several ruthenium phosphine complexes which are capable of generating hydrogen from formic acid amine adducts selectively at room temperature.^[7a,13] Unprecedented high rates at ambient temperature were obtained using *in situ* generated Ru/phosphine catalytic systems. Using $[\text{RuCl}_2(\text{benzene})_2]$ together with 1,2-bis(diphenylphosphino)ethane (dppe) a turnover number (TON = mol hydrogen/mol catalyst) of 1376 was obtained after 3 h using $5\text{HCO}_2\text{H}/2\text{NEt}_3$ at 40 °C. Except for argon and traces of the evaporated substrates, only H_2 and CO_2 were detected in the gas phase and no carbon monoxide was detected. Moreover we obtained improved catalytic performance (TON 3 h: 1469) using *N,N*-dimethylhexylamine instead of triethylamine at an increased amine to formic acid ratio (5:4 instead of 5:2). Hence, we combined for the first time the hydrogen generation unit with a polymer electrolyte fuel cell (PEMFC) and were able to consume online the produced hydrogen for conversion into electric energy. Thus, a power of 26 mW at 370 mV was obtained for more than 42 h. Further we investigated the influence of the nature and concentration of the present amine in the applied reaction solutions. Notably, the amine is not consumed during the reaction and can easily be recovered from the resulting mixture after full conversion.^[14] An active catalyst system containing *N,N*-dimethylhexylamine, $[\text{RuCl}_2(\text{benzene})_2]$ and 6 equiv. dppe was investigated both in batch and continuous mode. At room temperature (25 °C) more than 2.4 L of gas were obtained from a batch reaction applying 19.1 μmol Ru-catalyst resulting in a TON of 2616. Notably, this catalyst system can be recycled after full conversion simply by adding fresh HCO_2H . Applying this catalyst system no significant decrease of activity was observed even after 9 restarts of the reaction, *via* addition of formic acid, over a period of two months. Hence, a TON of 60,000 was achieved over this period and up to 2.9 L gas per hour were generated at 40 °C. Next, we investigated this catalyst system in continuous mode – constant dosage of FA – to investigate the long-time stability of this system. In a typical

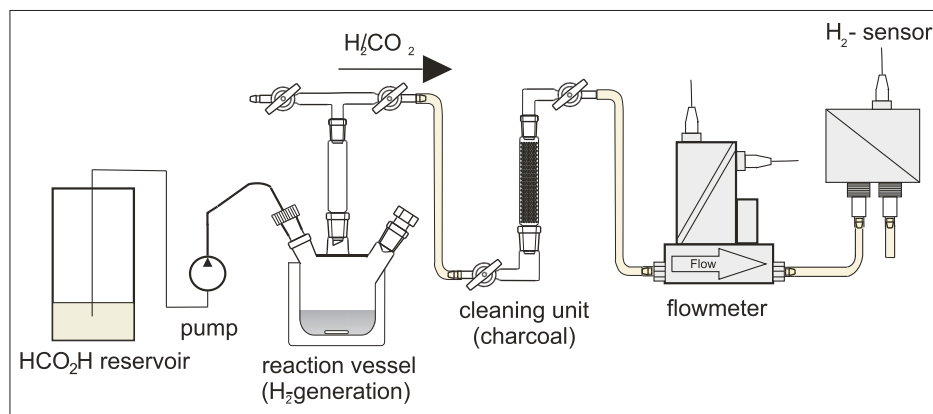


Fig. 2. Device for continuous hydrogen generation from formic acid.

experiment 0.74 mL formic acid per hour were added to the reaction vessel containing 9.55 mmol $[\text{RuCl}_2(\text{benzene})_2]/6$ equiv. dppe in 17.5 mL *N,N*-dimethylhexylamine (HexNMe_2). The reaction setup is shown in Fig. 2.

