

Current Status of Hydrogen Production Techniques by Steam Reforming of Ethanol: A Review

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Hydrogen is considered to be the most viable energy carrier for the future. Producing hydrogen from ethanol steam reforming would not only be environmentally friendly but also would open new opportunities for utilization of renewable resources, which are globally available. This paper reviews the current state of the steam reforming process of ethanol, examines different catalysts, and, finally, makes a comparative analysis. Different catalysts have been used for the steam reforming of ethanol. Depending on the type of catalysts, reaction conditions, and the catalyst preparation method, ethanol conversion and hydrogen production vary greatly. It was observed that Co/ZnO, ZnO, Rh/Al₂O₃, Rh/CeO₂, and Ni/La₂O₃-Al₂O₃ performed the best, in regard to the steam reforming of ethanol. Currently, hydrogen production from ethanol steam reforming is still in the research and development stage.

1. Introduction

Approximately 80% of the present world energy demand comes from fossil fuels.¹ Unlike fossil fuels, hydrogen gas (H₂) burns cleanly, without emitting any environmental pollutants.² In addition, H₂ is also abundantly available in the universe and possesses the highest energy content per unit of weight (i.e., 120.7 kJ/g), compared to any of the known fuels. H₂ is considered to be the energy carrier of the future¹ and could have an important role in reducing environmental emissions. The shifting of fuels used all over the world from solid to liquid to gas, and the “decarbonization” trend that has accompanied it, implies that the transition to H₂ energy seems inevitable.^{3,4} Consequently, there has been a surge in funding devoted for research on the production, distribution, storage, and use of H₂ worldwide, and especially the countries such as the United States, the European Union, and Japan.^{5–7} However,

H₂ has its own problems, and there is a strong debate on the subject. Some critics doubt that H₂ is the right solution for the energy-related environmental, security, and sustainability issues. They argue that the current technology for producing H₂ as an energy carrier is too costly and wasteful of energy.^{8–11} According to Romm,¹² there are two important pillars on which the H₂ economy rests on: pollution-free sources for the H₂ generation, and fuel cells for converting the H₂ to useful energy efficiently. This paper examines the first pillar, through the production of H₂ from ethanol (C₂H₅OH), which is a renewable source that would contribute to net-zero carbon dioxide (CO₂) emissions.

In nature, H₂ is always present in bound form, in organic compounds and water. H₂ can be produced from different sources, e.g., coal, natural gas, liquefied petroleum gas (LPG), propane, methane (CH₄), gasoline, light diesel, dry biomass, biomass-derived liquid fuels (such as methanol, C₂H₅OH, biodiesel), as well as from water. Among the liquid H₂ sources, C₂H₅OH is a good candidate for several reasons: (i) ethanol is renewable and is becoming increasingly available; (ii) it is easy to transport, biodegradable, and low in toxicity; (iii) it could be easily decomposed in the presence of water to generate a hydrogen-rich mixture; and (iv) it is free from

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catalyst poisons such as sulfur.^{13–15} In addition, the steam reforming of C_2H_5OH to produce H_2 is thermodynamically feasible.^{16,17}

Currently, almost 90% of the H_2 is produced via the reforming of natural gas or the light oil fraction with steam at high temperatures.¹ However, hydrogen production from natural gas is always associated with the emission of greenhouse gases and local pollutants. On the other hand, H_2 production from ethanol steam reforming would not only be environmentally friendly, but also would open a new opportunity for the utilization of the renewable resources that are globally available. Therefore, it would be beneficial for those interested in H_2 production research to get an idea about the current status of this industry, including the chemical processes involved, suitable catalysts, supporting materials, operating conditions for high C_2H_5OH conversion, and hydrogen selectivity. The objective of the paper is to review the literature on steam reforming of C_2H_5OH and make a comparative analysis.

