# Catalytic production of hydrogen from glucose and other carbohydrates under exceptionally mild reaction conditions†

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**A catalytic reaction system for the production of hydrogen from sugars and even water-insoluble biomass like cellulose is presented. The reaction system is based on an ionic liquid that has the role to dissolve the carbohydrate feedstock and a ruthenium catalyst. As hydrogen dissolves in this media at very low level, hydrogen consuming side reactions have been hindered, leading to a gaseous product mixture consisting mainly of hydrogen and carbon dioxide. Investigations with isotopic labelling suggest a reaction sequence in which glucose first thermally decomposes to formic acid followed by Ru-catalyzed decomposition of the latter to hydrogen and $CO_2$.**

## Introduction

In recent years, shrinking oil and gas reserves and growing concerns about global warming have created a world-wide interest in new concepts for sustainable future energy supplies. One important contribution to such a goal is expected to be the development of effective ways to produce hydrogen from biomass.[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 near future.[6,7]

Both gasification and reforming in supercritical water of biomass are energetically expensive processes. The former is performed at temperatures ranging from 800 °C up to 1300 °C, producing nitrogen-free synthesis gas. The raw gas product contains CO, $H_2$, $CO_2$, $CH_4$ and $H_2O$ in variable ratios depending on feedstock composition, temperature *etc.*[8-11] The latter is run at high pressures (typically 300 bar) and temperatures of 500–700 °C in the presence of a Ru supported on alumina catalyst.[12] The biomass is converted to gaseous products with a typical composition of 41% $CO_2$, 29% hydrogen and 27% of $CH_4$. The main drawbacks of these technologies are the high specific investment cost due to the demanding process conditions and the requirement of special reactor materials (especially for the corrosive nature of the supercritical water). Moreover, downstream processing is needed as the direct utilization of the produced hydrogen is hindered by the large amount of methane present in the final gas mixture.

As an alternative to the two aforementioned high temperature processes, aqueous phase reforming (APR) has been proposed by Dumesic and co-workers.[13-17] They described the reforming of alcohols or polyols (such as ethylene glycol, glycerol and sorbitol) in aqueous solution using heterogeneous catalysts at temperatures between 200 and 250 °C and pressures ranging between 15 and 50 bar, to produce primarily $H_2$ and $CO_2$. The reaction typically yields 35% of hydrogen, 40% of $CO_2$ and 25% of combined alkanes. The high amount of alkane formation originates eventually from intermediate CO hydrogenation and a Fischer–Tropsch (F-T) reaction;[18-21] those are thermodynamically favored in the above mentioned conditions. In order to get higher hydrogen selectivities, Dumesic and co-workers have focused on platinum and palladium catalysts. In fact, although metals like Ru, Ni, Ir and Rh are known to be more active catalysts for C–C cleavage[22] and for the water-gas shift (WGS) reaction,[23] their use will lead invariably to higher alkane content in the product: for example, Ru as a catalyst leads to alkane selectivity of up to 65%.[24] 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 glucose, the process can only be operated in very diluted systems to avoid rapid tar formation with consequent catalyst coking.[25-27]

In this contribution we describe for the first time a catalytic reaction system producing hydrogen in very high selectivity from glucose and even water-insoluble carbohydrates, such as cellulose, in very mild conditions. Our 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.[28] These liquid materials have attracted much interest in the last decade as solvents for catalytic reactions[29] and separation

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technologies (extraction, distillation).[30-35] Besides, they have found industrial applications as process fluids for mechanical[36] and electrochemical applications.[37] Finally, from the pioneering work of Rogers and co-workers, it has been demonstrated that ionic liquids are able to dissolve significant amounts of water-insoluble biopolymers (such as cellulose and chitin)[38] and even complex biopolymer mixtures, such as wood, have been completely dissolved in some ionic liquids.[39]

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 (detailed investigations of the hydrogen solubility in ionic liquids have been reported by *e.g.* Brennecke and co-workers[40]), thus inhibiting any possible collateral hydrogen-consuming processes, *i.e.* Fischer–Tropsch like processes.

## Results and discussion

The process was carried out using a pressure-less glass reactor, purged with a stream of argon (200 mL $min^{-1}$) 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 (a detailed description of the experiment can be found in the Supporting Information†). The amount of evolved hydrogen was determined by integrating the detector signal *vs.* time. The gas phase products were analyzed by GC-MS using a Varian GC 3900/MS Saturn 2100 T equipped with a PoraBond Q FS (25 m × 0.25 mm) column. Condensed liquid phases were analyzed with the same apparatus using a VF 5-ms (30 m × 0.25 mm) column.

