CATALYTIC STEAM REFORMING OF ETHANOL FOR HYDROGEN PRODUCTION: BRIEF STATUS

Article Highlights
- Ethanol is considered as a feedstock for hydrogen production
- Steam reforming of ethanol for hydrogen production is analyzed
- Various metals deposited on a support material are analyzed as promising catalyst for hydrogen production

Abstract
Hydrogen represents a promising fuel since it is considered as a clean energy carrier and also because during its combustion only water is emitted. It can be produced from different kinds of renewable feedstocks, such as ethanol. In this sense, hydrogen could be treated as biofuel. Three chemical reactions can be used to achieve this purpose: steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR). In this study, the catalysts implemented in steam reforming of ethanol were reviewed. A wide variety of elements can be used as catalysts for this reaction, such as base metals (Ni, Cu and Co) or noble metals (Rh, Pt and Ru), usually deposited on a support material that increases surface area and improves catalytic function. The use of Rh, Ni and Pt supported or promoted with CeO$_2$ and/or La$_2$O$_3$ shows excellent performance in ethanol SR catalytic process. The ratio of water to ethanol, reaction temperatures, catalysts loadings, selectivity and activity are also discussed, as they are extremely important for high hydrogen yields.

Keywords: hydrogen, ethanol, catalyst, steam reforming.

The current dependence on fossil fuels and issues related to climate change have increased the demand for solutions that simultaneously account for environmental sustainability, energy security, and feasibility. This perception has favored the emergence of alternative processes with low carbon emissions and created opportunities for new developments. According to Akande et al. (2006) [1] the demand for hydrogen has increased in the last years mainly due to progress in fuel cell technologies. Fuel cells are electrochemical devices described as continuously operating batteries and are considered as a clean source of electric energy, containing high energy efficiency, and its resulting emission is just water [2].

There is some criticism of hydrogen as an energy carrier, due to high costs and waste of energy involved in its production [3,4]. Despite this, hydrogen technologies are under constant improvement and the use of this gas has the potential to reduce the problems caused by using fossil fuels [5]. Hydrogen can be produced from different feedstocks, such as fossil fuels and renewable raw materials [6,7].

The use of ethanol as raw material presents several advantages because it is a renewable feedstock, easy to transport, biodegradable, has low toxicity, contains high hydrogen content, easy to store and handle, and carbon dioxide released in the process is reabsorbed during biomass growth [8-11].

Regarding catalytic reactions, hydrocarbons or oxygenated ones can be converted into hydrogen and carbon dioxide essentially by three reactions: steam reforming (SR, Eq. (1)), partial oxidation (POX, Eq. (2)), and autothermal reforming (ATR, Eq. (3)):

\[ C_{n}H_{m}O_{s} + (2n - k)H_{2}O \xrightarrow{\text{Catalyst}} \rightarrow nCO_{2} + (2n + \frac{m}{2} - k)H_{2} \]  \hspace{1cm} (1)

\[ C_{n}H_{m}O_{s} + (n - \frac{k}{2})O_{2} \xrightarrow{\text{Catalyst}} \rightarrow nCO_{2} + \frac{m}{2}H_{2} \]  \hspace{1cm} (2)

\[ C_{n}H_{m}O_{s} + nO_{2} + (2n - k - 2j)H_{2}O \xrightarrow{\text{Catalyst}} \rightarrow \frac{n}{2}CO_{2} + (2n + \frac{m}{2} - 2j)H_{2} \]  \hspace{1cm} (3)

SR is the most efficient reaction and requires an external heat source since the reaction is endothermic. Although POX is an attractive exothermic reaction, it yields low hydrogen content compared to SR. ATR combines the last two reactions to balance the power consumption required for SR and the energy produced by the POX; however, it results in lower overall system efficiency compared to SR [12,13]. These three reactions are able to produce hydrogen, but SR has seen the most extensive industrial practice [5]. Therefore, the prime objective of this paper is to review the current state of the catalysts applied in ethanol steam reforming in recent years.

