Green Chemistry

Hydrogen production from formic acid catalyzed by a phosphine free manganese complex: investigation and mechanistic insights†

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Formic acid dehydrogenation (FAD) is considered as a promising process in the context of hydrogen storage. Its low toxicity, availability and convenient handling make FA attractive as a potential hydrogen carrier. To date, most promising catalysts have been based on noble metals, such as ruthenium and iridium. Efficient non-noble metal systems like iron were designed but manganese remains relatively unexplored for this transformation. In this work, we present a panel of phosphine free manganese catalysts which showed activity and stability in formic acid dehydrogenation. The most promising results were obtained with Mn(pyridine-imidazoline)(CO)3Br yielding >14 l of the H2/CO2 mixture and proved to be stable for more than 3 days. Additionally, this study provides insights into the mechanism of formic acid dehydrogenation. Kinetic experiments, Kinetic Isotopic Effect (KIE), in situ observations, NMR labeling experiments and pH monitoring allow us to propose a catalytic cycle for this transformation.

Introduction

A vast majority of today’s energy sources are consumed much faster than it takes to produce them naturally on earth. In this context, transition to environmentally benign renewable sources is a growing field advocated by both academics and industries. Thus, several alternatives such as wind, solar and hydroelectric technologies are of growing importance. Unfortunately, they have an Achilles’ heel as they constitute intermittent energy sources. On the other hand, hydrogen, which can be easily produced by water electrolysis, is seriously considered as a better storable chemical energy vector. In this respect, safe storage and easy handling of H2 are of general interest for industrial supplying chains. Hitherto, Liquid Organic Hydrogen Carriers, also known as LOHCs, attracted much interest because of their convenient storage and transport. More specifically, cyclohexanes and heterocycles, ammonia, hydrazine, alcohols and formic acid (FA) showed encouraging results. The latter compound presents advantageous physicochemical properties and low toxicity enabling safe and easy handling, transportation and storage. Notably, FA can be reversibly generated by hydrogenation of carbon dioxide and subsequently dehydrogenated, thus making it an attractive carrier candidate. For the dehydrogenation process under mild conditions, homogeneous noble metal-based complexes, e.g., ruthenium, iridium and rhodium, constitute the state-of-the-art catalysts. For such molecularly defined systems, it has been shown that the structure of the ligand strongly influences the (de)hydrogenation reactions. Indeed, pH-tunable metal complexes bearing hydroxyl substituted bipyridine ligands led to significantly higher performance and stability. Additionally, complexes bearing tridentate phosphine–amine–phosphine pincer type ligands (PNP) reached very high TONs and TOFs. Obviously, regarding costs and availability, the use of precious metals and ligands possesses significant drawbacks for eventual applications. Consequently, in the last decade catalysts based on 3d metals attracted significant attention. As an example, our group reported the first iron based catalysts for FA dehydrogenation (DH) in 2010. In 2011, Milstein and co-workers described the first PNP pincer ligand with an iron metal center which initiated intensive further studies in this area. Apart from this, other systems including cobalt, aluminum and boron have been subject to investigations. However, except for Boncella’s recently reported complex ([IP3PNIP3P]Mn(OOCH)(CO)2 for...
FA DH\textsuperscript{19} and the very recent studies on \([\text{[Hb]PNNOP}Mn(CO)\text{]}}\) [Br],\textsuperscript{20} manganese remained quite unexplored for this transformation despite its abundance in the Earth crust. Furthermore, in the very recent year manganese has shown good results in other dehydrogenation transformations such as amine–alcohol coupling\textsuperscript{21} or methanol DH.\textsuperscript{22} Notably, all these complexes vide supra these complexes still make use of special, often highly sophisticated ligands. In fact, the costs of tailor-made PNP systems are determined by the ligand and not the metal. In nature, multi-dentate nitrogen ligands, such as porphyrins, are applied in combination with Fe (Heme A, B, C and O) or Co (vitamin B12) for various enzymatic redox processes.

