Ir(I)-NHC-phosphine complex catalyzed hydrogen generation and storage in aqueous formate/bicarbonate solutions with use of a flow reactor - dynamic response to changes in hydrogen demand[¶]

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Abstract

Hydrogen gas generation with dynamic response to changing application demands was achieved with use of a hydrogen battery based on aqueous cesium bicarbonate hydrogenation/ formate dehydrogenation, homogeneously catalyzed by an Ir(I)-N-heterocyclic carbene complex. In this device the storage solution was circulated through a small volume tubular reactor heated to the required high temperature to allow fast hydrogen evolution while the high volume reservoir was kept at ambient temperature at which no H_2 was generated. By simple control of the reactor temperature it was possible to regulate the rate of hydrogen evolution as required. The results also demonstrate the applicability of homogeneous catalysis for hydrogen generation in flow systems.

Keywords

1. Introduction

Harnessing the Sun by photovoltaic devices, wind turbines or by other means leads to fluctuating energy production which in turn highlights the need for temporary storage of energy.[1] Hydrogen is considered a suitable energy carrier for use in industry, transportation and in everyday life („hydrogen economy"), and its production using renewable energy could mitigate the fluctuations in available energy. In this case, the original problem of energy storage translates to the question of reversible hydrogen storage.[2] Among other possibilities, this can be achieved by reversible hydrogenation/dehydrogenation of suitable chemicals; processes which usually need catalysts.[3,4] Devices, in which the hydrogenation and dehydrogenation cycles (H_2 loading or delivery) are achieved simply by changing the hydrogen pressure can be termed hydrogen batteries.[5-7]

A widely studied way of hydrogen storage is the reversible formation and decomposition of formic acid (FA) and several highly active catalysts [8], both homogeneous [5-7, 9-18] and heterogeneous [19-21], have been discovered for decomposition of FA. In contrast, the catalytic hydrogenation of gaseous CO_2 to yield liquid FA is thermodynamically disfavoured.[22] Reaction of dissolved H_2 and CO_2 leads to high conversions to FA only in the presence of basic additives, [23-27] such as various amines, although a few processes are known leading to low concentrations of dissolved FA.[28-30] For this reason hydrogen storage devices based on reversible CO_2 hydrogenation/FA dehydrogenation can be constructed only with use of bases, of which the various ethanolamines, widely applied for CO_2-scrubbing from gases have received special attention.[31]

Although our early attempts [32] to achieve catalytic hydrogenation of CO_2 in aqueous media remained inconclusive, in later studies [33] bicarbonate was succesfully hydrogenated to formate in aqueous solutions. We also demonstrated that the processes of catalytic hydrogenation of bicarbonate and dehydrogenation of formate (as alkali metal salts) can be coupled, Eq. (1), to give working hydrogen batteries. The water-soluble complexes [{RuCl$_2$(*m*tppms-Na)$_2$}$_2$] [5] and [Ir(cod)(emim)(*m*tppms)] [6,34] in the presence of *m*tppms-Na and *m*tppts-Na$_3$, respectively (*m*tppms-Na = sodium-diphenylphosphinobenzene-3-sulfonate, *m*tppts-Na$_3$ = tris(meta-sulfonatophenyl)phosphine trisodium salt, cod = 1,5-cyclooctadiene, emim = 1-ethyl-3-methylimidazol-2-ylidene) were identified as active catalysts for both hydrogenation and dehydrogenation. Consequently, loading and delivery of H_2 (the charge-discharge process of the battery) could be simply regulated by the hydrogen pressure. An important feature is that in addition to the catalyst the aqueous reaction mixture

contains only inorganic salts with no other components, so the long-term operation of the battery depends only on the chemical stability of the catalyst.

In homogeneous catalysis the substrates and the catalysts reside in the same phase. In chemical hydrogen storage this can lead to unwanted H_2-generation when the battery is not in use. Furthermore, in case the reactions (either hydrogenation or dehydrogenation, or both) require elevated temperatures it is impractical to heat the entire storage solution (possibly of large volume). In the following we present a flow reaction system for reversible hydrogen storage/delivery based on the aqueous bicarbonate/formate equilibrium, Eq. (1) in which all the difficulties mentioned above are circumvented.

2. Materials and methods

[Ir(cod)(emim)($m$tppms)] [35], monosulfonated and trisulfonated triphenylphosphine, $m$tppms-Na [36], and $m$tppts-Na$_3$ [37], respectively, were synthetized by published procedures. $CsHCO_3$ and $CsHCO_2$ were purchased from Alfa Aesar GmbH. Ion-exchanged water ($S \leq 1\ \mu S$) was used throughout. All other reagents were high purity commercial products.

