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Priority Communication

Additive free, room temperature direct homogeneous catalytic carbon dioxide hydrogenation in aqueous solution using an iron(II) phosphine catalyst

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ABSTRACT

The negative consequences of the global warming require an important reduction of CO_2 emission; and the valorization of the carbon dioxide, its transformation into useful chemicals is essential. We present here our studies on the direct CO_2 hydrogenation reaction, yielding formic acid. In water, for the first time, an Fe(II) catalyst using meta-trisulfonated-tris[2-(diphenyl-phosphino)-ethyl]phosphine (PP_3TS) ligand, has been found active in CO_2 reduction. In homogeneous catalytic reactions, without any additives, at room temperature, under hydrogen and carbon dioxide gas pressures up to 0.5 M of formic acid is obtained, in acidic aqueous solutions. The same catalyst is active also in the reverse reaction, under different reaction conditions, i.e. at low pressure and high temperature. The CO_2 reduction and formic acid dehydrogenation catalytic cycle has been repeated several times; without deactivation of the catalyst, it is not sensitive to oxygen/air. The Fe(II)-PP_3TS complex could be a suitable catalyst in a chemical hydrogen storage/delivery system.

1. Introduction

Global warming and all the consequences, climate changes are the reality today. There is a consensus among the majority of scientists concerning the cause: augmentation of CO_2 level in the atmosphere (over 400 ppm today versus 345 thirty five years ago) [1]. CO_2 is a greenhouse gas, the heat is conserved at the surface of Earth. However, this is not the only issue, with more CO_2 in the atmosphere, the pH of the sea water will decrease, leading to the acidification of the oceans [2]. All these changes could have tremendous repercussions on the ecosystem of our planet. In response, both politicians and scientists should make effort to limit the carbon dioxide emission.

The main source of the CO_2 emission is the fossil fuel combustion. Increasing utilization of the renewable energy sources (hydroelectric, geothermic, wind and solar energy) is the first step toward the reduction of CO_2 production. An interesting, although minor contribution would be to use CO_2 in chemical syntheses. CO_2 can be used/is used as a C_1 building block for useful molecules (e.g. urea, salicylic acid, cyclic carbonates, epoxides, formaldehyde, etc) [3,4]. Nature uses CO_2 as carbon source for the living organisms. CO_2 can be also used as hydrogen vector, to store chemically the H_2 gas, an elegant contribution of CO_2 utilization.

Hydrogen is one of the most promising energy carriers. It has high gravimetric energy density and clean combustion pathways, but it is difficult to store it. Conventional hydrogen storage methods, like high pressure tanks and liquefaction, have safety and cost issues [5]. Therefore, the chemical hydrogen storage, the catalytic reduction of CO_2 into formic acid, into methanol or into other useful chemicals have both the advantage of storing hydrogen and adding value to carbon dioxide.

Formic acid (FA) has recently drawn attention in H_2 storage because its several advantages: It is liquid at room temperature with a volumetric hydrogen storage capacity of 53 g/L (it has a gravimetric hydrogen content of 4.4 wt%). FA has low toxicity and it is non-flammable below 85 vol% concentration (diluted with water), it is a good candidate for hydrogen storage [6,7]. Since 2006, a large number of studies dealt with the selective FA dehydrogenation [8,9]. A wide variety of metals and ligands have been used as catalysts for homogeneous and heterogeneous formic acid splitting into H_2 and CO_2, using either noble or non-noble metals, in a wide selection of solvents, reviewed recently [10].

The opposite reaction, the direct carbon dioxide hydrogenation to FA has got special attention as well, a large number of catalysts have been reported for the reduction of CO_2 [10]. However, in the overwhelming majority of the cases, this reduction has been

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carried out in the presence of a base and/or use carbonate and bicarbonate substrates instead of CO_2 gas. Indeed, CO_2 has a high thermodynamic stability; in gas phase it cannot be directly hydrogenated to FA (the Gibbs free energy for this reaction, $\Delta G^\circ$is positive, +33 KJ/mole). In basic aqueous solutions, CO_2 is transformed into bicarbonates (HCO_3^-) and carbonates (CO_3^{2-}), and these substrates can be reduced directly, the Gibbs free energy change then will be negative (around – 35 KJ/mole), hence favorable for the reaction [11].

Nevertheless, there are only a few reports for the direct reduction of CO_2 in acidic solutions, acidic conditions [10]. All these studies use, however, noble metal based catalysts and to the best of our knowledge there is no report for direct, homogeneous CO_2 hydrogenation, using a first row transition metal (non-noble metal) catalyst, in water. Combining both hydrogenation and dehydrogenation reactions, applying a cheap iron(II) complex could lead to the development of an affordable, battery-like energy/hydrogen storage system. This system could have a potential application in mobile energy supply.

2. Results

Recently we have studied the homogeneous formic acid dehydrogenation reaction with the Fe(II)-PP_3TS catalyst [12]. Now we have investigated the direct reduction of CO_2 in aqueous solution (that is in acidic medium), using the same iron(II) complex.

