Hydrogen production via aqueous-phase reforming for high-temperature proton exchange membrane fuel cells - a review

[version 1; peer review: 1 approved with reservations]

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First published: 20 Jul 2021, 1:81
https://doi.org/10.12688/openreseurope.13812.1
Latest published: 20 Jul 2021, 1:81
https://doi.org/10.12688/openreseurope.13812.1

Abstract
Aqueous-phase reforming (APR) can convert methanol and other oxygenated hydrocarbons to hydrogen and carbon dioxide at lower temperatures when compared with the corresponding gas phase process. APR favours the water-gas shift (WGS) reaction and inhibits alkane formation; moreover, it is a simpler and more energy efficient process compared to gas-phase steam reforming. For example, Pt-based catalysts supported on alumina are typically selected for methanol APR, due to their high activity at temperatures of circa 200°C. However, non-noble catalysts such as nickel (Ni) supported on metal-oxides or zeolites are being investigated with promising results in terms of catalytic activity and stability. The development of APR kinetic models and reactor designs is also being addressed to make APR a more attractive process for producing in situ hydrogen.

Keywords
Aqueous-phase reforming, methanol, hydrogen, catalyst, fuel cell, PEMFC

This article is included in the Societal Challenges gateway.
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Author roles: Lakhtaria P: Conceptualization, Investigation, Methodology, Writing – Original Draft Preparation; Ribeirinha P: Funding Acquisition, Methodology, Project Administration, Writing – Review & Editing; Huhtinen W: Writing – Original Draft Preparation; Viik S: Writing – Review & Editing; Sousa J: Writing – Review & Editing; Mendes A: Funding Acquisition, Project Administration, Supervision, Writing – Review & Editing

Competing interests: No competing interests were disclosed.

Grant information: This research was financially supported by the European Union's Horizon 2020 research and innovation programme under the grant agreement No 875081 (project EMPOWER). This project has also received Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE - funded by national funds through the FCT/MCTES (PIDDAC). The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

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How to cite this article: Lakhtaria P, Ribeirinha P, Huhtinen W et al. Hydrogen production via aqueous-phase reforming for high-temperature proton exchange membrane fuel cells - a review [version 1; peer review: 1 approved with reservations] Open Research Europe 2021, 1:81 https://doi.org/10.12688/openreseurope.13812.1

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Introduction

Energy decarbonization is critically needed to mitigate climate change and to contribute to economic growth and technological progress. The US Energy Information Administration predicts that between 2018 and 2050, world energy consumption will grow 50% in total and more than 30% in the industrial sector. According to the United Nations Sustainable Development Goals (goal 7), it is crucial that energy demand is met for the universal access of energy services since 13% of the world’s population still (2019) suffers from a lack of modern energy access. Fossil fuels such as oil and coal continue to dominate the global energy sector. Consequentially, greenhouse gas emissions, which are pointed to as the main cause of extreme climate change around the world, continue to climb; the UN recorded 1.3 million climate-related deaths between 1997–2017. This is one of the many reasons to make the transition towards more environmentally friendly and decarbonized energy. Therefore, new sustainable and renewable energy sources are crucial to meet the energy demands created by an increased world population, technological advancements and to mitigate global warming.

Hydrogen has emerged as a potential energy vector for a clean energy transition because it can be produced from a wide range of environmentally friendly sources and can be used for storing energy that is easily convertible into electricity and heat for long periods of time. Hydrogen can be produced from renewable feedstock such as biomass and synthetic fuels as well as from fossil fuels. Different technological pathways can be used to produce hydrogen, both for stationary and/or mobile applications. Hydrogen has a high weight energy density of 120 MJ/kg (lower heating value) compared to a traditional fuel such as gasoline (44 MJ/kg), although it has a very low volumetric energy density. Hydrogen can be used in combustion engines and turbines to produce mechanical energy and in electrochemical processes to produce electricity. These qualities make hydrogen a promising energy vector. Examples of these are the hydrogen driven trains in Germany, UK and France, and ferries in Norway. The European Commission has recently (March 10, 2020) announced the ‘clean hydrogen alliance’ as an initiative to develop hydrogen-based technologies.

Fuel cells are considered to be the next generation of propulsion systems in automotive, portable and stationary applications. In particular, hydrogen powered proton exchange membrane fuel cells (PEMFCs) are a promising clean power source due to low-emissions, rapid start times and high energy density and efficiency. Because of the very low volumetric energy density, hydrogen storage and transportation remain a challenge to overcome and a network of hydrogen delivering infrastructure has to be implemented. An inexpensive strategy that fulfills all the requirements for hydrogen storage and transportation has yet to emerge. Therefore, in situ hydrogen production is an exciting approach to overcome the challenges of hydrogen storage and transportation. Currently, the reforming of fossil fuels, such as methane, is the most widely used process to produce hydrogen, representing 71% of total hydrogen produced globally. Since this source of hydrogen is not renewable, research has shifted toward hydrogen production from renewable sources such as ammonia and alcohols (glycol, methanol and ethanol). A large number of studies can be found on catalytic steam reforming of alcohols because of its high hydrogen selectivity and yield. In addition to steam reforming, aqueous-phase reforming (APR) has emerged recently as a promising competitive approach. Contrary to steam reforming, which employs high temperatures and mild pressures, APR converts aqueous phase organic compounds into hydrogen at lower temperatures. In fact, APR operates at temperatures between 200°C and 250°C, and pressures close to bubble point feedstock, normally from 1.5 MPa to 5.0 MPa. These operating conditions make APR a potential technology for providing in situ hydrogen for automotive and mobile applications, allowing this fuel to be used as a direct hydrogen carrier. This review addresses the early state-of-the-art of APR process for in situ hydrogen production, targeting the integration with high temperature (HT)-PEMFCs.

Methanol APR

In 2002, Dumesic’s research group reported APR of an oxygenated hydrocarbon for the first time. Using group VIII metal-based catalysts, this research group successfully demonstrated the APR of sugar and alcohol (e.g. ethylene glycol and methanol) at ca. 226°C in a single reactor. Additionally, these authors proposed a mechanism for hydrogen formation, which became a steppingstone in the APR field.