Notably, no decrease of activity was observed over a period of 264 h resulting in a TON of 260,000 at a constant turn over frequency (TOF) of 900 h^{-1} at a reaction temperature of 25 °C, which represents so far the highest activity known for this temperature. With respect to feedstock, commercially available formic acid (99% grade, BASF) was used as received.^[15] This concept was proven to work in a small prototype model car driven by a hydrogen/air fuel cell, which was coupled to an on-board hydrogen generation system using formic acid and a similar catalyst.

More recently, we showed that ruthenium phosphine catalyst systems can be triggered and accelerated *via* irradiation with visible light.^[16] In comparison to the non photo-assisted system, a more than one order of magnitude increase of gas evolution is achieved in the light-accelerated reaction. Thus here the best catalyst productivity is observed with a $[\text{RuCl}_2(\text{benzene})_2]/\text{dppe}$ catalyst and the catalyst activity is almost double the activity of the best non-light activated system.

In addition to our efforts in the field of hydrogen generation from FA/amine adducts we also investigated the ruthenium-catalyzed bicarbonate hydrogenation to formates. For example, using $[\text{RuCl}_2(\text{benzene})_2]$ and 1,2-bis(diphenylphosphino)methane (dppm) or dppe sodium bicarbonate was hydrogenated with 30% yield (with dppm) at 70 °C with pure H_2 (80 bar) and a TON of 1374 was obtained.^[17]

A current goal in organometallic catalysis is the replacement of noble metal-based catalysts, such as ruthenium, iridium and rhodium, with non-precious metal catalysts such as iron compounds.^[18] Until now research on non-precious metal catalyst for these transformations is scarce.

Hydrogen Storage via FA Using Iron Catalysts

In 2010 we started our investigations towards the first non-precious metal catalyst system capable of dehydrogenating formic acid in the presence of amine.^[19] Therefore, we began our study with an initial catalyst testing of numerous non-noble metal precursors in combination with different phosphorus- and nitrogen-containing ligands. In a typical experiment a double-walled thermostatically controlled reaction vessel was charged with the metal complexes (60 μmol metal) and ligands (mostly one equivalent), which were added either as powders in a teflon crucible and 1 mL of solvent or from a freshly prepared stock solution (1 mL). 5 mL of $5\text{HCO}_2\text{H}/2\text{NEt}_3$ (FA/TEA) were placed in the vessel and the desired temperature was kept constant. The reactions were started after equilibration for at least 30 min. The volume of evolved gases was quantitatively measured using automatic gas burettes.^[13] In addition, H_2 and other evolved gases were qualitatively and quantitatively determined by GC (gas chromatograph HP6890N, carboxen 1000, TCD, external calibration). We found triiron dodecacarbonyl ($\text{Fe}_3(\text{CO})_{12}$) in the presence of triphenylphosphine (PPh_3), 2,2':6'2''-terpyridine (tpy) and dimethylformamide (DMF) capable of this transformation at elevated temperatures (>100 °C). However, the reaction did not proceed very selectively (H_2 or CO_2 : CO 1:5). To our delight, applying visible light (300 W PerkinElmer Cermax PE300BF Xenon Arc lamp with HOT Mirror) onto the reaction solution the temperature could be decreased to almost room temperature and also the selectivity of the reaction was enhanced (CO <100 ppm). Next, we investigated the influence of present ligands – PPh_3 and tpy (Table 1).

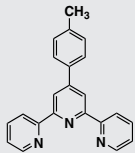
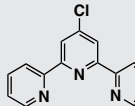
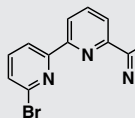
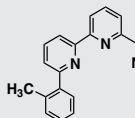
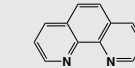
While $\text{Fe}_3(\text{CO})_{12}$ with 3 equiv. tpy (Fe/tpy 1:1) showed almost no activity, significant hydrogen evolution occurred with 3

Table 1. Dependence of catalytic activity on the ligand combination PPh₃, tpy and the presence of amine^a

