

**Catalysts for H₂ production using the ethanol steam reforming.
(A Review)**

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ABSTRACT

A short literature review of catalysts for the reforming reaction of ethanol from water vapor has been done at various operating conditions. In general, the ethanol/water vapor ratios most used range from 4 to 10, the latter being recommended. This reaction is endothermic and produce H₂, CO₂ and other products, when ethanol reacts under the best conditions from thermodynamic standpoint. However, there are undesirable products, such as CO and CH₄ which are also formed. Additionally other reactions also occur such as CH₃CHO ethanol dehydrogenation, dehydration CH₂ = CH₂, decomposition to CO and CH₄ or CO₂ and CH₄. The literature have mentioned and recognized that CH₃CHO and CH₂ = CH₂ are intermediates that may be formed during the reaction at relatively low temperatures prior to the formation of H₂ and CO₂ and has been observed the presence of coke on the catalyst. The reforming of ethanol with steam has been reported to produce small amounts of CO and CH₄. Catalysts having basic sites have shown good stability than other type of catalyst having acid sites.

1. Introduction

In the next future, H₂ will become a major source of energy. H₂ is a clean burning fuel which can be stored as a liquid or gas, is distributed via pipelines, and has been described as a long term replacement for natural gas [1]. The steam reforming of hydrocarbons, especially steam methane reforming is the largest and generally the most economical way to make H₂. If the electricity is available and relatively inexpensive, electrolysis of water offers an alternative commercial approach.

In the past (before 2000), the H₂ business have changed dramatically because H₂ was in plentiful supply with refineries being major sources of H₂, but that has all changed due to the refineries have become large net consumers of H₂ in an effort to reduce pollution [2]. H₂ offers a potentially non-polluting inexhaustible, efficient, and cost attractive fuel for energy demands. Future production of H₂ may be emerging from the selective oxidation of natural gas exclusively to CO and H₂, however research continues on photolysis, electrolysis and thermal processes for H₂ production. This work intends to provide an overview of the major catalytic studies for H₂ production by steam

reforming of ethanol from 2006 to 2013. Before this period of time, one review was found and by Hernandez and Kafarov [3].

From non fossil feedstocks such as ethanol, methanol and others, ethanol (or bio-ethanol) has several advantages as chemical hydrogen source for fuel cells, thanks to its storage facilities, handling and transport safely due to its low toxicity and volatility. Moreover, bio-ethanol is a chemical that can store hydrogen in amounts exceeding its density as liquid at atmospheric pressure and has a density of hydrogen volume greater than that of other compounds organics such as ethane, propane and methanol. As chemical storage compound the bio-ethanol has a total density of about 1 g/cm³ [4]. Therefore, it is within the substances most promising as storage means hydrogen for fuel cells.

According to existing literature, recently many works have been published and devoted to reforming of bioethanol in order to produce a gas rich in hydrogen for later use in fuel cells. Most of the investigations seek H₂ of the highest quality (which is achievable using noble metal catalysts) for use in fuel cells.

In the open literature, there are thermodynamic studies which demonstrating the feasibility of H₂ production from steam reforming of ethanol for applications in fuel cell [5-7]. In fact, two of the alternatives promising to carry out the process are the auto-thermal reforming, wherein the process is fed with ethanol, oxygen and steam and part of the ethanol is consumed to produce the necessary heat to maintain the reaction and steam reforming, where the heat for the endothermic reaction is supplied by a source of external energy. Of these two alternatives, the most efficient and with more advantages is the steam reforming, since it has a higher efficiency and higher concentrations of hydrogen [8].

Before 2007, Rh and Ni are the best and the most commonly used catalysts for ethanol steam reforming towards hydrogen production[9]. The selection of proper support for catalyst and the methods of catalyst preparation significantly affect the activity of catalysts. In terms of hydrogen production and long-term stability, MgO, ZnO, CeO₂, and La₂O₃ are suitable supports for Rh and Ni due to their basic characteristics, which favor ethanol dehydrogenation but inhibit dehydration. In accordance with Leung and Leung [9] Rh and Ni are inactive for water gas shift reaction (WGSR), and the development of bimetallic catalysts, alloy catalysts, and double-bed reactors is promising to enhance hydrogen production and long-term catalyst stability. Autothermal reforming of bioethanol has the advantages of lesser external heat input and long-term stability. Its overall efficiency needs to be further enhanced, as part of the ethanol feedstock is used to provide low-grade thermal energy. Development of millisecond-contact time reactor provides a low-cost and effective way to reform bio-ethanol and hydrocarbons for fuel upgrading. Despite its early research and development stage, bio-ethanol reforming for hydrogen production shows promises for its future fuel cell applications.

2.- Catalysts for steam reforming of ethanol

Some catalysts have been developed for the process of steam reforming of ethanol to produce H₂ which have been tested with different metals: Rhodium, Platinum, Nickel, Cobalt, Zinc, Iron, Copper, Gold, Palladium and Ruthenium

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with various metal oxide supports such as Al_2O_3 , CeO_2 , MgO , SiO_2 , ZnO , ZrO_2 , TiO_2 , V_2O_5 , La_2O_3 , Sm_2O_3 , Y_2O_3 and alkali promoters tested as K, Na and Li.