Both bicarbonate hydrogenations and formate dehydrogenations were carried out by using a H-Cube microfluidic hydrogenation flow reactor [38] (ThalesNano Nanotechnology Inc, Budapest, Hungary). Aqueous reaction mixtures containing the dissolved catalyst were pumped through the empty reactor heated to the appropriate reaction temperature. Volumes of the generated H_2 were measured with the use of a thermostated gas-burette kept at the appropriate $T \pm 0.1\ °C$ temperature by using a Haake K10 circulator.

Formate concentrations in the reaction mixtures were determined by HPLC (AGILENT 1220 INFINITY, Supelcogel 610H column, sample volume 20 µl, eluent 0.1% H_3PO_4 in water, flow rate 1 mL/min). Formate was detected at $\lambda = 210$ nm and its concentration was determined by integration of peak areas using a calibration curve.
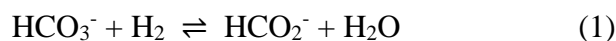
General procedure for homogeneous catalytic *dehydrogenation of aqueous Cs-formate*. Aqueous reaction mixtures containing the catalyst ([Ir(cod)(emim)($m$tppms)]) together with excess phosphine ($m$tppts-Na$_3$) and $CsHCO_2$ were prepared under argon in a Schlenk-tube (the reservoir) and pumped through the heated empty tubular reactor (CatCart, dimensions 30 (l) × 4 mm (i.d.)) of the H-Cube device. No H_2 was mixed into the flow. Flow rate was varied between 0.2-2.0 mL×min^{-1}. The reaction was studied in two ways. According to Method **A** (single pass) the reaction mixture was sampled and analyzed directly after leaving the reactor. According to Method **B** (cumulative), the reaction mixture leaving the

CatCart was continuously fed back to the stirred reservoir and the formate concentration of the resulting solution in the reservoir was then determined over time by HPLC. Volumes of the evolved hydrogen were measured with use of a thermostated gas-burette connected to the reservoir (see Figure 2).

General procedure for homogeneous catalytic *hydrogenation of Cs-bicarbonate.* Aqueous reaction mixtures containing the catalyst ([Ir(cod)(emim)(*m*tppms)]) together with excess phosphine (*m*tppts-Na$_3$) and Cs-bicarbonate were prepared in a Schlenk-tube (the reservoir) and pumped through the heated empty tubular reactor (CatCart, dimensions 30 (l) × 4 mm (i.d.)). Hydrogen, generated by the device electrolytically, was mixed into the liquid flow before entering the tubular reactor, where the hydrogen pressure was regulated in the range of 1-90 bar, and the temperature within 25-100 °C. Flow rate was varied between 0.5-2.0 mL×min^{-1}. Hydrogenation of CsHCO$_3$ was investigated using both Method **A** (single pass) and Method **B** (cumulative) – see previous paragraph. Composition of the reaction mixtures (formate concentration) were followed by HPLC.

3. Results and discussion

Hydrogenation of cesium bicarbonate and dehydrogenation of cesium formate (Equation 1) were studied in a microfluidic hydrogenation reactor (H-Cube [38]). [Ir(cod)(emim)(*m*tppms)] + *m*tppts-Na$_3$ was applied as catalyst.[6,34] Cesium salts were chosen due to their high aqueous solubilities [39]: CsHCO$_3$ – 209 g/100 g H$_2$O (15°C), CsHCO$_2$ – 450 g/100 g H$_2$O (20°C) and outstanding reactivities.[40-41] The catalyst was dissolved in the aqueous solutions of CsHCO$_3$ or CsHCO$_2$ and the reaction mixture was pumped through a tubular reactor held at a controlled temperature. The reactions could be conveniently followed in the 60-100°C temperature range.