Entry	ligand a	ligand b	V _{3h} [mL]	TON _{3h}
1	tpy	–	1.9	0
2	–	PPh ₃	16	5.4
3	tpy	PPh ₃	68 (131) ^b	23 (44) ^b
4 ^c	tpy	PPh ₃	5.6	1.9

^aReaction conditions: 20 μmol Fe₃(CO)₁₂, PPh₃, tpy, (Fe/PPh₃/tpy 1:1:1), 1 ml DMF, 5 mL 5HCO₂Hx2NEt₃, 40 °C, light irradiation by 300 W xenon lamp, 3 h reaction time, gas measured by automatic gas burette and analyzed *via* GC (H₂:CO₂ 1:1); ^b24 h; ^cwithout amine.

Table 2. Dependence of catalytic activity on various pyridine-type ligands^a

entry	P-ligand	N-ligand	TON _{2h}	TON _{3h}
1	PPh ₃	tpy	31	44
2	PPh ₃		20	27
3	PPh ₃		16	19
4	PPh ₃		52	56
5	PPh ₃		46	48
6	PPh ₃		26	39 (126) ^b

^aInfluence of pyridine-type ligands on the activity (TON) of H₂ generation from HCO₂H using 20 μmol Fe₃(CO)₁₂, PPh₃, N-type ligand, (Fe/PPh₃/N-type ligand 1:1:1) in 5 mL 5HCO₂Hx2NEt₃, 1 mL DMF, 60 °C, reaction time 3 h, light irradiation from 300 W xenon lamp; ^bafter 24 reaction time.

equiv. PPh₃ (Fe/PPh₃ 1:1) (Table 1, entries 1 and 2). However, in the presence of a catalyst system containing Fe/tpy/PPh₃ (ratio of 1:1:1) under irradiation a significantly higher activity is obtained, resulting in a TON of 44 (Table 1, entry 3) after 24 h. The absence of amine resulted in very low activity (Table 1, entry 4). Further, in order to improve the catalytic activity, a range of pyridine-type ligands were investigated at 60 °C (Table 2).

Among the tested pyridine-type ligands all showed significant activity compared to the standard ligand tpy (Table 2, entries 1–6). 4'-(4-methylphenyl)-2,2':6',2''-terpyridine (Table 2, entry 2) and 4'-(chloro)-2,2':6',2''-terpyridine (Table 2, entry 3) gave lower activities compared to terpyri-

dine itself. Interestingly, when changing the substituent in the 6,6''-positions of terpyridine from H to bromine or 2-methylphenyl groups an increase of activity is observed. 6,6''-(Bromo)-2,2':6',2''-terpyridine and 6,6''-(2-methylphenyl)-2,2':6',2''-terpyridine provided the highest activity with a turnover frequency (TOF) of 200 h⁻¹ for the bromo-substituted tpy compared to 84 h⁻¹ for terpyridine (Table 2, entries 4 and 5). However, the catalyst system derived from terpyridine provided higher stability. In addition, if 1,10-phenanthroline was applied, a significant enhancement of stability compared to tpy and bromo-substituted tpy was observed. After 24 h 1,10-phenanthroline gave a turnover number of 126 underlining the stability of these catalyst systems

Table 3. Investigation of various metal to ligand ratios on the decomposition of FA^a

Entry	equivalent PPh ₃	equivalent tpy	TON 3 h
1	1	0.2	72
2	1	0.33	71
3	1	2	20
4	0.33	1	28
5	0.5	1	33
6	1	1	44
7	2	1	19

^aReaction conditions: 20 μmol Fe₃(CO)₁₂ (60 μmol Fe), ratios refer to present [Fe], 5 mL preformed TEA/HCO₂H (2/5) mixture, 1.0 mL DMF, 60 °C, 3 h reaction time, 300 W Xe-light irradiation, gas mixture H₂/CO₂ = 1/1, gas volumes detected by automatic gas burettes, qualitative gas analysis by GC.

