Graphitic Nanofibres as Catalyst for Improving the Dehydrogenation Behavior of Complex Aluminium Hydrides

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Formic Acid – Convenient Liquid Hydrogen Storage for Mobile Applications

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1 Introduction

In the last decade hydrogen has become an increasingly attractive source for energy generation. Advancements in hydrogen technology such as the generation of hydrogen, its storage and its conversion to electrical energy are the prerequisite for the application of hydrogen as power source. Recently, the use of carbon dioxide as storage material for hydrogen and the controlled decomposition of formic acid to hydrogen have received considerable attention for energy storage [1].

In 2008, we have demonstrated that hydrogen can be generated from formic acid under mild conditions [2]. Commercially available Ru-catalysts are suitable for this reaction in the presence of amines. However, an improvement of the catalytic activity is possible applying in situ catalysts based on ruthenium and various phosphine ligands [3].

2 Results and Discussion

Unprecedented high rates at ambient temperature were obtained with a catalytic system which contains $[RuCl_2(benzene)]_2$ and the bidentate ligand dppe (1,2-bis(diphenylphosphino)ethane). This ruthenium/phosphine catalyst is able to generate hydrogen with high rates and high stability at room temperature. In order to allow for practical electric applications, >1 L H_2 per hour of hydrogen should be produced continuously for several hours. By application of $[RuCl_2(benzene)]_2$/dppe hydrogen evolution is achieved with up to 2.9 Liters per hour (Figure 1).

Besides the activity another important practical feature is the reuse of the catalyst system. Notably, our ruthenium phosphine complex showed no significant decrease of activity even after 10 restarts of the reaction by addition of formic acid during a period of two months! Hence, a total turnover number (TON) of approximately 60000 at 40 °C in 30 hours reaction time was obtained.

Applying the *in situ* ruthenium catalyst, usually the first run showed an induction period followed by a linear increase of gas evolution. The induction period is more pronounced for lower temperatures. The subsequent runs proceeded with an induction period of less than one minute (Figure 1).

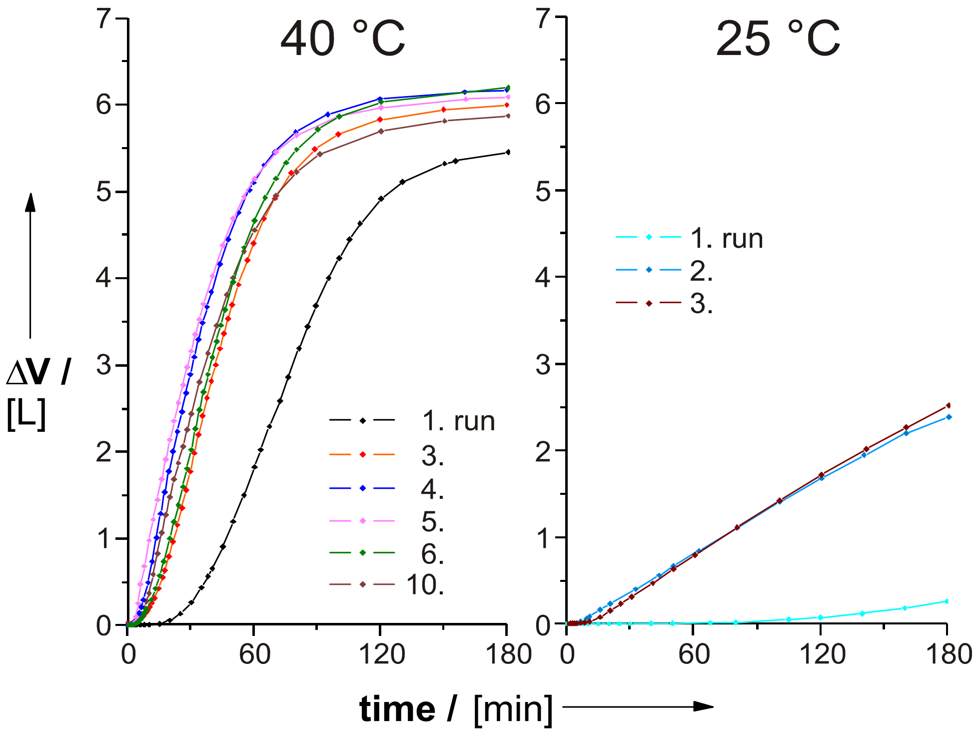


Figure 1: **Recycling experiments; 4.75 mL HCO_2H added to a solution of 9.55 µmol $[RuCl_2(benzene)]_2$ /3 equiv dppe in 17.5 mL $HexNMe_2$.**

