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OVERVIEW OF THE ETHANOL STEAM REFORMING FOR HYDROGEN PRODUCTION

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Abstract. Among the various hydrogen production technologies, steam reforming of hydrocarbons stands out due to its characteristics that can be applied in automotive systems on board as an internal combustion engine and as fuel cells. Ethanol has advantages such as easy handling, transport, storage, low toxicity, volatility, and is easily obtained from different biomasses such as sugarcane, corn and potatoes. The catalysts and supports applied in the reform help the conversion of ethanol into hydrogen. To obtain high rates of hydrogen, low coke deposition in catalysts and low concentrations of carbon dioxide, parameters such as catalyst composition and support, temperature and pressure applied during the process, steam-ethanol feed proportions and hydrogen selectivity are evaluated. This work is directed to a review of the literature on ethanol vapor reform, presenting several studies related to its area and its viability.

Keywords: Hydrogen, Ethanol, Steam Reforming, Renewable Sources, Energy

1. INTRODUCTION

In recent decades, global concerns about environmental consequences resulted by the high fossil fuels consumption have grown. Global warming and atmospheric pollution are examples of the consequence of use these energy sources. Due to this problem, hydrogen fuel stands out as a clean source of energy, with high calorific power and a promising substitute of fossil fuels for several applications.

Discovered in the 15th century by Paracelsus, hydrogen is the most abundant chemical element in the universe. Its usefulness was discovered in the eighteenth century by Henry Cavendish, who proved that by burning it in the air, the final product was only water. However, this element is not a primary source of energy, it needs to be fabricated. There are several methods of obtaining hydrogen, such as reactions between metals and acids, electrolysis of water, gasification, partial oxidation of oils and reforming of hydrocarbons (Balthasar, 1984).

When compared to any other fuel, hydrogen has a combustion power 2.5 times higher than commonly used hydrocarbons, such as methane, gasoline, and propane. Thus, the mass of hydrogen required to provide energy consumption is much lower than that of a hydrocarbon in the same application (Barreto; Makihira; Riahi, 2003).

2. CATALYTIC REFORMING

A widely known and widespread method in chemical industries for the hydrogen production is the catalytic reforming process. It is an endothermic process in which to use hydrocarbons, alcohols, and ammonia as a hydrogen source. The catalytic reforming needs a promoting substance of the reaction. This substance can be carbon dioxide, in the dry reforming, or water, in the steam reforming process (Casas-Ledón et al., 2012; Schwengber et al., 2016). Several catalysts are used, the noble metals being the most used due to their high catalytic activities, such as rhodium (Rh), ruthenium (Ru), palladium (Pd), iridium (Ir) and platinum (Pt) (Contreras et al., 2014; Greluk et al., 2016; Hedayati et al., 2015; Hou et al., 2014, 2015; Hung et al., 2012; Iulianelli et al., 2009; Mondal; Pant; Dalai, 2015; Murmura et al., 2015). Several studies have been published regarding the use of non-noble metals (for example, Co, Ni, Cu) blended in various supports such as Al_2O_3 , SiO_2 , La_2O_3 , ZrO_2 , CeO_2 and MgO (Akdim et al., 2008; Contreras et al., 2014; Ni;

Leung; Leung, 2007; Palma et al., 2014; Sharma et al., 2016, 2017; Sun et al., 2005; Wang et al., 2011) in furtherance of guarantee ideal metallic dispersion and to be also able to participate in the catalytic process (Cai et al., 2012).

