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ABSTRACT (Italiano)

Test di deidrogenazione rutenio-catalizzata di acido formico (FA) e idrogenazione di NaHCO_3 , reazioni importanti rispettivamente per il rilascio di idrogeno e suo stoccaggio utilizzando prodotti chimici organici, sono stati eseguiti in acqua in condizioni blande in presenza di una serie di mono- e bisfosfine (WSL **1-9**) recanti sostituenti alchilici e arilici aventi gruppi sulfonato per impartire la solubilità in acqua. Tutti i sistemi testati si sono dimostrati attivi per deidrogenazione di FA a 90°C ed e' stato possibile stabilire una scala di reattività. Alcune selezionate WSL hanno mostrato anche alte conversioni e velocità di reazione per la riduzione del bicarbonato a formiato a $50\text{-}80^\circ\text{C}$ sotto 80 bar di pressione di idrogeno senza aggiunta di basi. Dettagli preliminari del meccanismo di reazione sono inoltre stati ottenuti.

ABSTRACT (English)

Ruthenium-catalysed Formic Acid (FA) dehydrogenation and NaHCO_3 hydrogenation, important reactions for hydrogen release and storage using organic chemicals, were run in water under mild conditions in the presence of a series of mono- and bisphosphines (**WSL 1-9**) bearing alkyl and aryl substituents with sulfonate groups attached to the rings to impart water solubility. All systems tested were active for FA dehydrogenation at 90°C and a reactivity scale was established. Selected WSL showed also high conversions and rates for bicarbonate reduction to formate at $50\text{-}80^\circ\text{C}$ under 80 bar of hydrogen pressure without added base. Preliminary mechanistic details were also obtained.

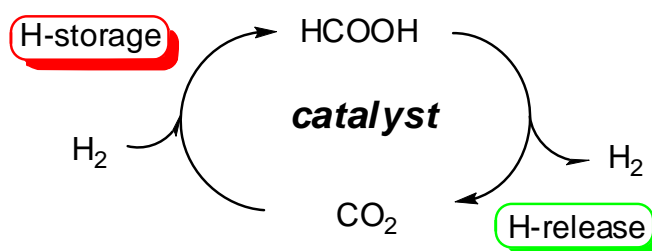
Introduction and Scope of the STM

The area of interest of this collaborative research project is connected to the field of Energy Storage, in particular the quest for novel catalysts for hydrogen production from chemical reservoirs in the frame of the emerging "Hydrogen Economy". Practical applications in the fields of electronics (hydrogen fuel cells technology) and in the automotive world (hydrogen reservoirs to be used on fuel-cell cars) are sought.

Continued strong interest in these energy vectors is demonstrated by the US DOE investing \$7 M in innovative hydrogen storage, in particular H₂-storage in liquids, porous materials, and regeneration technologies.¹ Ideally a suitable device should include the possibility to store hydrogen and release it on demand under mild temperature and pressure conditions.

Hydrogen can be in principle released from hydrogen-rich organic compounds by breaking and recombining chemical bonds. An example is the reaction involving Formic Acid (**FA**, HCOOH), which can be dehydrogenated into a mixture of CO₂ and H₂ gas in the presence of suitable homogeneous (soluble) or heterogeneous (solid) catalysts, able to decrease the activation energy of the reaction, enabling running the same under mild conditions of temperatures and atmospheric pressure. The reverse reaction, CO₂ hydrogenation, may in principle be used to regenerate FA under suitable conditions, enabling the sustainable use of such an “organic hydride” as H-storage material (Scheme 1).

As an alternative to its direct use in a fuel cell, formic acid readily decomposes into H₂ and CO₂ in the presence of a suitable catalyst as the reaction is thermodynamically downhill ($\Delta G^\ddagger = -32.8 \text{ kJ mol}^{-1}$). Conversely, the hydrogenation of CO₂ to make FA or formates (storage cycle) is uphill and requires higher temperatures and pressures in order to have significant yields and reaction rates. Hydrogenation of CO₂ is strongly inhibited from the thermodynamic point of view ($\Delta G^\circ > 0$, $\Delta S^\circ \lll 0$) but the formation of adducts between the acid and ammonia or amines makes the reaction possible.