2.1.- Noble metal catalysts

Studies carried out using noble metals as palladium on alumina (Table 1a) concluded that the selectivity to H_2 was proportional to the molar ratio of water / ethanol with complete conversion of ethanol. Also they obtained selectivity to hydrogen up to 95% with temperature close to 650°C and a production of CO minimum at a temperature close to 450°C [10]. Another metal that has been studied for the reforming of ethanol is rhodium supported: Rh/CeO_2 , Rh/ZrO_2 and $\text{Rh/CeO}_2\text{-ZrO}_2$ ($\text{Ce/Zr} = 4.2$ and 1), with an excess of water in the feed molar ratio of 1:8, which for the temperature range $400 - 500^\circ\text{C}$ all the catalysts showed total conversion of ethanol and a high selectivity to hydrogen (5 to 5.7 moles of hydrogen per mole of ethanol) [11-12].

Other studies have made comparisons between different metal catalysts and the same support as Au/CeO_2 , Pd/CeO_2 , Pt/CeO_2 and Rh/CeO_2 where the Au/CeO_2 catalyst presents increased production of CO_2 at low temperatures and low production of H_2 compared to the other catalysts [13].

The literature of noble metals supported or non-supported is very big and in some times very special because there are many factors which are involved, for example the metal dispersion, the metal-support interaction, the acidity, the total amount of noble metal (they are very expensive), the preparation method, the promoters. In an incipient review we can observe the follow metallic or bimetallic systems having these properties (Table 1b).

Table 1a. Summary of catalysts made of noble metals for ethanol reforming [3] (from 2003 to 2006)

Catalyst	X	S	T($^\circ\text{C}$)	EtOH H ₂ O	%CO (v/v)	%H ₂ (v/v)	Reference
2%-Ir/ CeO_2	100	96 c	650	1:3	16	72	B. Zhang, 2006
0,5%-Pd/ Al_2O_3	100 a	68 c	650	1:3	12	51	J. Breen, 2002
0,75%-Pd/ γ - Al_2O_3	100 a	73 c	700	1:3	18	55	F. Auprêtre, 2002
1%-Pd/ Al_2O_3	70	55	830	1:3	-	41,2 c	D. Liguras, 2003
5%-Pd/ Al_2O_3 (com.)	100 a	98 c	620	1:15	0,24	5,88	M. Goula, 2004
1%-Pd/C	99 a	58 c	330	1:8,1	14,6 c	43,4 c	V. Galvita, 2002
0,5%-Pd/ CeO_2 / ZrO_2	100 a	75 c	720	1:3	18	56	J. Breen, 2002
3%-Pd/MgO	66 a	75	650	S/C=4,2	17,5 c	56,2 c	F. Frusteri, 2004c
1%-Pt/ γ - Al_2O_3	100 a	61 c	700	1:3	13	46	F. Auprêtre, 2002
1%-Pt/ Al_2O_3	100 a	60 c	690	1:3	10	45	J. Breen, 2002
1%-Pt/ γ - Al_2O_3	95	75	850	1:3	-	56,2 c	D. Liguras, 2003
1%-Pt/ CeO_2 / ZrO_2	100 a	93 c	700	1:3	21	70	J. Breen, 2002

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0,5%-Rh/ γ - Al ₂ O ₃	99	90	780	1:3	-	67,5 c	A.Fatsikostas, 2002
0,5%-Rh/ γ - Al ₂ O ₃	99	95	825	1:3	-	71,2 c	D. Liguras, 2003
1%-Rh/ γ - Al ₂ O ₃		100 a	98 c	600	1:3	3 73,5	F.
Auprêtre, 2002							
1%-Rh/ γ - Al ₂ O ₃	100	95	800	1:3	-	71,2 c	D. Liguras, 2003
1%-Rh/ Al ₂ O ₃	100 a	93 c	690	1:3	19	70	J. Breen, 2002
2%-Rh/ γ - Al ₂ O ₃	100	96	810	1:3	-	72 c	D. Liguras, 2003
5%-Rh/ γ - Al ₂ O ₃	100 a	90 c	650	1:8,4	24% v/v	5,42mol	S. Cavallaro, 2003
5%-Rh/ γ - Al ₂ O ₃		100 a	92 c	650	S/C=4,2	9,6 c 69,2 c	S. Freni, 2001
Rh/ α - Al ₂ O ₃ /fecralloy	98 a	86	1000	S/C=3/1	-	-	E. Wanat, 2004
Rh-Ce/ α - Al ₂ O ₃ /fecralloy		100 a	98	950	S/C=3/1	-	E. Wanat, 2004
1%-Rh/CeO ₂	100 a	84 c	600	1:3	13,5	63	F. Auprêtre, 2002
2%-Rh/CeO ₂	100 a	92 c	450	1:8	3,5	69,1	C. Diagne, 2004
1%-Rh/12%CeO ₂ - γ - Al ₂ O ₃	100 a	85 c	600	1:3	7,5	63,5	F. Auprêtre, 2002
1%-Rh/Ce 0,63Zr 0,37O ₂	100 a	83 c	600	1:3	13	62	F. Auprêtre, 2002
1%-Rh/CeO ₂ /ZrO ₂	100 a	92 c	690	1:3	18	69	J. Breen, 2002
2%-Rh/1CeO ₂ -1ZrO ₂	100 a	94 c	450	1:8	1,5	70,3	C. Diagne, 2004
2%-Rh/2CeO ₂ -1ZrO ₂	100 a	92 c	450	1:8	1,6	69,2	C. Diagne, 2004
2%-Rh/4CeO ₂ -1ZrO ₂	100 a	94 c	450	1:8	1,6	70,5	C. Diagne, 2004
3%-Rh/MgO	100 a	92	650	S/C=4,2	7,75 c	69 c	F. Frusteri, 2004c
1%-Rh/ZrO ₂	100 a	76 c	600	1:3	5,5	57	F. Auprêtre, 2002
2%-Rh/ZrO ₂	100 a	96 c	450	1:8	2,1	71,7	C. Diagne, 2004
0,67%-Ru/ γ - Al ₂ O ₃	100 a	51 c	700	1:3	9	38	F. Auprêtre, 2002
1%-Ru/ γ - Al ₂ O ₃	83	65	860	1:3	-	48,7 c	D. Liguras, 2003
3%-Ru/ γ - Al ₂ O ₃	100	95	825	1:3	-	71,2 c	D. Liguras, 2003
5%-Ru/ γ - Al ₂ O ₃	100	98	820	1:3	-	73,5	D. Liguras, 2003
5%-Ru/MgO	100	98	840	1:3	-	73,5 c	D. Liguras, 2003
3%-Ru/TiO ₂	95	80	860	1:3	-	60 c	A.Fatsikostas, 2002
5%-Ru/TiO ₂	96	92	830	1:3	-	69 c	D. Liguras, 2003