For being easily decomposed in the presence of water during the Steam Reforming Process, alcohols are efficient sources of hydrogen. Although methanol is an abundant and widely distributed raw material, it is highly toxic and is produced from non-renewable fossil fuels, such as natural gas. In this way, ethanol appears as a good alternative to methanol, since it is already used as fuel in automotive vehicles and has advantages such as easy handling, transport, storage, low toxicity, volatility, besides being easily obtained from different biomasses as sugar cane, corn and potato (Bilal; Jackson, 2017; Deluga, 2004; Klouz et al., 2002; Roh et al., 2006). Moura et al. (2012) exposed that the H₂ catalyst selectivity during the reforming reaction is as following: Rh>Co>Ni>Ro>Pt,Ru,Cu and that a combination of catalysts can potentiate the selectivity of H₂ and CO₂. However, the catalyst properties are different for different supports and different reaction conditions, such as temperature, water/ethanol feed rate and space time of reforming.

2.1 Ethanol Steam Reforming

Ethanol Steam Reforming (ESR) is an endothermic process in which the fuel reacts with water in the presence of catalysts, responsible for increasing the rate of reactions, resulting in a mixture of gases generally containing hydrogen (H₂), carbon dioxide (CO₂), methane (CH₄), carbon monoxide (CO) and water (H₂O).

The ESR can be performed in fuel cells, where the cell itself assists the reaction stages and the reactions are activated more efficiently or in reformers. Solid Oxide Fuel Cells (SOFC) and Molten Carbonate Fuel Cells (MCFC) usually operate at elevated temperatures, while Proton Exchange Membrane Fuel Cells (PEMFC's) operate at lower temperatures (Sun et al., 2005). According to Akdim et al. (2008) PEMFC's are considered the most efficient and almost zero-emission power generation structures for mobile and stationary uses.

In fuel cells, when high-reforming temperatures are applied, CO formation is favored. Nevertheless, CO concentration must be low, once it is considered as a poison to the catalyst surface and it decreases the cell's efficiency and useful life. To reduce its concentration, conditions favoring low temperature are required to favor WGRS at the cost of reducing thermal efficiency (Roh et al., 2006).

For a catalyst to be considered efficient during ESR, it must dissociate efficiently C-C bonds, generate low concentrations of CO and CH₃CHO (poisons for fuel cells) and remain stable under catalytic operating conditions, avoiding coke deposits during the reaction. The catalyst support and the catalytic metal are the main sites of coke deposition. When it happens, the catalyst may be deactivated and lose its efficiency (Divins et al., 2015; Sharma et al., 2017).

Aiming the control of the catalytic surface and carbon deposition over it, several studies present the Temperature Programmed Desorption (TPD) as an efficient method of observation of the molecules adsorbed by the surface of the catalyst through the desorption. The method is used as an instrument to increase the perception of the reaction mechanisms of the ESR (Cai et al., 2008; de Lima et al., 2009; Sheng et al., 2007; Zeng; Li; Olsbye, 2015).

The global ESR reaction is (Ni; Leung; Leung, 2007):



This global reaction approaches the chemical mechanisms that describe ESR. To obtain higher rates of hydrogen production, lower coke deposition on catalysts and low concentrations of carbon dioxide, parameters such as catalyst composition and support, temperature and pressure applied during the process, steam-ethanol feed proportions and hydrogen selectivity for the catalyst must be evaluated. This global reaction approximates the chemical mechanisms that make the ESR up. Sutton et al. (2013) present and detail a scheme, Fig. 1, for the reaction mechanisms, indicating the most energetically favorable pathways for ethanol steam reforming. Authors emphasized the importance of dehydrogenation/hydrogenation reactions during the reforming. Solid lines represent the most energetically favorable pathway in the decomposition of ethanol in Pt (111)/Al₂O₃. Besides that, the solid (dotted) lines represent additional reactions when ethanol steam reforming occurs at 300 °C and for experimental feeding conditions of 12.5% ethanol and 37.5% H₂O. (*) indicates that the molecule was adsorbed by the catalyst. Nonactivated adsorption is observed for ethanol, acetaldehyde and CO, while methane is adsorbed by activated adsorption. The two key intermediates of the reaction are ethanol adsorbed and acetyl (CH₃CO*). Excess H* atoms were omitted from the scheme for better understanding. The initial dehydrogenation of ethanol is irreversible and the subsequent dehydrogenations are partially equilibrated until ketenyl (CHCO*) formation. At 300 °C, CO₂ production is limited by slow formation and carboxyl decomposition (COOH*).

