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

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Abstract

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,[1] 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).

$$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O \tag{1.1}$$

$$2\,H_2 \longrightarrow 4\,H^+ + 4\,e^- \tag{1.2}$$

This reaction leads to the production of heat, water and an electrical potential,[2] which is a major advantage over systems which produce CO_2. 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 tey fall short by taking into account the twelve principles of green Chemistry.[3] 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 biomass[4] 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 Methane steam reformation

Here we will look at the process of methane steam reformation, the most commonly used synthesis of hydrogen by industry. This section will discuss the common conditions under which the reaction is done, and why this reaction does not solve the current issue that the review is discussing. We will also find why this process is so widely used and what benefits it has over other lesser used techniques.

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 CH_4 methods

3.1 Thermal decomposition methods

In this section we will look at the synthesis of Fe−M (M=Mo, Ni, Pd) catalyst. We will then look at the differing temperatures for producing H_2 given different Fe/M ratios for each M. We will then look at a comparison between the various Fe−M with the use of pure Fe in terms of the temperature required for production of H_2. Finally we will discuss the advantages and disadvantages of the Fe−M catalysts for production of H_2.

3.2 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 0f the method and its greenness.

3.3 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 H_2O methods

4.1 Using $[Co(N_4 - Py)(H_2O)](PF_6)_3$ 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 H_2 from H_2O, the rate of H_2 production and how pH affects it.

4.2 Using GaN in photolytic H_2 production

This method needs to include how the compound is made and the relevance of theN_3^- conduction and valence-band to the oxidation and reduction potentials of H_2O. 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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