Editorial

The Role of Heterogeneous Catalytic Processes in the Green Hydrogen Economy

Eva Díaz *[ID] and **Salvador Ordóñez** [ID]

Catalysis, Reactors and Control Research Group (CRC), Department of Chemical and Environmental Engineering, Faculty of Chemistry, University of Oviedo, 33006 Oviedo, Spain; sordonez@uniovi.es
* Correspondence: diazfeva@uniovi.es

In a recent United Nations draft report (August 2021), a large number of scientists from the Intergovernmental Panel on Climate Change described the climate change over the past century as "unprecedented" and warned that the world will warm at an increasing rate, with unpredictable results, unless aggressive action to cut emissions of carbon dioxide and other heat-trapping gases is taken. Likewise, while benefits for air quality may come quickly, it could take 20–30 years to see global temperatures stabilize [1]. In agreement with this idea, and the importance of the planet's health for the future, on 11 December 2019, the European Commission presented its communication on the European Green Deal. The Green Deal is the new growth strategy of the EU, aiming to set Europe on the path of transformation into a climate-neutral, fair, and prosperous society, with a modern, resource-efficient, and competitive economy [2]. That is, the Green Deal looks for decarbonization of the economy, with the development of a carbon-neutral energy sector being a crucial step, since 75% of EU greenhouse gas emissions come from energy use and production. To achieve climate neutrality in the EU by 2050, hydrogen will play a key role, since it produces negligible CO_2 emissions when manufactured from renewable resources. In addition, hydrogen also contributes to buffering the discontinuous character of renewable resources by transforming local power surpluses into hydrogen.

Classical hydrogen production processes rely on the steam reforming of hydrocarbons, mainly obtained from fossil fuels such as natural gas; gasification of coal and petroleum coke; as well as the gasification and reforming of heavy oil [3]. This hydrogen obtained from fossil fuels, which releases uncaptured carbon dioxide, is called grey hydrogen. When the raw material is natural gas, a methane source, hydrogen is produced by steam methane reforming (SMR), where high-temperature steam (700–1000 °C) is used in a catalytic process. A further water gas shift reaction allows the global transformation of the methane into hydrogen and carbon dioxide. Among the reforming catalysts, Ni-based ones are the most common [4], and have some drawbacks such as catalyst deactivation (by thermal sintering or coke formation). In recent years, research in this field has moved in different directions: proposing new catalysts (as noble metal catalysts), or modifying reaction conditions (oxidative steam reforming, sorbent-enhanced steam reforming, etc.).

After the reforming reaction, a water gas shift reaction (WGSR) is needed for increasing hydrogen yields and converting CO into CO_2. Although this reaction has been well-known from many decades ago, it is today more challenging for various reasons: the maximum CO concentration at the WGSR reactor is lower each time (specially for electrochemical upgrading of the resulting hydrogen), and the lower WGSR feed temperature (due to improvements to the reforming, which is positive from a thermodynamic point of view, since the reaction is reversible and exothermic). These facts lead to the development of more active WGSR catalysts using new active phases (for example Au) or supports (ceria),

which can over perform as the typical Fe-Cr-based and Ni-based catalysts usually used for this reaction [5]. Additional hydrogen purification processes, such as preferential CO oxidation (PROX), are usually needed, especially for high purity requirements, such as fuel-cells.

Blue hydrogen uses the same process as grey hydrogen, with the addition of capturing and storing the carbon dioxide released in the reaction. This makes it much more environmentally friendly, but leads to added technical challenges and a big increase in cost. From the point of view of process intensification, the most attractive trend is trying to integrate into one unit the WGSR reaction and the H_2/CO_2 separation. The use of hydrogen permselective membranes is the logical choice for this purpose, since they allow simultaneously shifting the equilibrium and separating both gaseous products. The recent development of mixed membranes, replacing the dense palladium membranes, boosts this alternative [6].

Alternatively, green hydrogen is obtained from a renewable energy source, such as wind or solar power, which allows obtaining clean hydrogen from water, either by electrolysis driven by solar or wind energy, or photocatalysis using sunlight [7,8]. Water electrolysis is the process whereby water is split into hydrogen and oxygen through the application of electrical energy and, therefore, suffers from efficiency loses due to the use of electricity for the electrolysis of water; although it is the dominant technology for this process. Solar-driven hydrogen production from water using particulate photocatalysts could be considering an attractive alternative for producing green hydrogen, with negligible environmental impact. However, the efficiency of hydrogen production from water in particulate photocatalysis systems is still low [9]. As a reference, the most efficient solar hydrogen production schemes, which couple solar cells to electrolysis systems, can reach solar-to-hydrogen (STH) energy conversion efficiencies of 30% at a laboratory scale; whereas photocatalytic water splitting reaches notably lower conversion efficiencies, of only around 1% [10].