$$HCO_3^- + H_2 \rightleftharpoons HCO_2^- + H_2O \qquad (1)$$

Hydrogenation of cesium bicarbonate and dehydrogenation of cesium formate were investigated at various temperatures, pressures, and flow rates, using solutions of various substrate concentrations (Figures A.1-A.7). In both reactions the conversions increased with increasing temperature (Figures A.1, A.3); remarkably, no formate dehydrogenation was observed at 25°C. The conversion showed inverse dependence on flow rate (Figures A.4, A.5). At low substrate concentrations conversions as high as approximately 20% could be observed in a single pass of the reaction mixture through the heated tubular reactor for both

hydrogenation of bicarbonate and dehydrogenation of formate (see e.g. Figure A.3). Note that the catalyst was able to handle even high substrate concentrations, yielding very high TO values (e.g. TOF = 57800 h^{-1} for formate dehydrogenation at [CsHCO_2]:[Ir]=5000:1, Figure A.2). These observations are in agreement with our earlier findings obtained in batch reactions.[6] Furthermore, it was also found earlier [6] that the catalyst was stable under 100 bar H_2 pressure at room temperature for more than 71 days. Together with the results of the present measurements using a flow reactor, all the data show that aqueous $CsHCO_3^-/CsHCO_2^-$ solutions and the [Ir(cod)(emim)(*m*tppms)] catalyst have sufficiently chemical stability and may serve as basis for reversible hydrogen storage.

Figure 1 shows the results of an experiment when the reaction mixture was continuously circulated through the heated hydrogenation reactor. The solution in the reservoir was sampled over time and analyzed by HPLC (Method **B**). Under the conditions of Figure 1, bicarbonate was gradually hydrogenated to formate and the conversion reached 85 % in 200 min. At this point the H_2 pressure was decreased from 90 to 1 bar and the solution was further circulated at the same temperature (100 °C) with unchanged flow rate. The pressure drop resulted in formate dehydrogenation according to Eq. (1) with approximately 50% conversion in 100 min.
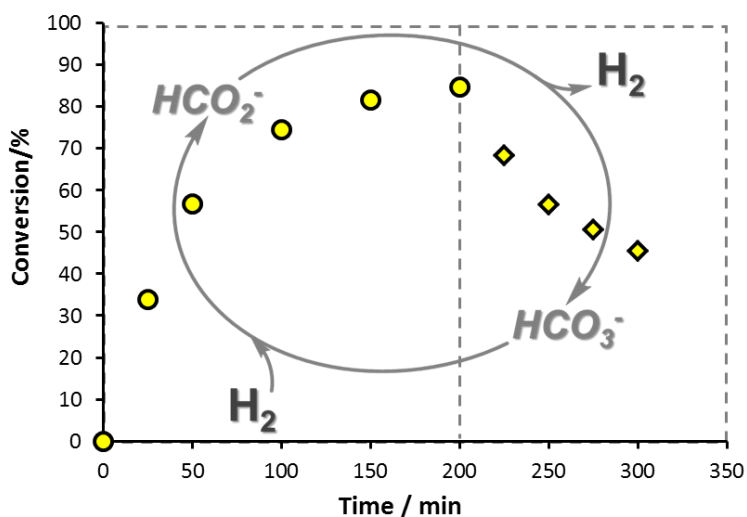

Figure 1. Hydrogenation of HCO_3^- to formate (○; 0-200 min) and dehydrogenation of HCO_2^- to bicarbonate (◇; 200-300 min) under flow conditions.

[CsHCO_3]/[Ir] = 75 (○,◇); [*m*tppts-Na_3]/[Ir] = 2; V(H_2O) = 25 mL; P(H_2) = 90 bar (0-200 min) or 1 bar (200-300 min), T = 100 °C; v = 1.0 mL×min^{-1}.

In other experiments the volume of the evolved H_2 was measured by using a gas-burette. The experimental setup is shown schematically on Figure 2 (in this case the burette and reservoir were kept at the same constant temperature). Note that the volume of the reservoir (at $T = 25$ °C) is about 66 times the volume of the heated flow reactor.

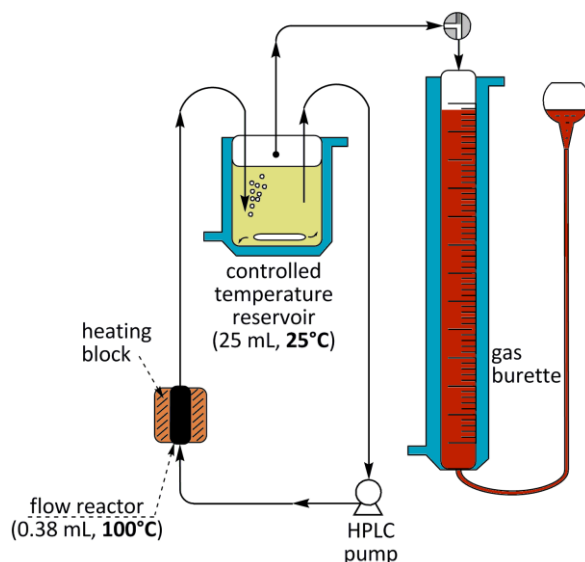**Figure 2.** Schematic figure of the coupled flow reactor - gas-burette system

