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P. Wasserscheid

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Hydrogen Production from Glucose in Ionic Liquids

D. W. Assenbaum, N. Taccardi, M.E.M. Berger, A. Bösmann, F. Enzenberger, R. Wölfel, P. Wasserscheid, Lehrstuhl für chemische Reaktionstechnik, Universität Erlangen-Nürnberg, Germany

1 Introduction

Depletion of oil and gas reserves and growing global warming concerns have created a world-wide interest in new concepts for future sustainable energy supplies. The development of effective ways to produce hydrogen from biomass is expected to be one important contribution to such a goal [1]. Nowadays, three main processes are considered for future industrial application, namely: gasification of biomass [2], reforming in supercritical water [3] and aqueous phase reforming [4,5]. Other technologies such as enzymatic decomposition of sugars or steam reforming of bio-oils suffer from low hydrogen production rates and/or complex processing requirements and can probably not be considered for industrial applications in the closer future [6,7]. On the other hand, either the gasification of biomass, which is typically carried out at temperatures above 800 °C using Ni or Fe catalysts [8,9,10,11], or the reforming in supercritical water, which is typically carried out in presence of Ru catalyst at pressures of 300 bar and temperatures ranging from 500 to 700 °C [12], suffer of poor energetic efficiency as a lot of energy is required to run the reactions. More recently, an alternative to the two aforementioned high temperature processes has been proposed as “aqueous phase reforming” (APR) by Dumesic and coworkers [13,14,15,16,17]. They achieved the reforming of polyols (such as ethylene glycol, glycerol and sorbitol) using heterogeneous catalysts at temperatures between 200 and 250 °C and pressure typically between 15-50 bar. The temperature level of the reaction allows generating hydrogen with low amounts of CO in a single reactor. The process typically forms 35 % of hydrogen, 40 % of CO₂ and 25 % of combined alkanes. The high amount of formed alkanes originates eventually from CO hydrogenation and Fischer-Tropsch (F-T) reaction [18,19,20,21], those are thermodynamically favored in the above mentioned conditions. However, heterogeneously catalyzed APR technologies suffer from the fact that the overall reaction rates are often restricted by mass and heat transport problems. Lastly, there are severe limitations concerning the feedstock selection as for some important substrates, such as e.g. glucose, the process can only be operated in very diluted systems to avoid rapid tar formation [22,23,24].

In this contribution we describe for the first time a catalytic reaction system producing hydrogen from glucose in astonishingly high selectivities using a single reaction step under very mild conditions. The catalytic reaction system is characterized by its homogeneous nature and comprises a Ru-complex catalyst dissolved and stabilized in an ionic liquid medium. Ionic liquids are salts of melting points below 100 °C [25]. These liquid materials have attracted much interest in the last decade as solvents for catalytic reactions [26] and separation technologies (extraction, distillation) [27,28,29,30,31,32]. Besides, these liquids have found industrial applications as process fluids for mechanic [33] and electrochemical applications [34]. Finally, from the pioneering work of Rogers and co-workers, it is known that

ionic liquids are able to dissolve significant amounts of water-insoluble biopolymers (such as e.g. cellulose and chitin)[35] and even complex biopolymer mixtures, such as e.g. wood, have been completely dissolved in some ionic liquids [36].

In our specific application, the role of the ionic liquid is threefold: a) the ionic liquid dissolves the carbohydrate starting material thus expanding the range of applicable carbohydrate to water insoluble polymers; b) the ionic liquid provides a medium to dissolve and stabilize the catalyst; c) the ionic liquid dissolves hydrogen at a very low level, so inhibiting any possible collateral hydrogen-consuming process (detailed investigation of the hydrogen solubility in ionic liquids have been reported by e.g. Brennecke and coworkers [37]).

2 Results and Discussion

The process was carried out using a pressure-less glass reactor, purged with a stream of argon (200 ml/min) and connected to a hydrogen analyzer (heat conductivity based hydrogen analysis, EMERSON Hydros 100). This set-up encloses a series of washing bottles and cooling traps in order to remove all condensables and to provide a selective gaseous product analysis. The amount of evolved hydrogen was determined by integrating the detector signal vs. time. The obtained results are given in Table 1.

