EFFICIENT PURIFICATION WITH PRECIOUS METALS CATALYTS

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Hydrogen will occupy a pivotal role in the necessary industrial transition towards a low-carbon emission industry. Nowadays, hydrogen is almost exclusively produced from fossil fuels and its demand reached an all-time high in 2022 of approximately 95 million t, mostly used across various processes within the petrochemical and chemical industry. However, according to an estimation from the International Energy Agency (IEA), the production and use of hydrogen was related to more than 900 million t of CO_2 emissions globally in 2022.[1] As the demand for hydrogen is expected to further increase significantly – to be used additionally as a substitute feed or energy vector in a wide range of applications and industrial processes – decarbonisation is key.

Two technological paths are likely to dominate the production of low-emission hydrogen in the coming decades: production from fossil fuels with subsequent capture and storage of carbon dioxide (CO_2) (blue hydrogen) and production via water electrolysis using renewable energy (green hydrogen).[1,2] Independent of the method of

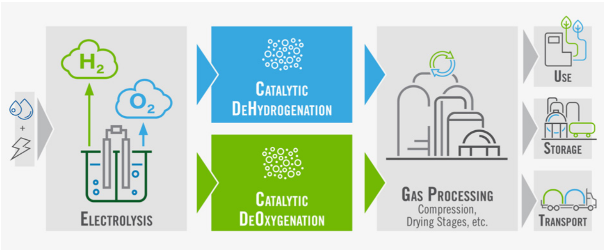

Figure 1. Green hydrogen process chain: hydrogen production by water electrolysis, followed by gas purification, gas processing and further utilisation or storage.

Figure 2. Palladium catalyst (2 - 4 mm spheres) for deoxygenation of hydrogen streams in a tubular fixed-bed reactor.

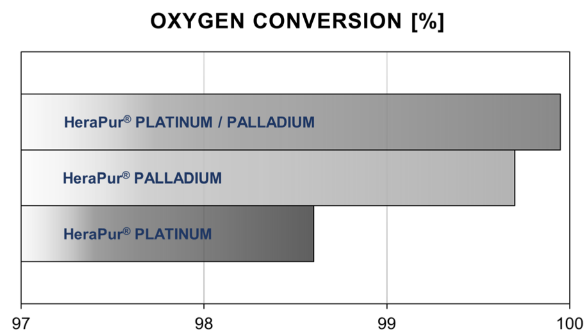

Figure 3. Performance comparison of Heraeus HeraPur® brand Pt-only, Pd-only and Pt-Pd mixed catalyst (same PGM loading) in deoxygenation of hydrogen streams in a stress test at high space velocities and in a wet feed close to the dewpoint. (Conditions were chosen to achieve an operative O_2 slip for comparability.)

production, the storage and utilisation of green or blue hydrogen requires further processing and the removal of impurities. Catalytic processes and precious metal catalysts assume an important function here.

The use of precious metal catalysts to efficiently remove oxygen or other trace components can be considered a core technology to provide the high purity necessary for various applications. Respectively, advancing the development and implementation of those catalytic materials has been subject to extensive ongoing R&D activities.

There are several approaches to electrolysis technologies and green hydrogen utilisation – however, the general process chain for hydrogen supply remains effectively the same (Figure 1). First, water is split into its elements, H_2 and O_2, by applying renewable electric power to the electrolyser. Yet, the separation of H_2 and O_2 is not perfect. Depending on the further on-site use or storage of hydrogen, it must pass through a series of processing steps for conditioning, which include the removal of impurities, drying stages and compression. Removal of oxygen is essential for any downstream utilisation of hydrogen, not only as it interferes with fuel cell applications or downstream catalytic reactors, but also because of safety considerations. There are various processes for hydrogen deoxygenation existing at industrial scale, such as adsorption methods (pressure swing adsorption, temperature swing adsorption), membrane separation, cryogenic separation and catalytic reactors.[3] This article will focus on the use of heterogeneous precious metal catalysts to remove oxygen from hydrogen streams as a common and easy-to-implement procedure. It will highlight important factors in the selection, application and performance of platinum and palladium catalysts for deoxygenation and discuss the advantages of using application-specific catalysts, allowing for the optimised and most efficient design of individual hydrogen supply units.

Precious metal catalysts for efficient hydrogen purification

Heraeus has experience in actively supplying and improving gas purification catalysts to reliably remove oxygen, hydrocarbons and other impurities from gas streams. As new demands from electrolysis and the production of hydrogen from renewable sources are emerging, the development of new generation, tailor-made HeraPur® deoxygenation catalysts has been one of the main objectives of Heraeus' R&D activities, factoring in the specific challenges of renewable hydrogen from different processes. This has been driven by both performance optimisation of the oxygen removal unit and economic considerations to minimise the cost of platinum group metals (PGM). Platinum and palladium-based catalysts are effective in removing traces of oxygen from hydrogen gas streams by H_2 oxidation at temperatures even below 60°C. Selectively promoting the reaction that converts oxygen to water, these catalysts can enable the use of efficient and compact fixed-bed purification systems (Figure 2) and thereby contribute to an overall process improvement and reduced energy consumption. The latter is of paramount importance in the context of green hydrogen supply, where energy efficiency and sustainability are key considerations.