To investigate the long time stability of our system, we constructed a device for continuous hydrogen generation (Figure 2). In a typical experiment 0.74 mL formic acid per hour were added to the reaction vessel containing 9.55 µmol $[RuCl_2(benzene)]_2$ / 3 eq. dppe in 17.5 mL *N,N*-Dimethylhexylamine ($HexNMe_2$). The gas mixture was quantified constantly with a gas flow meter “EL-FLOW” (Bronkhorst) and the hydrogen content was measured with a hydrogen sensor supported by GC analysis of the collected gas every 24 h.

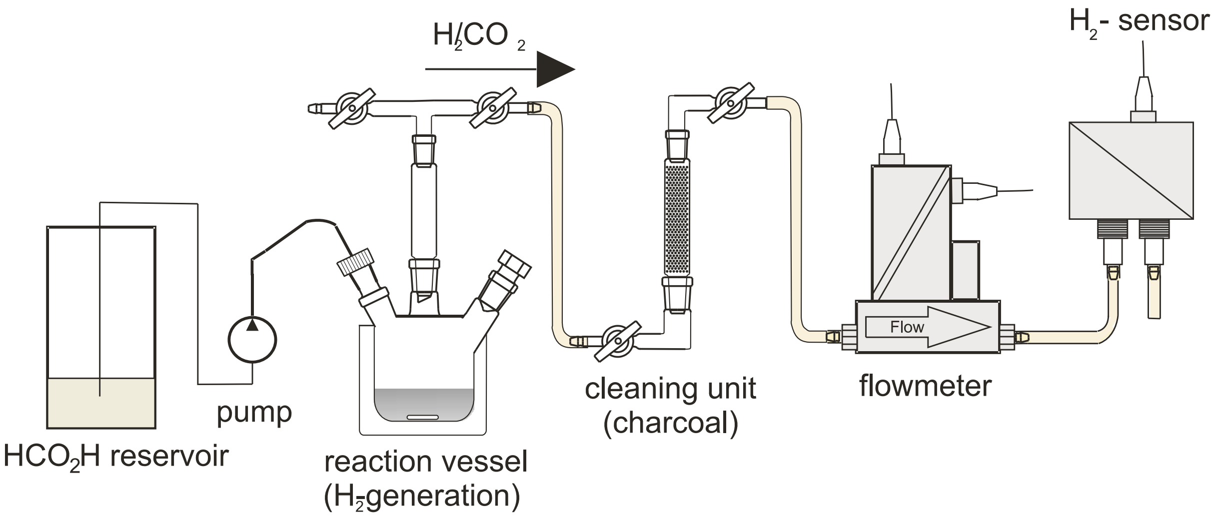


Figure 2: **Device for continuous hydrogen generation from formic acid.**

As shown in Figure 3 no decrease of catalyst activity was observed over a period of 264 h resulting in an outstanding TON of 260000! To the best of our knowledge, this is the highest value ever reported for selective formic acid decomposition. With respect to feedstock commercially available formic acid (99% grade, BASF) was used as received. Notably, also formic acid with 2% water content can be used without any loss of activity, underlining the robustness of the catalytic system. Applying the continuous conditions, the hydrogen outflow was approximately 0.45 L H_2/h [4].