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Table 1b. Catalysts prepared with Noble metals and some characteristic of catalytic activity (2006 to 2013).

Catalysts	Some characteristics.
Pt-Ni / CeO ₂	The bimetallic catalysts perform better [14]
Rh-Pt/La ₂ O	Long-term stability under favorable reaction conditions [15]
Rh-Pd/CeO ₂	Rh-Pd nanoparticles on cordierite monoliths [16]
Cox/ZnO, PtyCo10/ZnO	Pt was active for the dehydrogenation of ethanol and decomposition of acetaldehyde [17]
Rh/Al ₂ O ₃ , Pt/ Al ₂ O ₃	Hydrogen was always the main product over although products such as acetaldehyde, diethyl ether and acetone were also produced (<12%)[18]
Pt/Ni/ CeO ₂	catalysts for the renewable and clean H ₂ production via ethanol steam reforming [19]
Rh and Co/ CeO ₂ -	CO-Free, High-Yield H ₂ Generation at low-Temperature [20]
Ni-Cu/ ZrO ₂	Ni-Cu / ZrO ₂ by the homogenous urea co-precipitation technique [21]
CoIr/18CeZrO ₂ ;CoIr/ZnO	the influence of the support on the behavior of bimetallic CoIr-based catalysts[22]
Y ₂ Ce _{2-x} Ru xO ₇ (x=0~0.4)	On autothermal ethanol steam reforming reaction [23]
Ni/CeO ₂ - ZrO ₂	effect of addition of noble metals (Rh and Ru) [24]
Rh-Co/CeO ₂	CO-Free, High-Yield H ₂ Generation from Low-Temperature Ethanol Steam Reforming [25]
Pd-based membrane reactors	for producing ultra pure hydrogen: Oxidative reforming of bio-ethanol [26]
Rh- Co/ CeO ₂	H ₂ Generation from Low-Temperature Ethanol Steam [28]
Ru/alumina	Effect of temperature on activity, selectivity and carbon laydown [29]
Pd-Rh/CeO ₂	H ₂ production from ethanol over a metallic membrane reactor [30]
Ru/ Al ₂ O ₃	Steam reforming of ethanol at medium pressure over : Effect of temperature and catalyst deactivation[31]
Ni/ Al ₂ O ₃ addition of Zn and Pt	Ethanol steam reforming on promoted catalysts [32]
Pt-Ni and Pt-Co catalysts supported on CeO ₂	Pt/Ni/CeO ₂ catalyst shows a perfect agreement with equilibrium calculations yet at low contact times, although some carbon deposition occurs. Also the cobalt-based catalysts appear attractive [33]
2 wt % Pt/SBA-15 and 2 wt % Pt/ Al ₂ O ₃	The catalysts proved good activity determining a high conversion of ethanol [34]
Pt, Ir and Co/CeO ₂	Ceria-supported catalysts are prepared herein by the deposition- precipitation method and investigated for their suitability in the steam reforming of ethanol. [35].

