MCAT

Ruthenium-catalysed decomposition of formic acid: Fuel cell and catalytic applications

CrossMark

Lorenzo Piola[a], José A. Fernández-Salas[a], Fady Nahra[b], Albert Poater[c,d], Luigi Cavallo[d], Steven P. Nolan[b,e,*]

[a] *Departamento de Química Orgánica (Módulo 1), Facultad de Ciencias, Universidad Autónoma de Madrid, 28049-Madrid, Spain*
[b] *Universiteit Gent, Department of Inorganic and Physical Chemistry, Krijgslaan 281, S-3, B-9000 Ghent, Belgium*
[c] *Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, Campus Montilivi, 17003 Girona, Catalonia, Spain*
[d] *KAUST Catalysis Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia*
[e] *Department of Chemistry, College of Science, King Saud University, P. O. Box 2455, Riyadh 11451, Saudi Arabia*

ARTICLE INFO

ABSTRACT

The decomposition of formic acid into H_2 and CO_2 was successfully performed using a ruthenium hydride catalyst, without any concomitant CO evolution. The reaction mechanism is investigated by means of density functional theory calculations (DFT). The generated H_2 was further exploited in a fuel cell to produce electricity. The catalytic hydrogenation of conjugated olefins, using this dihydrogen generation procedure, is also reported.

© 2017 Elsevier B.V. All rights reserved.

Introduction

Nowadays, hydrogen is a valuable commodity in organic synthesis, mostly due to its use as a reducing agent in several chemical processes. Its importance is further highlighted in its growing use in fuel cells [1]. Solar energies are considered the major candidates for its production in order to maintain green and renewable processes [2]. Nevertheless, current methods of storage and transportation of hydrogen are inadequate [3–14]; storing liquid hydrogen presents safety risks, liquefaction and maintenance require a considerable amount of energy [15]. Therefore, alternative methods for hydrogen delivery are in dire need. To that end, recent reports on the activation of hydrogen-rich organic compounds (such as sodium borohydrides, ammonia borane, hydrazine and formic acid) [4–12] are receiving much attention from the scientific community. Among these strategies, formic acid (FA), which contains 4.4% hydrogen by mass, is considered one of the most promising compounds for the storage and useful source of hydrogen. Formic acid is

a liquid at room temperature, thus easily handled and transported. FA is also commercially available and relatively inexpensive, making it a valuable reagent for this type of process [4]. The products of its decomposition, H_2 and CO_2, could be used directly in chemical processes or could be captured and recycled to regenerate FA [16–19]. Indeed, many catalytic systems have shown that it is possible to reduce CO_2 using H_2, regenerating FA [19–24]. The latter can be decomposed following two pathways; *via* production of CO_2 and H_2 ($\Delta G° = $-38.3 kJ mol^{-1}) (Eq. (1)) or *via* production of H_2O and CO ($\Delta G° = $-9.66 kJ mol^{-1}) (Eq. (2)).

$$HCOOH \rightarrow CO_2 + H_2 \tag{1}$$

$$HCOOH \rightarrow CO + H_2O \tag{2}$$

The latter is highly undesired since small amounts of CO can poison fuel cells and deactivate catalysts. In 2008, Beller [25] and Laurenczy [26] reported, independently and for the first time, the use of ruthenium-based catalysts for the decomposition of formic acid showing no CO contamination. After these reports, various catalysts have been tested for this purpose: such as Fe [7,27–29], Ru [25,26,30–40] and Ir [41–46]. More recently Mo- [47] Pd- [48,49], and Ni-based [50] catalysts have also been shown to catalyse this transformation, with or without amine additives. In the former
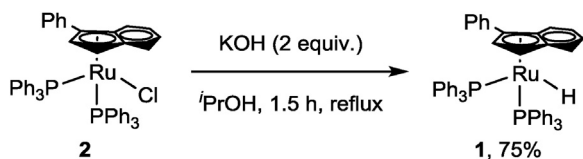
Scheme 1. Improved synthesis of **1**.

Table 1
Optimisation of the Ru-catalysed decomposition of formic acid.

Entry	n_{Ru} (mmol × 10^{-2})	Solvent	T (°C)	Conv (%)	TON
1	2.257	Tol	RT	70	14
2[a]	2.257	THF	RT	7	<5
3	**2.257**	**Tol**	**80**	**95**	**21**
4[b]	1.102	Tol	80	78	38
5[a]	0.226	Tol	80	37	73

Conditions: 20 μL of formic acid, 2 mL of solvent for 90 min.
[a] After 60 min.
[b] 1 mL of solvent was used.

case, the amine/FA ratio was a vital factor, and a constant addition of FA was required to maintain a continuous and viable reaction. Considering the metals previously mentioned, Ru-based catalysts showed distinctive activities; in particular, complexes containing a Ru-H bond proved to be highly reactive in the decomposition of formic acid [30,31,48]. To better understand the mechanism of this transformation and thus pave the way for more efficient and cost-effective catalyst design as well as develop a multifunctional system, active in chemical transformations and fuel cell technology, we describe herein the use of an easily accessible ruthenium hydride complex (**1**) [51] in the decomposition of FA.

