**BSc Literature Project**

**Group Name (same one for the entire project) -** Phenolmenal

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**Working Title of Project:** A comparison of methane decomposition and water-splitting reaction methods as a means to produce molecular hydrogen.

**Bibliography Week 4**

**Introductory statement**

In this literature review we will consider the synthesis of Hydrogen gas using inorganic complexes as catalysts to reduce the currently prohibitive energy costs. We will discuss the viability of a variety of processes which yield Hydrogen gas on an industrial scale with a special focus on sustainability; the hope of energy efficient Hydrogen production being to provide a long-term solution to fossil fuels. We will evaluate the progress currently made by considering the 12 principles of green Chemistry.

**Reference list**

1. R. Manisha, S. Arjun, R. Krishnan, *Physical chemistry chemical physics*, 2016, **18 (36)**, 25687-25692.

This paper discusses Hydrogen evolution from water using molybdenum oxide clusters in the gas phase, in particular modelling the potential energy surface of a proposed catalytic cycle using density-functional theory. The method allows for the production of H2 from feedstock by way of a catalytic cycle, in which a sacrificial reagent is used to reduce the Mo2O5- back to Mo2O4-. The paper goes on to evaluate the ideal sacrificial reagent for the reduction of H2O to H2. The proposed method is a two-step cycle: Step 1: Mo2O4 + H2O 🡪 Mo2O5 + H2, Step 2: Mo2O5 + X 🡪 Mo2O4 + XO. H2 is the clean fuel of the future and thus its sustainable production is essential.

1. P. Wang, G. Liang, C. Boyd, C. Webster, X. Zhao, *European journal of inorganic chemistry,* 2019, **15**, 2134-2139.

This article discusses the catalytic evolution of molecular hydrogen by a mononuclear cobalt complex {[Co(N4‐Py)(H2O)](PF6)3] where N4-Py = N‐methylpyridine‐2,11‐diaza[3,3](2,6)pyridinophane}. The proposed reactions are water splitting using either electrolytic or photolytic methods. Several reactions taking place at a variety of pH numbers with varying solvated species were attempted to evaluate the conditions which provide the highest yield. Their proposed method is clean and has the potential for industrial scale generation of H2; 200 mol of product is generated per 1 mol of spent catalyst. At larger scale this would make producing H2 for use in fuel cells a viable alternative to current technologies.

1. R. E. Rodríguez-Lugo, M. Trincado, M. Vogt, F. Tewes, G. Santiso-Quinones, H. Grützmacher, *Nature chemistry*, 2013, **5 (4)**, 342-347

A method is proposed in this paper of recreating the function of the enzyme group Alcohol Dehydrogenases (ADH), a biological molecule which serves to oxidise alcohol species to their corresponding aldehydes or ketones. This work demonstrates a process by which ruthenium complexes can be used to catalyse the dehydrogenation of methanol in a MeOH/H2O mixture under neutral conditions to H2 and CO2. During this, the entire hydrogen content is converted to molecular H2. Avoiding the production of CO gas has presented a major challenge as it can act as a catalytic poison. The ruthenium complexes are characterised, and a mechanistic schema is suggested.

1. K. Ohkawa, W. Ohara, D. Uchida, M. Deura, *The Japan Society of Applied Physics*, 2013, **52 (8)**, 08JH04-08JH04-3.

This paper looks at the use of a GaN catalyst with a NiO co-catalyst in the water splitting reaction producing H2 and O2. This catalytic cycle requires no sacrificial reagent however it has a relatively low energy efficiency (1% over 500 hours). There is also an issue with volume of production, with the paper reporting a volume of 184mL/cm2 of catalytic surface. This could lead to issues with increasing scale, although the research is promising more work is needed on both rate and efficiency for this to be a viable overall solution to the issue.

1. N. Sánchez‐Bastardo, R. Schlögl, H. Ruland, *Chemie ingenieur technik*, 2020, **92 (10)**, 1596-1609

This article is looking at the viability of methane as a means to produce H2 via radical pyrolysis. As C-H bonds have very strong bond energies traditionally this process must take place at 1100-1200oC, however the use of transition metals such as Ni, Fe and Co can mitigate the extreme reaction conditions required. This is facilitated by electron density transferring from the C-H bond to the 3d orbitals of the metal atoms and is further enabled by the crystal structure of the metals allowing for a high degree of diffusion throughout them. This article discusses how these metals can be used to create a CO2 free process of generating molecular hydrogen through methane pyrolysis as well as the associated challenges with using metal catalysts.