Oxygen impurities in the hydrogen stream are technically inherent in electrolysis. The degree of oxygen crossover can vary from a few 100 ppmv up to 0.6 vol.-% or more, and is influenced by electrolyser technology, its operating conditions and materials, as well as ageing of the separator membrane.[3,4] With regard to the hydrogen utilisation, oxygen limits may differ significantly depending on the downstream process requirements. For many follow-up catalytic reactions (e.g. in production of synthetic fuels or base chemicals), or for some applications in electronics and semiconductor manufacturing, oxygen removal down to single-digit ppm or even ppb levels is indispensable as residual oxygen can lead to quick degradation or deactivation of the materials and components. For fuel cells, different hydrogen purity requirements are defined by ISO 14687 limiting oxygen concentrations in the feed gas in a range of 5 - 200 ppm because the presence of oxygen negatively impacts performance and lifetime of the modules.[5] These examples illustrate that in most applications, the full conversion of oxygen is required, while in other cases, less strict limitations must be met. Platinum and palladium have proven to be excellent materials for low-temperature hydrogen oxidation. Heraeus' expertise in catalyst manufacturing enables the large-scale production of finely dispersed precious metal components on stable, high surface area supports that allow optimal performance with the least amount of PGM necessary for the individual application. Figure 3 shows an operating comparison of three different Heraeus' catalysts developed for oxygen removal. Catalytic experiments were performed as a stress test under highly challenging operating conditions at low temperatures to highlight differences in material performance. The platinum system reaches approximately 98.5% O_2 conversion, while the mixed Pt-Pd catalyst still achieves more than 99.9% conversion, even under the very demanding space velocities applied.

The reaction of hydrogen and oxygen can be carried out even below room temperature if promoted by precious metals. In practical use, however, there are restrictions regarding the lower temperature boundaries that require an adjustment of operating conditions. One of the key factors to consider in catalyst selection and reactor design is the amount of water present in the hydrogen feed. Near saturation, the catalyst can experience a decrease in activity due to water vapour adsorbing on the catalyst surface, which is especially relevant for the ultra-pure gas applications where conversion levels above 99.9% are required. Condensation must be avoided at any point of operation since it leads to reversible, but immediate deactivation of the active sites. Platinum is more sensitive to high water content of the feed gas in comparison to palladium or Pt-Pd mixed catalysts (Figure 4). Particularly at high space velocities, the drop-in activity can be substantial which is why operating above the dew point is crucial to ensure meeting the purification demands. As demonstrated in Figure 4, even a small increase in temperature of 5˚K can lift the conversion achieved by the Pt-based system to more than 99.5% in the tested space velocity range. The impact of the temperature increase is also noticeable for the palladium system at high space velocity, although it is less pronounced and in general the performance is superior to the platinum catalyst.

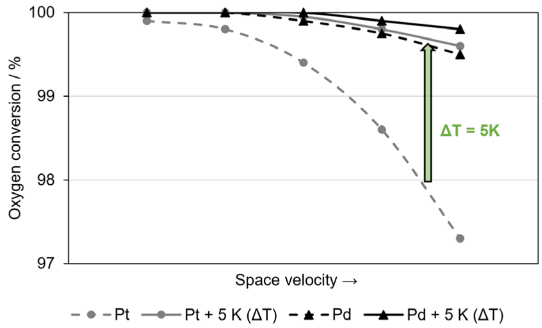

Figure 4. Oxygen conversion in fully saturated hydrogen over HeraPur® platinum- and palladium-based catalysts, and the impact of small temperature increase when operating near dew point.

In addition to their high activity at low temperatures, precious metals also excel in their durability and long-term activity in the absence of, or even to some degree, in the presence of catalyst poisons, thereby enhancing the reliability and availability of the gas purification system. Furthermore, at the end of the catalyst's lifetime, recycling and recovery of the precious metals is not only possible, but of the utmost importance from an ecological and economic standpoint. Heraeus offers the full PGM loop from catalyst synthesis to supply and recycling, hence contributing to a closed precious metal cycle. Re-applying recycled metals further contributes to saving greenhouse gas emissions related to primary mining, and the processing of metal ores as has been extensively demonstrated.[6]

Conclusion

In summary, precious metals have a significant impact on the entire process chain of renewable hydrogen production and utilisation. Their role is pivotal in advancing the development and adoption of high-purity green hydrogen for a wide range of applications in a future hydrogen-based economy. Heraeus has developed and commercialised a broad series of gas purification catalysts, enabling the safe and efficient use of low-emission hydrogen. The selection of the optimal catalyst system according to purity requirements is one of the most important steps in enhancing the overall efficiency of hydrogen supply and utilisation.

References

1. 'Global Hydrogen Review 2023', IEA, Paris https://www.iea.org/reports/global-hydrogen-review-2023, (2023).
2. 'Hydrogen Insights 2023', Hydrogen Council and McKinsey & Co., https://hydrogencouncil.com/en/hydrogen-insights-2023/
3. KIM, T., et al., International Journal of Hydrogen Energy, Vol. 47, Issue 59, (2022), https://doi.org/10.1016/j.ijhydene.2022.05.221.
4. NAITO, T., SHINAGAWA, T., NISHIMOTO, T., and TAKANABE, K., ChemSusChem 2022, 15, https://doi.org/10.1002/cssc.202102294
5. International Organization for Standardization, ISO 14687:2019 Hydrogen fuel quality– product specification
6. International Platinum Group Metals Association reports from 2022 and 2023