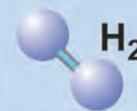# Hydrogen / Energy Storage and Delivery with the Carbon Dioxide Formic Acid Systems

Scope of project

Hydrogen storage is one of the great current challenges, and the on-demand decomposition of formic acid into hydrogen and CO_2 represents a cunning solution. We have developed the first example of a first row transition metal catalyst that efficiently and selectively performs formic acid dehydrogenation under mild conditions in aqueous solution.

Various renewable energy sources (e.g. wind and solar) have seen large-scale applications over the last decade and capacities are steadily increasing. In terms of energy distribution and storage, hydrogen is considered one of the ultimate energy vectors to connect a decentralized grid of power generators to various end users for «mobile applications». Particularly in combination with fuel cell technology, hydrogen has the potential to provide mobile application with an efficient and (locally) emission-free energy source. A hydrogen/energy storage-and-release cycle based on formic acid decomposition and carbon dioxide hydrogenation can be envisioned that could solve the inflexibility of decentralized power generation. The simplicity and elegance of the combination of formic acid and H_2/CO_2 as a reversible hydrogen storage system certainly sounds appealing, since the hydrogenation of CO_2/HCO_3^- over homogeneous catalysts has been achieved with excellent activities.

Status of project and main scientific results of workgroups

Quantitative aqueous phase formic acid dehydrogenation using Iron(II) catalysts

An ideal energy storage cycle would combine carbon dioxide with H_2 from renewable resources, or reduce CO_2 electrochemically with solar/wind-powered electricity to generate formic acid. Formic acid production is even possible in acidic media, under base-free conditions, as our group demonstrated recently. Stocks of formic acid then would be used as transportable fuels for on-demand remote power generation or even for mobile applications. Other research groups have also investigated the formic acid/CO_2 couple using different metal salts as pre-catalysts, such as ruthenium, iridium, or even their combination in bimetallic systems. Usually homogeneous catalysts offer greater selectivity towards the dehydrogenation reaction, although progress is being made with certain gold or palladium nanoparticles supported on various media,

or the use of non-metal catalyst such as boron. With the intent to combine the advantages of both homogeneous and heterogeneous catalysts, immobilization of the highly active and stable Ru(II)-mTPPTS catalyst on ion exchange resins, in polymers, on silica and zeolites was carried out in our group earlier.

Now we have investigated the homogeneous catalytic hydrogen production aqueous phase formic acid dehydrogenation using non-noble metal based pre-catalysts. This required the synthesis of *m*-trisulfonatedtris[2-(diphenylphosphino)ethyl] phosphine sodium salt (PP_3TS) as a water soluble polydentate ligand. New catalysts, particularly those with iron(II), were formed *in situ* and produced H_2 and CO_2 from aqueous formic acid solutions; requiring no organic co-solvents, bases or any additives. Manometry, multinuclear NMR and FT-IR techniques were used to follow the dehydrogenation reactions, calculate kinetic pa-

rameters, and analyse the gas mixtures for purity. The catalysts are entirely selective and the gaseous products are free from CO contamination. To the best of our knowledge, these represent the first examples of first row transition metal based catalysts that dehydrogenate quantitatively formic acid in aqueous solution.

Calorimetric and spectro-scopic studies of solvent/formic acid mixtures in hydrogenation storage

Solvents play a crucial role in many chemical reactions and additives can be used to shift the reaction equilibrium towards the product side. Herein we have assessed different solvents (water, organic solvents) and basic additives (amines, aqueous KOH) for carbon dioxide hydrogenation and formic acid dehydrogenation by determining the enthalpy of mixing with formic acid. From an efficiency perspective any heat evolving during these exothermic processes has to be reinvested to produce free
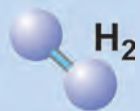
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Hydrogen / Energy Storage and Delivery with the Carbon Dioxide Formic Acid Systems

formic acid. In both scenarios, the addition of basic chemicals causes higher costs and reduces therefore the chances of a successful economic application.

The highest formic acid concentrations in direct catalytic carbon dioxide hydrogenation under acidic conditions were reached in dimethyl sulfoxide (DMSO). This solvent exhibits considerably stronger interactions with formic acid than water as it was revealed in calorimetric measurements. This difference can be ascribed, at least partly, to stronger hydrogen bonding of formic acid to DMSO than to water in the corresponding solutions, examined by a combination of infrared spectroscopic and quantum chemical studies. Furthermore, the investigation of the DMSO/formic acid and water/formic acid systems by ^{1}H- and ^{13}C-NMR spectroscopy revealed that only 1:1

aggregates are formed in the DMSO solutions of formic acid in the broad concentration range, while the stoichiometry and the number of the formic acid – water aggregates depend on the concentration of the aqueous solutions essentially.

We quantified the enthalpy of mixing for water and several organic solvents with formic acid by heat flow calorimetry. The heat of mixing for water and formic acid showed an unexpected behavior by reacting most exothermically at a certain mole fraction (X(water) = 0.7) and not in the beginning when the pure chemicals were combined as was observed for the other tested solvents. The enthalpies of mixing, collected under realistic conditions, are valuable information when it comes to developing a hydrogen battery since they demonstrate how effectively the solvent seques-

ters produced formic acid or formate and also to estimate the energy, which is necessary for hydrogen evolution under these circumstances. Mixtures of DMSO or water with formic acid were explored by spectroscopic measurements (multinuclear NMR and infrared ATR) and we identified different types of adducts in both systems, whose presence depends on the concentration. These data were further corroborated with quantum chemical calculations and finally used to draw mutual DMSO – formic acid and water – formic acid structures (Figure 1).

Acknowledgement

Figure 1:

B3PW91/aug-cc-pVTZ optimized structures of DMSO-FA (left) and 2 H₂O-FA (right) aggregates. The main characteristics of hydrogen bonds shown with dotted lines are the following:

DMSO-FA, d(H...O) = 1.61 Å;

vO-H = 2955 cm⁻¹;

2 H₂O-FA, d(H...O) = 1.62 Å;

vO-H = 2965 cm⁻¹.