2. Brief Review of Hydrogen Production Processes

Generally, the technologies for producing H_2 fall into four broad categories: (i) thermochemical, (ii) electrochemical, (iii) photobiological, and (iv) photoelectrochemical.¹⁸

2.1. Thermochemical Technology. Steam reforming is the most widely used thermochemical process to produce H_2 from raw materials such as natural gas, coal, methanol, C_2H_5OH , or even gasoline. Gasification and pyrolysis processes are used when the feedstocks are solids (such as coal, wood, and other biomass) or semisolid (such as heavy or residual oils).^{19–22} Thermochemical processes usually use catalysts in one or more elements of the conversion process. Currently, the steam reforming of natural gas comprises almost 50% of the world feedstock for H_2 production.^{6,23} In the United

States, ~95% of H_2 is currently produced through steam reforming.²⁴

2.2. Electrochemical Technology. The electrolysis of water is a mature technology that is used to produce H_2 .²⁵ Although the efficiencies of commercial electrolyzers are in the range of 60%–70%,⁵ the overall efficiencies of water electrolysis are in the range of only ~25%.²⁶ Electrolysis is energy-intensive; the energy requirements for current electrolysis systems are in the range of 53.4–70.1 kWh/kg of H_2 produced,²⁷ and the price of electricity contributes significantly to the production costs.²⁵ If the price of electricity is reduced from 7.89¢/kWh to 4.83¢/kWh, the cost of H_2 would be reduced by 31% for a system capacity of ~1000 kg of H_2 production per day.²⁷ This technology would be competitive only if low-cost electricity (1–2¢/kWh) is available.^{24,25}

2.3. Photobiological Technology. Photobiological systems generally use the natural photosynthetic activity of bacteria and green algae to produce H_2 . This technology covers a wide range of approaches, including direct and indirect biophotolysis, photofermentation, and dark-fermentation. Detailed reviews on this technology could be found elsewhere.^{1,28–30} One major limitation of this technology is the relatively slow production rates. Different rates of photobiological H_2 production have been noted, which ranged from 0.07 mmol H_2 L^{-1} h^{-1} in direct biophotolysis with *Chlamydomonas reinhardtii* to 96 mmol H_2 L^{-1} h^{-1} in photoheterotrophic water gas shift (WGS) with *Rubrivivax gelatinosa* CBS.³⁰ Because of lower mass transfer and slower kinetics, biological WGS reactors are not yet considered to be economical to replace catalytic WGS reactors.³¹ Also, these technologies are still immature and in the experimental stage, and the practical applicabilities are unclear.³⁰

2.4. Photoelectrochemical Technology. The photoelectrochemical process produces H_2 in one step, splitting water by illuminating a water-immersed semiconductor with sunlight. However, this technology is also

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Table 1. Cost and Energy Efficiency from the Selected Technologies to Produce Hydrogen

plant size and technology	cost (\$/kg H ₂) ^a	energy efficiency (%)
central plant		
natural gas steam reforming	2.11	66 ^b
coal gasification	2.17	60 ^c
midsize plant		
methane steam reforming	3.94	70 ^d
biomass gasification	7.07	45–50 ^c
distributed plant		
water electrolysis	7.36	27 ^c
natural gas steam reforming	3.68	70–80 ^c
water electrolysis	6.82	56–73 ^e

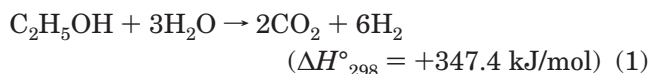
^a Data taken from ref 4. ^b Data taken from ref 37. ^c Data taken from ref 38. ^d Data taken from ref 12. ^e Data taken from ref 27.

in the early stages of development.³² There are some barriers for developing durable, high-efficiency photoelectrochemical systems for H₂ production.^{33,34} Some of the major obstacles are (i) poor matching of the semiconductor band gap with the solar spectra, (ii) instability of the semiconductor materials in the aqueous phase, (iii) difference between the semiconductor band edges and the electrochemical reactions, and (iv) poor kinetics of the H₂ generation reaction.