Ethanol steam reforming

Ethanol SR occurs at relatively lower temperatures compared with other hydrocarbon fuels [9,11] and has been widely studied due to the high yield provided for the formation of hydrogen (Eq. (4)). In this reaction, water and ethanol react over a catalyst to produce a mixture of hydrogen rich gas. Usually, the water to ethanol molar ratio in the reaction is higher than the stoichiometric value in order to prevent coke formation [14]. Some authors suggest the direct use of ethanol, i.e., without distillation, in fuel processors coupled in fuel cells in order to decrease the final cost of the fuel and improve energetic balance of the system, since distillation consumes a lot of energy in the industry [15]:

\[ C_{2}H_{5}OH(g) + 3H_{2}O(g) \xrightarrow{\text{Catalyst}} \rightarrow 2CO_{2(g)} + 6H_{2(g)}, \Delta H' = 173.3 \text{ kJ/mol} \]  \hspace{1cm} (4)

In ethanol SR several reactions can occur in parallel, such as: dehydrogenation, dehydration, products decomposition, methanation, Boudouard reaction, water gas shift (WGS), etc. [9]. Thus, it is of crucial importance to define both a good catalyst and reactor operating conditions to favor the desired routes to maximum hydrogen content and suppressing undesirable pathways to prevent catalyst deactivation [16,17]. Among all, the WGS reaction (Eq. (5)) becomes particularly important because it converts the carbon monoxide (CO) formed during reaction to carbon dioxide and hydrogen:

\[ CO + H_{2}O \rightleftharpoons CO_{2} + H_{2} \]  \hspace{1cm} (5)

WGS is a reversible reaction that at lower temperatures shifts the equilibrium to the right favoring the formation of the hydrogen and carbon dioxide and at higher temperatures the reaction kinetic is faster and reaction toward to lower conversion of CO. As a result, this reaction usually occurs in two different steps: high-temperature shift (HTS) and low-temperature shift (LTS), which can remove CO at acceptable levels [11,12,18].

In order of substitute the conventional two-step process by a single step, a new concept of WGS reaction in a heat exchanger microchannel reactor is proposed by Baier and Kolb [19], which suggests one step with a temperature profile along the reactor. The authors showed that it was possible to achieve a temperature profile close to the optimum and concluded that that concept was able to reduce the total reactor length and eliminated the needs for connections between different components.

Catalysts for steam reforming of ethanol

The main issue for ethanol SR is avoiding the coke formation over the catalysts, since it reduces the catalytic activity and leads to the material deactivation [20,21]. A wide variety of elements have been studied for this reaction, most of them focus on metals such as Ni, Cu and Co or noble metals such as Rh, Pt and Ru. Although these metals are characterized with high activity, alone they are not enough to achieve desirable hydrogen production. Thus, the active metal is usually deposited on a support material that increases surface area and improves catalytic function [9,11,21,22]. Table 1 summarizes the catalysts used for ethanol SR process analyzed in this review.