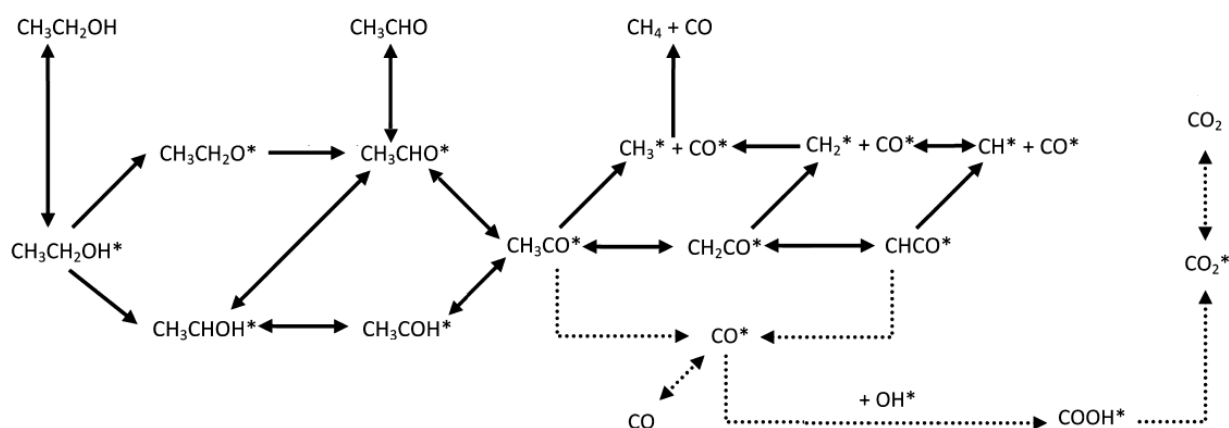


Figure 1. Reaction scheme mechanism of ESR [adapted from (Sutton et al., 2013)]

2.2 Catalyst composition

The choice of catalyst is extremely important in ESR. Each catalyst type presents different performances during the process and can be joined in different proportions. Hung et al. (2012) studied the oxidative ethanol steam reforming (OESR) by co-feeding steam and oxygen on ten different metal catalysts (Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, Au) supported on Al_2O_3 . The reaction was studied in the temperature range of 400-600 °C at atmospheric pressure. The OESR performance is influenced by all M/ Al_2O_3 different chemical properties. Ru, Rh and Ir revealed high H_2 yield and low selectivity to CH_3CHO and C_2H_4 . Cu, Ag and Au showed high selectivity to CH_3CHO , while Co, Ni, Pd and Pt showed high selectivity to C_2H_4 , due to the preferential ethanol dehydration reaction. In addition, experimental values indicated that ethanol can easily interact with all metals and Al_2O_3 is an efficient catalyst for the dehydration of ethanol.

In ESR processes, Rh is used to assist the breakage of C-C and C-H bonds and to promote the hydrogenation reaction. Platinum (Pt), though, may exhibit high rates of carbon deposition, even being highly selective to hydrogen. Nevertheless, the union of these two metals, creating the Rh-Pt bimetallic catalyst presents high activity in the SRE and in the Water Gas Shift reaction (WGS), presenting low susceptibility to the formation of coke (Cifuentes et al., 2016; Contreras et al., 2014; Roh et al., 2006; Sharma et al., 2016). Sheng et al. (2007) studied the use of bimetallic catalyst Rh-Pt and concluded that for an efficient ethanol decomposition and high hydrogen production, Rh-Pt presence is required. A considerable decrease in the formation rate of acetaldehyde byproducts (such as benzene and ketene) was detected, which are considered as poisons for the reforming cells.