APR offers a number of advantages compared with conventional steam or autothermal reforming; APR is more energy efficient, since it eliminates the vaporization of the aqueous/oxygenated hydrocarbon solutions. Additionally, operating at lower temperatures improves the stability of catalysts, avoiding coke formation, sintering and oxidation. The low operating temperatures favors the water-gas shift (WGS) reaction, which minimizes the formation of carbon monoxide; and finally, it mitigates undesired decomposition reactions related to carbohydrates. Contrary to the multi-stage and multi-reactor steam reforming process, APR is an easy single-step and single reactor process.

Of all alcohols, methanol is the most convenient hydrogen carrier. With only one carbon, methanol is the simplest alcohol displaying the highest hydrogen to carbon ratio (Figure 1), meaning that more molecular hydrogen can be extracted from methanol compared to other feedstock. Methanol displays 12.6 wt. % of hydrogen content, it is liquid at room temperature, it is biodegradable and can be easily produced from biomass and or synthesized. Methanol reforms – via either steam reforming or APR – at the lowest temperature compared to ethanol or methylene, because it has no C-C bonds.

Reaction mechanism

The methanol APR mechanism involves cleaving C-H and O-H bonds to produce hydrogen (H2) and CO (Equation 1). The produced CO then reacts with water to form H2 and CO2 via the WGS reaction (Equation 2).
APR of oxygenated hydrocarbons (Equation 1–Equation 2) occurs at low temperatures between 200°C and 250°C and are exothermic reactions. However, in both cases (Equation 1–Equation 2), the reactions thermodynamically favored by higher temperatures. On the other hand, WGS reaction equilibrium (Equation 2), which converts CO into CO₂ and H₂, is favored by lower temperatures and is an endothermic reaction\(^{17,18}\). The reaction products of APR are broader than just CO₂ and H₂. APR conditions thermodynamically unstable, where the cleavage of the C-O bond followed by hydrogenation can form alkanes and water. For methanol APR, methane and water is produced via methanation of CO and Fischer-Tropsch reaction of CO₂ (Equation 3–Equation 4)\(^{17–19}\). Figure 2 shows a schematic representation of methanol APR reaction pathways.

\[
\begin{align*}
\text{CO} + 3\text{H}_2 & \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H^\circ < 0 \quad (3) \\
\text{CO}_2 + 4\text{H}_2 & \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H^\circ < 0 \quad (4)
\end{align*}
\]

**Catalysts**

The focus has been placed on finding suitable catalysts that show high activity for promoting reforming reactions at low temperatures (Equation 1–Equation 2) and inhibit side reactions (Equation 3–Equation 4)\(^{17–19}\). Various catalysts have been used for methanol APR based on noble (Pt, Ru) and non-noble (Ni, Cu) metals, yet the most commonly used catalyst for methanol APR is Pt-based. Dumesic’s group\(^{18}\) made significant advances in APR by using Pt supported on aluminum oxide catalysts. Many authors opted for Pt as it is very active and displays high selectivity towards H₂\(^*^{18,26,27}\). Despite its high catalytic activity for methanol APR, Pt shows lower C-C cleavage activity compared to other metals (Ru, Ni and Ir)\(^{28}\), needed for the APR of heavier alcohols, and reasonable activity for the WGS reaction as shown in Figure 3\(^29\). Additionally, metals such as Cu show the highest activity for WGS but no activity for C-C bond breaking. Different supports, with large surface areas, have also been studied with the objective of increasing the Pt loading in catalysts to increase catalytic activity of Pt-based catalysts\(^{22,26,30}\).

Nickel-based catalysts have also been investigated for the APR reaction. Although Ni-based catalysts show lower stability and H₂ selectivity, they favor the WGS shift reaction and are inexpensive compared to Pt. Davda et al.\(^{17}\) determined the catalytic activities of various silica supported noble metals (based on the rate of CO₂ production) for ethylene glycol APR and found that they decrease in the following order: Pt ~ Ni > Ru > Rh ~ Pd > Ir. To improve stability and H₂ selectivity of Ni-based catalysts, various support materials have been considered\(^{15,20,31–33}\). However, reports on methanol APR via Ni-based catalysts are still limited. Shabaker et al.\(^{34}\) and Coronado et al.\(^{31,32}\) made significant advances in this field. The
least studied catalysts are of Cu, Ce or Ru. These metal-based catalysts have been used as bi-metallic combinations or their complexes, however. For example, a Ru complex for methanol APR showed high H₂ yield with turnover frequency of 4700 h⁻¹ and low amounts of unwanted side products (CO and CH₄) ³⁶.