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Ir/CeO ₂	Ageing analysis of a catalyst in ethanol steam reforming [36]
Pt-RuMg/ZrO ₂	OSRE (oxidative steam reforming reaction) requires a higher temperature (T _R ~ 390°C) to achieve 100% ethanol conversion than the SRE reaction (T=2500°C)[37]
Pd and Pd-Cu membranes	Experimental and kinetic studies of the ethanol steam reforming reaction equipped with ultrathin film for improved conversion and hydrogen yield [38]
Ni-Ru/ La ₂ O ₂ CO ₃	Ru is more active in the ethanol dehydration reaction to form ethylene than Ni. The presence of Ru could improve the selectivity for hydrogen of Ni catalyst. TG results reveal that Ni-Ru/ La ₂ O ₂ CO ₃ has excellent resistance to carbon deposition [39]
Rh and Co/Hydrotalcites	The Mg-Al oxide-supported rhodium and cobalt catalyst was the most promising sample to produce hydrogen by ethanol reforming, showing the highest hydrogen yield, low ethene selectivity and high specific surface area during reaction [40]
Ir/CeO ₂	Oxidative steam reforming of ethanol over Ir/CeO ₂ catalysts: A structure sensitivity analysis [41]
M/ CeO ₂ /YSZ (M = Ru, Pd, Ag)	Hydrogen production from ethanol steam reforming on M/CeO ₂ /YSZ (M = Ru, Pd, Ag) nanocomposites [42]
Ru-Pt/CeO ₂	Ru/CeO ₂ and Ru-Pt/CeO ₂ have considerable similarities while that of Pt/CeO ₂ was considerably different [43]
Ir/ CeO ₂ , Ir/Ce _{0.9} Pr _{0.1} O ₂	PrOx-doping have significantly promoted the oxygen storage capacity and thermal stability of the catalysts by incorporation into the ceria lattice[44]
Pd promoted ZnO/Al ₂ O ₃	The Pd promotion does not prevent the formation of coke on the ZnO/Al ₂ O ₃ [45] catalysts.
Pd-Cu membranes	Preparation of thin Pd-Cu membranes and their application in a membrane reactor for the ethanol steam reforming [46]
Pd-Ag based membranes	At 450°C with a reaction pressure of about 400kPa and a water/ethanol feed flow rate of 5gh ⁻¹ , maximum values of hydrogen yield (5.5) and hydrogen recovery factor (close to 100) have been measured [47]
Rh and Pt/zirconia	The results were compared with those obtained on a commercial steam reforming catalyst (15 wt-% NiO/Al ₂ O ₃ [48]
Pt-Ni and Pt-Co/CeO ₂	The aim of this work is to study bimetallic Pt based catalysts for the low temperature Ethanol Steam Reforming (SRE) reaction in concentrated reaction mixture. Preliminary results concerning economic aspects are also reported.[49]
PtRu/ZrO ₂ modified with Na and Mg	The preferential Pt-Ru-Na ₁ /ZrO ₂ catalyst shows active at temperatures as low as 300 °C and produces less CO (< 0.2%) at temperatures lower than 340 °C [50]
Rh/CeO ₂ / Al ₂ O ₃	The stability test performed on 2%Rh/20%CeO ₂ /Al ₂ O ₃ at 500 °C for Oxidized SRE showed that the catalyst was stable for ~40 h and then started to deactivate slowly. The comparison between packed bed reactor and micro-channel reactor showed that the micro-channel reactor can be used for OSRE to produce hydrogen without any diffusional effects in the catalyst layer. [51]
Rh/CeO ₂	Catalyst deactivation occurs from the deposition of carbon on the catalysts during both reactions. However, no carbon formation is observed on the Rh/CeO ₂ high surface area catalyst during steam reforming due to a higher surface fugacity of O from species adsorbed on the support that react to remove carbon [52].
Fe-Rh	For the first time, a novel iron-promoted Rh catalyst is developed to produce CO-free H ₂ through steam reforming of ethanol at low temperatures,[53]

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Rh-Co/ZrO ₂	catalysts exhibited high activity in the reaction of ethanol steam reforming. The equilibrium composition of reaction products was attained at 500-700°C and a reaction mixture space velocity of 10000 h ⁻¹ . C[54]
Ni xOy-, FexOy-, and Co xOy-Pd loaded Zeolite Y	The H ₂ production was maximized to 98% over CoxOy-Pd(50.0 wt%)/Zeolite Y at the conditions of reaction temperature 600 °C, CH ₃ CH ₂ OH:H ₂ O = 1:3, and GHSV 8400 h ⁻¹ . In the mechanism that was suggested in this work, the cobalt component played an important role in the partial oxidation and the CO activation for acetaldehyde and CO ₂ respectively, and eventually, cobalt increased the hydrogen yield and suppressed the CO generation.[55]
Pt/ZrO ₂	The major carbon-containing products were CH ₄ , CO ₂ , and CO. Small amounts of acetaldehyde, acetone, and ethylene were produced, showing that the partial ethanol steam reforming reaction [56]
Pt/ Al ₂ O ₃ -ZrO ₂	The decay in the selectivity of H ₂ and CO ₂ caused by the surface acetate species on Pt/Al ₂ O ₃ decreased in the presence of ZrO ₂ . [57]
Rh- Ni/Y ₂ O ₃ - Al ₂ O ₃	It was established that the catalytic behaviour of the Rh/Y-Al base catalyst is widely improved by the addition of Ni. Nickel incorporation leads to the formation of both dispersed nickel phase and nickel aluminate species. Basic properties of the support were not modified by the addition of Ni.[58]
Co/ZnO, Rh and Co/ZnO	The difference in the reaction pathway is shown to favor Co-based catalysts for selective hydrogen production under elevated system pressures (up to 15 bar) of industrial importance. Co/ZnO is a more suitable catalyst system for steam reforming of ethanol due to the low methane selectivity, low cost and the possibility of regeneration with mild oxidation [59]
Rh/Y ₂ O ₃ :	Rh/Y ₂ O ₃ is found to produce the highest rate of hydrogen in steam reforming of ethanol (SRE) at a high reaction temperature of 650-800 °C, with the order of catalyst activity as follows: Rh/Y ₂ O ₃ > Rh/CeO ₂ > Rh/La ₂ O ₃ > Rh/Al ₂ O ₃ [60]
Pd-Ru/Nb ₂ O ₅ -TiO ₂	Parallel reactions occurred in all conditions studied according to what was observed by the presence of H ₂ , CO ₂ , CH ₄ , CO, C ₂ H ₄ , C ₂ H ₆ , C ₂ H ₄ O and (C ₂ H ₅) ₂ O. [61].
CeZrO ₂ and Pt/CeZrO ₂	Unpromoted CeZrO ₂ was quite stable whereas Pt/CeZrO ₂ catalyst deactivated for all feed compositions studied. the loss of the Pt-support synergy leads to a buildup of carbonaceous residue, which is the likely reason of the deactivation of Pt/CeZrO ₂ [62]
Rh/CeO ₂	The co-precipitated catalyst was effective for the production of hydrogen by steam reforming of ethanol. The main products identified in the gaseous products for all catalysts were H ₂ , CO, CH ₄ , and CO ₂ . The CO formation decreased with increase in space time, ethanol conversion, and steam to ethanol molar ratio. The selectivity of H ₂ , CO, CH ₄ , and CO ₂ were non zero at conversions close to zero. [63]
Rh-Pd/CeO ₂	bimetallic catalyst breaks the carbon-carbon bond of ethanol at low temperature <400 K, as evidenced by the presence of adsorbed CO species. [64]
Ir/CeO ₂	Under reaction conditions, acetaldehyde was the primary product below 673 K, which decomposed mainly to methane and carbon monoxide at higher temperatures, whereas methane reforming and the water-gas shift were the major reactions above 773 K. The Ir/CeO ₂ catalyst demonstrated rather high stability for the reactions at 823 and 923 K with no apparent deactivation for 60 h on stream [65].
Ru/ Al ₂ O ₃ and Pt-Ru/ Al ₂ O ₃	These catalysts outperformed a commercial Ru/Al ₂ O ₃ catalyst, as well as catalysts that had been prepared from inorganic salts using the conventional impregnation Method [66]