Investigations of the catalytic performance

In the past decade, noble metal complexes with heterocyclic ligands, especially those bearing an N–H moiety, showed high efficiency in the DH of formic acid\textsuperscript{24–27} or the hydrogenation of carbon dioxide.\textsuperscript{28,29} In this context, a panel of manganese complexes was synthesized and tested for the DH of FA (Table 1).

Little gas evolution was noted when Mn(CO)\textsubscript{5}Br was used as a catalyst (entry 1). Similarly, bipyridine based complexes showed negligible activities (entries 2 and 3). In contrast, ligands containing an N–H moiety as a part of an aromatic heterocycle – such as pyrazole or imidazole – clearly showed improved gas evolution (entries 4, 5 and 6). Modification of the imidazole based ligand (entry 4) to the imidazoline based ligand (entry 7) resulted in further enhanced gas production. In the case of catalyst 3a, the electronic nonbonding pair on the nitrogen is involved in the aromaticity of the imidazole and the proton in the N–H moiety is more acidic (entry 4) unlike catalyst 4a (entry 7), where this electron doublet is localized on the nitrogen and thus not involved in the aromaticity. Extending the heterocycle from a 5 to a 6 membered ring did not benefit the reaction (entry 8). Interestingly, the N-methylated version of this pyridine-imidazoline based complex yielded almost identical results (entry 9). Therefore, catalysts 4a (entry 7) and 4c (entry 9) led to equally efficient activity, suggesting that H in N–H is not mandatory. Ultimately, systems bearing non-aromatic ligands such as 5a and 5b (entries 10 and 11) gave higher initial gas evolution but were prone to deactivation yielding lower activities (Fig. S5†).

Finally, at the end of this iterative catalyst screening, the in situ generated complex 4a was tested, which yielded identical results compared to the use of the defined complex (Fig. S6†).

Table 1 Tested catalysts for the FA dehydrogenation\textsuperscript{a}

| Entry | Cat. | H\textsubscript{2} + CO\textsubscript{2} (mL) | TON (3 h) | TOF (h\textsuperscript{-1}) |
|-------|------|-----------------|----------|---------------------|
| 1     | 1    | 4.1             | 17       | 6                   |
| 2     | 2a   | 12              | 50       | 17                  |
| 3     | 2b   | 4.7             | 19       | 6                   |
| 4     | 3a   | 37              | 151      | 50                  |
| 5     | 3b   | 43              | 175      | 58                  |
| 6     | 3c   | 54              | 220      | 73                  |
| 7     | 4a   | 138             | 564      | 188                 |
| 8     | 4b   | 134             | 549      | 183                 |
| 9     | 4c   | 141             | 577      | 192                 |
| 10    | 5a   | 136             | 556      | 185                 |
| 11    | 5b   | 116             | 473      | 158                 |

\textsuperscript{a} Reaction conditions: HCOOH (37 mmol), KOH (40 mmol), Mn catalyst (0.005 mmol), H\textsubscript{2}O (9 mL), triglyme (4 mL), time (180 min), light exclusion. Gas evolution monitored with manual burettes, corrected by the blank volume (2.7 mL) and content of the gas phase analyzed by gas chromatography (GC). Ratio H\textsubscript{2} : CO\textsubscript{2} in all cases 1:1; CO content in between 78 ppm (quantification limit) and 2632 ppm. Experiments were performed at least twice (except entries 1–3) with reproducibility differences between 0.8 and 10%.

Results and discussion

Next, the influence of important reaction parameters was investigated (Table 2). As expected, the observed gas evolution increased along with the catalytic loading (entries 1–5). KOH base can be successfully changed for HCOOK (entry 6). Performing the DH of FA in various organic solvents showed that triglyme remained superior (entry 6) to dioxane (entry 9), NMP (entry 10), DMSO (entry 7) or DMF (entry 11).

Interestingly, plotting the gas evolution over time indicated that the triglyme based reaction led to much higher initial gas evolution (Fig. S7†). Thus, special care is needed to minimize light exposure.