The importance of the support material for ethanol SR has been demonstrated in some studies, which emphasize that catalysts development is focused on both the active metal phase and in support material [23,24]. Wu et al. [25] analyzed four catalyst compositions: Ni/ZnO, Ni/La2O3, Ni/MgO and Ni/Al2O3. They found that Ni/ZnO presented the best performance achieving a hydrogen selectivity of 89.1% at 650 °C using 10% of Ni loading and water to ethanol mole ratio of 8. The effects of catalyst loading and water molar ratio were also studied. It was observed that with the increasing the mole ratio of water in reaction mixture up to 9 the selectivity of hydrogen grows to 91%. Also, this elevates carbon dioxide formation and suppresses the formation of carbon...
<table>
<thead>
<tr>
<th>Catalyst/metal loading</th>
<th>T range, °C</th>
<th>Ethanol conversion</th>
<th>H₂ selectivity</th>
<th>Catalyst preparation</th>
<th>Type of reactor</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% Ni/Al₂O₃; 10% Ni/MgO; 10% Ni/La₂O₃; 10% Ni/ZnO</td>
<td>650</td>
<td>−100</td>
<td>78.2–89.1</td>
<td>Support prepared by decomposition of precursors; active phase deposited by incipient wetness impregnation</td>
<td>Fixed-bed</td>
<td>[25]</td>
</tr>
<tr>
<td>10% Co/Al₂O₃; 10% Co/ZnO; 10% Ni/Al₂O₃; 10% Ni/MgO; 5% Rh/Al₂O₃; 5% Rh/MgO; 5% Ru/Al₂O₃; 5% Rh-10% Ni/Al₂O₃; 5% Rh-10% Ni-15% CeO₂/Al₂O₃</td>
<td>400-600</td>
<td>9.2–100</td>
<td>6.8–80.8</td>
<td>Support deposited by wash coating suspension; active phase deposited by incipient wetness impregnation</td>
<td>Microchannel reactor</td>
<td>[26]</td>
</tr>
<tr>
<td>2% Ir/CeO₂</td>
<td>400-650</td>
<td>50-100</td>
<td>40-65</td>
<td>Support prepared by precipitation of precursors and deposited by wash coating suspension</td>
<td>Microchannel reactor</td>
<td>[27]</td>
</tr>
<tr>
<td>10% Co/CeO₂</td>
<td>350-500</td>
<td>32.6-84.4</td>
<td>25-80*</td>
<td>Support prepared by hydrothermal method; active phase deposited by incipient wetness impregnation</td>
<td>Fixed-bed</td>
<td>[28]</td>
</tr>
<tr>
<td>20% Co/20% CeO₂-γ-Al₂O₃</td>
<td>400-600</td>
<td>88.4-99.7</td>
<td>0.93-4.4*</td>
<td>Support prepared by thermal stabilization of γ-Al₂O₃ followed by impregnations; active phase deposited by incipient wetness impregnation</td>
<td>Fixed-bed</td>
<td>[29]</td>
</tr>
<tr>
<td>20% CeO₂/La₂O₃-CeO₂</td>
<td>500</td>
<td>91-99</td>
<td>0.6-3.25*</td>
<td>Catalyst prepared by polymerization method</td>
<td>Fixed-bed</td>
<td>[30]</td>
</tr>
<tr>
<td>1% Rh/CeO₂</td>
<td>500</td>
<td>98-100</td>
<td>50-76</td>
<td>Support prepared by calcinations and precipitations; active phase deposited by incipient wetness impregnation</td>
<td>Fixed-bed</td>
<td>[31]</td>
</tr>
<tr>
<td>30% Ni/CeO₂-ZrO₂; 1%Rh-30%Ni/CoO₂-ZrO₂</td>
<td>600</td>
<td>81-90.1</td>
<td>58.9-72.8*</td>
<td>Support prepared by co-precipitation method; active phase deposited by incipient wetness impregnation</td>
<td>Fixed-bed</td>
<td>[32]</td>
</tr>
<tr>
<td>1% Rh/Al₂O₃-La₂O₃-CeO₂</td>
<td>500</td>
<td>72-100</td>
<td>42-79</td>
<td>Supports prepared by successive wet impregnation; active phase deposited by incipient wetness impregnation</td>
<td>Fixed-bed</td>
<td>[33]</td>
</tr>
<tr>
<td>9% Ni/Al₂O₃; 8% Ni/6% CeO₂-5%Al₂O₃; 8% Ni/6% La₂O₃-Al₂O₃; 8% Ni/6% CeO₂-ZrO₂; 8% Ni/6% La₂O₃-ZrO₂</td>
<td>150-350</td>
<td>15-100</td>
<td>30-55*</td>
<td>Supports prepared by wet impregnation and precipitation; active phase deposited by incipient wetness impregnation</td>
<td>Fixed-bed</td>
<td>[34]</td>
</tr>
<tr>
<td>1% Pt/CeO₂; 10% Ni/CeO₂; 1% Pt10% Ni/CeO₂</td>
<td>300</td>
<td>18-62</td>
<td>40-55</td>
<td>Supports prepared by precipitation; active phase deposited by incipient wetness impregnation</td>
<td>Fixed-bed</td>
<td>[20]</td>
</tr>
<tr>
<td>10% Ni/Al₂O₃; 10% Ni/15% La₂O₃-Al₂O₃; 10% Ni/15% La₂O₃-5% CeO₂-Al₂O₃; 10% Ni/15% La₂O₃-10% CeO₂-Al₂O₃; 10% Ni/15% La₂O₃-15% CeO₂-Al₂O₃</td>
<td>400-650</td>
<td>15-100</td>
<td>25-90</td>
<td>Supports prepared by successive wet impregnation; active phase deposited by incipient wetness impregnation</td>
<td>Fixed-bed</td>
<td>[37]</td>
</tr>
<tr>
<td>3% Pt-10% Ni/CeO₂</td>
<td>250-600</td>
<td>48-100</td>
<td>10-55*</td>
<td>Support prepared by calcination of CeO₂, followed by successive wet impregnations</td>
<td>Fixed-bed</td>
<td>[38]</td>
</tr>
</tbody>
</table>

*H₂ Yield = 100(mol H₂ produced)/(6×mol converted ethanol); **H₂ Yield = mol H₂ produced/mol converted ethanol.
over the catalyst. Increasing the Ni loading from 5 to 20% did not affect the ethanol conversion, but resulted in higher selectivity and suppressed methanation conversion.