**Platinum-based catalysts.** As previously mentioned, Pt is the favoured metal for APR reactions, showing high activity and selectivity for reforming of oxygenated hydrocarbons ¹⁸, although low C-C cleavage activity ¹⁷. To enhance the stability and activity of the Pt-based catalyst, different supports have been investigated such as ZnO, ZrO₂, TiO₂ and carbon black ¹⁷. However, studies on Pt-based catalysts for methanol APR are limited and mostly focused on Pt supported on γ-Al₂O₃. Shabaker et al. ¹⁹ performed a detailed study of methanol APR reaction kinetics using a Pt catalyst supported on alumina (Pt/γ-Al₂O₃), reporting 100% selectivity for H₂ concerning alkane formation. γ-Al₂O₃ showed very high H₂ yield compared to other supports, followed by α-Al₂O₃ and δ-Al₂O₃ ²⁷. In contrast, α-Fe₂O₃ and CeO₂ showed low methanol conversion and low H₂ yield ²⁷. Furthermore, Pt/γ-Al₂O₃ showed improved WGS activity since it had the highest rate of CO₂ production amongst various Pt-based catalysts. However, under APR reaction conditions, γ-Al₂O₃ is hydrated to boehmite (AlO(OH)). This reaction reduces the support surface area and promotes the sintering and encapsulation of the Pt nanoparticles. Consequently, it decreases the metal dispersion over the surface of the support, which affects APR performance due to the reduction of the catalyst active sites ³⁸,³⁹. Additionally, it also increases the surface acidity of the catalyst, leading to the formation of undesired side products ³⁹. Therefore, it is crucial to find suitable supports for Pt-based catalysts that increase catalytic activity and stability. Following this, Li et al. ⁴⁰ prepared Pt supported on nickel aluminate (NiAl₂O₄) spinel. They observed that the H₂ yield from Pt/NiAl₂O₄ catalyst was four times higher than that of a Pt/Al₂O₃ catalyst. The authors attributed the noticeably higher dehydrogenation rate of methanol to the NiAl₂O₄ spinel structure and synergy between Pt and NiAl₂O₄. The large amount of oxygen vacancies over Pt/NiAl₂O₄ stabilize Pt and significantly improved WGS activity. Interestingly, they report negligible activity of
NiAl$_2$O$_4$ in APR tests, which indicates clearly a synergistic effect between Pt and NiAl$_2$O$_4$. The performance and stability of this catalyst for APR is also affected by the oxidation state of Pt on NiAl$_2$O$_4$, which should be reduced to metallic Pt from PtOx. Zeolites have also been tested as a potential support for methanol APR catalysts. Pt supported on NaY zeolite shows a slight increase in methanol conversion and H$_2$ selectivity compared with a Pt/Al$_2$O$_3$ catalyst. This fact was attributed to the synergistic effect between Pt and NaY, where the high electron density of the microporous zeolite surface stabilizes Pt and enhances the hydrogen retention capacity in Pt/NaY catalysts. The highest H$_2$ production rate reported was achieved using Pt supported on various structures of molybdenum carbide (α-MoC, β-MoC), as can be seen in Table 1. Lin et al. using density functional theory (DFT) calculations showed that the enhanced APR activity is due to high interaction between Pt and MoC caused by highly atomically dispersed Pt atoms on the MoC surface. Increasing Pt loading usually leads to higher H$_2$ yield and production rate. They observed a sharp increase in H$_2$ production rate when Pt loading increased from 2 wt. % to 2.2 wt. %.$^{27}$ Higher Pt load leads to the increased number of active sites for the reaction. Figure 4 shows the methanol conversion as a function of the Pt load.

**Ni-based catalysts.** Ni-based catalysts have been investigated for the APR process, since they show appreciable H$_2$ production and are less expensive than Pt-based catalysts. Table 2 summarizes the Ni-based catalysts reported in the literature for methanol APR. Ni-based catalysts are more susceptible to oxidation in hydrothermal APR conditions. Additionally, sintering, agglomeration and coke formation leads to the

<table>
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<tr>
<th>Support</th>
<th>Pt loading (wt. %)</th>
<th>Preparation method</th>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>Methanol concentration (wt. %)</th>
<th>WHSV (h$^{-1}$)</th>
<th>Methanol conversion (%)</th>
<th>H$<em>2$ production rate (µmol/min/g$</em>{catalyst}$)</th>
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**Figure 4.** Effect of Pt loading in methanol aqueous-phase reforming. Reprinted with permission from 26. Copyright 2009. American Chemical Society.

**Table 2.** Ni-based catalysts for hydrogen production in methanol aqueous-phase reforming (IWI – incipient wetness impregnation, WI – wetness impregnation, WHSV – weight hourly space velocity).

<table>
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<tr>
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<td>11.8</td>
<td>IWI</td>
<td>230</td>
<td>3.2</td>
<td>2</td>
<td>0.8</td>
<td>8.6</td>
<td>32</td>
<td></td>
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<tr>
<td>SiO₂</td>
<td>10</td>
<td>IWI</td>
<td>230</td>
<td>3.2</td>
<td>2</td>
<td>1</td>
<td>10.1</td>
<td>32</td>
<td></td>
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<tr>
<td>γ-Al₂O₃</td>
<td>11.4</td>
<td>IWI</td>
<td>230</td>
<td>3.2</td>
<td>2</td>
<td>6</td>
<td>60.6</td>
<td>32</td>
<td></td>
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<tr>
<td>R-NiSn</td>
<td>14</td>
<td></td>
<td>225</td>
<td>2.5</td>
<td>18.6</td>
<td>1.43</td>
<td></td>
<td>34</td>
<td></td>
</tr>
</tbody>
</table>
deactivation of Ni-based catalysts.\textsuperscript{38,44} To overcome these issues, Ni has been supported on various materials to increase H\textsubscript{2} production along with stability. Raney nickel offers a notably high surface area, thermal and structural stability; adding Sn does not influence the reaction rate of Raney nickel catalysts, but increases the selectivity for H\textsubscript{2} by weakening CO and H adsorption, which lowers the methanation reaction rate.\textsuperscript{44} The rate of H\textsubscript{2} production, selectivity and stability of Raney NiSn is comparable to Pt/Al\textsubscript{2}O\textsubscript{3} catalysts. Ni has been supported on metal oxides, such as Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} but also on CeO\textsubscript{2} and ZrO\textsubscript{2} (Table 2). It should be emphasised that both CeO\textsubscript{2} and ZrO\textsubscript{2} have catalytic activity themselves, making them attractive for APR. For instance, ZrO\textsubscript{2} enhances WGS activity.\textsuperscript{45} The use of mixed oxides (bimetallic supports) such as CeO\textsubscript{2}-ZrO\textsubscript{2} and La\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} improved methanol conversion, hydrogen production and catalyst stability.\textsuperscript{46} The addition of CeO\textsubscript{2} increases oxygen storage capacity, catalyst mobility and promotes redox properties. Ni supported on [CeO\textsubscript{2}]\textsubscript{0.17}-[ZrO\textsubscript{2}]\textsubscript{0.83} mass fractions showed superior performance compared to Ni supported on [CeO\textsubscript{2}]\textsubscript{0.25}-[ZrO\textsubscript{2}]\textsubscript{0.75} or compared to a Ni/ZrO\textsubscript{2} catalyst.\textsuperscript{47} However, compared to the performance of Ni supported on CeO\textsubscript{2}-ZrO\textsubscript{2}, NiCeO\textsubscript{2} based catalysts showed worse results; poor metal dispersion due to a lesser surface area was pointed to as the main reason.\textsuperscript{42,43} Ni has also been tested as a catalyst without using any support material. Shabaker et al.\textsuperscript{44} used a Sn modified Ni catalyst for reforming various hydrocarbons and concluded that adding Sn was required to suppress the alkane formation reaction. Nevertheless, Ni without any support showed better H\textsubscript{2} selectivity since it avoids the often-observed dehydrogenation of the catalyst support.