Finally, different working temperatures were investigated (entries 11–14). Although the activity increased, it should be noted that heating the system would favor the dehydration of FA, leading to water and carbon monoxide, which is detrimen-
A stable system could not be designed. The best results were obtained using a phosphate buffer with a strength of 1.5 mol L\(^{-1}\) reaching a TON of 338 at 46% conversion in 180 minutes (Fig. S13†). Higher concentrated phosphate buffers were not investigated since the concentration could not be increased. Even though the use of an organic base such as dimethyl-octylamine (DMOA) or triethylamine (TEA) proved to be more suitable for hydrogen release, in these cases the attractive aqueous feature of the reaction was lost (Fig. S14†). Thus, alternatively we considered continuous flow experiments. Controlled dosage of FA in our system should permanently maintain the pH at a desired value and therefore lead to a steady and fast gas evolution over an extended period of time.

### Towards a continuous flow process

In a preliminary investigation, FA was added to the system after 180 minutes, when the deactivation occurred (Fig. S14†). To our delight, we noted that gas evolution was resumed (1 : 1 H\(_2\) : CO\(_2\) analyzed by GC). This result suggested that our catalyst did not irreversibly deactivate, but was rather out of its optimum pH zone as proposed above. Next, we concentrated our effort on designing a FA continuous dosage system. The initial experiments showed that injecting FA every 30 minutes yielded a stable and steady gas evolution for the given reaction time. Satisfying results were obtained both in a buffer system (Fig. S15†) and in water (Fig. S16†) reaching TONs of 584 (47% conversion, 1425 mL of H\(_2\) : CO\(_2\)) and 508 (41% conversion, 1240 mL of H\(_2\) : CO\(_2\)) respectively. Those periodic dosage experiments were transposed into a continuous flow, carried out on a longer time scale.

Finding an optimal rate to steadily maintain the rapid initial gas evolution (7 mL min\(^{-1}\)) was challenging. Indeed, an imprecise dosage would irremediably lead to an accumulation of FA and the inhibition of the reaction. In this context, our best result – a TON of 5763 (67% conversion, 14073 mL of H\(_2\) : CO\(_2\) mixture), was obtained after 45 hours. Unfortunately,
even under these conditions deactivation slowly occurred and the gas evolution stopped (Fig. S17†). As pointed out before, accumulation of FA acidified the solution and inhibited the reaction as shown by the final pH (3.5). As a result, we performed a long term stability experiment with a lower dosage rate to tackle FA accumulation. In this context, a TON of 2637 was reached (78% conversion, 6442 mL of H2 : CO2) within 87 h. We should note that the gas evolution throughout the reaction is found to be constant on average (Fig. 2).

Mechanistic studies

The dehydrogenation of formic acid has been widely explored for numerous metal complexes including iron,15,31,32 rhenium13 or ruthenium25,34,35 based PNP systems. More recently, mechanistic investigations of iridium21,26,27 and ruthenium25,36,37 catalysts bearing bis-heterocyclic ligands revealed interesting features. Notably, the role of the ligand pointing out a proton relay transfer through an N–H moiety was believed to be crucial for this transformation.38,39 Based on these elegant studies, a proposal for the mechanism is shown in Fig. 3. First, dissociative substitution of I by HCOO− leads to the formate complex [L₆Mn–OOĈH] II. Himeda and coworkers reported the formate complex as a starting point, for their highly active iridium catalyst.24 Furthermore, many other authors proposed this species as the resting state.18 Additionally, substitution of the leaving group (LG) by water has been proposed as an intermediate step.39 β-Hydride elimination releasing CO₂ forms the hydride complex [L₆Mn–H₃] III.28 Protonation of the hydride results in the hydrogen complex [L₆Mn–H₄] IV. This step is accepted as a protonation done by H₂O, HCOOH or H₂O⁺ species in solution.40 The active catalyst II is regenerated and H₂ is released during the last step of the catalytic cycle. Milstein and co-workers41 followed by other groups32,40 reported the protonation of the hydride complex leading to [L₆M–H₃] which undergoes liberation of H₂ and regeneration of [L₆M–OOĈH].