Men et al. [26] studied wide range of catalysts in a microchannel reactor varying temperature from 400 to 600 °C. The active metals involved Rh, Ru, Ni and Co and support materials Al₂O₃, CeO₂ and MgO. Among others, Ru was considered unsuitable for ethanol SR while Rh showed higher activity and hydrogen selectivity due to ability to break the C-C bond. However, the combination of a bimetallic composition (Rh-Ni) and promoting Al₂O₃ with CeO₂ resulted in higher selectivity and suppressing undesirable reactions. The use of 10% Ni loading suppresses the ethylene formation, which is extremely important to practical applications due to coke formation. In addition, it was reported that ethanol SR proceeds better at temperatures over 500 °C.

Using the concept of microchannel reactor Cai et al. [27] realized a study over Ir/CeO₂. The catalyst showed a better performance comparing with fixed-bed reactor but was not active for WGS reactions.

Ozkan et al. [28] performed the experiments with Co catalysts supported on CeO₂ nanorods and nanocubes under the temperature range from 350 to 500 °C and using water to ethanol molar ratio of 10. Lower conversions and hydrogen yields to Co/CeO₂-nanorods catalyst were observed, which was attributed to the lack of activity on C-C bond cleavage and a great affinity for dehydration reaction. However, a conversion of approximately 84 and yield of 80% were achieved by Co/CeO₂-nanocube. This performance was due to higher Co dispersion, density of surface basic sites and oxygen mobility.

Cobalt-based catalysts were also investigated by Assaf et al. [29]. The catalysts were supported on Al₂O₃, as well as CeO₂. It was observed that support material led to higher surface area of CeO₂-Al₂O₃ which increases for 75% the hydrogen yield at 600 °C. In another study, Assaf et al. [30] realized this reaction using a mixture of Co₂O₃/La₂O₃/CeO₂ at 500 °C and water to ethanol molar ratio of 3. They found that the mixture of these oxides was a better catalyst than the association of just two of them. A maximum of 99% of ethanol conversion and a yield of 54% were achieved at mentioned temperature.

Noronha et al. [31] performed an investigation over Rh/CeO₂ at temperature of 500 °C and water mole ratios of 3 and 10, by using CeO₂ with low (14 m²/g) and high (275 m²/g) surface area. The results indicate that the addition of 1% of Rh improves the hydrogen selectivity due to ability to break C-C bound. Nonetheless, it was observed a significantly decrease Rh/CeO₂ stability characterized by low surface area due to ethylene formation and consequently the carbon deposition over the catalyst. This effect was not observed with high surface area Rh/CeO₂ catalyst, which showed good stability during the deactivation tests. Furthermore, the increasing on the water to ethanol mole ratio up to 10 improved the stability for both catalysts and also towards to hydrogen selectivity.

The use of Rh was also compared by Dalai et al. [32] which tested two different compositions of prepared catalyst and identified an ethanol conversion of 86% and a hydrogen selectivity of 73%. The authors used crude bioethanol with the water to ethanol mole ratio of approximately 11. In agreement with other studies, the addition of Rh increases the ethanol conversion and hydrogen yield due to its ability of breaking the C-C bonds. In addition, they identified that this promotor favored WGS and methane SR reactions and suppressed coke formation. The Rh catalyst was considered more stable than Ni/CeO₂-ZrO₂ in time on stream tests because the ethanol conversion decreased from 91 to 86% after 12 h and remained stable up to 48 h of operation.