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Rh/MgO	Catalytic tests performed at molten carbonate fuel cell (MCFC) operative conditions (TR = 923 K) clearly show a structure-sensitive reaction since the turnover frequency (TOF) significantly increases with the mean Rh particle size [67]
Al ₂ O ₃ and CeO ₂ -supported noble metals	It was found that water enhanced the stability of ethoxide surface species formed in the dissociation of ethanol. Dehydrogenation of molecularly adsorbed ethanol was proposed as a key reaction step[68].
Co, Ir and Ni /CeO ₂	long-term stability test revealed that the Ir/CeO ₂ catalyst showed rather stable catalytic performance for 300 h time-on-stream without any deactivation. The improvement was attributed to the effective prevention of the sintering of the highly dispersed Ir particles through the strong interaction between Ir and CeO ₂ and to the significant resistance to coke deposition of ceria based on its higher oxygen storage-release capacity [69].

2.2.- Catalysts based on no-noble metals

In tests with cobalt catalysts,(Table 2) Co/ Al₂O₃, Co/SiO₂, and Co /MgO, it was found that the sites CoO are active for the steam reforming of ethanol, the conversion was 70% to hydrogen and 30% of a gas mixture of CO, CO₂ and CH₄ [70]. In the case of catalysts with Co/ZnO (10 wt.% Co) using as precursors nitrates and cobalt carbonyls (Co₂(CO)₈), a catalyst was highly stable and selective to the production of CO-free hydrogen (73% H₂ and 25% CO₂) at temperatures of 623K [71]. These experiences with Co catalysts were extended by the same authors to other supports as Al₂O₃, CeO₂, SiO₂, ZnO, TiO₂, V₂O₅, La₂O₃, and Sm₂O₃, obtaining a conversion of 100% ethanol and a selectivity of up to 73.8% for H₂ and 24.2% for CO₂ [72]. These authors also tested the effect of the promoter for different Na concentrations, a positive effect was observed in the ethanol conversion, obtaining total conversions at temperatures between 623 and 723K . It was observed an increased production of hydrogen from 5 to 8% when the molar ratio was 1:13 [73].

Studies have also been conducted using oxide copper supported on ceria CuO/CeO₂ presenting the formation of acetaldehyde and hydrogen at 260 °C and hydrogen and acetone (2 moles of hydrogen per of ethanol) at 380 ° C, obtaining low selectivity to hydrogen[74]. Ni has been the metal most studied, and catalysts of Ni/Al₂O₃ were tested at temperatures between 573 and 773K using different ratios of ethanol/water obtaining a 91% of selectivity to hydrogen at a temperature of 773K with a feed ratio of 6:1 water / ethanol [75]. Also been made comparisons with different media such as Y₂O₃, La₂O₃ and Al₂O₃, where supported catalysts of Y₂O₃ and La₂O₃ showed high activity for the reforming of ethanol at 250 ° C with conversions of 81.9% and 80.7% and selectivity to hydrogen of 43.1% and 49.5% respectively [76-77]. Other researchers compared nickel catalysts supported on La₂O₃, Al₂O₃, YSZ and MgO again found a high activity for the Ni/La₂O₃ catalyst [78] and high stability over time.

Additionally, we have investigated the effect of promoters alkali on nickel catalysts such as the case of Ni / MgO promoted with potassium (1-3 wt.%) as which improved catalyst activity and stability achieving a production of more than 5 moles of hydrogen per mole of ethanol fed [22], although the addition of Li and Na are affected negatively catalyst dispersion [79-80]. For ethanol reforming process also bimetallic catalysts were tested as Cu- Ni/

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Al₂O₃ which proved able to produce appreciable amounts of hydrogen at atmospheric pressure and 300 ° C [81] and Cu-Ni/SiO₂ with which mixtures were obtained from 33% hydrogen, suitable to feed SPFC fuel cells [82].