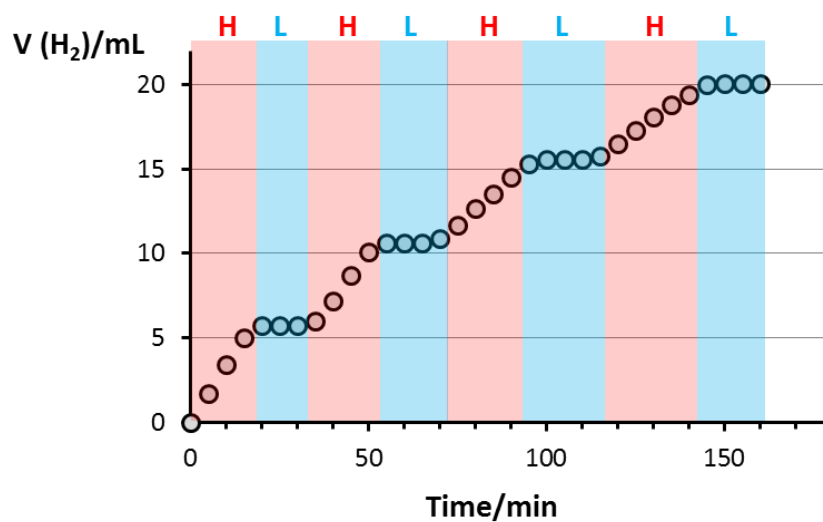**Figure 3.** Hydrogen evolution in subsequent high temperature (100 °C; **H**) and low temperature (25 °C; **L**) intervals during temperature controlled dehydrogenation of aqueous Cs-formate.

[CsHCO$_2$] = 0.081 M; [Ir-NHC] = 0.1 mM; [$m$tppts-Na$_3$]/[Ir] = 2; V(H$_2$O) = 25 mL; v = 2.0 mL×min^{-1}, $T = 100$ °C (**H**) or 25 °C (**L**).

Figure 3 shows the effect of temperature on the dehydrogenation of aqueous cesium formate. It can be seen that the reaction proceeds with high rate in the reactor set at 100 °C. However, hydrogen evolution stops immediately when the reactor temperature is switched to 25 °C. Apparently, the heat capacity of the entering cold reaction mixture is sufficient to cool the reactor in a few seconds. By switching the reactor temperature back and forth between 100 °C and 25 °C, generation of gaseous H_2 can be initiated and stopped at will. Such a possibility provided by flow systems may have high importance in the case of mobile devices (e.g. vehicles) where hydrogen supply must be dynamically adjusted to the feed requirements. It was also observed, that the temperature of the reaction mixture in the reservoir did not increase significantly even in the absence of temperature control; air cooling of the solution travelling through the capillary tube connection between the reactor and reservoir was efficient enough to keep the reservoir at room temperature.

Conclusions

A reversible hydrogen storage reaction system, based on hydrogenation of aqueous cesium bicarbonate and dehydrogenation of cesium formate both homogeneously catalyzed with the water-soluble [Ir(cod)(emim)($m$tppms)] was analyzed in a flow reactor (H-Cube). Fast switches of the reactor temperature between high (e.g. 100 °C) and low (e.g. 25 °C) values allow precise and dynamic adjustment of the H_2 generation rate to application demand. Furthermore, depending on the relative volumes of storage solution and the flow reactor, only a fraction of the reaction mixture has to be heated avoiding undesired H_2 evolution. Until now, soluble complex catalysts were used only in heterogenized form on solid supports but mostly failed in the long run due to leaching of the anchored complexes. This work also demonstrates the practical feasibility of using homogeneous catalysis for hydrogen generation in flow systems provided it meets the following requirements: a) the catalytic H_2-storage reaction has sufficiently high activation energy to allow fast H_2-evolution at high temperatures with no or negligible H_2-formation at ambient temperature; b) all reaction partners of the storage reaction as well as the dissolved catalyst have high chemical stability, and c) the catalyst is able to catalyze the storage reaction (such as e.g. Eq. 1) in both directions.

Acknowledgement

Appendix A. Supplementary data

Supplementary data related to this article can be found at …..

Declarations of interest: none

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