Based on previous reports on the dissolution of biopolymers and sugars in ionic liquids,[41-44] the ionic liquids 1-ethyl-3-methylimidazolium acetate ([EMIM][acetate]), 1,3-dimethylimidazolium dimethylphosphate ([MMIM][$Me_2PO_4$]), 1-ethyl-3-methylimidazolium methyl-methylphosphonate ([EMIM][Me-P(OMe)$O_2$]) and 1-ethyl-3-methylimidazolium methylphosphonate ([EMIM][H–P(OMe)$O_2$]) were chosen as reaction media. The compound [(p-cymene)$RuCl_2$]$_2$ and TMEDA as a stabilizing ligand were selected as the catalytic system, the choice being based on a report by Beller and co-workers, in which this complex was applied to the dehydrogenation of isopropanol and showed remarkable long time stability at relatively high temperature.[45] The obtained results are given in Table 1.

Analysis of the gas phase showed no evidence for CO, methane or other higher alkanes' formation (below detection limit). Apart from hydrogen, the only detectable gas product was $CO_2$, whereby hydrogen and $CO_2$ were detected in a 1 : 1 ratio. The extremely low alkane formation supports the above stated assumption that a low hydrogen concentration in the IL system suppresses effectively hydrogenation side reactions. The lack of CO and alkane formation is technically very relevant. Comparison runs with the same ionic liquids and glucose feedstock but without added Ru-catalyst showed no hydrogen formation.

**Table 1** Overview of glucose hydrate ($C_6H_{12}O_6 \cdot H_2O$) dehydrogenation experiments using different ionic liquids at 180 °C and [(p-cymene)$RuCl_2$]$_2$/TMEDA as the catalyst

| entry | ionic liquid | $H_2$ production/ mL $h^{-1}$/Yield (%)[a] | TON |
|---|---|---|---|
| 1 | [EMIM][H–P(OMe)$O_2$] | 56 (2.5) | 35 |
| 2 | [EMIM][Me–P(OMe)$O_2$] | 65 (2.9) | 40 |
| 3 | [EMIM][acetate] | 49 (2.2) | 31 |
| 4 | [MMIM][$Me_2PO_4$] | 18 (0.8) | 11 |

Reaction conditions: $C_6H_{12}O_6 \cdot H_2O$ 3.00 g (15 mmol), [(p-cymene)$RuCl_2$]$_2$ 40 mg, TMEDA 300 mg, IL 50 g, 180 °C, 1 h; [EMIM]= 1-ethyl-3-methylimidazolium, [MMIM]= 1,3-dimethylimidazolium.[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 moles $H_2$ from one mol of glucose.

Another important outcome of these preliminary experiments was the fact that all the tested ionic liquid/glucose mixtures remained liquids and did not show any visible solid formation throughout the entire reaction time. This is a promising result, given the fact that the dehydration reaction with consequent solid formation has complicated so far the successful application of heterogeneous catalyzed aqueous phase reforming 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.[46] Nevertheless, the behavior of the IL system described here is yet to be confirmed under technical conditions.

In order to improve the hydrogen production, the reaction time was prolonged. This resulted in a better yield only in the case of [EMIM][acetate] and [EMIM][H–P(OMe)$O_2$] with 445 mL and 779 mL of hydrogen being produced respectively after 8 h. However, in the case of [EMIM][acetate], NMR analysis of the reaction mixture and the condensed products showed clear evidence of ionic liquid decomposition *via* a retro-alkylation mechanism under the applied conditions ($T = 180$ °C, 8 h reaction time). The basic and nucleophilic acetate reacted with the 1-ethyl-3-methylimidazolium generating methylacetate and *N*-ethylimidazole, the latter being presumably further decomposed in the reaction mixture with consequent production of hydrogen. Additional GC head space analysis showed clearly the presence of amines. Consequently, a baseline experiment without addition of glucose also showed constant hydrogen production over time with this particular ionic liquid.