Table 2. Summary of catalysts (no-noble metal) for ethanol reforming [3] (from 2001 to 2006)

Catalyst	X	S	T(°C)	<u>EtOH</u> H ₂ O	%CO (v/v)	%H ₂ (v/v)	Reference
Ni/Al ₂ O ₃ (comercial)	100	76 c	400	15%	-	57c	A.Therdthianwong, 2001
5%-Ni/Al ₂ O ₃	100 a	57 c	720	1:3	24	43	J. Breen, 2002
9,7%-Ni/γ-Al ₂ O ₃	100 a	100 c	600	1:3	0	75	F. Auprêtre, 2002
10%-Ni/γ-Al ₂ O ₃	100	77 c	650	1:8	11	57,7 c	Y. Yang, 2006
16,1%-Ni/Al ₂ O ₃	86,4 a	64 c	300	1:3	0,7	47,7	J. Sun, 2005
17%-Ni/γ-Al ₂ O ₃	100 a	88	750	1:3	-	66 c	A. Fatsikostas, 2002
35%-Ni/γ-Al ₂ O ₃	100 a	87 c	500	1:6	-	65	J. Comas, 2004
10%-Ni/CeO ₂	100 a	84 c	600	1:3	8	63	F. Auprêtre, 2002
15%-Ni/CeO ₂	100	87 c	450	1:3	21	65	B. Zhang, 2006
10%-Ni/12%CeO ₂ -γAl ₂ O ₃	100 a	87 c	600	1:3	3	65	F. Auprêtre, 2002
10%-Ni/Ce 0,63Zr 0,37O ₂	100 a	83 c	600	1:3	9	62	F. Auprêtre, 2002
10%-Ni/La ₂ O ₃	100	89 c	650	1:8	6,1	66,9 c	Y. Yang, 2006
15,3%-Ni/La ₂ O ₃	100 a	72 c	350	1:3	16,9	54,3	J. Sun, 2005
17%-Ni/La ₂ O ₃	100 a	90	750	1:3	-	67,5 c	A.Fatsikostas, 2002
20%-Ni/(La ₂ O ₃ /γ-Al ₂ O ₃)	99	98	830	1:3	-	73,5 c	A.Fatsikostas, 2002
5%-Ni/MgO(MM)	45	27 c	650	1:8,4	-	20,2 c	S. Freni, 2003
10%-Ni/MgO	100	84 c	650	1:8	4,4	63,3 c	Y. Yang, 2006
17%-Ni/MgO	100 a	80	750	1:3	-	60 c	A.Fatsikostas, 2002
18%-Ni/MgO(UBE)	100	87,5 c	650	1:8,4	-	67,5 c	S. Freni, 2003
20%-Ni/MgO(MM)	55	38 c	650	1:8,4	-	28,5 c	S. Freni, 2003
21%-Ni/MgO	65 a	96	650	S/C=4,2 5,6 c		72 c	F. Frusteri, 2004c
21%-Ni/MgO	45 a	70 c	650	S/C=4,2 8,7 c		52,5 c	F. Frusteri, 2004a
21%-Ni/MgO	47 a	93	650	S/C=4,2 0,08 c		69,7 c	F. Frusteri, 2004b
1%-K-21%-Ni/MgO	65 a	77 c	650	S/C=4,2 7,9 c		57,8 c	F. Frusteri, 2004a
1%-K-21%-Ni/MgO	60 a	91	650	S/C=4,2 0,06 c		68,2c	F. Frusteri, 2004b

Table 2. Summary of catalysts for ethanol reforming

Catalyst	X	S	T(°C)	<u>EtOH</u> H ₂ O	%CO (v/v)	%H ₂ (v/v)	Reference
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3%-K-21%-Ni/MgO	62 a	65 c	650	S/C=4,2	5,9 c	48,8 c	F. Frusteri, 2004a
1%-Na-21%-Ni/MgO	55 a	92	650	S/C=4,2	0,07 c	69 c	F. Frusteri, 2004b
1%-Li-21%-Ni/MgO	83 a	90	650	S/C=4,2	0,07 c	67,5 c	F. Frusteri, 2004b
Ni/Y2O3(3)	100 a	80 c	550	1:3	3	60	J. Sun, 2004
20,6%-Ni/Y2O3	95,3 a	71,5 c	320	1:3	6,4	53,6	J. Sun, 2005
17%-Ni/YSZ	100 a	91	750	1:3	-	68,3 c	A.Fatsikostas, 2002
10%-Ni/ZnO	100	89 c	650	1:8	5,5	66,8 c	Y. Yang, 2006
20%-Ni/ZnO	100	95	550	1:8	6,6 c	71,2 c	Y. Yang, 2006
Ni/ZrO2	100	93 c	700	S/C=4.84	15	70	M. Benito, 2005
6%-Ni/ZrO2	100	44 c	550	1:3	-	33	V.Bergamaschi, 2005
10%-Ni/ZrO2	100 a	91 c	600	1:3	7	68,5	F. Auprêtre, 2002
20%-NiO/40%-CeO2 -							
40%ZrO2	95	90 c	550	1:8	3,7	67,5	D. Srinvas, 2003
30%-NiO/35%-CeO2 -							
35%ZrO2	95	92 c	550	1:8	3,7	69	D. Srinvas, 2003
40%-NiO/5,4%-CeO2 -							
54%ZrO2	95	91 c	550	1:8	3,2	68	D. Srinvas, 2003
40%-NiO/30%-CeO2 -							
30%ZrO2	95	91 c	550	1:8	2,9	68	D. Srinvas, 2003
40%-NiO/ 60%-CeO2	95	90,5 c	550	1:8	3	67,9 c	D. Srinvas, 2003
3%-Cu/ γ -Al2O3	76	51 c	300	1:2,5	0	38 c	F. Mariño, 2001
6%-Cu/ γ -Al2O3	78	49 c	300	1:2,5	0	36,7 c	F. Mariño, 2001
9,1%-Cu/ γ -Al2O3	100 a	53 c	700	1:3	12	40	F. Auprêtre, 2002
Cu/ZrO2	30	53 c	700	S/C=4,84	-	-	M. Benito, 2005
3%-Cu/ZrO2	100	51 c	550	1:3	-	38	V.Bergamaschi, 2005
20%-CuO/Al2O3	100 a	25 c	350	1:5	-	18,8	T. Nishiguchi, 2005
20%-CuO/CeO2	95,7 a	33 c	380	1:5	-	25	T. Nishiguchi, 2005
CuO 0,05g - CeO2 0,45g	89,7 a	26 c	320	1:5	-	19,5	T. Nishiguchi, 2005
6%-Ni/3%-Cu/ZrO2	100	80 c	550	1:3	8	60	V.Bergamaschi, 2005