Scheme 1: the hydrogen storage and release cycle based on the FA/CO₂ couple

Both precious (Ru) and non-precious (Fe, Co)² d-block metals stabilized by suitable ligands, were used to obtain active catalysts for homogeneous FA dehydrogenation and CO₂ hydrogenation. These processes can also be run in water, a cheap and environmentally safe solvent, with high efficiency by use of adequate water soluble ligands (WSL) such as sulfonated aryl phosphines, as stabilizers for the catalytically active metal species.³

The research unit (RU) at EPFL directed by Prof. Gabor Laurenczy is traditionally interested in the used of WSL in transition metal catalysed reactions in water under gas pressures with particular attention to develop HP NMR (high pressure NMR) analytical techniques to study reaction mechanisms in situ. Recently, Laurenczy and coworkers have disclosed cutting-edge results on FA dehydrogenation and CO₂ hydrogenation in water phase, establishing the benchmark for such processes in this media.³

The RU at ICCOM under the scientific responsibility of the Applicant has a strong interest in the field of water phase and biphasic homogeneous catalysis,⁴ and has recently developed catalysts for FA dehydrogenation.⁵ Mechanistic studies are commonly run based on model reactions, both under experimental in vitro and theoretical in silico techniques. The two RUs have collaborated in the past in the field of CO₂ hydrogenation to formate, and the results were published in the scientific literature as joint papers.⁶ On the basis of these results, the two teams have decided to investigate together some aspects of Ru-catalysed FA dehydrogenation and CO₂ hydrogenation under gas pressure using HPNMR tubes and by in situ NMR analysis in the presence of selected mono- and bidentate WSLs during the STM of the Applicant at EPFL. The preliminary results obtained are hereby summarized.

Results and Discussion

Part 1: FA dehydrogenation tests under endogenous pressure.

A series of mono- and bidentate water-soluble phosphine ligands bearing alkyl, aryl and biaryl groups bearing sodium sulfonate (-SO₃Na) as hydrophilic substituent, **WSL 1-9**, were brought to EPFL to test their activities in Ru-catalysed FA dehydrogenation and CO₂ hydrogenation under various conditions. All the ligands were prepared and fully characterised in solution and were previously tested at ICCOM for FA dehydrogenation using ambient pressure (open) thermostated reactors. In order to check the reproducibility and general trend of structure-reactivity correlation for such systems, it was agreed to test the same ligands under endogenous pressure conditions, using HPNMR tubes as closed reaction vessels. At EPFL, routinary tests are carried out under such conditions, by connecting the tubes containing the reaction mixtures to automated pressure monitoring systems, as shown in Figure 1.



Figure 1 (left): A setup of four different FA dehydrogenation tests using HPNMR tubes; (right) pressure evolution monitoring by automated digital system.

The tube was charged with the reagents, connected to the measurement system and placed into a thermostated jacket set at 90 °C. Once the required temperature was set, the experiment was started and the gas pressure evolution monitored to produce pressure (bar) vs. time (min) curves from which kinetic and activity data can be extrapolated and treated offline.

Therefore, in the first part of the STM, five different monodentate (**WSL 1-5**) and four bidentate water soluble phosphines (**WSL 6-9**) were tested in the presence of $\text{RuCl}_3 \times 3 \text{H}_2\text{O}$ as metal precursor (details in the Experimental Section). The ligands differ in the nature (alkyl, aryl) and degree (1-3) of sulfonation on the ligand. After a first cycle, when the maximum conversion was reached, the tube was depressurised and more FA was added. Then, the tube was again inserted into the thermostated jacket and a second run was monitored to assess recyclability. In selected cases a third run was also carried out.