3. Hydrogen Production via the Catalytic Steam Reforming of Ethanol

Steam reforming of natural gas to produce H₂ is the most energy-efficient technology currently available.^{35,36} Furthermore, the reforming process could extract H₂ not only from the hydrocarbon fuels but also from water. The reaction is fast, although H₂ production is limited by thermodynamic balance.⁶ In addition, catalytic steam reforming of natural gas is, by far, the most cost-effective process, when applied at large-scale production,²⁴ compared to the other technologies (Table 1).

Steam reforming is a cost-effective and an efficient process. In addition to ethanol being a biorenewable resource, the steam reforming of ethanol is a promising choice in H₂-based energy systems. Stoichiometrically, the overall steam reforming reaction of C₂H₅OH could be represented as follows.³⁹



However, there are several reaction pathways that could

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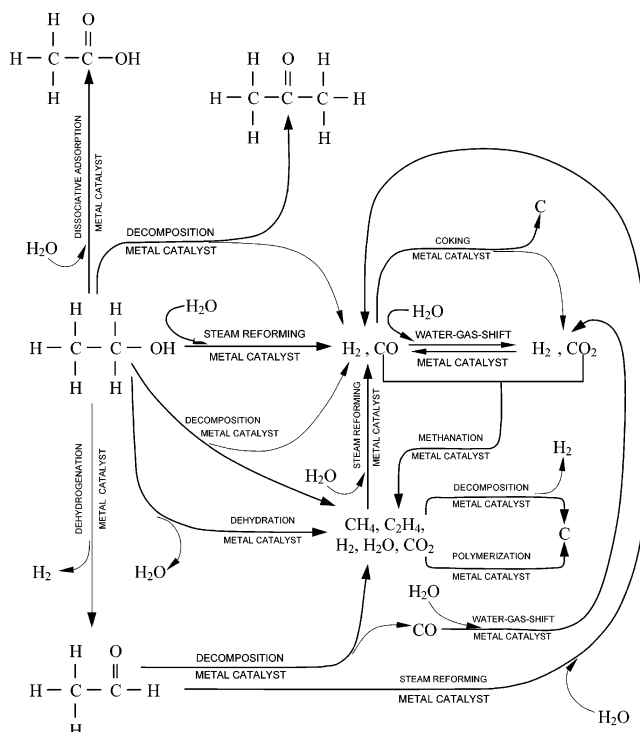


Figure 1. Reaction pathways that can occur during ethanol steam reforming over metal catalysts.

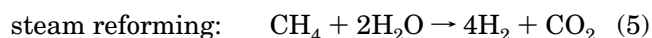
occur in the C₂H₅OH steam reforming process, depending on the catalysts used; Figure 1 shows some such reactions.

A breakdown of the reactions is given below:

(1) C₂H₅OH dehydration to ethylene (C₂H₄) and water, followed by polymerization of C₂H₄ to form coke.^{14,40–43}



(2) C₂H₅OH decomposition or cracking to CH₄, followed by steam reforming.⁴²



(3) C₂H₅OH dehydrogenation to acetaldehyde (C₂H₄O), followed by decarbonylation or steam

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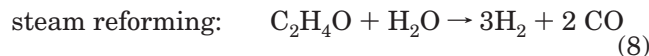
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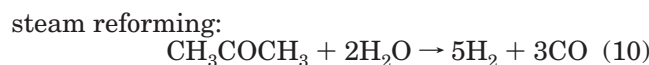
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reforming of C₂H₄O:^{14,40–50}



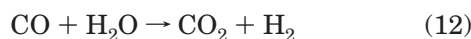
(4) C₂H₅OH decomposition into acetone (CH₃COCH₃), followed by steam reforming:^{44,45,50,51}