Regarding the role of manganese in this transformation, it is important to consider the work of Gonsalvi’s group, who reported the synthesis of a [Mn(PNP)₂H₂-iPr)κ¹(OCOO)(CO)₂] complex in their studies on the reverse reaction (CO₂ hydrogenation).42 In addition, the group of Boncella synthesized a similar complex [[(iPrPNP)Mn(OOCH)(CO)₂] dehydrogenating FA.19 Additionally, manganese hydride complexes have previously been synthesized and characterized.43

Last but not least, previous investigations on FA dehydrogenation using noble metal complexes pointed out several subtle aspects that should be mentioned here. The computational studies performed by Zhang et al.44 showed the capacity of formic acid to form stable dimers. As a result, the transition state leading to the hydride protonation would be assisted by the N–H moiety. In a similar manner, J. Xiao, N. G. Berry and co-workers have proposed a mechanism involving formic acid pre-positioned, thanks to the N–H moiety, able to protonate the hydride complex.45 The role of this amine function was furthermore demonstrated by Ikiy and Kayaki where the N–H moiety assists in [M – H] protonation via a proton relay mechanism involving water, leading to the [M – H₃] complex.46

Kinetics experiments and crystal structure of intermediate II

To gain additional insights into our specific transformation, investigations have been carried out to consolidate the mechanistic proposal presented in Fig. 3. First, general kinetic experiments were performed. Both reaction orders in manganese catalysts and formic acid/formate were found to be 1 (Fig. S21 and S22†). This means that one manganese complex and one entity of formate are involved in the catalytic cycle.
We therefore cross out the eventuality of a dimer type mechanism. Then, a standard catalytic experiment was carried out and the reaction solution was extracted with an organic solvent. Liquid diffusion at −32 °C yielded X-ray crystals of the formate complex suitable for X-ray analysis (Fig. 4) (crystal data: Fig. S18, NMR data: Fig. S20†).

To further confirm the hypothesis of the formate complex as the active species in this transformation, NMR studies of the reaction mixture were performed showing the major presence of the formate complex in solution (Fig. 5).

The obtained spectrum (Fig. 5) revealed the characteristic signals of the pyridine at 9.04, 8.23, 8.12 and 7.75 ppm, respectively. Additionally, the broad signal at 8.91 ppm was likely to be the formate signal. The imidazoline ring signals are not shown since they are overlapped by the triglyme approximately.

The imidazoline proton. The singlet at 8.07 ppm is assigned to the imidazoline proton. The singlet at 7.99 ppm is attributed to the formate signal. The imidazoline ring signals are not shown since they are overlapped by the triglyme signals. All those signals match the NMR data of the formate complex crystalized (Fig. S20†).

**Labeling NMR scale experiment using H^{13}COONa**

Next, labeling experiments were carried out, using H^{13}COONa as a formate source, on the NMR scale coupled to GC analysis. \(^1\)H NMR (Fig. S23†) showed the starting complex with several signals of a much lower intensity that are assigned to the formate complex [Mn−OO\(^{13}\)CH], but accurate interpretation was not possible. Additionally, a hydride signal was observed at −17.3 ppm, which might be [Mn−H]. In the corresponding \(^1\)C NMR (Fig. S25†) the main signals of the starting material were observed along with side signals of a complex of much lower intensity that should belong to the formate complex.