At first, a series of experiments (Exp 1-7) were run after preparing the NMR tube in the open air. It was observed that immediately after the addition of $\text{RuCl}_3 \times 3\text{H}_2\text{O}$, the solutions changed from colourless to greenish-black and not all the solid was dissolved for the less water soluble ligands. Therefore, all tests were repeated by preparing the reaction mixtures under nitrogen in Schlenk tubes, then transferring them into the NMR tube by syringe. In this way, all solids were dissolved and generally a deep red solution was obtained. After the first cycle, depressurisation and FA addition was also carried out under nitrogen. A visual comparison of the ligand effects on FA dehydrogenation performance can be seen in Figures 2 and 3, showing the reaction profiles of all systems in the first runs (generated pressure vs. time) at 800 and 60 min elapsed time, respectively.

Figure 2: Reaction profiles for first run FA dehydrogenation experiments with ligands WSL 1-9 after 800 min at 90 °C. Y axis = P (bar); X axis = t (min).

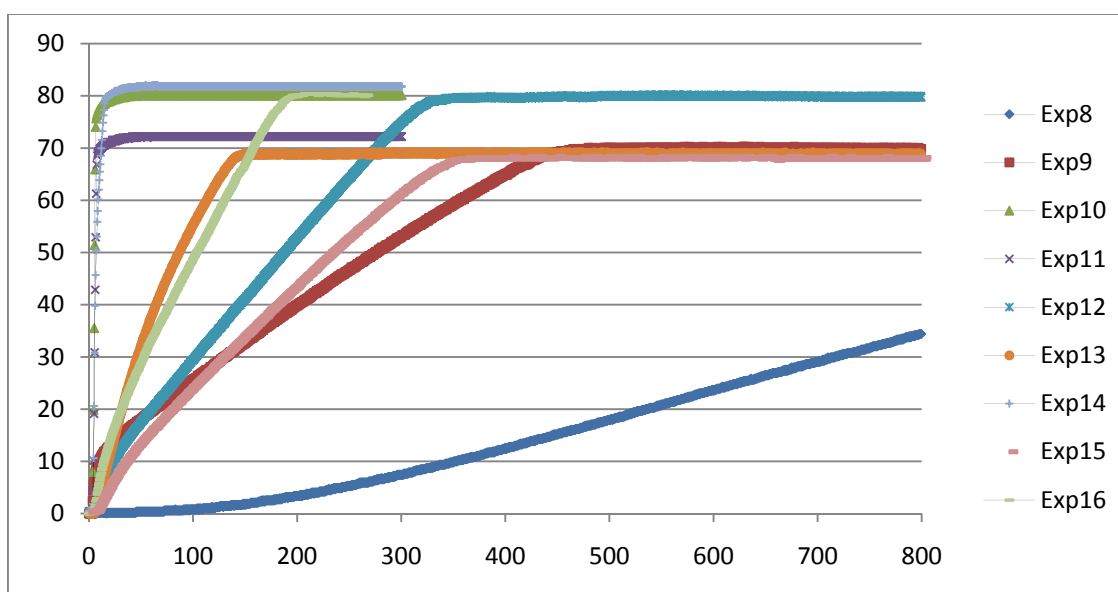
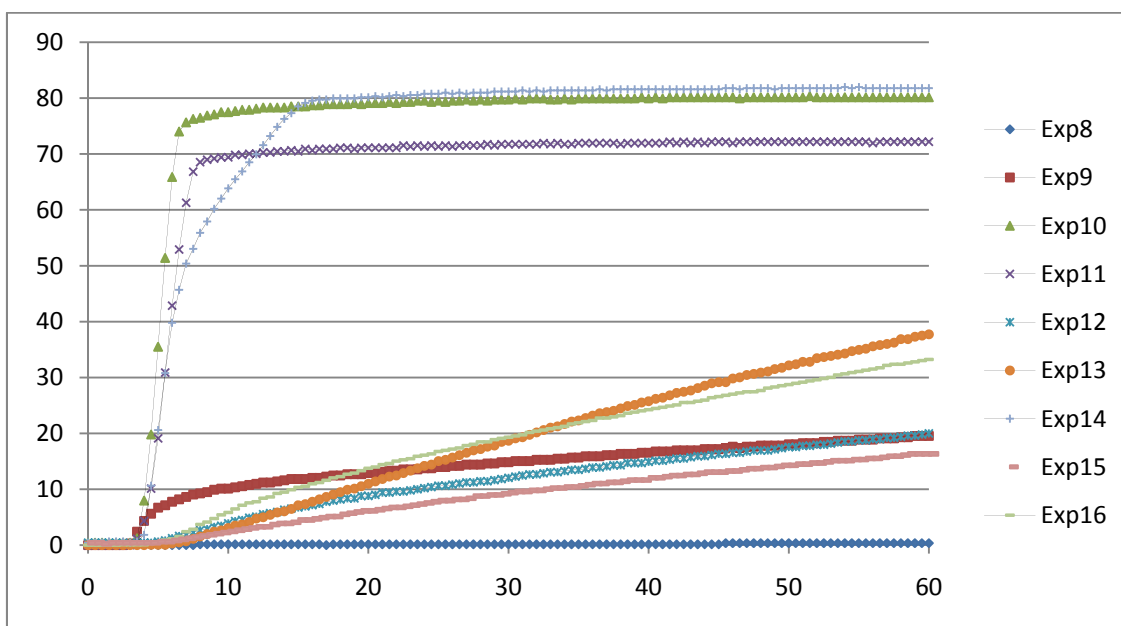