Nickel (Ni) catalyst promotes the breakdown of the bonds of the ethanol molecule into O-H, -CH₂-, C-C and -CH₃ and is useful in decreasing carbon deposition. Zeng; Li; Olsbye (2015) evaluated the effect of incorporating 2 wt.% Ni^{2+} to $\text{Mg}(\text{Al})\text{O}$ at 500 °C. The catalyst mainly produced C_2H_4 , CH_3CHO , H_2 as byproducts under all tested conditions, while CO and CO_2 were detected only when a larger space-time was used. Without incorporation of Ni^{2+} , $\text{Mg}(\text{Al})\text{O}$ exhibits high selectivity to C_2H_4 , while its incorporation reveals high selectivity to CH_3CHO . González-Gil et al. (2015) presented the effect of incorporation of Rh to Ni/ Al_2O_3 for ethanol and acetone reform in a temperature range of 200 to 700 °C at atmospheric pressure. They verified that Rh promotes the total conversion of acetone, in addition to a greater production of hydrogen, with minimum deposition of carbon. As for the Ethanol Reform, Rh reduces the formation of intermediates such as acetaldehyde and ethylene, even in minimal proportions of Rh-Ni.

Cobalt (Co) catalysts can be active in low temperature reactions and increase the reactions of Water Gas Shift (Contreras et al., 2014; Sharma et al., 2016). Ethanol steam reforming studies on Co/ CeO_2 catalysts (da Silva et al., 2010; de Lima et al., 2009) indicated that the reaction at low temperatures may favor acetate formation, while higher temperatures assist the conversion of acetate to methane, which is decomposed on Co metal particles to produce H_2 and carbon. To avoid catalyst deactivation rates during the reform, high H_2O /ethanol feed ratios can be applied. Furthermore, increasing space-time during the reaction might increase hydrogen selectivity and decrease acetaldehyde selectivity. Moretti et al. (2015) evaluated the use of nickel, cobalt and nickel/cobalt-supported ceria in the production of hydrogen from the ESR. Authors emphasize the importance of the metal-support interaction for high efficiency. Results showed that the best support was the mixture of nickel and cobalt, with respect to the higher conversion of ethanol and the production of hydrogen compared to the monometallic supports. The conversion efficiency of ethanol reached 90% at a temperature of 500 °C.

2.3 Support composition

The choice of support is of extreme importance in ESR, since the strong interaction between metal and support leads to lower coke generation. It is important to have high selectivity and deactivation resistance, besides promoting H_2 formation and CO conversion in the WGS during ESR (Cifuentes et al., 2016; Sharma et al., 2017).

Alumina (Al_2O_3) is a thermally stable metal oxide and acts as an acidic support in catalytic reactions due to the acidic centers present on its surface. It promotes ethanol dehydration and leads to the formation of ethylene, a primary source of coke, known as a catalyst deactivator (Bilal; Jackson, 2017; Contreras et al., 2014; Sharma et al., 2017). Sharma et al. (2016) compared the catalytic activity of Rhodium catalysts supported by Al_2O_3 and CeZrO_2 at 600 °C. The conversion of 99.9% of the ethanol is achieved on the surface of both catalysts; however the amount of gaseous products, including H_2 , CO , CO_2 and CH_4 was higher on Rh/CeZrO_2 and the amount of coke deposited on $\text{Rh/Al}_2\text{O}_3$ catalyst was 150% higher than Rh/CeZrO_2 , which can be attributed to the acidic nature of alumina.