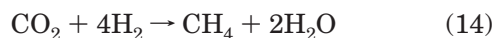
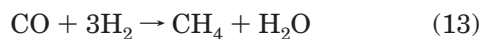
(5) Steam reforming of C₂H₅OH to syngas (CO + H₂):¹⁴



(6) Water gas shift:



(7) Methanation:



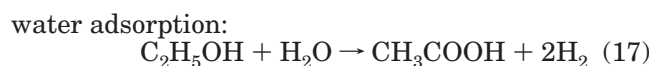
(8) Coking from the decomposition of CH₄:



(9) Coking from the Boudouard reaction:



(10) Dissociative adsorption of water to form acetic acid (CH₃COOH):¹³



The intent of the reforming process is to make as much H₂ and CO₂ as possible by cracking C₂H₅OH in the presence of steam over a catalyst. However, from the reaction network, it is clear that the overall reaction is very complex and involves over a dozen of potential

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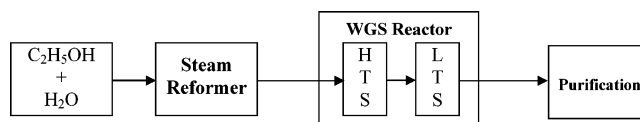
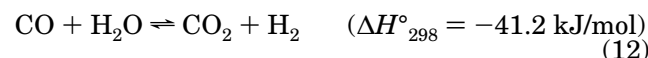
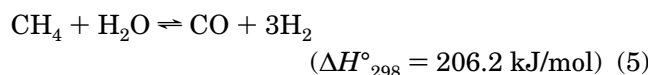
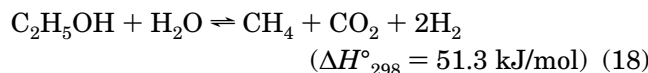


Figure 2. Scheme of steam reforming of ethanol. (Legend of abbreviations: WGS, water-gas shift; HTS, high-temperature shift; and LTS, low-temperature shift.)

products. Therefore, it is important to reduce the production of undesirable intermediate compounds. Reactions to avoid are those that lead to C₄ species and C₂H₄. The presence of C₂H₄ especially hinders the overall H₂ production reaction by inducing the pathways toward carbon production and thus causing “coking” of the catalysts.⁵² Section 4 will discuss the catalysts that have been tried thus far, and an attempt will be made to identify the promising catalysts to drive the ethanol steam reforming reaction with less byproducts.

Typically, a reforming process consists of three major steps: steam reforming, WGS, and methanation or purification, as depicted in Figure 2.

3.1. Steam Reforming. Steam reforming is the first step of the H₂ production process. This process occurs with a catalyst at a temperature of ~1023–1073K. In this stage, C₂H₅OH is introduced into a reformer or reactor, where the liquid is thermochemically broken down into shorter-chained carbonaceous species. These compounds would react with steam over the catalyst to produce a mixture of H₂ and other compounds, such as carbon monoxide (CO), CO₂, C₂H₄O, C₂H₄, or CH₃COCH₃. Conversion of the C₂H₅OH to H₂ may occur through the reactions depicted below (reactions 18, 5, and 12).⁴³



3.2. WGS Reaction. Almost all catalysts used for the steam reforming of C₂H₅OH produce CO.^{46,53–55} The WGS reaction is an important step in the reforming process. During the WGS reaction, CO is converted to CO₂ and H₂ through a reaction with steam. CO is poisonous to the noble-metal catalysts, and therefore, the formation of CO is typically reduced by performing the reaction in excess steam. At the end of the WGS

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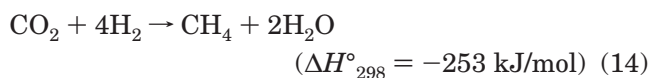
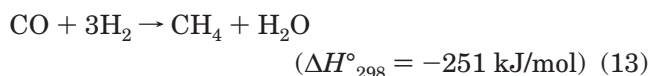
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reaction, the CO concentration is between 0.5 mol % and 1 mol %. The chemical reaction for WGS is as shown in reaction 12. This reaction is the basis for most industrial H₂ production in the world. The WGS reaction is reversible, and, therefore, the reaction equilibrium shifts to the right and favors the formation of the H₂ and CO₂ as products at lower temperatures. At higher temperatures, the equilibrium shifts to the left, limiting the complete conversion of CO.