The ionic liquids listed in Table 1 were chosen on the base of previous reports on the dissolution of biopolymers and sugars in ionic liquids [38,39,40,41]. The [(p-cymene)RuCl₂]₂/TMEDA system was selected as catalyst, because of its remarkable long time stability at relatively high temperature, as reported by Beller and coworkers, in which this complex was applied for the dehydrogenation of isopropanol [42].

Table 1: Overview of glucose hydrate (C₆H₁₂O₆·H₂O) dehydrogenation experiments using different ionic liquids at 180°C and [(p-cymene)RuCl₂]₂/TMEDA as the catalyst.

entry	ionic liquid	H ₂ production 1h /ml (Yield / %) ^a	TON (1h)
1	[EMIM][HP(OMe)O ₂]	56 (2.9)	35
2	[EMIM][MeP(OMe)O ₂]	65 (2.5)	40
3	[EMIM][acetate]	49 (2.2)	31
4	[MMIM][Me ₂ PO ₄]	18 (0.8)	11

Reaction conditions: C₆H₁₂O₆·H₂O 3.00g (15mmol), [(p-cymene)RuCl₂]₂ 40mg, TMEDA 300mg, IL 50g, 180°C; [EMIM]= 1-ethyl-3-methylimidazolium, [MMIM]= 1,3- dimethyl-imidazolium. ^a) Evolved hydrogen determined through integrating the detector signal over the time; total hydrogen yields refer to the production of hydrogen from glucose, i.e. 100% yield corresponds to the formation of 6 mols H₂ from one mol of glucose; total hydrogen yield refers to the production of hydrogen from glucose, i.e. 100% yield corresponds to the formation of 6 mols H₂ from one mol of glucose.

Analysis of the gas phase showed no hints for CO, methane or other higher alkanes formation (below detection limit). Apart from hydrogen, the only detectable gas product was CO₂. Hydrogen and CO₂ were detected in a 1:1 ratio. The lack of CO and alkane is technically very interesting as a pure hydrogen/CO₂ mixture would greatly facilitate the downstream hydrogen purification processes or, in principle, could be direct used for feeding

fuel-cells. Another important outcome of these experiments was the fact that all the tested ionic liquid/glucose mixtures remained liquids and did not show any visible solid formation under the entire reaction time. This is remarkable, given the fact that the dehydration reaction with consequent solid tars formation has prevented so far the successful application of heterogeneous catalyzed APR approaches for glucose. Moreover, in aqueous systems, hydrogen consuming side reactions (formation of alkanes) have been observed if glucose is used as the feedstock. These limitations require the use of highly diluted feedstock solutions (usually < 1 % for glucose) and the processing of excessive amounts of water [43].

Aimed to improve hydrogen production, the reaction time was prolonged. With the only exception being the ionic liquid [EMIM][CH₃P(OMe)O₂], in all cases either decomposition of the cation ([EMIM][acetate]) or of the anion [EMIM][HP(OMe)O₂] was observed. However, no improvement of the hydrogen yield was achieved. Thus, the reason of the low yields was addressed. At first glance, it could be alleged the possible *in situ* N-heterocyclic carbene (NHC) complexes formation as reason for the low activity observed. It is well known [44] that the proton at carbon 2 of the imidazolium ring possesses enough acidity to be abstracted (even by relatively weak bases such as acetate) with consequent generation of a NHC, which coordinates the metal centre and blocks the coordination sites. Recently, such chemistry has also been observed for the protons in position 4 or 5 of the imidazolium ring (abnormal NHC) [45]. Therefore, we shifted from imidazolium to phosphonium salts. The ionic liquid tetrabutylphosphonium methylphosphonate ([Bu₄P][CH₃P(OH)O₂]) was prepared by simply reacting an aqueous solution of phosphonium hydroxide with a solution of methylphosphinic acid in the same solvent. After water evaporation, a waxy solid was obtained that was fully characterized. The results of the comparison between [EMIM][CH₃P(OMe)O₂] and [Bu₄P][CH₃P(OH)O₂] are presented in Table 2.