Ceria (CeO_2) is a catalyst support with high Oxygen Storage Capacity (OSC) leading to the carbon oxidation deposited on the catalyst surface (Cai et al., 2012; Sharma et al., 2017). Its catalytic property is unstable at temperatures above 400 °C and it is efficient in three-way catalysis (TWC), in which harmful gases are converted in to harmless ones (Murmura et al., 2015; Wang et al., 2011). Cifuentes et al. (2016) present CeO_2 as a promising basic support for Rh, Pt and Rh-Pt catalysts, as it promotes a high dispersion of the active sites, i.e. the metal atoms, on the surface of the support. There are strong interactions between the Ce^+ species of CeO_2 with the active sites, which facilitates the decomposition of the alcohols. In addition, da Silva et al. (2011) introduced a new support cleaning mechanism of Ceria, which showed continuous coke-removal properties during the reaction and, besides that, validated Ceria's ability to donate oxygen during the reforming.

Titanium oxide (TiO_2) is typically used in the generation of photocatalytic hydrogen from ethanol or water. However, carbonaceous deposition is not a problem in the photocatalytic conversion of ethanol to hydrogen, but the rupture of C-C bonds under ambient conditions is still a challenge to increase yield in hydrogen (Contreras et al., 2014; Sharma et al., 2017).

2.4 Influence of temperature and pressure

SRE is an endothermic reaction with positive ΔH° and its equilibrium constant increases as the temperature increases. Based on the Le Chatelier's principle, the ESR temperature increase leads to a higher formation of products. The use of catalysts reduces the activation energy of the reaction, promoting a higher rate of reaction and formation of products. Cobalt catalysts supported in alumina are among the most active metal catalysts for SRE at high temperatures (Hou et al., 2015). According to Greluk et al. (2016) the temperature of 540 °C allows complete ethanol conversion and is satisfactory for the generation of hydrogen-rich gas with small yield of byproducts.

Sheng et al. (2007) studied the reforming of ethanol as a function of temperature over Rh-Pd/CeO_2 . During the period of 2 hours, no catalytic deactivation was detected. At low temperature <500 K (around 480 K) signs of acetaldehyde and acetone were seen and at higher temperatures they were not detected. According to TPD results, ethylene was not observed at any temperature evaluated. At temperatures >650 K, ethanol conversion was almost complete. Results showed that the 550–650 K temperature interval is very critical for CO and CO_2 production. Authors say that it is independent of reaction flow rate. Besides that, above 700 K hydrogen production increases, however, the amount of CO also increases.

SRE studies are mostly carried out at atmospheric pressures, since, according to the Le Chatelier's principle, an increase in the pressure of the overall reaction of the reform causes a shift in the equilibrium of the SRE to reduce the formation of products and increase the formation of reagents (Klouz et al., 2002). (Zeng; Li; Olsbye, 2015) performed the ESR at 500 °C at atmospheric pressure. Using the partial pressure ratio of $P_{\text{C}_2\text{H}_5\text{OH}}: P_{\text{H}_2\text{O}}: P_{\text{Inerte}} = 0.0163: 0.0500: 0.93$ (atm), they noticed that Water and Ethanol competed with the same active sites on the surface of the catalyst. Also, both the increase of $P_{\text{C}_2\text{H}_5\text{OH}}$ and of $P_{\text{H}_2\text{O}}$ led to a decrease in the yield of the byproducts CH_3CHO and C_2H_4 , but favored the selectivity of C_2H_4 .

2.5 Summary

The table summarizes the key results found listed in this review on the ethanol steam reforming.