Reyes et al. [33] tested the SR reaction over a Rh/Al₂O₃-La₂O₃ promoted with CeO₂ and verified that the addition of CeO₂ in loadings from 2.5 to 10% improved the catalyst stability and decreased carbon formation, at 500 °C and the water to ethanol mole ratio of 3. However, negative effects over the stability and hydrogen selectivity were observed when the amounts of CeO₂ loading exceed 15%. This consequence was attributed to Boudouard reaction and ethylene polymerization. Concerning the catalyst stability, it was shown that the ethanol conversion and hydrogen selectivity ranged from 100 to 99% and from 100 to 60%, respectively, during 48 h of time on stream. The authors also verified that was possible to recover part of the original the catalyst activity subjecting to an oxidation and reduction process.

Lazar et al. [34] investigated the behavior of Ni/Al₂O₃ and Ni/ZrO₂ modified with La₂O₃ and CeO₂ at 150 to 350 °C and the water to ethanol mole ratio of 30. The results suggest that the promoter La₂O₃ over Ni/ZrO₂ improved the catalyst structure better than others tested, and elevated the hydrogen yield to approximately 60% at 350 °C. Comparing with similar catalyst [35,36], they concluded that without excess of water this result was achieved just when those oxides were used in temperatures above 550 °C. Reyes et al. [37] confirmed that the addition of La₂O₃ and CeO₂ over NiAl₂O₃ improved the catalyst stability and dec-
reased the carbon deposition rate comparing with Ni supported on bare Al2O3.

Considering low temperature steam reforming (LTSR) Noronha et al. [20] examined the effect of Pt addition on Ni/ CeO2 catalysts. Time on stream experiments realized at 300 °C with stoichiometric mole ratios revealed very low carbon deposition rate with PtNi/ CeO2 catalyst. The maximum ethanol conversion ranged from 65 to 37% and the hydrogen selectivity remained around 48% during 28 h in stream experiments. Using a comparable catalyst Palma et al. [38] also found very low carbon deposition rates and a complete ethanol conversion was achieved in temperatures above 300 °C. These catalysts were considered excellent in C-C bond cleavage.

CONCLUSIONS

Based on the observations from recent research on reforming catalysts, it is possible to infer that the use of Rh, Ni and Pt supported or promoted with CeO2, and/or La2O3 shows excellent performance for hydrogen synthesis using ethanol steam reforming process. The combinations of these materials in different proportions are exceptional in producing a very low carbon deposition on catalyst surface. In addition, the use of these catalysts allows achieving high ethanol conversion and hydrogen selectivity.

The ratio of water to ethanol has an important function in ethanol steam reforming process, especially in hydrogen selectivity. The excess of water favors the water gas shift reaction, improving hydrogen content and helping minimize the negative effects of carbon deposition. Furthermore, recycling catalyst tests are extremely important for technical and economic evaluation, but still need to be considered in future studies.

Despite the difficult of break C-C bond in low temperature steam reforming (LTSR), very promising results have been shown and more attention should be given to it. This is an important issue, since the energetic balance at low temperatures tends to be better, which will result in more efficient energy conversion devices for good sustainability and environment development.

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REFERENCES

KATALITIČKO REFORMOVANJE ETANOLA VODENOM PAROM ZA PROIZVODNJU VODONIKA: KRATAK PREGLED

Vodonik predstavlja interesantno gorivo jer se smatra nosiocem čiste energije budući da tokom sagorevanja emituje samo vodu. Dobija se iz različitih obnovljivih sirovina, na primer etanola. Imajući sve ovo u vidu, vodonik se može smatrati biogorivom. Tri hemijske reakcije se primjenjuju u njegovoj proizvodnji: reformovanje vodenom parom (RVP), delimična oksidacija (DO) i autotermičko reformovanje (ATR). U ovom istraživanju, izvršen je pregled upotrebe katalizatora za reformovanje etanola vodenom parom. Ka o katalizatori u ovoj reakciji mogu se koristiti veliki broj različitih hemijskih elemenata, na primer alkalni metali (Ni, Cu i Co) ili plemeniti metali (Rh, Pt i Ru), obično nanešeni na nosač da bi se povećala površina i pospešila katalitička funkcija. Rh, Ni i Pt, nanešeni na CeO$_2$ i/ili La$_2$O$_3$ nosačima, pokazuju odlične učinke u procesu katalitičkog RVP etanola. U radu su takođe razmatrani odnos voda/etanol, reakcionalna temperatura, količine katalizatora, selektivnost i aktivnost zbog njihovog izuzetnog značaja za postizanje visokih prinosa vodonika.

Ključne reči: vodonik, etanol, katalizator, reformovanje vodenom parom.