Table 2: Overview of [(p-cymene)RuCl₂]₂/TMEDA catalyzed dehydrogenation experiments using different methylphosphonate ionic liquids.

entry	ionic liquid	feedstock	H ₂ produced in 1h / ml (Yield /%) ^a	TON (1h)
1	[EMIM][MeP(OMe)O ₂]	C ₆ H ₁₂ O ₆ ·H ₂ O	56 (2.5)	35
2	[EMIM][MeP(OMe)O ₂] ^b	C ₆ H ₁₂ O ₆ ·H ₂ O	93 (4.2)	58
3			54 (2.9)	37
3.1			75 (3.6)	47
3.2			61 (3.0)	39
3.3			56 (2.7)	35
3.4			41 (2.0)	26
3.5	[Bu ₄ P][CH ₃ P(OH)O ₂] ^{c, d}	C ₆ H ₁₂ O ₆ ·H ₂ O	44 (2.2)	28
4	[Bu ₄ P][CH ₃ P(OH)O ₂] ^{b, e}	C ₆ H ₁₂ O ₆ ·H ₂ O	116 (5.2)	72

Reaction conditions: C₆H₁₂O₆·H₂O 3.00g (15mmol), [(p-cymene)RuCl₂]₂ 40mg, TMEDA 300mg, IL 50g, 180°C; [EMIM]= 1-ethyl-3-methylimidazolium, [Bu₄P]= tetrabutylphosphonium; ^a) Evolved hydrogen determined through integrating the detector signal over the time; total hydrogen yields refer to the production of hydrogen from glucose, i.e. 100% yield corresponds to the formation of 6 mols H₂ from one mol of glucose; ^b) reaction at 150°C; ^c) 3.00g aliquots of glucose were added to the system after hydrogen production ceased; ^d) dry ionic liquid; ^e) ionic liquid contained 5% of water.

The results obtained allowed us to exclude a possible intermediation of NHC-complexes (entries 1 and 3). On the other hand, it has to be highlighted that the catalytic system showed to be robust, as demonstrated by experiment in entry 3, where other 5 successive additions of glucose were made over 48 h at 180 °C (Figure 1). By the slope of the curves in Figure 1, it could be deduced that after the first addition a catalytic species formed in the system that was more active than the parental [(p-cymene)RuCl₂]₂/TMEDA system.

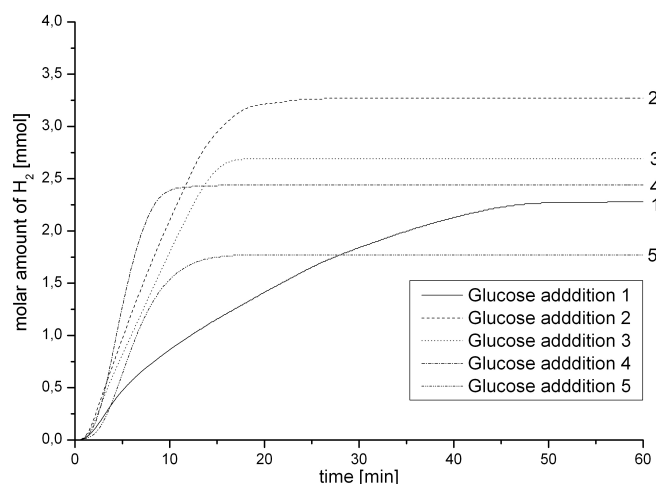


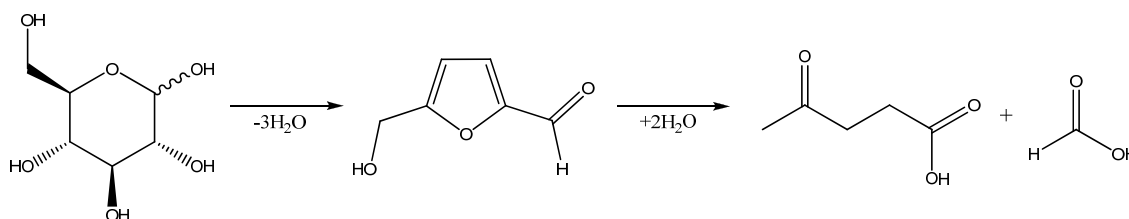
Figure 1: Hydrogen evolution vs. time for the different glucose additions in [Bu₄P][CH₃P(OH)O₂] at 180 °C.

