

A comparison of methane decomposition and water splitting reaction methods as a means to produce molecular hydrogen.

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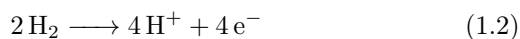
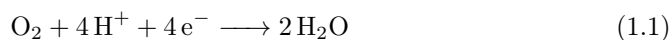
Abstract

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1 Introduction

As the global energy demand continues to increase, a sustainable alternative to fossil fuels is desperately needed. Hydrogen gas potentially presents an innovative solution, but the energy costs for production are currently prohibitive. An efficient synthesis could be a revolutionary step towards a more sustainable future as the hydrogen fuel cell has many advantages over current energy sources; a hydrogen storage tank can be refilled much more quickly than a battery can be recharged,⁴ making it far more practical for use in transport.

In a fuel cell, electricity is produced by reducing oxygen at the cathode (1.1) and hydrogen at the anode (1.2).



This reaction leads to the production of heat, water and an electrical potential,² which is a major advantage over systems which produce CO₂. These reasons alone make investigating the sustainability of hydrogen production a worthwhile endeavour.

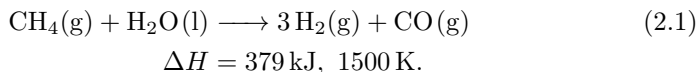
We will start by discussing the traditional methods of synthesis and where they fall short by taking into account the twelve principles of green Chemistry.⁵ Then we will look at new approaches in the areas of methane decomposition and water splitting reactions, and how these compare to the traditional synthetic techniques. The most promising method from each feedstock will be analysed further, concluding on if and how these new approaches can solve the problems preventing widespread adoption of hydrogen as a fuel.

We will focus on how the use of metal catalysts and how they can improve the rate of reaction, allow for more mild reaction conditions, and reduce the cost of reactions. While we are concerned with the environmental impact of these processes, this review will not discuss the sourcing of the feedstock for each reaction, but will assume the methane being used in these reactions comes from carbon neutral sources such as biomass⁶ and not from petrochemical routes. We also realise that in order for a process to be viable on an industrial scale it must be possible to scale up the reaction, however the practical implications of scaling up will not be discussed in this review.

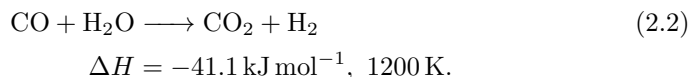
2 Traditional Methods

2.1 Steam methane reformation

The steam methane reformation reaction is an extremely inexpensive and widespread method for producing molecular hydrogen in a commercial setting. The reaction follows the scheme:⁵



There is also a secondary mechanism for extracting hydrogen from the carbon monoxide by-product of this first stage reaction, which runs at a lower temperature and is called a water gas shift reaction.^{5,7}



This basic reaction scheme is applied to generate approximately 40% of the global hydrogen demand;⁸ primarily due to using readily available reagents, it is a mature technique and it is inexpensive.

Although both reactions (2.1) and (2.2) can proceed without the use of a catalyst one is often employed for the water gas shift reaction (2.2) in order to increase the hydrogen yield. Iron-chromium or copper-zinc compounds are often used dependant on if the reaction is a low- or high-temperature shift. EXPAND on this.

2.2 Uncatalysed electrolysis

This section will discuss uncatalysed water splitting via electrolytic methods, with specific focus on why this method is an important foundation and the theory behind it. There will also be a discussion of why this method alone is not a suitable solution to the problem of producing hydrogen on an industrial scale.

2.3 Enzyme catalysed production

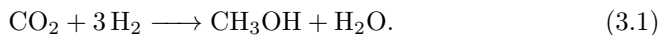
This will discuss how the [FeFe]–hydrogenases can generate molecular hydrogen in the body as a molecule for energy storage. It will discuss the mechanism of this process, the transition metal centres employed as well as how it came to be, the biological significance of hydrogen and also some attempts to replicate this using bioinorganic chemistry. We can also discuss the application of using organisms to generate hydrogen industrially.

2.4 Discussion

In this section we will discuss and evaluate the current methods, their drawbacks and the reason that none of these methods can currently meet the demands of a hydrogen fuel based society. We will also outline the criteria that an alternative method must be able to meet in order to be a viable solution to energy efficient production of hydrogen for use in fuel cells.

3 CH₄ methods

This research is looking to use the H₂ from methane decomposition to upcycle waste gases, such as CO₂, from industry:



For this, a steady stream of H₂ gas is needed, which simply cannot be provided by water electrolysis due to the reasons outlined previously. Methane pyrolysis has an enthalpy of reaction ($\Delta_R H$) of 37.5 kJ mol⁻¹, while the electrolysis of water has a $\Delta_R H$ of 268 kJ mol⁻¹, making methane decomposition more thermodynamically favourable than the electrolysis of water. Methane pyrolysis occurs via a free radical dissociation reaction, involving one of a selection of catalysts available. The initial step is the chemisorption of methane onto the catalytic surface.

This reaction mechanism gives rise to no waste gases such as CO₂ but does has the issue of elemental carbon production which can lead to the degradation of the catalyst as carbon is deposited upon the catalyst surface (catalytic poisoning).

Methane pyrolysis occurs via a free radical dissociation reaction, involving one of a selection of catalysts available. The initial step is the chemisorption of methane onto the catalytic surface.

Equations 3-81

This reaction mechanism gives rise to no waste gases such as CO₂ but does has the issue of elemental carbon production which can lead to the degradation of the catalyst as carbon is deposited upon the catalyst surface (catalytic poisoning).