The case of [EMIM][H–P(OMe)$O_2$] was revealed to be fairly more complex. On the one hand, blank tests without glucose showed neither significant hydrogen production (about 4 mL in the first hour) nor NMR spectral changes over 4 h in the presence of the Ru-catalyst at 180 °C. On the other hand, NMR analysis of the mixtures after the reactions showed no cation decomposition but modification of the anion. Initially, this was attributed to the hydrolysis of the anionic phosphonic ester caused by the water arising from the thermal dehydration of glucose.[47] The former reaction reasonably led to the new species [H–P(OH)$O_2$]$^-$ and methanol. The latter, was detected in the condensate sample. However, after deeper investigations, the

**Table 2** Overview of $[(p\text{-cymene})RuCl_2]_2$/TMEDA catalyzed dehydrogenation experiments using different methylphosphonate ionic liquids

| entry | ionic liquid | feedstock | $H_2$ produced in mL $h^{-1}$/Yield (%)[a] | TON |
|---|---|---|---|---|
| 1 | [EMIM][Me-P(OMe)$O_2$] | $C_6H_{12}O_6 \cdot H_2O$ | 65 (2.9) | 40 |
| 2 | [EMIM][Me-P(OMe)$O_2$][b] | $C_6H_{12}O_6 \cdot H_2O$ | 93 (4.2) | 58 |
| 3.1 | [$Bu_4$P][Me-P(OH)$O_2$][c,d] | $C_6H_{12}O_6 \cdot H_2O$ | 54 (2.6) | 37 |
| 3.2 | | $C_6H_{12}O_6 \cdot H_2O$ | 75 (3.6) | 47 |
| 3.3 | | $C_6H_{12}O_6 \cdot H_2O$ | 61 (3.0) | 39 |
| 3.4 | | $C_6H_{12}O_6 \cdot H_2O$ | 56 (2.7) | 35 |
| 3.5 | | $C_6H_{12}O_6 \cdot H_2$ | 41 (2.0) | 26 |
| 4 | [$Bu_4$P][Me-P(OH)$O_2$][b,e] | $C_6H_{12}O_6 \cdot H_2O$ | 116 (5.2) | 72 |
| 5.0 | [$Bu_4$P][Me-P(OH)$O_2$] | cellulose | 41 (2.0) | 26 |
| 5.1 | | cellulose | 31 (1.5) | 19 |

Reaction conditions: $C_6H_{12}O_6 \cdot H_2O$ 3.00 g (15 mmol), $[(p\text{-cymene})RuCl_2]_2$ 40 mg, TMEDA 300 mg, IL 50 g, 180 °C, 1 h; [EMIM] = 1-ethyl-3-methylimidazolium, [$Bu_4$P] = 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 moles $H_2$ from one mol of glucose. [b] Reaction at 150 °C. [c] 3.00 g aliquots of glucose were added to the system after hydrogen production ceased. [d] Dry ionic liquid. [e] Ionic liquid contained 5% of water.



phosphonic anion turned out to be unstable in the presence of water and ruthenium catalyst. In fact, reacting a water-donor, $Na_2SO_4 \cdot 10H_2O$, with [EMIM][H–P(OMe)$O_2$] in the presence of $[(p\text{-cymene})RuCl_2]_2$/TMEDA also resulted in the formation of hydrogen. The use of a hydrated salt as a water donor was mandatory in order to ensure slow release of water and to avoid immediate evaporation from the reaction system. Therefore, the higher yields over a longer time observed using the ionic liquid [EMIM][H–P(OMe)$O_2$] had to be attributed to the reaction between the anion and water. Water in our reaction system originated from the glucose monohydrate feedstock and from the dehydration of glucose itself at 180 °C.

Among the ionic liquids tested, the one containing the [Me–P(OMe)$O_2$]$^-$ anion was identified as the most stable system for the dehydrogenation of glucose. Therefore, our subsequent investigations addressed the reason for the relatively low hydrogen yields obtained with this system. At first, we considered the possibility of *in situ* N-heterocyclic carbene (NHC) complex formation as a reason for the low activity. It is well known[48] that the proton at C2 of the imidazolium ring possesses enough acidity to be abstracted even by relatively weak bases such as acetate. Consequently an NHC is generated, 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).[49] Therefore, we decided to shift from imidazolium systems to phosphonium salts.

The ionic liquid tetrabutylphosphonium methylphosphonate ([$Bu_4$P][Me–P(OH)$O_2$]) was prepared by simply reacting an aqueous solution of tetrabutylphosphonium 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]-[Me–P(OMe)$O_2$] and [$Bu_4$P][Me–P(OH)$O_2$] are presented in Table 2.