Typically, WGS reactors use metallic catalysts in a heterogeneous gas-phase reaction with CO and steam. Although equilibrium favors formation of products at lower temperatures, reaction kinetics are faster at elevated temperatures. For this reason, the catalytic WGS reaction is performed in two steps: high-temperature shift (HTS) and low-temperature shift (LTS). The HTS reactor typically operates at temperature of 623–643 K. To achieve higher conversions of CO to H₂, the gas leaving the HTS reactor is then cooled to 473–493 K and passed through a LTS reactor. Thereby, ~90% of the CO is converted to H₂ in the first HTS reactor and 90% of the remaining CO is converted in the LTS reactor. However, care should be taken when choosing WGS catalysts, because the feed composition affects the catalytic activity. A summary of the catalysts used in WGS reaction is given in section 4.

3.3. Purification. Further reduction in the amount of CO in the reformate can be achieved by catalytic methanation. Methanation reactor converts any residual carbon oxides back to CH₄ so that CO concentration becomes <10 ppm. Note that H₂ would be consumed for the process, and the chemical reactions are shown below.



In addition to methanation, other methods could be used to purify H₂, such as pressure swing adsorption, cryogenic distillation, or membrane technology in which ~99.9% purity of H₂ can be produced, so that methanation is no longer needed.⁵⁶

Three processes—namely, steam reforming, WGS, and methanation—may occur simultaneously in a single steam reforming reactor (reformer), depending on the type of catalysts used. Different catalysts lead to different reaction pathways and different effluent compositions. The following section will discuss the role of catalysts in the steam reforming of ethanol.

4. Catalysts

Reforming and WGS reactions in steam reforming of C₂H₅OH are reversible and not simple to maintain.²³ On the other hand, complete C₂H₅OH conversion is essential for the process to be economical. The catalyst has an important role in achieving this, because it increases the rate of reaction in such a way that the

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Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
Period																				
1		1																2		
		H																He		
2		3	4										5	6	7	8	9	10		
		Li	Be										B	C	N	O	F	Ne		
3		11	12										13	14	15	16	17	18		
		Na	Mg										Al	Si	P	S	Cl	Ar		
4		19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
		K	Ca	Sc	Ti	V	Cr	Mn	Fe	Cu	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5		37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
		Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6		55	56	*	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
		Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
7		87	88	**	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
		Fr	Ra		Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Uuu	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
		*Lanthanoids		*	57	58	59	60	61	62	63	64	65	66	67	68	69	70		
					(La)	(Ce)	Pr	Nd	Pm	(Sm)	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
		**Actinoids		**	89	90	91	92	93	94	95	96	97	98	99	100	101	102		
					Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Figure 3. Elemental compounds that were tried as catalysts in ethanol reforming (denoted by circles). (Source of Periodic Table: Webelements.⁷⁹)

system tends toward thermodynamic equilibrium.³⁵ However, different catalysts induce different pathways to produce H₂ (see Section 3). Therefore, the choice of the catalyst has a vital role in the reforming process.

Table 2 presents various catalysts from selected research that have been used for H₂ production via the steam reforming of ethanol. These include oxide catalysts,^{42,57} metal-based (Ni, Cu, Co) catalysts,^{14,41–43,45,46,48,49,58–60} metal-mixture-based catalysts,^{13,39,61} and noble-metal-based catalysts.^{14,23,40,46–48,50,60,62–64}

Elemental compounds that had been attempted as catalysts for the ethanol reforming process are also shown in Figure 3 and marked with a circle. The figure shows that most of the catalysts attempted were metals, both base and noble compounds. Some studies^{14,63,78} imply that metals alone do not assist H₂ production significantly. These studies suggest that the performances of metal catalysts could be improved using suitable supporting materials.