Figure 3: Reaction profiles (zoom) for first run FA dehydrogenation experiments with ligands WSL 1-9 after 60 min at 90 °C. Y axis = P (bar); X axis = t (min).



It was observed that all WSL promote the Ru-catalysed FA dehydrogenation reaction, giving conversions for the first run ranging from ca. 74 to 84 % at 90 °C in neat water as solvent. The highest activities were obtained with WSL 3, 4 and 5. Secondly, upon recycling a general trend was observed showing a decrease in the maximum conversion reached by a comparable degree, regardless on the nature of the WSL (mono, bidentate, degree of sulfonation). Finally, a marked difference could be observed in the rate of reactions as shown in Figure 3. The initial reaction rates follow the order:

$$\text{WSL 3} \approx \text{WSL 5} > \text{WSL 4} \gg \text{WSL 8} > \text{WSL 9} > \text{WSL 7} \approx \text{WSL 6} \approx \text{WSL 2} > \text{WSL 1}$$

It is worth of notice that the most active and fastest systems, based on the monodentate tris-, di- and monosulfonated aryl phosphines WSL 3, 4 and 5, however showed a marked decrease in the rate for the second and third cycle. Future work will involve running again some of the tests using the same experimental conditions to check for reproducibility of these data.

Part 2: Mechanistic details by HPNMR techniques.

The mechanism of Ru-catalysed FA/formate dehydrogenation in the presence of TPPTS (trisulfonate triphenylphosphine) was described by Laurency et al. using HPNMR analysis of ^{13}C , ^{31}P and ^1H NMR data.^{3b} During the STM, a similar approach was used to try and identify structural changes of the pre-catalysts during the course of the reaction. This aspect could be of importance to understand the structure-activity relationship related to ligand effects in catalysis.

Some WSL were selected to run HPNMR experiments, observing the evolution of ^{31}P and ^1H NMR spectra with time (using a water signal suppression pulse sequence for the latter). Different complementary approaches were used.

a) At the end of a catalytic run carried out as described above in Part 1, the NMR tube was transferred to the NMR probe and ^{31}P and ^1H NMR spectra were measured at 25 °C. In this way, stable metal complexes

formed during the reaction and/or the resting state of the catalyst could in principle be observed. The behaviour of systems based on ligands WSL 1- 4 under these conditions was observed. In general, a large amount of phosphine oxide was observed to be present in solution in each case, which were identified by comparison with known data. In some cases weak ^{31}P NMR signals which could be due to the formation of Ru-phosphine complexes were observed, however more synthetic work has to be carried out to identify correctly the nature of these complexes. In the corresponding ^1H NMR spectra, signals at negative ppm values, indicative of Ru-H bond formation, were often observed. Also in this case, it was not possible to attribute these signals unequivocally and further work is planned to clarify this point.