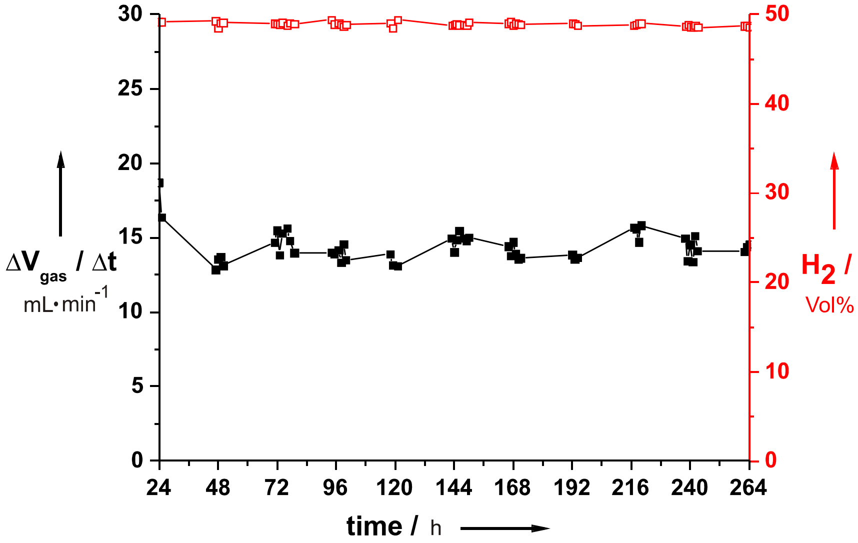


Figure 3: Continuous hydrogen production at room temperature.

The produced hydrogen (1:1 mixture with CO_2) meets already the qualitative and quantitative requirements for an application in small electric devices. It contains < 10 ppm CO and can be directly used in fuel cells. For demonstration we successfully implemented our hydrogen generation unit in a commercial available PEMFC toy car (Figure 4).

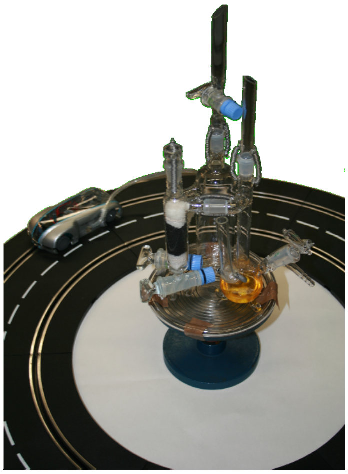
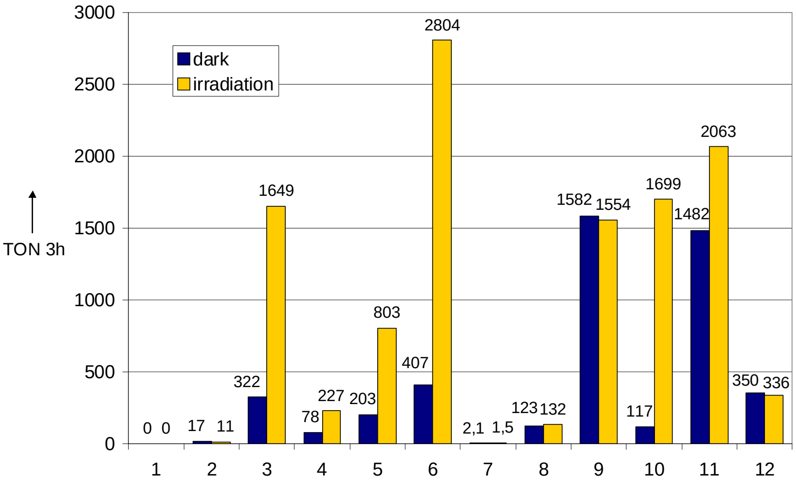


Figure 4: HCO_2H based H_2 supply for a commercial PEMFC toy car.

It is noteworthy to mention that the hydrogen generation can be accelerated by light and in fact can be triggered by switching on and off the light source (Figure 5).



1 PPh_3[a]
2 $[RuCl_2(benzene)]_2$
3 $[RuCl_2(benzene)]_2$ + 12 PPh_3
4 $[RuCl_2(benzene)]_2$ + 12 $P(C_6H_4$-4-OMe)
5 $[RuCl_2(benzene)]_2$ + 12 $P(C_6H_4$-4-$CF_3)$
6 $[RuCl_2(benzene)]_2$ + 6 dppe
7 $[RuCl_2(benzene)]_2$ + 12 PCy_3
8 $[RuCl_2(benzene)]_2$ + 12 $P(OPh)_3$
9 $[RuCl_2(benzene)]_2$ + 12 TPPTs
10 $[Ru(cod)(methylallyl)_2]$ + 6 PPh_3
11 $RuCl_3 \cdot x\, H_2O$ + 6 PPh_3
12 $RuH_4(PPh_3)_3$

Figure 5: Influence of light on the performance of Ru-catalysts. (5.0 mL 5 HCO_2H • 2 NEt_3, 19.1 µmol [Ru], 3h at 40 °C, Xe-Arc lamp/hot mirror; P : Ru = 6. [a] no hydrogen detected by GC.