Table 2. Summary of catalysts for ethanol reforming

Catalyst	X	S	T(°C)	$\frac{\text{EtOH}}{\text{H}_2\text{O}}$	%CO (v/v)	%H2 (v/v)	Reference
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3%-Cu-1%Ni-0,15%K/ γ -Al ₂ O ₃	79	48 c	300	1:2,5	2,2 c	36,3 c	F. Mariño, 2001
3%-Cu-2,5%Ni-0,15%K/ γ -Al ₂ O ₃	81	43 c	300	1:2,5	12 c	32,4 c	F. Mariño, 2001
3%-Cu-6%Ni-0,15%K/ γ -Al ₂ O ₃	83	42 c	300	1:2,5	14 c	31,5 c	F. Mariño, 2001
6%-Cu-1%Ni-0,15%K/ γ -Al ₂ O ₃	77	47 c	300	1:2,5	2,9 c	35,4 c	F. Mariño, 2001
6%-Cu-2,5%Ni-0,15%K/ γ -Al ₂ O ₃	85	48 c	300	1:2,5	8,9 c	35,7 c	F. Mariño, 2001
6%-Cu-6%Ni-0,15%K/ γ -Al ₂ O ₃	90	50 c	300	1:2,5	20,7 c	37,8 c	F. Mariño, 2001
Cu(6)-Ni(4)-K/ γ -Al ₂ O ₃	81,7	92 c	300	1:2,5	0,5	5,5	F. Mariño, 2004
1%-Co/ γ -Al ₂ O ₃	100 a	0,11 c	450	1:13	0	0,8	J. Llorca, 2002
8%-Co/ γ -Al ₂ O ₃	74	89 c	400	1:3	5	70	M. Batista, 2004
18%-Co/ γ -Al ₂ O ₃	99	89 c	400	1:3	1	70	M. Batista, 2004
20%-Co/ γ -Al ₂ O ₃	83	62	850	1:3	-	46,5 c	A.Fatsikostas, 2002
1%-Co/CeO ₂	93,7 a	93 c	450	1:13	0	69,6	J. Llorca, 2002
15%-Co/CeO ₂	100	93 c	700	1:3	18	70	B. Zhang, 2006
1%-Co/La ₂ O ₃	85 a	84 c	450	1:13	0	63,1	J. Llorca, 2002
1%-Co/MgO	29,3 a	73 c	450	1:13	0,4	55	J. Llorca, 2002
5%-Co/MgO(MM)	18	3 c	650	1:8,4	-	2,25 c	S. Freni, 2003
20%-Co/MgO(MM)	40	27 c	650	1:8,4	-	20,2 c	S. Freni, 2003
21%-Co/MgO	90 a	91	650	S/C=4,2	7,62 c	68,2 c	F. Frusteri, 2004c
1%-Co/SiO ₂	87 a	66 c	450	1:13	2,9	49,8	J. Llorca, 2002
8%-Co/SiO ₂	89	93 c	400	1:3	10	70	M. Batista, 2004
18%-Co/SiO ₂	97	93 c	400	1:3	3	70	M. Batista, 2004
1%-Co/Sm ₂ O ₃	85,9 a	86 c	450	1:13	0	64,7	J. Llorca, 2002
1%-Co/TiO ₂	16,4 a	63 c	450	1:13	0	47,4	J. Llorca, 2002
1%-Co/V ₂ O ₅	100 a	71 c	450	1:13	0	53,5	J. Llorca, 2002

Table 2 Summary of catalysts for ethanol reforming

Catalyst	X	S	T(°C)	$\frac{\text{EtOH}}{\text{H}_2\text{O}}$	%CO (v/v)	%H ₂ (v/v)	Reference
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1%-Co/ZnO(1)	100 a	88 c	450	1:13	0	66	J. Llorca, 2002
1%-Co/ZnO(2)	100 a	98 c	450	1:13	0	73,8	J. Llorca, 2002
10%-Co(CO)/ZnO	100 a	100 c	400	1:13	0	74,9	J. Llorca, 2003b
10%-Co(N)/ZnO cal	97,6 a	83 c	450	1:13	0	62,2	J. Llorca, 2003b
10%-Co(N)/ZnO red	100 a	98 c	400	1:13	0	73,2	J. Llorca, 2003b
0,06-NaCoZn	100 a	97,5 c	450	1:13	0,7	73,1	J. Llorca, 2004
0,23-NaCoZn	100 a	98 c	350	1:13	0	73,9	J. Llorca, 2004
0,78-NaCoZn	100 a	99 c	400	1:13	0	74,2	J. Llorca, 2004
0,98-NaCoZn	100 a	99 c	450	1:13	0	74,4	J. Llorca, 2004
Co/ZrO ₂	100	93 c	700	S/C=4,8	10	70	M. Benito, 2005
8,7%-Fe/ Al ₂ O ₃	100 a	59 c	700	1:3	10	44	F. Auprêtre, 2002
9,8%-Zn/ γ - Al ₂ O ₃	100 a	56 c	700	1:3	16	42	F. Auprêtre, 2002
GIAP-16	100	98 c	335-650	1:8	8,5	73,6 c	V. Galvita, 2001
CeO ₂	16,1 a	24 c	320	1:5	-	17,9	T. Nishiguchi, 2005
ZrO ₂	100	37 c	550	1:3	-	28	V.Bergamaschi,2005

a).- These conversions were obtained in the presence of an inert component.

c).- These values were calculated by the authors [3] using the technical information reported.