When we have pressurized with hydrogen and carbon dioxide the aqueous solution of $Fe(BF_4)_2$; in presence of meta-trisulfonated-tris[2-(diphenylphosphino)ethyl]phosphine sodium salt (PP_3-TS – Fig. 1); we could detect the formation of formic acid in the reaction mixture, even at room temperature. 10 mm high pressure sapphire NMR tubes were used to carry out these reactions, a mixing device was applied to solubilize H_2 and CO_2, to reach always the saturation concentrations. FA concentrations were measured *in situ* under pressure by quantitative ^1H and ^{13}C NMR (see Experimental).

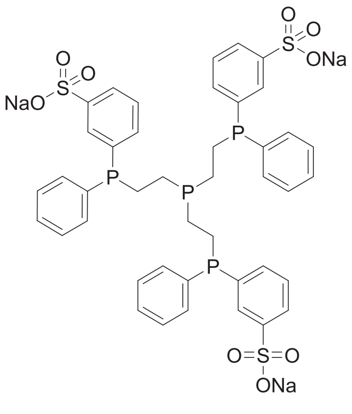

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Fig. 1. *Meta*-trisulfonated-tris[2-(diphenylphosphino)ethyl]phosphine sodium salt (PP_3TS, **1**).

When we have pressurized an aqueous solution of $Fe(BF_4)_2$ (0.05 M) and PP_3TS (0.05 M) with 50 bar of H_2 and 50 bar of CO_2 in a 10 mm sapphire NMR tube; heated this tube to 50 °C and mixed it for several hours, more than 0.1 M formic acid solution was detected by ^1H and ^{13}C NMR in the solution.

We have investigated the effect of the catalyst concentration on the formic acid production/yield, and the iron(II) to phosphine ligand ratio, using $Fe(BF_4)_2$ salts as catalyst precursors. Pressure (50 bar H_2 and 50 bar CO_2) and temperature (25 °C) were kept constant during the whole reaction (generally 60 h – checking several times the formic acid concentration, verifying to arrive to equilibria), Table 1. The ratio of the iron salt with respect to the ligand was kept constant while varying the concentration of the catalyst complex.

The catalyst concentration does not influence the formic acid yield significantly (Table 1), indicating that the limiting factor for the conversion is thermodynamic. It should be the hydrogen and CO_2 equilibrium concentration under pressure in water. The catalyst concentration certainly influences the reaction rate.

The reaction requires gas solubilization under pressure (CO_2 and H_2), it is necessity to have an intensive mixing. The quantitative NMR technique gave the only possibility for FA concentration determination *in situ,* under pressure (time-consuming measurements, long acquisitions). For these reasons we were not able to do precise kinetic analysis for this reaction. We are working on to find a suitable experimental setup to collect detailed kinetic information on this reaction.

In Table 2 the results concerning the effect of the ligand to iron (II) ratio has been shown. The ratio of the iron salt with respect to the ligand was varied between 2:1 and 1:3. Different iron salt were tested as precursors ($FeCl_2$, $Fe(BF_4)_2$ and $(NH_4)_2Fe(SO_4)_2$. A poisoning effect has occurred when $FeCl_2$ was used (at high chloride concentrations the formation of chloride bridged dimers is possible), the catalytic activity of this precursor were lower.

Using half equivalent of PP_3TS ligand could lead to bimetallic complex formation, with reduced catalytic activity. In case of large PP_3TS ligand excess, the formation of the ML_2, ML_3 type complexes could reduce the available active coordination sites around the Fe(II) ion. The excess of the PP_3TS ligand blocks the access of the substrate to the iron(II) cation, avoiding catalytic reduction.

As it is can be seen from variation of the chemical shift of the ^{31}P signal of the tris-ethylene linked P atom in meta-trisulfonated-tris [2-(diphenylphosphino)ethyl]phosphine (PP_3TS) at acidic and neutral solutions, this P atom can be protonated (Fig. 2a), while the other PPh_2 type P atoms not, in the studied pH range. Indeed, the ^{31}P NMR peak, corresponding to the triethylenephosphine bridgehead phosphorus, it was shifted from −20 ppm to 15 ppm under acidic conditions with decreasing pH, while the chemical shift of the signal corresponding to PPh_2 phosphorus atoms practically does not change. From the ^{31}P NMR shifts it was possible to

Table 1
Formic acid yield dependence on the catalyst concentration.

$Fe(BF_4)_2$ concentration [mM]	8.3	10	15	25	30	50	75	100
Final formic acid conc. [M]	0.21	0.13	0.19	0.27	0.21	0.30	0.23	0.25
	0.25	0.18	0.20	0.27	0.24	0.22	0.22	0.20
	0.20	0.15	0.23	0.28	0.21	0.23	0.23	0.23
Average	0.22	0.15	0.21	0.28	0.22	0.25	0.23	0.23
std[a]	0.04	0.04	0.04	0.03	0.03	0.06	0.03	0.04

PP_3TS/Fe(II) ratio = 1; 50 bar H_2 and 50 bar CO_2, room temperature, final pH 2.0–2.5, reaction time: 60 h.

[a] Estimated standard deviation, reproducibility.