This is the first example of the light-accelerated hydrogen generation reaction from formic acid with a catalyst system based on a ruthenium precursor and arylphosphines. In comparison to the non photo-assisted system, a more than one order of magnitude increase of gas evolution is achieved in the light-accelerated reaction. Thus the productivity of our best catalyst system $[RuCl_2(benzene)]_2$/dppe could be further increased [5]. Hence, the catalyst activity is almost double the activity of the best non-light activated system.

A careful analysis of our results reveals that irradiation has at least two effects: first the generation of the active species is promoted and second the deactivation of the catalyst is prevented.

Notably, this offers the opportunity to control hydrogen generation with light. After an initial formation of a stable photo-active catalyst, gas evolution could be almost stopped by switching off the light source, and restarted after turning it on again. Thus in addition, we could demonstrate for the first time that hydrogen evolution can be triggered by switching on and off the light source! (Figure 6)

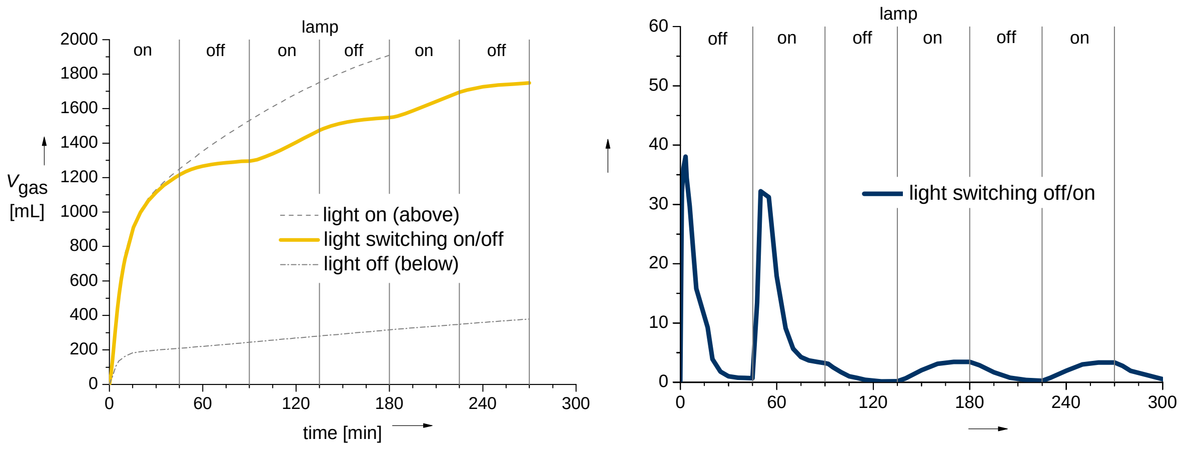


Figure 6: Light-triggered gas evolution from 5 mL 5 HCO_2H • 2 NEt_3 with $[RuCl_2(benzene)]_2$ / 12 PPh_3 (320 ppm Ru).

Left: After an initial formation of a stable photo-active catalyst, gas evolution can be almost stopped switching off the light source, and restarted after turning it on again.

Right: (Differential plot) Irradiation with light after 45 min further activates the catalyst in the first cycle of irradiation. In the following irradiation cycles, hydrogen generation is started and stopped by turning the light on or off.

In the light assisted reaction ruthenium can be substituted by the non noble metal iron. Recently the first light-driven iron-based catalytic system for hydrogen generation from formic acid could be developed. The catalyst is formed in situ from inexpensive $Fe_3(CO)_{12}$, 2,2':6'2''-terpyridine and triphenylphosphine.

3 Conclusion

Active and stable catalysts for the generation of hydrogen from formic acid at ambient conditions could be developed, which allow for an application of formic acid as hydrogen source especially in portable electric devices. Here the combination of hydrogen generation from formic acid and a PEMFC could be a suitable alternative for direct methanol fuel cells.

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