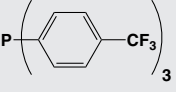
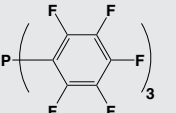
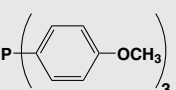
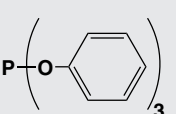
(Table 2, entry 6). The present study of different pyridine-type ligands suggests that these co-ligands accelerate the transformation of Fe₃(CO)₁₂ into an active species – especially the 6,6'' substituted – and are responsible for stabilization as well.

In order to investigate the necessity of the standard ratio of phosphine and tpy ligand to Fe (mostly 1:1:1) on the catalytic activity we performed numerous reactions with various metal to ligand ratios (see Table 3).

As presented previously (Table 1) without PPh₃ no activity was observed, even at 60 °C. However without tpy significant catalytic activity was observed at 60 °C. In Table 3 the results of the investigation of various ligand to iron ratios are presented. Interestingly, with a ratio of 0.2 or 0.33 tpy per Fe an increased catalytic activity was observed (Table 3, entries 1 and 2) with TON of 72 and 71, respectively. A ratio of 2 (tpy/Fe) resulted in a significant decrease of activity (Table 3, entry 3). Altering the ratio of PPh₃ to iron led to a decrease in activity, thus the optimum was found at 1.0 (Table 3, entries 4–7). These findings additionally underline that tpy may be needed only for stabilization purposes.

Further, we investigated additional phosphine and phosphite ligands in the presence of Fe₃(CO)₁₂ and tpy.^[19,20] Selected results from this ligand variation are shown in Table 4. Whereas considerable activity was observed with tris(4-fluoromethylphenyl)phosphine and tris(4-methoxyphenyl)phosphine (Table 4, entries 2 and 4), significantly less activity was observed applying tris(pentafluorophenyl)phosphine or triphenylphosphite (Table 4, entries 3 and 5). Among the different ligands studied, only those bearing benzyl groups showed improved activity compared to our previous triphenylphosphine-based catalyst.

Table 4. Influence of various phosphine and phosphite ligands on the iron-catalyzed decomposition of FA^a

Entry	Fe-source	Fe conc. [μmol]	ligand	V 3 h [mL] (15 h)	TON 3 h (15 h)
1	Fe ₃ (CO) ₁₂	60	PPh ₃	129	44
2	Fe ₃ (CO) ₁₂	60		68	23
3	Fe ₃ (CO) ₁₂	60		5	1.7
4	Fe ₃ (CO) ₁₂	60		91	31
5	Fe ₃ (CO) ₁₂	60		2.0	2.1
6	Fe ₃ (CO) ₁₂	30	PPh ₃	96 (153)	65 (104)
7	Fe ₃ (CO) ₁₂	30	PBn ₃	203 (1033)	138 (702)
8	Fe ₃ (CO) ₁₂	30	P(Ph ₂ Bn) ₃	132 (344)	90 (234)
9	Fe ₃ (CO) ₁₂	30	P(etPh) ₃	31 (272)	21 (185)

^aReaction conditions: Fe₃(CO)₁₂, *P*-ligand, tpy, (Fe/PPh₃/tpy 1:1:1), 5 mL preformed TEA/HCO₂H (2/5) mixture, 1.0 mL DMF, 60 °C, 3 or 15 h reaction time, 300 W Xe-light irradiation, gas mixture H₂/CO₂ = 1/1, gas volumes detected by automatic gas burettes, qualitative gas analysis by GC.

Compared to PPh₃, tribenzylphosphine (PBn₃) and benzyldiphenylphosphine (P(Ph)Bn₂) showed significantly improved activity as well as stability (Table 4, entries 6–8). The turnover number for PPh₃ after 3 h is 65 (Table 4, entry 6) and the system is deactivated. However, tribenzylphosphine gave a TON of 138 and more importantly the stability is increased giving a total TON of 702 after 15 h. Notably, this effect is limited to benzyl-substituted phosphines. The more benzyl moieties are present in the ligand, the higher the activity and stability of the system (Table 4, entries 6–8).

