Hydrogen generation from glucose catalyzed by organoruthenium catalysts under mild conditions

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Concerns about the depletion of fossil fuel reserves and environmental pollution make hydrogen an attractive alternative energy source. Here, we first describe a catalytic reaction system that produces H₂ from glucose using a homogeneous catalyst \([p\text{-cymene}]\text{Ru(NH₃)}\text{Cl}_2\) with the maximum TOF = 719 h⁻¹ at 98 °C and an initial pH = 0.5.

According to the Greenhouse Gas Bulletin released by the World Meteorological Organization in 2016, atmospheric carbon dioxide concentration surpassed the upper limit of 400 ppm in 2015 and is forecast to reach a peak over the next few years. To cope with global warming, it is important to reduce anthropogenic CO₂ emissions and develop renewable resources. Because of its high energy efficiency and clean combustion characteristics, hydrogen is not only one of the most important chemicals in the chemical industry but also an important fuel for internal combustion engines and fuel cells in the future.

So far, the production of hydrogen is mainly through reforming reactions which require a lot of energy input to drive the reactions. Furthermore, hydrogen storage is facing a bottleneck, as conventional liquid-hydrogen or pressed-hydrogen storage methods greatly increase the cost of hydrogen. Recently, the hydrogen storage processes of organic small molecules at normal temperatures and pressures have been widely investigated, and significant results have been achieved. The TOF values of formic acid dehydrogenation have exceeded 480 000 in succession. The TOF value of a new Pd–Ag nanofacet catalyst that was synthesized recently by the Zhou group has exceeded 3 million. Generally, the preparation processes of common hydrogen storage materials such as formic acid, methanol, ethanol, etc. involve the modification of massive quantities of fossil fuels. The higher the production yield of such substances, the greater the pressure on the environment.

The full transition to a hydrogen society can be realized only when hydrogen is produced via renewable resources such as biomass and water. As they are representatives of biomass, glucose and cellulose can be prepared without causing any pollution. P. Wasserscheid and Dumesic and his co-workers have already achieved great success in biomass hydrogen production, making it possible for biomass to produce hydrogen efficiently. However, the current processes of biomass dehydrogenation such as gasification and steam reforming are restricted to harsh external conditions. The former needs to proceed with temperatures higher than 800 °C to obtain a relatively pure gaseous product. The latter is carried out at temperatures ranging from 500 °C to 700 °C, as well as high pressures of typically 300 bar being essential. Other processes, such as the photocatalytic reforming of biomass, are restricted to extra specific light source. So it is difficult to meet the requirements of wide applications in the near future.

Here, we first describe a glucose dehydrogenation process at temperatures below 100 °C and atmospheric pressure using a water-soluble ruthenium-based p-cymene pincer complex \([p\text{-cymene}]\text{Ru(NH₃)}\text{Cl}_2\). No additional organic matter is required, and hydrogen generation was observed with an excellent turnover frequency (719 h⁻¹).

Inspired by these recent studies, herein, the catalytic activities of a series of water-soluble organo Ru, Rh, and Ir complex catalysts for glucose dehydrogenation were first investigated. Equal amounts of different catalysts were added into the catalytic system, and all of the experiments were carried out at 98 °C. The reaction methods used in this system have many advantages, such as easily available raw materials, mild reaction conditions, a short synthetic route, and the fact that no alkaline medium is needed, and these advantages offer the possibility for their practical industrial application. The overall reaction is shown as follows:
Catalytic activities of a series of organo Ru, Rh, and Ir complexes for β-glucose hydrate (C₆H₁₂O₆·H₂O) dehydrogenation at 98 °C

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Vₐ/V (%)</th>
<th>TOF₀₉₈ (h⁻¹)</th>
<th>TOF₉₈ (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[(p-Cymene)Ru(NH₃)]Cl₂</td>
<td>60</td>
<td>270</td>
<td>719</td>
</tr>
<tr>
<td>2</td>
<td>[RhCp*(NH₃)]Cl₂</td>
<td>36</td>
<td>71.5</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>[RhCp*(bpym)]Cl₂</td>
<td>2.88</td>
<td>6.8</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>[(p-Cymene)Ru(bpym)]Cl₂</td>
<td>0.29</td>
<td>0.75</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>IrCp*(bpym)]Cl₂</td>
<td>0.15</td>
<td>0.42</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>IrCp*(phen)]Cl₂</td>
<td>0.1</td>
<td>0.08</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>[(p-Cymene)Ru(bpym)]Cl₂</td>
<td>0.02</td>
<td>0.04</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>[(p-Cymene)Ir(H₂O)]SO₄</td>
<td>0</td>
<td>0</td>
<td>—</td>
</tr>
</tbody>
</table>

Reaction conditions: β-C₆H₁₂O₆·H₂O (0.26 g, 15 mmol), deionized H₂O (2 mL), sulphuric acid (pH = 0.5, 5 μmol), and catalyst (1 mg).

\[
\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} \xrightarrow{\text{catalyst}} 12\text{H}_2 + 6\text{CO}_2
\]

\[\Delta G_m^\circ = -32.58 \text{ kJ mol}^{-1}\]