b) Ru-hydrido species relevant for catalysis may form during FA dehydrogenation reactions due to the release of hydrogen gas. Thus, it was of interest to observe whether such species could form in the presence of Ru and WSLs under a pressure of H_2 . To test this, a mixture of $\text{RuCl}_3 \times 3\text{H}_2\text{O}$ and WSL (2.2 equiv for WSL 4 and WSL 5, 1.1 equiv for WSL 7) in H_2O (2.5 mL) were placed in a HPNMR tube which was then pressurised with H_2 (100 bar). The tube was placed in the NMR probe which was then heated to 50-70 °C, recording the corresponding $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra over 2h. It was observed that also under these conditions Ru-hydrido species were formed, however further work and better WSL purity (i.e. lower initial concentrations of phosphine oxides in the samples) were needed to repeat the experiments and draw conclusions on the nature of the complexes which are formed under a pressure of hydrogen and heating.

Part 3: NaHCO_3 hydrogenation tests by HPNMR techniques.

The reverse reaction of Ru-catalysed FA/formate dehydrogenation, i.e. CO_2 hydrogenation to formate (Scheme 1), was also studied in the presence of selected mono- and bidentate WSLs. Thus, WSL 4, 5 and 7 were chosen, in analogy with the NMR experiments carried out as in Part 2b. In these experiments, a solution of $\text{NaH}^{13}\text{CO}_3$ (0.1 M in H_2O , 2.5 mL) was added to $\text{RuCl}_3 \times 3\text{H}_2\text{O}$ (0.028 mmol) and WSL (2.2 equiv for WSL 4 and 5, 1.1 equiv for WSL 7) in a HPNMR tube which was pressurised with H_2 (80 bar) and placed in the NMR probe then heated to 50-80 °C. The conversion of bicarbonate to formate was monitored by following the decrease of the $^{13}\text{C}\{^1\text{H}\}$ NMR signal at 159.5 ppm (bicarbonate) and the increase of the signal at 171.4 (formate) overnight. $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra were also recorded at the beginning and the end of the reaction.

For WSL 4, very fast conversion (16 min) was observed at 50 °C, to reach almost complete conversion after 80 min at 70 °C. The final $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra showed signals at 33.96 ppm and 56.26 ppm and -7.76 ppm, respectively, in close analogy with the values observed in the experiments in Part 2b. Also for WSL 5, fast conversion was observed at 70 °C, reaching completeness after 90 min. The final $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra showed signals at 33.90 ppm (P=O) and 56.30 ppm and -8.02 ppm, respectively. Finally, for the bisphosphine WSL 7, the hydrogenation experiment, run at 50 °C, was more sluggish and a maximum 70 % conversion was observed after 12h.

Conclusions

In conclusion, a series of FA dehydrogenation experiments was carried out in the presence of the novel watersoluble mono- and diphosphines WSL 1-9. All the ligands showed to promote the reaction reaching high conversions to H₂ and CO₂ with very high reaction rates for selected examples. This allowed to establish a general trend of reactivity which will be considered for further synthetic work to reach tailored design of new water soluble ligands. Mechanistic HPNMR experiments showed that Ru-hydrido species were formed under at the end of the catalytic runs and in model tests using hydrogen pressure only, however more detailed studies are needed to clarify the nature of such complexes. Finally, selected WSL showed very high activities for bicarbonate reduction to formate under relatively mild conditions of temperatures and pressures, without the need for an added base, which paves the way for interesting applications of such ligands also for this reaction.

Future work

At the end of the STM, it was agreed to continue with the experimental and mechanistic work at EPFL, in particular to extend the bicarbonate reduction tests to all the other ligands which were not explored for time constraint. Selected FA dehydrogenation experiments will also be repeated to find out the cause of loss of activity upon recycling. Further collaborative work involving the two teams has been planned and will be carried out by exchange of chemicals and/or more visits in both directions to gain expertise in synthetic chemistry and HPNMR techniques.

References

¹ <http://www1.eere.energy.gov/hydrogenandfuelcells/storage/index.html>

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