Iron can also be used as a catalyst, its catalytic activity is lower than that of nickel and cobalt, however it is more resistant catalytic deactivation. This is because carbon has higher rate of diffusion in iron, meaning it does not deposit itself upon the active site of the catalyst. It also has the advantage of being able to operate at high temperatures 700 to 1000°C. It is also cheaper and less toxic than nickel and cobalt catalysts.

Both supported and non-supported iron catalysts have been tested such as: [Fe(CO)₅], [Fe(cp)₂]. However, these types of clusters can give result in unwanted gases meaning the H₂ has to be separated from the gaseous mixture. A catalyst with strong support increases the carbon dispersion and reducibility of the metal along with preventing sintering of metal particles. However, an excessively strong support may hamper the reducibility of metal oxides. A supported catalyst has a better performance as it balances the carbon dispersion resulting in a longer lasting catalyst while maintaining the reducibility of the metal species.

Ni-Pd or Ni-Cu can be used as a catalyst promoter; they have high lattice constants meaning they have a high capacity for waste carbon build up meaning they are longer living catalysts. While these alloys are longer lasting, they have a lower rate of reaction. The palladium or copper in the alloy serve as dopants, helping to initiate the hydrogen spill over effect.

Metal catalysts have reduced performance as the reaction progresses as the active sites become encapsulated by elemental carbon, therefore carbon-based catalysts should be considered. These catalysts need higher operating temperatures have lower catalytic activity but are lower cost, have a high resistance to temperature and have a high stability, do not deposit toxic materials into the carbon by-product, tolerate impurities in the reaction such as sulphur and produce zero CO₂ emissions as the catalyst doesn't need to be regenerated.

There are three types of carbon catalyst; highly ordered, less ordered, and disordered. Disordered carbon catalysts have free valence sites or coordination sites these are known as high energy sites (HES). The more HES's there are the faster the rate, as these are thought to initiate the mechanism. More oxygenated catalysts have a higher activity but release COx.

This is because as COx is produced new active sites are created on the surface of the catalyst. The reaction mechanisms for many of these carbon catalysts are not known.

3.1 *Radical chain reactions*

Here we will start by discussing the pros and cons of free radical chemistry and the general reaction pathway. We will then talk about how the use of each of the catalysts can change the reaction conditions and pathway and give the advantages and the disadvantages of the method and its greenness.

3.2 *Discussion*

This section will deal with evaluating the methane decomposition methods given above; why they are relevant, and which shows more promise. The work outlining each method will be briefly discussed, relating each of them back to how they can provide a solution to the initial problem and where they fall short.

4 H₂O methods

4.1 *Using [Co(N₄ - Py)(H₂O)](PF₆)₃ as a catalyst*

We will begin by discussing the synthetic method for producing this catalyst and similar catalysts along with their redox potentials. We will include discussion of the thermodynamics of the method for producing H₂ from H₂O, the rate of H₂ production and how pH affects it.

4.2 *Using GaN in photolytic H₂ production*

This method needs to include how the compound is made and the relevance of the N₃⁻ conduction and valence-band to the oxidation and reduction potentials of H₂O. The thermodynamics of the process and its rate of reaction along with the reaction conditions and its efficiency are also important to this approach and will be analysed. Another point to include is the advantages of the reaction like its greenness but also its disadvantages such as power usage, degradation of the Xe lamp and poor rate of reaction.

4.3 Photocatalysts for H_2O splitting with graphene oxide- TiO_2

We will start with a comparison of the initial activity of hydrogen for various metal sulphide catalysts with differing methods of loading a Pt co-catalyst. We will then look at $CuGaS_2$ in particular, comparing the initial H_2 activity under different conditions (i.e. with or without Pt and with or without a reduced graphene oxide (RGO)- TiO_2 co-catalyst). Next we will look at a comparison of various metal co-catalysts with Pt. Finally evaluate the advantages and disadvantages of metal sulphide and (RGO)- TiO_2 co-catalysts.

4.4 Dehydrogenation of methanol in $MeOH/H_2O$ using Ru with a chelating ligand as a catalyst

We will start by looking at the generation of the catalyst, its use in the catalytic cycle which produces H_2 . Then we will look at the rate, thermodynamics and yield of the reaction. Finally we will give some analysis of the advantages and disadvantages of this method and its greenness.

4.5 Thermo-photo catalytic water splitting reactions using methanol as the sacrificial reagent

We will start by looking at the generation of the $NiOX/TiO_2$ and its use in the thermo-photo catalytic water splitting with methanol as the sacrificial agent on a light-diffuse-reflection SiO_2 substrate. Then we will look at the effect of conditions on yield and the optimum production rate achieved. Finally give some analysis of the advantages and disadvantages of this method compared to the traditional methane reformation method and consider the sustainability of this process taking into account the 12 principles of green chemistry.

4.6 Discussion

This section will deal with evaluating the water electrolytic methods given above; why they are relevant, and which show more promise. The work outlining each method will be briefly discussed, relating each of them back to how they can provide a solution to the initial problem and where they fall short.

5 Evaluation

This section will look broadly at the two methods which have been outlined in the chapters above. We will look at which approach has more promise and more viable solutions to the question, as well as where they both fall short of meeting the task. Finally there will be a discussion of the challenges associated with making these techniques scalable.

6 Conclusion

6.1 Evolution of the most promising methodology

6.2 Future innovations

References

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