Introduction of an ethyl bridge into the ligand did not result in a stable system and low activity is observed (Table 4, entry 9), thus making it unlikely that electronic properties of the ligands account for the different activity. Notably, also here both light as well as base are essential for catalysis. Finally, a TON of 1266 (3728 mL gas) after 51 h with 20 μmol Fe₃(CO)₁₂/3 equiv. PBn₃/3 equiv. tpy in 10 mL 5HCO₂Hx 2NEt₃ at 60 °C could be obtained! This represents the highest productivity for any non-noble metal catalyzed hydrogen production from formic acid and is one order of magnitude higher than all previously reported catalysts.

Further, we investigated the mechanism *via* MS and HRMS studies applying

ESI-TOF, NMR, *in situ* IR, UV-VIS and DFT calculations with the *in situ* catalyst Fe₃(CO)₁₂/PPh₃/tpy. We found [HFe(CO)(PPh₃)₃(tpy)]⁻ and [Fe(CO)₃(PPh₃)₂] present in the reaction mixture. Further [Fe(CO)₃(PPh₃)₂] was found to be a catalytically active species which is generated during catalysis. Notably, the reaction rate for the *in situ* catalyst system and the defined complex were comparable within the first hour confirming the same active

species. Then, the molecular defined precatalyst [Fe(CO)₃(PPh₃)₂] is rapidly deactivated, which is not the case for the *in situ* catalyst mixture, where terpyridine is included (Fig. 3). Therefore we conclude that terpyridine is needed mainly for stabilization purposes.

In situ IR spectroscopy of the reaction solution together with DFT calculation, at the B3PW91/6-31G* and B3PW91/6-311G** levels of theory, and NMR spectroscopy led to the conclusion that PPh₃ dissociates from [Fe(CO)₃(PPh₃)₂] under light irradiation, which is considered to be the first step of selective dehydrogenation of formic acid. Further loss of PPh₃ or CO, which decreases the catalytic activity, can be prevented *via* the terpyridine co-ligand. Indeed, we found that PPh₃ loss is more likely to occur than CO loss (~4 kcal/mol). However, we found that CO loss of the generated [Fe(CO)₃(PPh₃)₂] complex is responsible for the ultimate deactivation of the catalytic system. Next, we wanted to have a closer look on the formed catalytic active species.

Testing these different *P*-ligands, no clear tendency of electronic or steric parameters was observed. Apparently, the significant difference in activity and stability is not caused by these factors. On the other hand, comparing PPh₃ and PBn₃, the latter offers the opportunity of a cyclometallation towards a five-membered metallacycle, which could account for the increased stability. To find indications for this proposal, we carried out additional NMR-experiments as well as theoretical calculations which both strongly support the formation of ortho-metallated intermediates in the case of [Fe(CO)₃(PBn₃)₂]. Indeed, we found from DFT calculations that a ortho-metallation of the intermediate [Fe(CO)₃(PBn₃)] is favored with ~10 kcal/mol (Fig. 4). Hence, characteristic NMR shifts of the ortho-metallated species could be detected.