To increase basicity of the APR reaction and consequently the selectivity for H\textsubscript{2}, calcia-stabilized ZrO\textsubscript{2} (CSZ) and ytrria-stabilized ZrO\textsubscript{2} (YSZ) have been tested as supports. The results showed that adding calcia to ZrO\textsubscript{2} improves the APR performance with higher methanol conversion and H\textsubscript{2} yield, while ytrria-stabilized ZrO\textsubscript{2} had no impact on performance. However, increasing the loading of calcia for CSZ did not necessarily increase H\textsubscript{2} production. Lanthanum (La) has been employed with Ce and Zr to increase WGS activity and catalyst stability. Adding La\textsubscript{2}O\textsubscript{3} to a CeO\textsubscript{2} support increases oxygen vacancies, provides better metal-support interactions and leads to higher H\textsubscript{2} production due to better Ni dispersion.\textsuperscript{45}

\textbf{Effect of dopants.} Adding Cu to Ni-based catalysts supported on Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} significantly increases WGS activity and makes methane formation less favorable, as depicted in Table 3.\textsuperscript{32} This behavior is less evident in other types of support. Coronado et al.\textsuperscript{31}, using CeO\textsubscript{2}-ZrO\textsubscript{2} supports, reported higher H\textsubscript{2} selectivity for alcohol dehydrogenation for Ni-Cu/[CeO\textsubscript{2}]\textsubscript{0.25}-[ZrO\textsubscript{2}]\textsubscript{0.75} in comparison to Ni/[CeO\textsubscript{2}]\textsubscript{1.25}-[ZrO\textsubscript{2}]\textsubscript{0.75}, despite the lower methanol conversion and H\textsubscript{2} yield. The authors justified the lower performance with the lower loading of nickel in Ni-Cu/[CeO\textsubscript{2}]\textsubscript{1.25}-[ZrO\textsubscript{2}]\textsubscript{0.75}. On the other hand, adding Ce to Ni catalysts supported on Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} showed slight improvements in methanol conversion.\textsuperscript{32} The opposite effect was observed for CeO\textsubscript{2}-ZrO\textsubscript{2} supports,\textsuperscript{31} due to an increase in the nickel particles' size. Similar results were obtained by Goma et al.,\textsuperscript{45} using a Ni-based catalyst doped with CeO\textsubscript{2} over different supports (ZrO\textsubscript{2}, calcia-stabilized ZrO\textsubscript{2} and ytrria-stabilized ZrO\textsubscript{2}). The results showed that the CeO\textsubscript{2} doped catalysts have lower performances than those without CeO\textsubscript{2}. The reduction properties and basic nature of Ce reduces the CO selectivity. Moreover, the CeO\textsubscript{2} layer additionally hindered the basic sites of calcia and ytrria, lowering the methanol conversion and H\textsubscript{2} production.

\textbf{Noble metal-based catalysts.} Besides Pt-based catalysts, other noble metals such as Ru, Ir, Rh and Pd have been employed in APR of alcohols,\textsuperscript{17,20} but only Ru and Ir were studied for methanol APR. The dehydrogenation of methanol at low temperatures between 89°C and 95°C, using Ru-based pincer complexes in alkaline solution, showed that decreasing the base concentration (NaOH) negatively affects the catalytic performance.\textsuperscript{46} The presence of formate as an intermediate to produce H\textsubscript{2} and CO\textsubscript{2} was identified by Raman spectroscopy. The use of the Ru complex allows high H\textsubscript{2} yield with a turnover frequency of 4700 h\textsuperscript{-1} and low amounts of CO and CH\textsubscript{4} with long-term stability.\textsuperscript{36,46} Ir-based catalysts supported on SiO\textsubscript{2}, TiO\textsubscript{2} and ZrO\textsubscript{2} have also been used in methanol APR. Adding Re to Ir/SiO\textsubscript{2} and Ir/ZrO\textsubscript{2} increased the H\textsubscript{2} formation rate by four times and five times, respectively,\textsuperscript{42} by forming nanostructured clusters that decreased the H\textsubscript{2} adsorption sites on Ir. Meanwhile, adding Mo to Ir/TiO\textsubscript{2} created a thin monolayer of MoO\textsubscript{2} on TiO\textsubscript{2} that is responsible for improving the water reactivity. This hydration process over the monolayer leads to an increased H\textsubscript{2} production rate.