Table 2a. Some catalysts evaluated in 2013 (no-noble metals)

Catalysts	Some characteristics.
NiLaZr and NiCuLaZr	All catalysts were active in runs of ethanol steam reforming, leading to the formation of gaseous mixtures containing H ₂ , CO, CO ₂ and CH ₄ . Deactivation due to carbon formation was observed at the lowest reaction temperature tested (500°C).[83]
hydrotalcite-like compounds with Ni/Fe	With a Ni/Fe ratio of 1, a remarkable improvement in catalytic activity as well as selectivity to hydrogen is observed with respect to the catalyst with Ni/Fe ratio of 0.5[84]
Ni-Cu catalysts supported over ZrO ₂	homogenous urea coprecipitation method for catalytic steam reforming of ethanol[85]
Co- and Cu-based catalysts /SiO ₂ and TiO ₂	flame pyrolysis (FP) technique are proposed as possible substitutes for Ni-based catalysts, very active for the Ethanol Steam Reforming reaction, but showing poor stability towards coke formation when operating at relatively low temperature [86]
LaNiO ₃ perovskite	The ethanol conversion reached 100% at 300 °C with 70% hydrogen selectivity. The highly catalytic activity of the reduced catalyst was due to the well-dispersion of Ni particles on the surface of active catalyst was formed in the in situ reduced catalyst.[87]

As it was shown in Table 1 and 2, is abundant number and variety of catalysts tested for bio-ethanol reforming process to various conditions of operation, which include temperatures from 300 °C to 1000 °C and relationships of ethanol/ water in the feed from 1/2.5 to 1/13 and the working pressure is near 1 atm.

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According with Hernández et al. [3], The Table 1 shows that in some works cited, the catalysts were tested under a feed stream including a carrier gas, which dilutes the concentration of reactants (water and bioethanol) to the reactor. This has two disadvantages, one is that these studies could not be scaled economically, and the other is that it masks the actual conversion process. The latter is due to the conversion using a carrier gas is different from the conversion that would be obtained without a carrier gas.

This reaction occurs using reactants without gas carriers For this reason, the catalysts listed in Table 1 was selected initially forming a subgroup by those were tested in their work without carrier gas. Subsequently in this subgroup were selected those catalysts that presented a conversion of 100% and a selectivity to hydrogen greater than 90%, which reduces the number of catalysts to 11. Additionally, the stability over time is also an important property when choosing a catalyst, therefore tests were reviewed stability for this group of catalysts, which these assessments are only recorded for five of them and are presented in Table 3.

Table 3. Stability of selected catalysts for ethanol reforming

Catalizador	Estabilidad	Referencia
Ni/ZrO ₂	10 h	M. Benito, 2005
Co/ZrO ₂	60 h	M. Benito, 2005
15% - Co/CeO ₂	50 h	B. Zhang, 2006
2% - Ir/CeO ₂	300 h	B. Zhang, 2006
1%-Pd/C y (24-26)% NiO-(14-16)%CaO/(55-59)% γ - Al ₂ O ₃ GIAP-16	100 h	V. Galvita, 2001

Thus, from the viewpoint of selectivity hydrogen the best alternative would be to use a reformer two consecutive catalyst beds, one from 1%-Pd / C and a (24-26)% NiO-(14-16)% CaO / (55-59)% γ - Al₂O₃ GIAP-16. Moreover, the catalyst having stability is 2% -Ir/CeO₂ although is the second with 96% selectivity. As shown, the above results, the catalysts including noble metals in the active phase are more efficient compared to those catalysts without noble metals such as nickel and cobalt.

On the other hand, the use of catalysts with noble metals such as iridium, palladium and rare earth oxides such as cerium, as supports have a comparatively high cost with respect to materials be included in the base metals (no noble metals).

In the group of catalysts Selected shown in Table 2, the characteristics of the present catalysts Co/ZrO₂ and Ni/ZrO₂ have been of, 10 and 60 h respectively, and their selectivity to hydrogen was 93%.

Recently catalysts having basic sites like hydrotalcites, have shown good stability than other type of catalyst having acid sites.

3.- Conclusions

This reaction is endothermic and produce H_2 , CO_2 and other products, when ethanol reacts under the best conditions from thermodynamic standpoint. However, there are undesirable products, such as CO and CH_4 which are also formed. Additionally other reactions also occur such as CH_3CHO ethanol dehydrogenation, dehydration $CH_2 = CH_2$, decomposition to CO and CH_4 or CO_2 and CH_4 . The literature have mentioned and recognized that CH_3CHO and $CH_2 = CH_2$ are intermediates that may be formed during the reaction at relatively low temperatures prior to the formation of H_2 and CO_2 and has been observed the presence of coke on the catalyst. The reforming of ethanol with steam has been reported to produce small amounts of CO and CH_4 .

Ni, Co, Rh, Ir and Ru were the most active phases supported on CeO_2 , ZnO, like compounds Hydrotalcites and ZnO. The best experimental conditions were made using high H_2O /ethanol ratio and low pressure. Catalysts having basic sites have shown good stability than other type of catalyst having acid sites.

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