Results and discussion

In the present report, an improved synthesis of **1** was also developed (Scheme 1) starting from complex **2** [52–54]. The previous procedure used NaOMe in methanol to achieve good yields of **1** (77%) [51]. In the current process – NaOMe is replaced by the inexpensive and safer alternative KOH – and the toxic methanol is replaced by the greener solvent, isopropanol. In that manner, the procedure is now considered more practical and hopefully more attractive.

Preliminary tests were performed in a J-Young NMR tube, at room temperature and under argon, by mixing **1** and HCOOH in d_8-toluene; the presence of H_2 was confirmed by ^{1}H NMR, and the GC analysis of the gaseous products obtained showed no formation of CO (see Supporting Information). Encouraged by these results, controlled reactions were next carried out using a closed vessel with a pressure sensor (Man On The Moon Apparatus, see Supporting Information). This system allowed the controlled addition of formic acid while regulating the pressure over time. Reaction conditions were explored and the optimal parameters were determined (Table 1).

A slow evolution of gas is observed when the reaction is performed at room temperature (Table 1, entry 1). The solvent plays a fundamental role in the generation of H_2. THF completely inhibited the reaction (Table 1, entry 2); This is probably due to its polarity and high coordinating power. It should be noted that other solvents such as water, alcohols and halogen-based solvents are not tolerated by the catalyst in this reaction. A higher temperature increased the performance of the system and the evolution of gas became instantaneous (Table 1, entry 3). When the catalyst loading was decreased (Table 1, entries 4–5), a reduction in conversion was observed, however, an increase in the reaction TON was also noted.
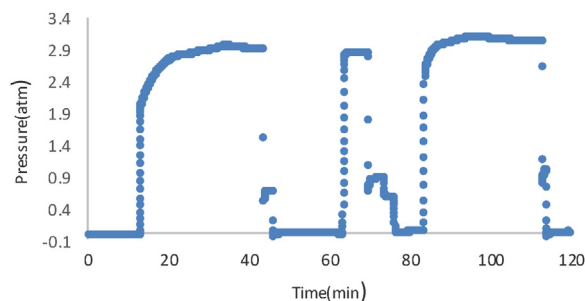

Fig. 1. Pressure variation over time of entry 3 in Table 1.
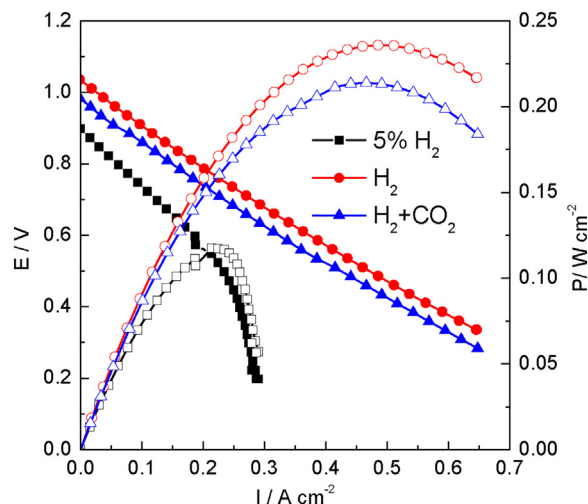

Fig. 2. Intensity *vs* Voltage curves.

Using the optimal conditions of entry 3 (Table 1), several additions of fresh FA were performed without any noticeable loss in catalyst efficiency (Fig. 1, see Supporting information). In that manner, after each injection of fresh FA, gas evolution was observed with increased pressure till a plateau was reached (no more decomposition); at that point, the pressure was relieved and fresh FA was added again (overall, this was repeated 3 times, see Fig. 1). We then proceeded to connect a fuel cell to the system, feeding the cell with the generated gas mixture in order to produce electricity with the liberated H_2. The fuel cell was also tested with two different gas combinations: pure H_2 and 5% H_2 in argon as standards to allow comparison. Results showed comparable activity when pure H_2 and our system were used (Fig. 2). Following this promising proof-of-concept, an electrical windmill was connected to the fuel cell, showing how the electricity produced from the fuel cell can be readily employed (See Supporting information for video).

The hydrogen (or even the gas mixture of CO_2 and H_2 generated from our decomposition experiment) can also be used as a chemical reagent. Chemical reductions, especially using molecular hydrogen [55], are ubiquitous in synthetic endeavours that involve the construction or manipulation of molecular architectures. However, the usual requirement of high pressures of gaseous H_2 renders these procedures less practical or even dangerous at times. Therefore, we envisaged that the hydrogen liberated during the decomposition of the HCOOH could be used for the reduction of unsaturated compounds. Recently, a similar strategy has been reported by Grela and co-workers, describing a tandem metathesis/hydrogenation protocol using various Grubbs' catalysts and subsequent addition of HCOOH under basic conditions [56]. Indeed, initial tests, using *trans*-stilbene, showed a certain degree of conversion (See Table 2 and Supporting information). When the reaction was performed at