Table 1 shows that the rate of H₂ production is largely dependent on the kind of the reactive metal and the organic ligands. [(p-Cymene)Ru(NH₃)]Cl₂ exhibited the highest activity, displaying a maximum TOF value of up to 719 h⁻¹. When the reaction reached a stable stage, 60% hydrogen content can be observed in the gaseous product. [(p-Cymene)Ru(bpym)]Cl₂ showed quite a low rate compared with [(p-cymene)Ru(NH₃)]Cl₂. The rhodium catalysts followed a weaker activity trend than that observed for the ruthenium analogues; [RhCp*(NH₃)]Cl₂ displayed a higher dehydrogenation rate compared to [RhCp*(bpym)]Cl₂. Intriguingly, catalysts bearing the phen ligand had poor reactivity. The iridium complexes coherently displayed low reaction rates. We suspect that catalysts bearing the phen ligand had poor reactivity. The iridium catalysts showed quite a low rate compared with [(p-cymene)Ru(NH₃)]Cl₂. The rhodium catalysts followed a weaker activity trend than that observed for the ruthenium analogues; [RhCp*(NH₃)]Cl₂ displayed a higher dehydrogenation rate compared to [RhCp*(bpym)]Cl₂. Intriguingly, catalysts bearing the phen ligand had poor reactivity. The iridium complexes coherently displayed low reaction rates. We suspect that the higher the activity of the catalysts, the higher the number of empty coordination sites of the ligands bound to the active site.

As shown in Fig. 1, we obtain a relationship between the gas volume and reaction time of the glucose dehydrogenation using [(p-cymene)Ru(NH₃)]Cl₂. Apparently, the gas volume increases rapidly with time in the initial 10 min. Then, the gas production rate decreases from 0.74 mL min⁻¹ to 0.012 mL min⁻¹. It is worth noting that the low conversion rate measured in the stable stage is not caused by the deactivation of the catalyst, as the longer reaction time of the [(p-cymene)Ru(NH₃)]Cl₂ catalyst may lead to further reactant consumption. To consider the complex products from the decomposition, the components of the gaseous product need to be detected. We used GC to measure the contents of the gaseous product during the total process of glucose decomposition.

The analysis of the gas phase shows that besides hydrogen, the only detectable gaseous product was CO₂ (Fig. 2a). No evidence of CO (below the detection limit) was detected in the generated gas (Fig. 2b). Fig. 2c shows that, during the first 10 h, the mole ratio of H₂ and CO₂ (rH₂/CO₂) decreases from about 12 to 4. Remarkably, in the initial 10 minutes, no CO₂ was detected in the gas chromatogram (Fig. S6, ESI†). The content of the carbon dioxide increased gradually with the time increase, whereby hydrogen and CO₂ were detected in a nearly 4:1 balance ratio. The control experiment, which operates with the same reactants [deionized water and glucose] but without the addition of the Ru-catalyst, showed no hydrogen production or gas volume change. As shown in Fig. S3 (ESI†), the effect of water vapor is negligible relative to the amount of gas evolved from the glucose decomposition.

The effects of the reaction parameters, such as reaction temperature, the initial concentration of glucose, and the pH value of the reaction solution, on the hydrogen evolution were systematically investigated. Fig. 3a shows that a higher temperature can greatly accelerate the dehydrogenation of glucose, and the TOF value can reach up to 270 h⁻¹ at 98 °C. Simultaneously, we can obtain the apparent activation energy (E_a) using the excellent linear correlation between ln(TOF) and (1/T). According to the high correlation coefficient, which exceeds 0.99 in Fig. 3a, the E_a value could be determined accurately. The E_a value for [(p-cymene)Ru(NH₃)]Cl₂ (2.8 μmol) is 97.0 kJ mol⁻¹.

As exhibited in Fig. 3b, there is an optimal catalytic activity under different glucose concentrations. The H₂ evolution increases with the increase in glucose concentration and reaches a maximum at C_glucose = 0.66 mol L⁻¹, followed by a sharp decrease upon increasing the concentration to 2.52 mol L⁻¹. This can be an indication of H₂O taking part in the dehydrogenation process, and the overall reaction of glucose with water over
formic acid accompanied by its decomposition into H₂ and CO₂. It has been reported that glucose was first thermally decomposed into water, resulting in a mixture of hydrogen and carbon dioxide gas. The side reactions of the hydrogen consumption strongly affect the hydrogen production. On the whole, the H₂ evolution rate increases with decreasing pH and reaches a maximum at pH = 0.5, followed by a decrease upon decreasing the pH to 0. Therefore, acidic conditions favour the hydrogen production process, whereas alkaline conditions have adverse effects on the reaction. This is also consistent with the other studies that reported that the decomposition of glucose is more prone to happen under acidic conditions.

The pH of the solution has a significant effect on the hydrogen evolution. Generally, the Ru–H intermediate (Ru = \([p\text{-cymene}]\text{Ru(NH}_3\text{)}\text{Cl}_2\)) will be produced during the dehydrogenation process of an alcohol or an aldehyde. Similarly, glucose dehydrogenates via a dehydrogenation process of the intermediate: the H⁺ ions in the solution combine with the dehydrogenation at 98 °C. The primary AWS reaction pathway of hydrogen production from glucose using \([p\text{-cymene}]\text{Ru(NH}_3\text{)}\text{Cl}_2\) in the aqueous phase, and no additional organic matter was required. Renewable hydrogen with a low CO concentration can be produced at 98 °C and constant pressure with a remarkable TOF value of 719 h⁻¹, which makes this system promising for application in hydrogen fuel cells in the future. The TOF reaches a maximum at \(C_{\text{glucose}} = 0.66 \text{ mol L}^{-1}\). The stronger the buffer solution acidity, the more beneficial it is to hydrogen production (pH ≥ 0.5). The primary AWS reaction only produced hydrogen, and no carbon dioxide was detected here. Formic acid was generated as an intermediate as the reaction went on, which was the rate-determining step. The mechanism of the reaction needs further investigation. The reaction is of great
significance for solving the current environmental pollution and energy crisis, and furthermore, to achieve a true carbon recycling process and ultimately achieve zero emissions of carbon.

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References