Additionally, 3 intense singlets, due to the labeling, were observed at 161.34 (\(^1\)\(^3\)CO\(^2\) trapped as H\(^1\)\(^3\)CO\(^3\)), \(^1\)H NMR (Fig. S23). The last two signals are attributed to the formate complex and free formate. \(^1\)C no dec. NMR (Fig. S26†) showed that the singlet at 161.3 ppm did not couple to any proton, which is in agreement with \(^1\)\(^3\)CO\(^2\) trapped as H\(^1\)\(^3\)CO\(^3\). Two formate signals (H\(^{13}\)CO) were observed at 172.2 (\(J = 197.6\) Hz) and 171.6 (\(J = 190.2\) Hz). The signal at 171.6 ppm is identified as the H\(^{13}\)COONa formate reagent (Fig. S27†). While [Mn−OO\(^{13}\)CH] appears at 172.2 ppm. 2D correlation NMR indicated the correlation between \(C_{\text{formate}}\) (172.2 ppm) and \(H_{\text{formate}}\) (7.99 ppm) (Fig. S28 and S29†). \(^1\)H NOESY NMR (Fig. S30) was performed to investigate the eventual correlation between \(H_{\text{formate}}\) and \(H_{\text{imidazoline}}\) but nothing could be observed. Therefore, the signal at 7.99 ppm (172.2 ppm) corresponds to the formate complex. Ultimately, GC analysis showed both H\(^2\) and CO\(^2\) in the gas phase. Carbon monoxide is also detected resulting from the dehydration of formic acid. We can conclude that this experiment allowed us to directly and indirectly observe and confirm each step of the catalytic cycle proposed above (Fig. 2).

**Kinetic isotope effect**

Ultimately, kinetic isotope effect (KIE) experiments have been carried out to investigate which is the rate limiting step for our catalyst. It has been suggested before that the rate limiting step in the presence of an Ir-catalyst is the β-hydride elimination or the hydride protonation.\(^{24}\) Our results are shown in Table 3.

| Entry | Substrate | Solvent | TON | KIE |
|-------|-----------|---------|-----|-----|
| 1     | HCOOH + HCOOK | H\(_2\)O | 40  | —   |
| 2     | HCOOH + HCOOK | D\(_2\)O | 39  | 1.02 |
| 3     | DCOOD + DCOOK | H\(_2\)O | 21  | 1.89 |
| 4     | DCOOD + DCOOK | D\(_2\)O | 19  | 2.08 |

\(^{a}\) Reaction conditions: HCOOH or DCOOD (1 mmol), HCOOK or DCOOK (6.4 mmol), Mn(pyridine-imidazoline)(CO)\(_3\)Br (100 mmol), \(H\(_2\)O/D\(_2\)O (1.8 mL), triglyme (0.8 mL), \(J_{\text{set}} (92.5 \ ^\circ\text{C}), \) time (180 min), gas evolution measured with manual burettes and gas mixture analyzed by GC. \(^{\beta}\) TON calculated at 10 minutes. \(^{\delta}\) KIE calculated at 10 minutes.
Using D₂O instead of H₂O (entry 2) does not really impact the outcome of the reaction. Therefore, we can conclude that the role of water is rather minor in this process. Hence, the idea of the hydride complex protonation by water being the rate limiting step could be excluded. However, using DCOOD and DCOOK instead of HCOOH and HCOOK showed a significant KIE effect (entry 3). This suggests that the β-hydride elimination of the formyl proton leading to the hydride complex might be the rate limiting step for this transformation.

Conclusions

A panel of manganese complexes bearing biomimetic κ²-NN type ligands was synthesized. Compared to previous manganese systems, catalyst 4a showed improved activity with a maximum TON of 5746 (corresponding to 14 073 mL of H₂:CO₂ mixture; 67% conversion) under optimized conditions. The present complex is highly stable as shown by continuous hydrogen production for >3 days. Mechanistic investigations showed that, under aqueous conditions, consumption of FA led to the pH increase which can directly be correlated with a significant drop in the activity. Additional experiments such as varying the starting pH, using a buffer or periodically/continuously adding HCOOH, led us to the conclusion that those manganese type catalysts are efficient under neutral conditions. Crystallization of the formate complex directly from a crude reaction, NMR (¹³C labeling coupled to GC, in situ NMR) and kinetic experiments (reaction order, KIE) suggested β-hydride elimination of intermediate II as the rate limiting step for this transformation.

Conflicts of interest

There are no conflicts to declare.

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