1. N. Shah, D. Panjala, G. P. Huffman, *Energy Fuels,* 2001, **15 (6),** 1528–1534

This article presents early research on the use of transition metal catalysis for the production of H2 from the decomposition of methane. The temperatures required for this thermal decomposition are compared for various Fe-M (M=Pd, Mo and Ni) compounds. The reaction uses these nanoscale catalysts supported on alumna and demonstrates a 400-500oC variation in the temperature at which methane will thermally decompose with catalysis versus without. This research is valuable as the metals used are non-noble, although there is also comparison to an Fe-Pd catalyst which obtains the lowest temperatures and highest hydrogen concentration (80%) in the product stream.

1. K. Iwashina, A. Iwase, Y. H. Ng**,** R. Amal**,** A. Kudo**,** *J. Am. Chem. Soc.,* 2015, **137 (2)**, 604–607

This paper compares the usefulness of various metal sulphide compounds as photocatalysts for water splitting reactions in the context of producing H2, with graphene oxide-TiO2 as an O2 producing catalyst. The initial activity of H2 for each catalyst was measured, with CuGaS2 with 0.1 Pt by weight loaded by adsorption having the highest activity. The paper goes on to compare a range of co-catalysts for the CuGaS2 and determines that Pt was the most suitable. This paper shows the usefulness of non-noble metal catalysts in water splitting reactions, even if small amounts of Pt are required for the best results.

1. Y. Xu, M. Gao, Y. Zheng, J. Jiang, S. Yu, *Angewandte Chemie* *(International ed.)*, 2013, **52 (33)**, 8546-8550

This paper presents a noble-metal free method of producing H2 from an electrolytic water splitting process, in acidic conditions by use of Ni/NiO/CoSe2 nanocomposite deposited on a glassy carbon electrode. This hybrid produced superior results by way of a greater reduction potential than any of the individual components. This is a demonstration of the potential of non-noble metal catalyst hybrids in the hydrogen evolution reaction. Despite this potential there was still a significant gap in efficacy between the proposed method and a traditional commercial Pt/C catalyst.

1. S. Fang, Z. Sun, Y. Hang Hu, *ACS Catal.*, 2019, **9 (6),** 5047–5056

In this paper, NiO on a TiO2 substrate is discussed as a catalyst for the thermo-photo catalytic water splitting reaction. Methanol is the sacrificial agent used, with the research demonstrating a hydrogen evolution rate five orders of magnitude greater than room temperature at 260oC and approximately twice the rate under simulated AM 1.5G sunlight at the same temperature. NiO-TiO2 catalysts could find use in thermo-photo catalytic settings where constant illumination does not present any challenge. Using methanol in the reaction means that the reagent can be obtained by the conversion of biomass.

1. Y. Zhang, J. Zhou, Y. Chen, Z. Wang, J. Liu, K. Cen, *International journal of hydrogen energy*, 2008, **33 (20)**, 5477-5483

This paper uses a slightly different approach and instead uses a nickel-ceria catalyst to split HI in the sulphur iodine cycle. The paper compares the HI conversion rates of pure CeO2 with Ni loading G, Ni doping G, Ni loading P and using no catalyst at varying temperatures. The paper suggests that adding Ni to the CeO2 causes an increase in the catalyst surface area and therefore an increase in effectiveness over pure CeO2 which itself is a huge improvement over using no catalyst at all, thereby showing the possibility of HI splitting as a viable method of hydrogen production.

**Conclusion**

From the selected works we can see that there are some very promising looking developments that use a variety of different catalysts and environmental conditions in order to produce Hydrogen gas in an energetically less demanding way than current and classical processes. This research becomes critical when discussing hydrogen as a wide-spread clean energy source; there is currently a prohibitive energy cost preventing production at scale. None of the processes discussed above are perfect - many rely on rare and expensive elements in order to yield significant results, and those which do not are yet to be proven at scale.