\textbf{Supports and preparation methods.} The performance of the catalyst relies on the active surface area of the support, the dispersion of the metal over the support surface and the size of the active metal nanoparticles. Therefore, it is necessary to optimize the preparation method in order to achieve catalysts with highly dispersed metal over the support surface. The most commonly used methods for catalyst preparation are derivations from co-precipitation and wet-impregnation. It is important to opt for an appropriate aforementioned preparation method (depending on metal precursors and supports) in order to achieve optimal catalytic activity. Incipient wetness impregnation (IWI) is a commonly used method for preparation of catalysts for methanol APR. However, the use of metal nitrates often offers poor dispersion of the catalyst. Studies on Fe and Ni precursors attributed the reason for low dispersion to redistribution during the drying process. Adding viscosity-increasing agents or chelating citrate salts to aqueous nitrates solutions can avoid redistribution problems.\textsuperscript{48,49} Figure 5 shows one example of the effect of surface area in methanol APR. As seen in this figure, the use of an alumina support with a larger surface area (\(\alpha\)-Al\textsubscript{2}O\textsubscript{3}) corresponds to higher H\textsubscript{2} yield. The reason behind this could be that the
Table 3. Ce and Cu doped Ni-based catalysts for hydrogen production in methanol aqueous-phase reforming at 230°C and 3.2 MPa (5 wt. % methanol concentration) (IWI – incipient wetness impregnation, WI – wetness impregnation, WHSV – weight hourly space velocity).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Support</th>
<th>Metal loading (wt. %)</th>
<th>Preparation method</th>
<th>Methanol conversion (%)</th>
<th>WHSV (h⁻¹)</th>
<th>H₂ yield (%)</th>
<th>H₂ production rate (µmol/min/g&lt;sub&gt;catalyst&lt;/sub&gt;)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cu</td>
<td>[CeO&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;0.25&lt;/sub&gt;-[ZrO&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;0.75&lt;/sub&gt;</td>
<td>Ni 10 Cu 5</td>
<td>IWI</td>
<td>38</td>
<td>3.6</td>
<td>101</td>
<td>2100</td>
<td>31</td>
</tr>
<tr>
<td>Ni-Cu</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Ni 10 Cu 5</td>
<td>IWI</td>
<td>2</td>
<td>1.0</td>
<td>10.9</td>
<td>10.9</td>
<td>32</td>
</tr>
<tr>
<td>Ni-Cu</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Ni 10 Cu 5</td>
<td>IWI</td>
<td>2</td>
<td>6.2</td>
<td>63.5</td>
<td>63.5</td>
<td>32</td>
</tr>
<tr>
<td>Ni-Cu</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Ni 10 Cu 5</td>
<td>IWI</td>
<td>2</td>
<td>6.2</td>
<td>63.5</td>
<td>63.5</td>
<td>32</td>
</tr>
<tr>
<td>Ni-Ce</td>
<td>[CeO&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;0.25&lt;/sub&gt;-[ZrO&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;0.75&lt;/sub&gt;</td>
<td>Ni 10 Ce 5</td>
<td>IWI</td>
<td>12</td>
<td>3.6</td>
<td>18</td>
<td>620</td>
<td>31</td>
</tr>
<tr>
<td>Ni-Ce</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Ni 10 Ce 5</td>
<td>IWI</td>
<td>19</td>
<td>3.6</td>
<td>28</td>
<td>950</td>
<td>31</td>
</tr>
<tr>
<td>Ni-Ce</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Ni 10 Ce 5</td>
<td>IWI</td>
<td>2</td>
<td>3.4</td>
<td>34.19</td>
<td>34.19</td>
<td>32</td>
</tr>
<tr>
<td>Ni-Ce</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Ni 10 Ce 5</td>
<td>IWI</td>
<td>2</td>
<td>8.3</td>
<td>84.7</td>
<td>84.7</td>
<td>32</td>
</tr>
<tr>
<td>Ni-Ce</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Ni 5.9 Ce 12.6</td>
<td>IWI</td>
<td>40</td>
<td>4</td>
<td>34</td>
<td>40</td>
<td>42</td>
</tr>
<tr>
<td>Ni-Ce</td>
<td>Calcia-stabilized ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Ni 5.9 Ce 13</td>
<td>IWI</td>
<td>68</td>
<td>4</td>
<td>57</td>
<td>57</td>
<td>42</td>
</tr>
<tr>
<td>Ni-Ce</td>
<td>Calcia-stabilized ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Ni 5.5 Ce 13.5</td>
<td>IWI</td>
<td>44</td>
<td>4</td>
<td>33</td>
<td>33</td>
<td>42</td>
</tr>
<tr>
<td>Ni-Ce</td>
<td>Yttria-stabilized ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Ni 5.5 Ce 12.7</td>
<td>IWI</td>
<td>54</td>
<td>4</td>
<td>40</td>
<td>40</td>
<td>42</td>
</tr>
</tbody>
</table>

Figure 5. Catalyst Brunauer–Emmett–Teller (BET) surface area and hydrogen yield in methanol aqueous-phase reforming, 230°C, 3.2 MPa, WHSV 2 h⁻¹, Ni loading 11.8 wt. % for Ni/α-Al<sub>2</sub>O<sub>3</sub> catalyst, Ni loading 13 wt. % for Ni/γ-Al<sub>2</sub>O<sub>3</sub> (figure created using data obtained from 32).
larger surface area of the support allows for a better dispersion of Ni than for the support with lower surface area (γ-Al₂O₃).

**Alkane formation.** In APR, methanation and Fischer-Tropsch reactions are responsible for alkane formation. For APR of methanol, only CH₄ is formed as side product alkane. The formation of undesired CH₄ can be suppressed to some extent by using suitable metal and/or support materials. Alkane formation heavily depends on the acidity of the catalyst material. Additionally, using catalysts of basic nature not only suppresses alkane formation, it is also favorable for WGS activity. Huber et al. reported that alkane selectivity increased as acidic sites were added to the non-selectivity Pt/Al₂O₃ catalyst.

As previously mentioned, different metals have their own methanation activity rate (Ni shows a higher tendency to form alkanes than Pt). In order to decrease alkane selectivity and favor higher H₂ formation, non-acidic dopants or supports must be used with a Ni-based catalyst during dehydrogenation reactions. Not only the metal of the catalyst, but also the support plays an equally vital part in APR reactions. Acidic supports like SiO₂-Al₂O₃ tend to favor higher alkane formation compared to basic or neutral supports such as Al₂O₃. Ni-based catalysts have been doped with Cu in order to increase H₂ production and to suppress CH₄ formation; however, adding Cu had no noticeable effect on increasing H₂ production. Use of a Ce doped Ni-based catalyst also limits CH₄ formation, which could be the result of a synergetic effect between Ni and Ce. Calcia and ytria have been added to ZrO₂ in Ni-based catalysts to increase the surface basicity. This resulted in promoted WGS activity that decreased the selectivity of alkane formation.