The system remained liquid along the whole experiment, as the formation of tarry solid seemed to be substantially suppressed in the ionic liquid. Interestingly, the presence of water seemed to play an important role on the process efficiency (entries 3 and 4). In particular, it could be seen that although the lower reaction temperature (the system could not reach the foreseen temperature of 180 °C due to the reflux of water), it was possible to get a slight improvement of yields.

The evidences collected so far, namely the nature of gaseous products and the effect of water suggested that this new catalytic system could not follow a common alcohol dehydrogenation mechanism [42 and references cited therein]. In order to elucidate this hypothesis, we investigated the system by means of ¹³C-NMR spectroscopy using fully ¹³C-labelled glucose (99 % ¹³C). The fate of the ¹³C-labeled substrate was investigated during two sets of experiments: in the first set, thermolysis at 150 °C of ¹³C₆-glucose was carried out in the ionic liquids without any Ru-catalyst. The second set of experiments was mimicking the catalytic process, with the thermolysis carried out in presence of [(p-cymene)RuCl₂]₂/TMEDA. In all the ionic liquid tested, complete disappearance with decomposition of glucose was observed within 90 min. By comparing the spectra of the Ru-free and the Ru-containing samples, only one pronounced difference could be noticed: an intense singlet in the region 170÷176 ppm appearing in the Ru-free samples that was missing in the respective Ru-containing systems (Figure 2). This singlet peak can be easily attributed to formic acid, which formed during the thermal degradation of glucose [46]. Obviously, this formic acid is

immediately transformed to hydrogen and CO₂ in the presence of the Ru-catalyst [47]. The above hypothesis was also supported by the observation of a 1:1 ratio H₂:CO₂ in the gas phase. The GC-MS analysis of gaseous product revealed an enrichment of ¹³CO₂ up to 90 % (the missing ¹³C could be attributed either to experimental error or contamination during the gas handling with atmospheric CO₂).

In this view, the role of water could also be explained. In fact, it has been reported that the formation of formic acid from glucose proceeds through a de-hydration/re-hydration sequence (scheme 1) [48].



Scheme 1: Formation of formic acid via de-hydration/re-hydration of D-glucose [48].

As depicted in the scheme, the re-hydration step is responsible for the formation of formic acid, thus the lower the water content in the system the slower its formation.

3 Conclusion

In conclusion we have demonstrated the feasibility of a new ionic liquid based catalytic system that allows the conversion of glucose to hydrogen. The issue of a suitable ionic liquid for such application was addressed and the new ionic liquid [Bu₄P][CH₃P(OH)O₂] was synthesized and characterized. The ionic liquid/catalyst system showed to be robust and stable up to 48 h at 180 °C, allowing up to six consecutive glucose dehydrogenation reactions without formation of tarry solid materials. Isotopes labelling studies allowed us to gain new insights about the reaction mechanism and to identify a reasonable reaction scheme for the carbohydrate dehydrogenation. It was found that in ionic liquid glucose thermally decomposed yielding formic acid. The generated formic acid was quickly and selectively decomposed to CO₂ and hydrogen in a Ru-catalyzed process. The outcomes of this study are important as new scenarios for exploiting bio-feedstock are described. As a matter of fact, a catalytic IL based system was developed for the direct conversion of biomass to hydrogen and carbon dioxide in very high selectivity. This kind of hydrogen production could be potentially integrated into advanced bio-refinery concepts, as almost all existing bio-refinery schemes suffer from the lack of “non-fossil” hydrogen to balance the shortage of hydrogen in going from biogenic polyols to fuel components like alkanes or ethers. Clearly, the presented process is still in its infancy and its efficiency has to be improved for practical applications.

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