Table 1: State of art

Catalysts/Supports investigated	Temperature (°C)	Conversion (%)	Conclusions
Ni/Mg(Al)O Zeng; Li; Olsbye (2015)	500 °C		The catalyst mainly produced C ₂ H ₄ , CH ₃ CHO, H ₂ as byproducts under all tested conditions; Without incorporation of Ni ²⁺ , Mg(Al)O exhibits high selectivity to C ₂ H ₄ , while its incorporation reveals high selectivity to CH ₃ CHO.
(Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, Au)/Al ₂ O ₃ Hung et al. (2012)	400-600 °C.	Best conversion rates: Rh:(84% at 400 °C) (87%, at 450 °C) (92% at 500 °C) Au:(96% at 550 °C) Ni, Rh, Ag, Au: (97% at 600 °C)	The OESR performance is influenced by all M/Al ₂ O ₃ different chemical properties. Ru, Rh and Ir revealed high H ₂ yield and low selectivity to CH ₃ CHO and C ₂ H ₄ . Cu, Ag and Au showed high selectivity to CH ₃ CHO, while Co, Ni, Pd and Pt showed high selectivity to C ₂ H ₄ , due to the preferential ethanol dehydration reaction.
Rh-Pt/CeO ₂ , Rh-Pd/CeO ₂ , Sheng et al. (2007)	Around 500 K and 700 K		Authors concluded that for an efficient ethanol decomposition and high hydrogen production, Rh-Pt/Pd presence is required. The study in Rh-Pd/CeO ₂ as a function of temperature showed that acetaldehyde and acetone are detected at low temperature (<500 K) and that above 700 K hydrogen production increases, however, the amount of CO also increases
Rh-Ni/Al ₂ O ₃ González-Gil et al. (2015)	200-700 °C	70% at 700 °C	Hydrogen-rich gas is produced at temperatures higher than 673 K in with maximum mole fraction of 0.6-0.7. Rh reduces the formation of intermediates such as acetaldehyde and ethylene, even in minimal proportions of Rh-Ni.
Ni/CeO ₂ , Co/CeO ₂ , Ni-Co/CeO ₂ Moretti et al. (2015)	250-750 °C	90% at 500 °C.	Results showed that the best support was the mixture of nickel and cobalt, with respect to the higher conversion of ethanol and the production of hydrogen compared to the monometallic supports.
Rh/Al ₂ O ₃ Rh/CeZrO ₂ Sharma et al. (2016)	600 °C	99.9%	The conversion of 99.9% of the ethanol is achieved on the surface of both catalysts; however the amount of gaseous products, including H ₂ , CO, CO ₂ and CH ₄ was higher on Rh/CeZrO ₂ and the amount of coke deposited on Rh/Al ₂ O ₃ catalyst was 150% higher than Rh/CeZrO ₂ , which can be attributed to the acidic nature of alumina.
PtKCo/CeO ₂ Greluk et al. (2016)	T < 600 °C		SRE over PtKCo/CeO ₂ avoids formation of ethylene and methane. However, it favours acetaldehyde production. The temperature of 540 °C allows complete ethanol conversion and is satisfactory for the generation of hydrogen-rich gas with small yield of byproducts.
Pt (111)/Al ₂ O ₃ Sutton et al. (2013)	300-400 °C		Authors emphasized the importance of dehydrogenation/hydrogenation reactions during the reforming. Nonactivated adsorption is observed for ethanol, CH ₃ CHO and CO, while CH ₄ is adsorbed by activated adsorption. The two key intermediates of the reaction are ethanol and CH ₃ CO adsorbed. The initial dehydrogenation of ethanol is irreversible and the subsequent dehydrogenations are partially equilibrated until ketenyl formation. At 300 °C, CO ₂ production is limited by slow formation and carboxyl decomposition (COOH*).

3. CONCLUSIONS

The present work was developed with the objective of evaluating an Ethanol Steam Reforming, process that is being developed to hydrogen production to internal combustion engine and fuel cells. From the analyzed studies, it was possible to observe some important parameters responsible for the success of the hydrogen formation from the ESR, such as the temperature of the reform, the type of catalyst and the pressure, the latter interfering directly in the degree of the global reaction, and thus in the production of hydrogen.

Studies have shown that the appropriate temperature for ESR should be above 500  C and the pressure at 1 atm. Regarding catalysts, they are key elements in the conversion of liquid and gaseous fuels into hydrogen. Thus, the choice of the appropriate catalyst is of extreme importance, and those with the best conversion efficiencies were those containing Ni, Rh and Pt supported on Ceria.

4. ACKNOWLEDGEMENTS

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