**Effect of experimental conditions**

Methanol APR can be carried out in the range 200°C – 250°C within the pressure range of 1.5 MPa – 3.5 MPa. Therefore, it becomes necessary to observe the effect of system pressure and temperature for optimized H₂ production. Pan et al. studied the effect of pressure on H₂ production along with the production rates of CO₂ and CH₄ in APR of 5 wt. % ethylene glycol aqueous solution for Ni₃SnAl₉, hydroalumina derived catalyst. It was reported that H₂ production decreased significantly with increased pressure (from 2.6 MPa to 3.0 MPa) whereas the production rate of CH₄ was unaffected. The decrease in CO₂ production was also observed with increasing operating pressure. This effect was ascribed to blockage of available catalytic sites and results in dehydration and hydrogenation of intermediate products at the expense of produced H₂. This results in the decrease of H₂ production.

Additionally, partial H₂ pressure becomes a limiting factor to H₂ production. Methanol APR forms H₂, CO, CO₂, and sometimes CH₄ in gaseous form, which is in the form of gas bubbles within the aqueous solution. The total pressure inside the bubble is calculated to be the same as the total system pressure considering vapor-liquid equilibrium. The high H₂ pressure blocks catalytic sites and lowers the surface concentration of CO₂, which reduces the activity of the WGS reaction. Additionally, changes in total system pressure influence the gaseous bubble density and size distribution. Such changes affect the performance of the catalyst by modifying their wetting behavior. In the same manner as pressure, system temperature also influences H₂ production. For example, at high temperature water can corrode the catalyst and active metal and/or support can be washed away into the effluent. However, thermodynamic analysis of methanol APR show higher H₂ selectivity at higher temperatures (>187°C). On the contrary, CH₄ formation decreases with temperature increase (and increases with pressure increase). Since CH₄ formation is an exothermic process, the methanation reaction is thermodynamic unfavored by higher temperatures.

**APR kinetics and modeling**

Kinetic modelling is a way to shed light on the reaction pathways leading to rate of formation of the products of various catalysts at given temperatures. Ribeirinha et al. studied empirical and mechanistic models for the high performance catalyst CuO/ZnO/Ga₂O₃ for methanol steam reforming (MSR). Simulating a packed bed reactor, they found that these models accurately fit to the experimental results, after appropriate parameter estimation. Lotrić et al. developed a power-law empirical model for the same catalyst CuO/ZnO/Ga₂O₃ and reported good fitting with experimental data. There are several kinetic models reported in the literature for MSR for various catalysts, reaction temperatures and types of reactor. In contrast, APR kinetic models are scarce as the technology is still in its development phase. Coronado et al. presented a kinetic model for C₃-C₅ alcohols derived from Fischer-Tropsch synthesis over Ni supported on ceria-zirconia using power law and phenomenological models. The authors evaluated three different reaction rate equations. The first equation was a Langmuir–Hinshelwood reaction rate expression based on the work by Murzin et al. for xylitol APR (Equation 5), and the two other equations (Equation 6–Equation 7) were simple power law models.

\[
R_A = k_A \frac{C_{\text{alcohol}}}{(1 + k_{\text{alcohol}}C_{\text{alcohol}})} 
\]

\[
R_B = k_B C_{\text{alcohol}}^m 
\]

\[
R_C = k C_{\text{alcohol}}^C 
\]

The authors considered only alcohols as being able to adsorb on the active sites of the catalyst. The adsorption equilibrium constants of alcohols (K), the rate constants (k) and the reaction orders (m) were considered as lumped parameters to avoid system over-parametrization. Water concentration was considered constant and the WGS reaction was assumed to be dependent on the concentration of CO and H₂O. The Arrhenius and Van’t Hoff equations were used to calculate the temperature dependency of the reaction rate constants and adsorption equilibrium constants, respectively. However, the availability of APR kinetics modelling is still limited and in its preliminary stage. Further study and development in the field of APR kinetic models are required in order to better understand APR reaction kinetics that can help optimize and upscale APR.
Feasibility of reforming for fuel cell applications

Low-temperature PEMFCs (LT-PEMFCs) such as Nafion based polymer electrolyte membrane fuel cells are state-of-the-art fuel cells that operate below 100°C. Despite the excellent proton conductivity, the poor CO tolerance at the anode, slow oxygen reduction reaction kinetics and complex water management system hinders cost reduction and performance improvement of LT-PEMFCs. Operating at temperatures above 100°C has the benefits of enhanced catalytic activities and simplified water management. HT-PEMFCs are also more tolerant to fuel impurities and have low dependency on heat removal systems\textsuperscript{66,67}. Such attributes of HT-PEMFCs provide the potential of \textit{in situ} hydrogen production using fuel processors based on reforming or oxidation processes. One of the most important reasons for \textit{in situ} H\textsubscript{2} production is the non-availability of a viable H\textsubscript{2} storage material\textsuperscript{68–70}. In this sense, \textit{in situ} H\textsubscript{2} production has been extensively researched in recent years as a source of H\textsubscript{2} feedstock for fuel cells. The integration of fuel cells with a steam reformer is thermally advantageous since fuel cells are exothermic, while reformers are endothermic. Several studies investigating the thermal integration of low temperature steam reforming with HT-PEMFCs can be found in the literature\textsuperscript{23,71–75}. However, the operating temperature remains a hurdle to overcome in the integration of steam reformers and HT-PEMFCs. HT-PEMFCs have the operating temperature range of 120°C – 180°C, whereas the steam reforming of alcohols occurs at temperatures between 220°C and 500°C\textsuperscript{76,77}. The operating temperature for state-of-the-art HT-PEMFCs cannot exceed 200°C, as it would lead to problems such as degradation and loss of proton conductivity. Additionally, the temperature difference between HT-PEMFCs and steam reformers is more of a challenge for rapid startup\textsuperscript{78,79}.