From the comparison of entries 1 and 3, a possible intermediation of NHC-complexes in the imidazolium ionic liquid can be excluded as results in the phosphonium and in the imidazolium ionic liquid are quite similar.

It has to be pointed out that the catalytic system applied here appeared to be quite robust. After 5 successive additions of glucose to the test system (Entries 3.1–3.5) within 48 h at 180 °C, the system still showed comparable catalytic activity (Fig. 1). From the slope of the curves, it can be deduced that after the first glucose addition a catalytic species is formed *in situ*, which was more active than the parental $[(p\text{-cymene})RuCl_2]_2$/TMEDA system. Analogous activation behavior was also observed in recent studies on hydrogen production from formic acid with other Ru-complexes by the group of Dyson.[50] Remarkably, glucose additions from 2 to 5 showed very similar slopes of hydrogen production, indicating a very similar catalytic activity of our system in all subsequent runs. However, a certain decrease in hydrogen yield from glucose addition 2 to glucose addition 5 was also observed. This behavior could be attributed to the accumulation of non-volatile by-products in the reaction mixture that interferes with the glucose thermolysis (see mechanistic discussions, further in the text).

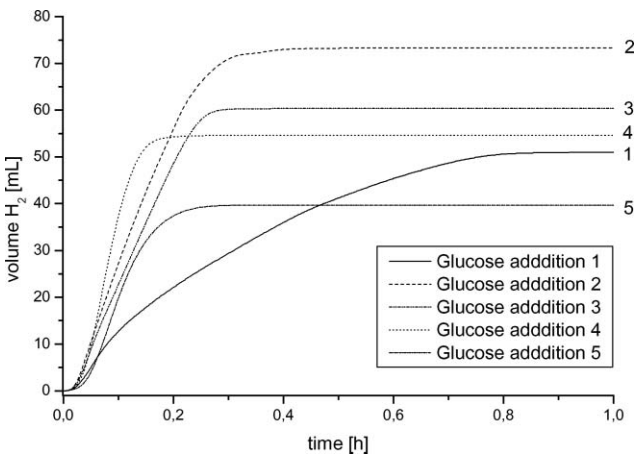



**Fig. 1** Hydrogen evolution *vs.* time for the different glucose additions in [$Bu_4$P][Me–P(OH)$O_2$] at 180 °C.

It is worth noting that the system remained liquid under reaction conditions throughout the whole experiment, as the formation of tarry solid did not occur in the ionic liquid.

Interestingly, the presence of a small amount of water in the ionic liquid seemed to play a beneficial role for the efficiency of

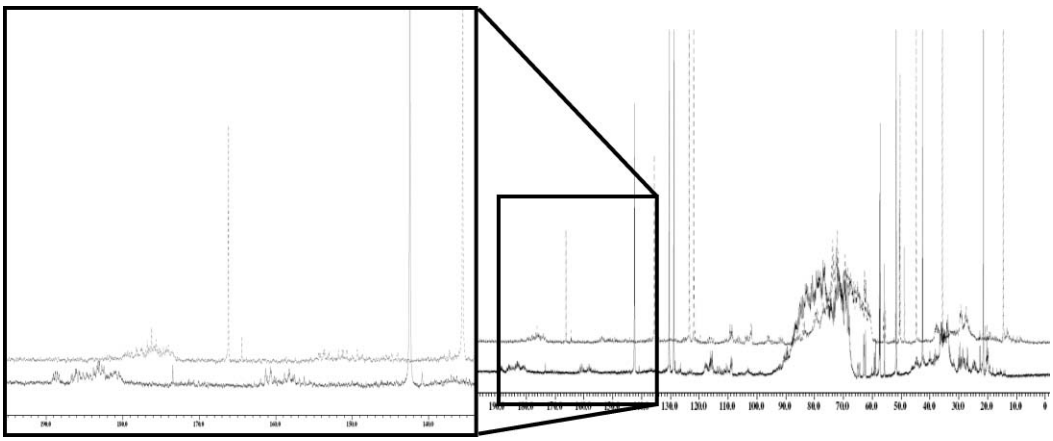
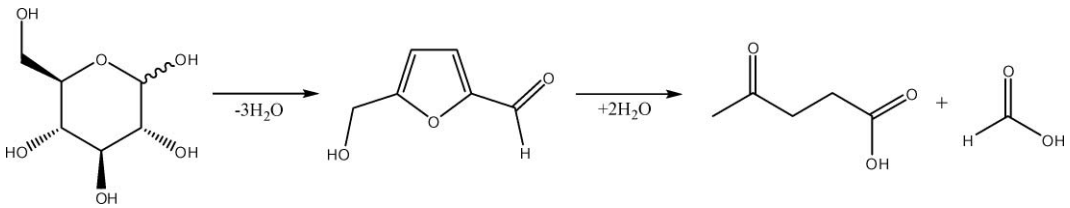