Among the photocatalysts, TiO_2 is the most common for water splitting; however, it cannot utilize the visible light spectrum, as its band gap (3.2 eV) lies in the UV region. Oxides, sulfides, and nitrides of transition metal cations were also used as photocatalysts for water splitting: CdSe, CdS, Ta_3N_5, TaON, C_3N_4, SiC, $BiVO_4$, WO_3, Cu_2O, Fe_2O_3, etc. [11]. Added to this, earth-abundant and metal-free catalysts like γ-C_3N_4, C_3N_3, C_5N_3, $C_{10}N_3$, graphene, graphene oxide, carbon nanotubes, and carbon quantum dots have also been tested [12]. The choice of photocatalyst is a key point in increasing H_2 production. While, recyclability, reusability, and stability also become critical factors when considering photocatalysts for industrial applications, and all these fields constitute a great challenge in order to increase the small percentage of hydrogen (<2%) that today is obtained from electrolysis [13].

With these precedents, biomass, especially lignocellulosic materials that avoid competing with food uses (e.g., wood, forestry side-products, and agricultural wastes), through thermochemical processes, could be an alternative to obtain green hydrogen. In a recent work, Lepage et al. [14] priced from 1.21 to 2.42 USD/kg the hydrogen production cost from biomass in the case of gasification. This cost, although still high in comparison to fossil fuels, is economical in relation to hydrogen produced from water by electrolysis (3 to 5.3 USD/kg). The main primary thermochemical routes are gasification and aqueous phase reforming. Gasification converts organic materials at high temperatures (>700 °C), without combustion, with a controlled amount of oxygen and/or steam, into syngas (i.e., a mixture of H_2 and CO) and carbon dioxide. The carbon monoxide then reacts with water to form carbon dioxide and more hydrogen by the previously mentioned WGSR. The process changes according to the oxidizing agent, and it can be designated as air gasification, oxygen gasification, or steam gasification. The latter promotes steam reforming and increases the yield of H_2; with Ni-based catalysts, alkaline metal oxides, and dolomite being the most common catalysts [14]. Likewise, nickel and cerium catalysts prevent coke deposits. Finally, aqueous phase reforming mainly converts oxygenated compounds into H_2. The

catalysts are metal-based ones, with basic and neutral supports being the ones preferred to increase H_2 selectivity.

Another renewable resource for hydrogen production is biogas, a mixture of CH_4 and CO_2 obtained in anaerobic fermentation. Biogas dry reforming allows direct conversion into syngas by reforming. The removal of CO_2 is not required, which avoids substantial costs related to gas purification. The most common catalyst for biogas reforming is nickel, followed by a wide range of materials including CeO_2, ZrO_2, and Al_2O_3 [15]. In this sense, the simultaneous side reactions and coke formation, among other issues, are authentic challenges from the point of view of catalysis.

All these efforts to increase the efficiency of electrolysis cells and processes, based on biomass gasification followed by a water gas shift reaction, require effective hydrogen storage and transport. However, this is still a major challenge for the development of the hydrogen economy. Although several approaches have been proposed (compression, chemical activation, etc.), the use of liquid organic hydrogen carriers (LOHC) seems to be a very promising alternative. This interest can be numerically expressed by comparison of energy density with respect to volume; that is, the volume required to obtain the same amount of energy, 11.4 MJ (1 Nm^3): hydrogen gas (1 m^3), Li-ion battery (6.1 L), H_2 at 70 MPa (1.43 L), methylcyclohexane, a LOHC (1.7 L) [16]. LOHC systems enable hydrogen storage without binding or releasing other substances from, or to, the atmosphere. Pure H_2 is obtained from LOHC dehydrogenation after appropriate condensation of the liquid, ideally using a high-boiling point carrier molecule such as toluene (toluene/methylciclohexane system), naphthalene (naphthalene tetralin/decalin system), or benzyltoluene (benzyltoluene H0-BT/perhydrobenzyltoluene) [17]. The hydrogen rich LOHC compound can be stored for extended times without energy losses and transported over long distance using energy transport logistics for liquid fuels; that is pipelines, ships, etc. This enables the transition towards a hydrogen economy. Catalysis plays a key role in hydrogen storage using LOHC systems, both for hydrogenation and dehydrogenation. Ni, Ru, and Pt have been described as active phases in the hydrogenation reaction [17], at temperatures between 120 and 260 °C and pressures between 50 and 200 bar, depending on the molecules. In the case of dehydrogenation reactions, precious metal catalysts (e.g., Pt, Pd, Rh, and Ru) were used as catalytic phases, supported either on Al_2O_3 and activated carbon, as more common supports [18], or at low temperatures (150–200 °C). However, the development of LOHC-based systems is still immature, and aspects such as the stability of the LOHCs in successive hydrogenation/dehydrogenation cycles, the development of selective and stable catalysts, and the optimized design of hydrogenation and dehydrogenation reactors must be further optimized to ensure the competitiveness of these technologies.