Fuel processors for fuel cells applications

Fuel processors are complex devices that convert hydrocarbons into H\textsubscript{2}. A typical fuel processor consists of a steam generator, preheater, catalytic fuel reformer, WGS reactor, exhausters, condenser and catalytic after burner (Figure 6). Catalytic fuel reforming is undoubtedly the most crucial part of the cogeneration system as it produces H\textsubscript{2} for the fuel cell. A vaporizer or heater is another important component of the fuel processor that is required to heat fuel and water to meet the catalytic reaction conditions of the hydrocarbon. Many fuel processors are equipped with CO removal systems, such as WGS reactors\textsuperscript{80,81}. When using LT-PEMFCs, it becomes critical to feed in pure H\textsubscript{2} to avoid the contamination of the fuel cell anode catalyst; therefore, more complex purification systems are required, such as pressure-swing adsorption (PSA) units. Since methanol reforming involves production of CO\textsubscript{2}, it is critical to install a CO\textsubscript{2} capture system at the outlet to avoid adding to CO\textsubscript{2} emissions\textsuperscript{82–84}.

Fuel processors make the overall HT/LT-PEMFCs a complicated system, as it is vital to maintain the temperatures of various subsystems. This in turn can make the thermal integration of the system a challenging task (especially for relatively small fuel cell systems) since the temperatures for different subsystems can vary across wide ranges. The thermal efficiency of a fuel processor ($\varepsilon_{FP}$) (Equation 8) is calculated using the higher heating value (HHV) of H\textsubscript{2} produced via reforming divided by the HHV of the input fuel (e.g. methanol). The total thermal efficiency of the fuel processor is brought down by the energy required to run the fuel processor subsystem (e.g. pumps, condenser, exhaust fans, etc.). Brett et al.\textsuperscript{81} reported that if one counts the (electrical) efficiency...

\textbf{Figure 6. Schematic diagram of an integrated fuel (methanol) processor with fuel cell.} Reproduced from 85 (open access, Creative Commons Attribution (CC BY 4.0) license. Licensee MDPI, Basel, Switzerland.)
of the whole system, in reality it is one third to one fifth lower than the efficiency counted for only the fuel cell stack.

$$\epsilon_{FP}(\%) = \frac{\Delta H_{HHV},H_2}{\Delta H_{HHV},fuel}$$ (8)

APR integration with HT-PEMFC

Internal reforming of methanol or integration of a methanol reformer with a fuel cell is distinctly advantageous compared to fuel processor systems due to the complex thermal management, water management and eventual loss in overall efficiency due to many subsystem components. To overcome this issue, researchers have studied lowering the temperature of MSR for integration with HT-PEMFC\textsuperscript{24,36-38}. Lotrić \textit{et al.}\textsuperscript{74} followed a different approach, by considering a higher HT-PEMFC stack operating temperature of 255°C. The authors investigated the integration of MSR with fuel cells and reported that HT-PEMFC shows higher system efficiency than LT-PEMFC in an integrated system. However, operating fuel cell stacks at 255°C requires novel electrolytes capable of proton conduction at such a temperature in absence of water, using expensive gaskets to withstand high temperatures, and development of a new catalyst support, as widely used carbon supports corrode faster at high temperatures\textsuperscript{39}.

These issues can be avoided, to some extent, via methanol APR. Integrating methanol APR with HT-PEMFCs can be seen as a potential technology to increase efficiency and to overcome the complexity of MSR integration into HT-PEMFCs. As discussed earlier, methanol APR, using catalysts such as Pt/MoC, can be performed at temperatures below 200°C with considerably high H\textsubscript{2} production\textsuperscript{32}. Additionally, APR is an exothermic process, which makes its integration with fuel cell a simpler and more efficient method of H\textsubscript{2} and electricity production\textsuperscript{33}. Using methanol APR with HT-PEMFCs is advantageous since the undesired byproducts of reforming are easy to control, except for CH\textsubscript{4} and CO, where the concentration is below the limits of HT-PEMFC tolerance. Integrating APR with HT-PEMFCs can also make the whole system more compact since methanol APR is an easy single-step, single reactor process. The methanol APR reaction conditions are far better suited for integration with HT-PEMFCs than MSR. APR integrated HT-PEMFCs have potential for higher CHP fuel cell system efficiency and performance than MSR integrated HT-PEMFCs.

Challenges with integration. Although the integration of APR and HT-PEMFCs has several advantages, there are also distinct barriers. Challenges are related to the low maturity of the APR technology, elementary APR catalyst research, and the feasible conditions of the integrated system.

To improve the overall efficiency of the HT-PEMFC system and to make the integration of APR and HT-PEMFCs more attractive, the waste heat recovered from the FC stack should be utilized as the heat source of the APR unit. In thermal integration, the waste heat of the FC stack is utilized with a heat transfer fluid recycled in the overall system. Thermal integration would enhance the benefits of APR and compensate for the lower methanol conversions and hydrogen production rates compared to the high values attained with MSR technology. Due to thermal losses in the heat recovery process, the operation temperature of the APR unit is below the operation temperature of the FC stack. Moreover, even though the operation temperature of the HT-PEMFC may vary in the range of 120–200°C, the degradation of the stack is faster at higher operation temperatures\textsuperscript{40}. Therefore, in the thermal integration of APR and HT-PEMFC technology, the selection of operation temperature is based on the optimization of APR catalyst activity and stack lifetime.

Since the reforming temperature should remain below 200°C, a major challenge is the lack of data related to APR systems at decreased temperatures. As presented in Table 1 and Table 2, the methanol conversion and hydrogen production rate drop when the reforming temperature is decreased. A high conversion rate is essential for the system to reach high system efficiency. Furthermore, the anode of the HT-PEMFC tolerates only limited amounts of vaporized feed solution; even a 3% volume fraction of methanol-water vapor would degrade the FC performance\textsuperscript{40}. To avoid this, either a more efficient catalyst or a cold trap for vapor collection is necessary for the integrated system.