**Fig. 2** Thermolysis *vs.* catalysis in [EMIM][Me–P(OMe)$O_2$]. Dotted line: thermolysis of $^{13}C_6$-D-glucose; continuous line: dehydrogenation of $^{13}C_6$-D-glucose in the presence of [(p-cymene)$RuCl_2]_2$/TMEDA.




**Scheme 1** Formation of formic acid *via* de-hydration/re-hydration of D-glucose.[52]

hydrogen formation process (comparison of hydrogen formation in entries 3.1–3.5 and 4). System 4 containing a small amount of water in the ionic liquid gave an improved yield even under the milder operating conditions of 150 °C that were caused by the reflux of condensing water in our catalytic reactor. The role of additional water in the [$Bu_4P$][Me–P(OH)$O_2$] [(p-cymene)$RuCl_2]_2$/TMEDA system will be discussed in more detail in the analytical part below.

Next, we processed pure cellulose as a potential technical feedstock for this kind of catalytic ionic liquid based hydrogen production process. Surprisingly, it was possible to convert cellulose directly into hydrogen in the applied ionic Ru-catalyst solution. No further pretreatment of the cellulose was necessary and very mild conditions could be applied as for the conversion of glucose. The values of evolved hydrogen were in a comparable order of magnitude to those obtained with glucose. To the best of our knowledge, this is the first report on the direct catalytic production of hydrogen from cellulose without any chemical pretreatment. Thus, these experiments may open new perspectives for the catalytic conversion of cellulose in ionic liquids.

The evidence collected so far, namely the nature of gaseous products and the effect of water, suggested that this new catalytic system does not follow the common alcohol dehydrogenation mechanism (ref. 45 and references cited therein). In order to elucidate this hypothesis, we investigated the system by means of $^{13}$C-NMR spectroscopy using fully $^{13}$C-labeled glucose (99% $^{13}$C). The distribution of the $^{13}$C-labeled atoms was investigated during two sets of experiments: in the first set, thermolysis at 150 °C of $^{13}C_6$-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 the presence of [(p-cymene)$RuCl_2]_2$/TMEDA.

In all the ionic liquids tested, complete decomposition of glucose was observed within 90 min, except in [MMIM]-[$(MeO)_2PO_2$], where the glucose showed remarkable chemical stability. Furthermore, comparing the spectra of the Ru-free and the Ru-containing samples, only one pronounced difference was obvious: an intense singlet in the region 170–176 ppm appearing in the Ru-free samples that is missing in the respective Ru-containing systems (Fig. 2). This singlet peak can be easily attributed to formic acid, which formed during the thermal degradation of glucose.[51] Obviously, this formic acid is immediately transformed to hydrogen and $CO_2$ (in the observed 1 : 1 ratio) in the presence of the Ru-catalyst.[50] Accordingly, the worst system for glucose dehydrogenation was the one based on [MMIM][$(MeO)_2PO_2$], whose $^{13}$C-NMR monitoring showed no significant formic acid formation over 90 min. The GC-MS analysis of the gaseous product revealed an enrichment of $^{13}CO_2$ up to 90% (the missing $^{13}$C can be attributed to some $^{12}$C impurities in the labeled glucose feedstock, to experimental error or to contamination during the gas handling with atmospheric $^{12}CO_2$).

In this context, the role of water can be explained, too. It has been reported that the formation of formic acid from glucose proceeds through a de-hydration/re-hydration sequence (Scheme 1).[52]

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 by re-hydration.

This conclusion was further confirmed by glucose dehydrogenation experiments in [EMIM][Me-P(OMe)$O_2$] in the

presence of tolane (diphenylacetylene). The latter is acting as a "hydrogen trap" by its hydrogenation to stilbene. When 1,2,3,4,5,6,6-heptadeuteroglucose was dehydrogenated, incorporation of deuterium was found in the final stilbene (GC-MS analysis) as expected. However, when dehydrogenation was carried out with normal glucose, but in presence of deuterated water, even enhanced incorporation of deuterium in the final stilbene was observed (Fig. 3).