In summary, the transition towards a hydrogen economy seems to be clearly linked to the development of both catalysts and catalytic processes, in which the metal loading, the support selection, and the structural properties are important characteristics in the operation process design.

References

1. IPCC Working Group I Report, Climate Change 2021: The Physical Science Basis. Available online: https://www.ipcc.ch/report/ar6/wg1/ (accessed on 9 September 2021).
2. A European Green Deal. Available online: https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_en (accessed on 9 September 2021).

3. Naimi, Y.; Antar, A. Hydrogen Generation by Water Electrolysis, Advances in Hydrogen Generation Technologies, Murat Eyvaz, IntechOpen. 2018. Available online: https://www.intechopen.com/chapters/60944 (accessed on 9 September 2021).
4. Oh, Y.-S.; Roh, H.-S.; Jun, K.-W.; Baek, Y.-S. A highly active catalyst, Ni/Ce-ZrO$_2$/γ-Al$_2$O$_3$, for on-site H$_2$ generation by steam-methane reforming: Pretreatment effect. *Int. J. Hydrogen Energy* **2003**, *28*, 1387–1392. [CrossRef]
5. Chen, W.-H.; Chen, H.-Y. Water gas shift reaction for hydrogen production and carbon dioxide capture: A review. *Appl. Energy* **2020**, *258*, 114078. [CrossRef]
6. Marín, P.; Díez, F.V.; Ordóñez, S. Fixed bed membrane reactors for WGSR-based hydrogen production: Optimisation of modelling approaches and reactor performance. *Int. J. Hydrogen Energy* **2012**, *37*, 4997–5010. [CrossRef]
7. Hisatomi, T.; Domen, K. Reaction systems for solar hydrogen production via water splitting with particulate semiconductor. *Nat. Catal.* **2019**, *2*, 387–399. [CrossRef]
8. Kim, J.H.; Hansora, D.; Sharma, P.; Jang, J.-W.; Lee, J. Toward practical solar hydrogen production—An artificial photosynthetic leaf-to-farm challenge. *Chem. Soc. Rev.* **2019**, *48*, 1908–1971. [CrossRef] [PubMed]
9. Guo, S.; Li, X.; Li, J.; Wei, B. Boosting photocatalytic hydrogen production from water by photothermally induced biphase systems. *Nat. Commun.* **2021**, *12*, 1343. [CrossRef] [PubMed]
10. Nishiyama, H.; Yamada, T.; Nakabayashi, M.; Maehara, Y.; Yamaguchi, M.; Kuromiya, Y.; Tokudome, H.; Akiyama, S.; Watanabe, T.; Narushima, R.; et al. Photocatalytic solar hydrogen production from water on a 100 m^2-scale. *Nature* **2021**. [CrossRef] [PubMed]
11. Li, X.; Yu, J.; Low, J.; Fang, Y.; Xiao, J.; Chen, X. Engineering heterogeneous semiconductors for solar water splitting. *J. Mater. Chem. A* **2015**, *3*, 2485–2534. [CrossRef]
12. Tentu, R.D.; Basu, S. Photocatalytic water splitting for hydrogen production. *Curr. Opin. Electrochem.* **2017**, *5*, 56–62. [CrossRef]
13. International Energy Agency (IEA). The Future of Hydrogen, Japan. 2019. Available online: https://bit.ly/3tK7OcU (accessed on 9 September 2021).
14. Lepage, T.; Kammoun, M.; Schmetz, Q.; Richel, A. Biomass-to-hydrogen: A review of main routes production, processes evaluation and techno-economical assessment. *Biomass Bioenergy* **2021**, *144*, 105920. [CrossRef]
15. Zhao, X.; Joseph, B.; Kuhn, J.; Ozcan, S. Biogas Reforming to Syngas: A Review. *iScience* **2020**, *23*, 101082. [CrossRef] [PubMed]
16. Sekine, Y.; Higo, T. Recent trends on the dehydrogenation catalysis of liquid organic hydrogen carrier (LOHC): A review. *Top. Catal.* **2021**, *64*, 470–480. [CrossRef]
17. Preuster, P.; Papp, C.; Wasseerscheid, P. Liquid Organic Hydrogen Carriers (LOHCs): Toward a hydrogen-free hydrogen economy. *Acc. Chem. Res.* **2017**, *50*, 74–85. [CrossRef] [PubMed]
18. Rao, P.C.; Yoon, M. Potential Liquid-Organic Hydrogen Carrier (LOHC) Systems: A review on recent progress. *Energies* **2020**, *13*, 6040. [CrossRef]