Additionally, a challenge with the APR catalysts is the lack of long-term activity experiments. Li \textit{et al.}\textsuperscript{32} reached excellent hydrogen production rates with a Pt/a-MoC catalyst, but their experiments lasted less than two hours, which provides no information on long-term catalyst activity. When the APR unit is integrated with the HT-PEMFC stack, the stability of the APR catalyst should correspond with the durability of the HT-PEM membrane electrode assemblies (MEAs), which have recently reached a lifetime of 9,000 hours without any problems\textsuperscript{31}. In \textit{situ} re-reduction of deactivated catalyst demands more complexity from the FC system and therefore it should be avoided if possible.

Even though high-pressure hydrogen storage is not required when hydrogen is produced \textit{in situ} with APR, the pressure conditions of APR are relatively high. To perform APR, the reforming pressure should be above the bubble point pressure of the feed mixture. If the methanol molar fraction in the feed solution is 30%, the bubble point pressure of the solution is over 9 bar at 150°C and over 29 bar at 200°C\textsuperscript{25,33}. Since the HT-PEMFC is operated at around atmospheric pressure, the reforming pressure should be maintained with a back-pressure regulator.

In three-phase reforming systems, such as APR, mass transfer limitations cause challenges. Typically, they are solved with nitrogen co-feeding, which enhances the removal of hydrogen molecules from the porous catalyst surfaces. Nevertheless, when the APR is integrated with the HT-PEMFC, nitrogen co-feeding would dilute the feed gas, which is unfavorable. The separation of nitrogen and hydrogen is possible with
novel membrane separation techniques\(^4\),\(^5\). However, such a separation system would increase the complexity and capital expenditure (CAPEX) of the FC system, and thus is not considered a reasonable solution. Instead, usage of a micro-channel reactor or novel catalyst coating on a structured catalyst have been suggested to improve the mass transfer properties of the APR system\(^1\).

**Conclusion**

In recent years, research on methanol APR for hydrogen production has been increasing, with a focus on developing new catalysts. Pt-based catalysts are the best performing catalysts and the highest hydrogen production was reported using MoC and NiAl\(_2\)O\(_4\) as supports. Unconventional supports such as Zeolite and MoC performed better than conventional supports such as alumina and silica. Non-noble metal-based catalysts, such as Ni-based catalysts, show promising results and are the focus of most methanol APR catalytic developments. Ni has been supported on various metal oxides such as CeO\(_2\) and ZrO\(_2\), which increased overall hydrogen production by promoting WGS reaction. The addition of Cu to produce a bi-metallic Ni-based catalyst leads to higher WGS activity and suppressed methanation, whereas adding Ce only leads to increased hydrogen yield. Ru, Re and Ir are other less frequently used metals that showed promising results and need to be further explored.

Methanol APR has the potential to be considered as a prominent hydrogen production technology. However, methanol APR using non-noble metal catalysts need further development to reach Pt-based catalyst activity, where the supports play a major role. Furthermore, kinetic models need to be developed for better understanding of APR reaction mechanisms, as well as being important tools for scaling, designing and optimizing processes.

**Data availability**

No data are associated with this article.

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**References**


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Open Peer Review

Current Peer Review Status:  

Version 1

Reviewer Report 09 August 2021

https://doi.org/10.21956/openreseurope.14891.r27272

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The review manuscript deals with an interesting overview about the advantages due to the combination of the aqueous phase reforming of methanol process with high temperature PEM fuel cells. It describes carefully the role of the various catalysts, the kinetics and the benefits of the aqueous phase reforming of methanol for hydrogen generation compared to the gas phase process. The main comment is related to the absence of discussion about the potential of the membrane reactor technology utilization to carry out the aqueous phase reforming reactions. It is suggested to add a paragraph on the membrane reactor technology and the possible benefits due to its utilization in the aqueous phase reforming of methanol process, based on the examples present in literature for other reaction processes such as “Neira D’Angelo, M. F., Ordomsky, Van der Schaaf, J., Schouten, J. C., & Nijhuis, T. A. (2014). Carbon-coated ceramic membrane reactor for the production of hydrogen via aqueous phase reforming of sorbitol. ChemSusChem, 7(7), 2007-15”.

In the following, a few minor comments are reported further:

1. A schematic about the aqueous phase reforming reactor should be added and discussed. Furthermore, a diagram of the APR reactor integrated to the HT-PEMFC should be provided like to Fig. 6.

2. The CO tolerance for both LT and HT-PEMFCs should be reported numerically in the paragraph “Feasibility of reforming for fuel cell applications”.

3. Regarding to the main performance of the APR reactors present in literature, information about the by-products compositions should be added (a dedicated table is suggested).

4. Regarding to the sentence “However, the operating temperature remains a hurdle to overcome in the integration of steam reformers and HT-PEMFCs. HT-PEMFCs have the operating temperature range of 120°C - 180°C, whereas the steam reforming of alcohols occurs at temperatures between 220°C and 500°C” reported in the paragraph “Feasibility of reforming for fuel cell applications”, neither
ref. 76 nor 77 refer to the range of temperatures for carrying out the steam reforming of alcohols as reported in the aforementioned sentence.

The following references are suggested to be used instead of ref. 77:
- Amiri et al. - Chemical Engineering & Processing: Process Intensification, 157 (2020) 108148
- Palma et al. – Catalysts, 10 (2020) 665

5. The quality of Figure 4 should be improved.

6. A list of symbols and acronyms should be added.

**References**

**Is the topic of the review discussed comprehensively in the context of the current literature?**
Yes

**Are all factual statements correct and adequately supported by citations?**
No

**Is the review written in accessible language?**
Yes

**Are the conclusions drawn appropriate in the context of the current research literature?**
Yes

**Competing Interests:** No competing interests were disclosed.

**Reviewer Expertise:** Hydrogen generation by reforming reactions; catalytic membrane reactors for hydrogen production; fuel cells; membrane gas separation.

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.