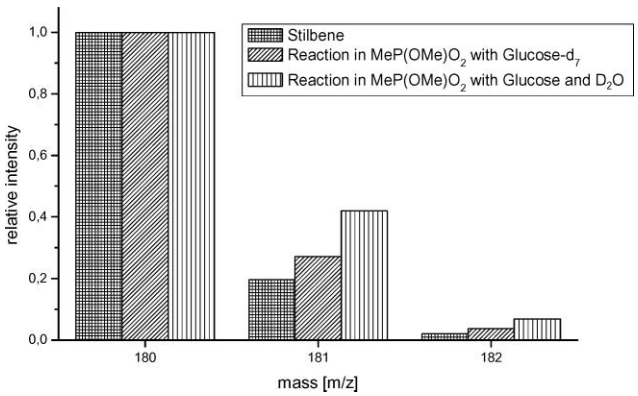



**Fig. 3** Mass spectra comparison between pure stilbene and stilbene obtained through tolane hydrogenation in the $[Bu_4P][Me–P(OH)O_2]$ [(p-cymene)$RuCl_2]_2$/TMEDA hydrogen production system in the presence of deuterated glucose and deuterated water, respectively.

This led us to the conclusion that, in the case of glucose, two processes were on-going in the system simultaneously, namely: 1) the thermal decomposition of glucose to formic acid and other unidentified products; 2) the fast catalytic decomposition of the resulting formic acid, promoted by the ruthenium catalyst. The same steps are expected to proceed also in the case of cellulose. However in this case, it is reasonable to assume that the thermal de-polymerization of cellulose in the ionic liquid/water system is a pre-requisite for hydrogen production. As a matter of fact, Barthel *et al.*[53] reported that noticeable degradation of cellulose already occurred by dissolution in ILs at around 100 °C. Therefore, it is assumed that under our reaction conditions cellulose is depolymerized to glucose, the latter undergoing the above mentioned reaction sequence. In the light of this mechanism, the hydrogen yields indicated in Tables 1 and 2 have to be reconsidered. While our initial calculation of the hydrogen yield was based on a theoretical hydrogen production of 6 moles $H_2$ per glucose unit (see also sub-titles), the mechanistic work proved that this is not realistic. Based on the latter it is reasonable to refer the hydrogen yield to a mechanism that produces a maximum of one mole of formic acid (and thus one mole of hydrogen) per mole of glucose unit. Consequently, all yields indicated in Tables 1 and 2 have to be multiplied with a factor of six to obtain the correct values in the light of this mechanism. This results in a maximum hydrogen yield *via* formic acid of 31.2% (run 4, Table 2) with glucose as substrate and a maximum yield *via* formic acid of 12.0% based on cellulose (run 5, Table 2).

## Conclusion

In conclusion we have demonstrated the feasibility of a new ionic liquid based catalytic system that allows the production of hydrogen from glucose and, more importantly, from cellulose. The issue of a suitable ionic liquid for such an application was addressed and the new ionic liquid $[Bu_4P][Me–P(OH)O_2]$ was synthesized and characterized. The ionic liquid/catalyst system was shown to be robust and stable up to 48 h at 180 °C, allowing up to six consecutive glucose dehydrogenation reactions without formation of solid tarry materials. Isotopic labeling studies allowed us to gain new insights into the reaction mechanism and to identify a reasonable reaction scheme for the carbohydrate dehydrogenation. It was found that glucose thermally decomposes in the applied ionic liquids through a dehydration/re-hydration process, yielding one mol formic acid per mol glucose. The generated formic acid was quickly and selectively transformed to $H_2$ and $CO_2$ in a Ru-catalyzed process. When cellulose was used as a feedstock, similar yields were achieved. Remarkably, the applied ionic liquid/Ru-catalyst system is able to promote the thermal depolymerization of cellulose, the thermal decomposition of glucose, and the hydrogen formation from formic acid, simultaneously, in one single reactor. Thus our study presents a new approach for exploiting a non-edible bio-feedstock as a feedstock for the catalytic production of hydrogen.