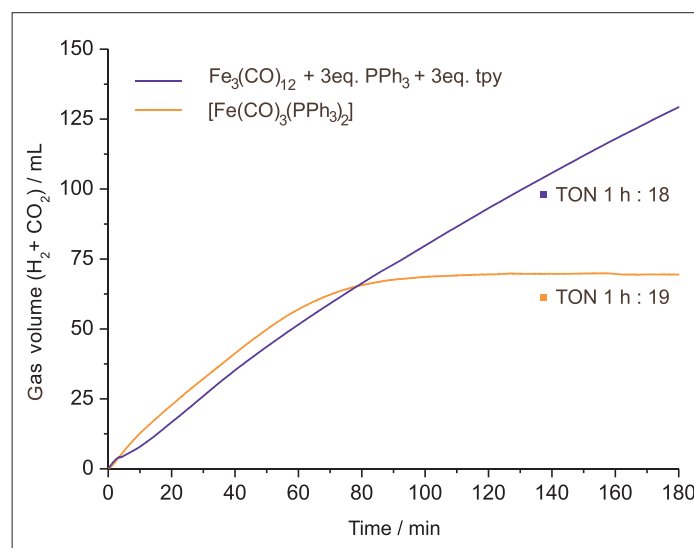


Fig. 3. Comparison of the catalyst activity of the *in situ* generated catalyst from Fe₃(CO)₁₂/PPh₃/tpy and [Fe(CO)₃(PPh₃)₂] for H₂ generation from HCO₂H using 20 μmol Fe₃(CO)₁₂/PPh₃/ligand (Fe/P/ligand 1:1:1) or 60 μmol [Fe(CO)₃(PPh₃)₂] in 5 mL 5 HCO₂Hx 2NEt₃ + 1 mL DMF, ambient pressure, 60 °C, reaction time 3 h, light irradiation from 300 W xenon lamp (385 nm cut-off by hot mirror).

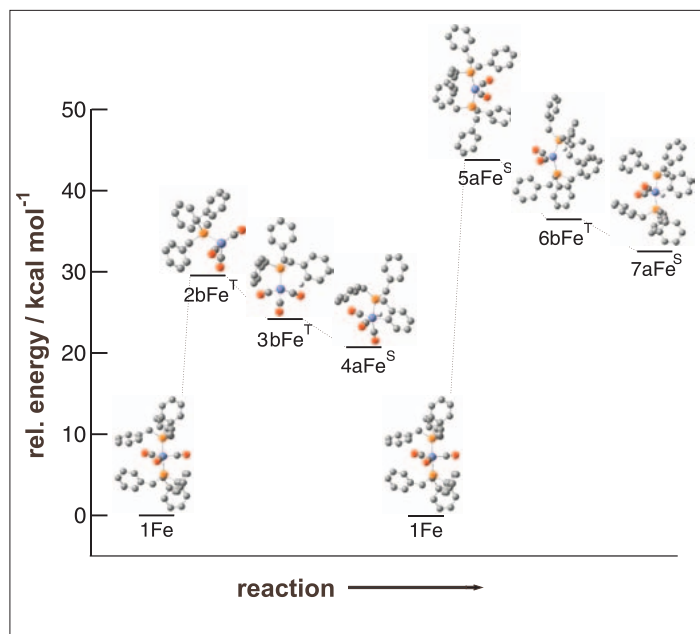


Fig. 4. DFT calculation at the B3PW91/6-31G* and B3PW91/6-311G** levels of theory for the ortho metallation reaction starting from $[\text{Fe}(\text{CO})_3(\text{PBN}_2)_2]$.

Conclusions

We have shown that formic acid is an ideal, easily applicable hydrogen storage material. Under ambient conditions it is a non-toxic liquid with 4.4 wt% of hydrogen. Through catalytic hydrogenation of CO_2 and subsequent catalytic dehydrogenation of FA a CO_2 neutral hydrogen storage cycle can be envisioned. However, during the last 40 years CO_2 hydrogenation has been in the focus of many scientists, and selective dehydrogenation of formic acid towards H_2 and CO_2 is comparably less studied. We explored whether hydrogen storage in formic acid amine adducts is conceivable with ruthenium and iron catalysts. With respect to ruthenium-based catalysts, we identified several active catalysts for the selective dehydrogenation of FA and moreover the hydrogenation of appropriate starting material (CO_2 , bicarbonate). The highest activity known to date for the dehydrogenation of FA was observed applying $[\text{RuCl}_2(\text{benzene})_2]$ and dppe. With this catalyst system we could show TONs of more than 260,000 at room temperature, which is the highest activity known to date. In addition, also hydrogenation of CO_2 and bicarbonate was possible with this catalyst, which enhances the applicability. For the first time a hydrogen generation unit equipped with this ruthenium catalyst was coupled to a fuel cell to demonstrate the general principle. Although this highly active ruthenium-based catalyst was identified we also investigated possible non-precious metal catalyst systems. To our delight we observed also remarkable activity with iron-based systems. A catalyst system consisting of $\text{Fe}_3(\text{CO})_{12}$, tribenzylphosphine and tpy showed over 51 h a TON of 1266, which claims the highest value for a non-