Despite the fact that there are some open issues that have to be addressed, *i.e.* the hydrogen yield has to be substantially increased and regeneration of the ionic liquid by removal of biomaterial degradation products, it can be hypothesized that this kind of cellulose based hydrogen production technology could be integrated into advanced bio-refinery concepts, as almost all existing bio-refinery schemes suffer from the lack of "non-fossil" hydrogen; *e.g.* for fuel production from biogenic polyols a considerable amount of hydrogen is required in order to decrease the oxygen content and obtain a fuel like quality product.

Identification of superior ILs, development of new and stable catalysts and optimization of reaction parameters are aspects currently under investigation in our group, in order to advance this challenging concept towards higher process efficiency.

## Experimental

All reagents, catalysts and ionic liquids were commercial and used as received. Cellulose was purchased from J. Rettenmaier & Söhne & Co. GmbH in the form of micro-fiber. The $^{1}H$, $^{31}P$ and $^{13}C$-NMR were recorded on a JEOL ECX-400 MHz. GC-MS were recorded using a Varian GC 3900/MS Saturn 2100 T equipped with a VF 5-ms (30 m × 0.25 mm) column for liquid phase analysis and with a PoraBond Q FS (25 m × 0.25 mm) column for gaseous product analysis. Hydrogen was detected with an EMERSON Hydros 100 TCD. The identity of gaseous products was confirmed *via* GC analysis. The water content of the ionic liquids was determined with K–F.

### Synthesis of tetrabutylphosphonium methylphosphonate ($[Bu_4P][Me-P(OH)O_2]$)

500 mL of an aqueous $[Bu_4P][OH]$ solution (40% w/w) were charged in a 1 L flask. The required stoichiometric amount of $Me–P(OH)_2O$ (1 eq) was dissolved in the minimal amount of water and the resulting solution added drop wise to the

[$Bu_4P$][OH] solution over 10 min. When the addition was completed, the flask was transferred to a rotavapor and the water evaporated. The final very viscous liquid was further dried overnight (15 mbar, 60 °C). Quantitative yield of an off-white waxy solid was obtained. Water content: 5%; $^1$H-NMR ($D_2O$): 0.73 (12H, t, $CH_3CH_2$); 1.08 (3H, d, $CH_3P$); 1.26 (8H, tt, $CH_2CH_2CH_3$); 1.35 (8H, tt, $CH_2CH_2CH_2$); 1.96 (8H, dt, $CH_2CH_2P$). $^{13}$C-NMR ($D_2O$): 23.5; 23.3; 22.9; 22.8; 17.8 (d, $CH_3P$). $^{31}$P-NMR ($D_2O$): 33.9 (1P, $P(^nBu)_4$); 24.7 (1P, $CH_3PO_3H$).

### Dehydrogenation reaction (general procedure)

The dehydrogenation reactions were carried out in glass equipment using a TCD as a hydrogen detector (see Supporting Information†). The ionic liquid (50.0 g), [(p-cymene)$RuCl_2$]$_2$ (40 mg), TMEDA (300 mg) and the feedstock (3.0 g) were charged in the apparatus. The system was evacuated and purged with argon (3 times), then the heating was switched on and the reaction started.

### $^{13}$C labeling experiment

60 mg of $^{13}C_6$-glucose were dissolved in the relevant ionic liquid. This solution was divided into two parts. One was charged in a NMR tube for thermolysis, the second one was charged in a NMR tube containing [(p-cymene)$RuCl_2$]$_2$ (2–3 mg) and TMEDA (18–20 mg). Both tubes were put in an oil bath at 150 °C for 90 min. After the reaction time was over, $D_2O$ (0.5 mL) was added and content analyzed.

### $^2$H labeling experiment

Two screw-capped test tubes were charged with [EMIM][Me–P(OMe)$O_2$] (500 mg), tolane (100 mg), [(p-cymene)$RuCl_2$]$_2$ (3 mg) and TMEDA (20 mg). In one test tube 1,2,3,4,5,6,6-D-heptadeuteroglucose (60 mg) and $H_2O$ (25 mg) were added. In the second one, D-glucose (60 mg) and $D_2O$ (25 mg) were added. Both tubes were placed in an oil bath at 150 °C for 90 min. After the reaction the content of the tubes was diluted with water (5 mL) and extracted with chloroform (1 mL, 3 times). The chloroform extracts were dried over $MgSO_4$ and analyzed with GC-MS.

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