precious metal catalyst system capable of selectively dehydrogenating formic acid.

Acknowledgements

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- [1] a) J. O. M. Bockris, *Science* **1972**, *176*, 1323; b) G. W. Crabtree, M. S. Dresselhaus, M. V. Buchanan, *Phys. Today* **2004**, *57*, 39; c) N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729.
- [2] a) J. A. Turner, *Science* **2004**, *305*, 972; b) N. Armbaroli, V. Balzani, *Angew. Chem. Int. Ed.* **2007**, *46*, 52; *Angew. Chem.* **2007**, *119*, 52; c) A. Züttel, L. Schlapbach, *Nature* **2001**, *414*, 353; d) F. A. Armstrong, J. C. Fontecilla-Camps, *Science* **2008**, *321*, 498; e) W. Lubitz, W. Tumas, *Chem. Rev.* **2007**, *107*, 3900.
- [3] a) N. Armbaroli, V. Balzani, *ChemSusChem*; **2011**, *4*, 21; b) U. Eberle, A. Felderhoff, F. Schüth, *Angew. Chem. Int. Ed.* **2009**, *48*, 6608; c) K. M. Thomas, *Catal. Today* **2007**, *120*, 389; d) A. W. C. van den Berg, C. O. Areán, *Chem. Commun.* **2008**, 668; e) L. J. Murray, M. Dinca, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294; f) R. E. Morris, P. S. Wheatley, *Angew. Chem. Int. Ed.* **2008**, *47*, 4966; g) F. Schüth, B. Bogdanovic, M. Felderhoff, *Chem. Commun.* **2004**, 2249; h) R. B. Biniwale, S. Rayalu, S. Devotta, M. Ichikawa, *Int. J. Hydrog. Energy* **2008**, *33*, 360; i) R. H. Crabtree, *Energy Environ. Sci.* **2008**, *1*, 134.
- [4] For a review of physical hydrogen storage see: R. von Helmolt, U. Eberle, *J. Power Sources* **2007**, *165*, 833.
- [5] For recent reviews on hydrogen release from formic acid and other chemical hydrides see: a) B. Loges, A. Boddien, F. Gärtner, H. Junge, M. Beller, *Top. Catal.* **2010**, *53*, 902; b) T. C. Johnson, D. J. Morris, M. Wills, *Chem. Soc. Rev.* **2010**, *39*, 81; c) H.-L. Jiang, K. Singh, J.-M. Yan, X.-B. Zhang, Q. Xu, *ChemSusChem* **2010**, *3*, 541; d) P. Makowski, A. Thomas, P. Kuhn, F. Goettman, *Energy Environ. Sci.* **2009**, *2*, 480; e) S. Enthaler, J. von Langermann, T. Schmidt, *Energy Environ. Sci.* **2010**, *3*, 1207; f) C. W. Hamilton, R. T. Baker, A. Staubitz, I. Manners, *Chem. Soc. Rev.* **2009**, *38*, 279; h) S. Fukuzumi, *Eur. J. Inorg. Chem.* **2008**, *9*, 1351.
- [6] a) J. Reunanen, P. Oinas, T. Nissinen, 'A process for recovery of formic acid', *PCT Int. Appl.* **2009**; b) A. Kruse, A. Gawlik, *Ind. Eng. Chem. Res.* **2003**, *42*, 267; c) D. J. Hayes, S. Fitzpatrick, M. H. B. Hayes, J. R. H. Ross, in 'Biorefineries-Industrial Processes and Products', Ed. B. Kamm, P. R. Gruber, M. Kamm, Wiley-VCH, Weinheim, **2006**, p. 139.
- [7] B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2008**, *47*, 3962; b) C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem. Int. Ed.* **2008**, *47*, 3966; c) C. Fellay, N. Yan, P. J. Dyson, G. Laurenczy, *Chem. Eur. J.* **2009**, *15*, 3752.
- [8] a) S. Gladioli, E. Alberico in 'Transition metals for organic synthesis', Vol. 2, Ed. M. Beller, C. Bolm, Wiley-VCH, Weinheim, **2004**, p. 145; b) S. Gladioli, E. Alberico, *Chem. Soc. Rev.* **2006**, *35*, 226.
- [9] For a recent publication on transfer-hydrogenation via TEAF see: P. Hauwert, R. Boerleider, S. Warsink, J. J. Weigand, C. J. Elsevier, *J. Am. Chem. Soc.* **2010**, *132*, 16900.
- [10] S. Ogo, T. Abura, Y. Watanabe, *Organometallics* **2002**, *21*, 2964.
- [11] a) W. Leitner, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2207; b) P. G. Jessop, F. Joó, C. C. Tai, *Coord. Chem. Rev.* **2004**, *248*, 2425; c) P. G. Jessop in 'The Handbook of Homogeneous Hydrogenation', Ed. J. G. de Vries, C. J. Elsevier, Wiley-VCH, Weinheim, **2006**; p. 489.
- [12] a) S. Enthaler, *ChemSusChem* **2008**, *1*, 801; b) F. Joó, *ChemSusChem* **2008**, *1*, 805.
- [13] A. Boddien, B. Loges, H. Junge, M. Beller *ChemSusChem* **2008**, *1*, 751.
- [14] H. Junge, A. Boddien, F. Capitta, B. Loges, J. R. Noyes, S. Gladioli, M. Beller, *Tetrahedron Lett.* **2009**, *50*, 1603.
- [15] A. Boddien, B. Loges, H. Junge, F. Gärtner, J. R. Noyes, M. Beller, *Adv. Synth. Catal.* **2009**, *351*, 2517.
- [16] B. Loges, A. Boddien, H. Junge, J. R. Noyes, W. Baumann, M. Beller, *Chem. Commun.* **2009**, 4185.
- [17] C. Federsel, R. Jackstell, A. Boddien, G. Laurenczy, M. Beller, *ChemSusChem* **2010**, *3*, 1048.
- [18] For recent reviews and highlights on iron catalysis see: a) 'Iron Catalysis in Organic Chemistry', Ed. B. Plietker, Wiley-VCH, **2008**; b) S. Enthaler, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2008**, *47*, 3317; c) S. Gaillard, J.-L. Renaud, *ChemSusChem* **2008**, *1*, 505; d) C. Bolm, J. Legros, J. L. Paith, L. Zani, *Chem. Rev.* **2004**, *104*, 6217; e) A. Correa, O. G. Mancheño, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108; f) B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500; g) A. Fürstner, *Angew. Chem. Int. Ed.* **2009**, *48*, 1364; h) R. M. Bullock, *Angew. Chem. Int. Ed.* **2007**, *46*, 7360.
- [19] A. Boddien, B. Loges, F. Gärtner, C. Torborg, K. Fumino, H. Junge, R. Ludwig, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 8924.
- [20] A. Boddien, F. Gärtner, R. Jackstell, H. Junge, A. Spannenberg, W. Baumann, R. Ludwig, M. Beller *Angew. Chem. Int. Ed.* **2010**, *49*, 8993; *Angew. Chem.* **2010**, *122*, 9177.