4.1. Oxide Catalysts. Alumina (Al₂O₃) and vanadia (V₂O₅) exhibited high activity in which they were able to convert 100% C₂H₅OH at a temperature of 623 K.⁴⁴ However, these two catalysts produced only small amounts of H₂, as well as high amounts of C₂H₄ and/or C₂H₄O. The activity of the Al₂O₃ catalyst was attributed to its large adsorption capacity toward C₂H₅OH,⁴² whereas the low H₂ yield was attributed to C₂H₅OH dehydration to C₂H₄ that dominates the reaction pathway.^{42,44}

Among the oxide catalysts, zinc oxide (ZnO) exhibited the best performance for the steam reforming of C₂H₅OH. This catalyst not only completely converted C₂H₅OH, but also produced considerable amounts of H₂ and only

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Table 2. Catalysts Used in the Process of Hydrogen Production via the Steam Reforming of Ethanol

catalysts involved	research highlight	references
Oxide Catalyst Group		
MgO; Al ₂ O ₃ ; V ₂ O ₅ ; ZnO; TiO ₂ ; La ₂ O ₃ ; CeO ₂ ; Sm ₂ O ₃ ; La ₂ O ₃ -Al ₂ O ₃ ; CeO ₂ -Al ₂ O ₃ ; MgO-Al ₂ O ₃	ZnO is the most promising catalyst. At 723 K, ZnO catalyst converts C ₂ H ₅ OH totally and produces H ₂ with no CO. H ₂ yield is 5.1 mol per mol of reacted C ₂ H ₅ OH.	14, 42, 44
Co-oxide Catalyst Group		
Co/Al ₂ O ₃ ; Co/La ₂ O ₃ ; Co/SiO ₂ ; Co/MgO; Co/ZrO ₂ ; Co-ZnO; Co/TiO ₂ ; Co/V ₂ O ₅ ; Co/CeO ₂ ; Co/Sm ₂ O ₃ ; Co/CeO ₂ -ZrO ₂ ; Co/C	Haga ⁵⁸ reported Co/Al ₂ O ₃ showed high selectivity by suppressing the methanation of CO and decomposition of C ₂ H ₅ OH. Llorca ⁶⁵ reported that Co/ZnO as the best for C ₂ H ₅ OH steam reforming. Co/ZnO catalyst produces 5.51 mol H ₂ and 1.87 mol CO ₂ , which converts to 92% of stoichiometrical coefficients.	45, 46, 57, 58, 65-68
Ni-oxide Catalyst Group		
:Ni/La ₂ O ₃ ; Ni/(La ₂ O ₃ -Al ₂ O ₃); Ni/Al ₂ O ₃ ; Ni/MgO; Ni-Cu/SiO ₂ ; Ni-Cu/γ-Al ₂ O ₃ ; Ni-Cu-K/γ-Al ₂ O ₃	Ni/Al ₂ O ₃ converted 100% C ₂ H ₅ OH and produced 70 vol % H ₂ . ⁴³ At a temperature more than 773K and steam to C ₂ H ₅ OH molar ratio 6:1, Ni/γ-Al ₂ O ₃ gave 5.2 mol H ₂ with 91% H ₂ selectivity. ⁶⁹ Ni/Al ₂ O ₃ deactivated because of coke formation. ⁷⁰ Ni/(La ₂ O ₃ -Al ₂ O ₃) showed good activity and stability. ⁴⁹ At temperatures of > 600 °C, C ₂ H ₅ OH conversion was 100% and H ₂ selectivity 95%, with CH ₄ as the only undesirable product. However, a small deactivation was observed. ⁷⁰	13, 42, 43, 46, 49, 61, 71-74
Rh-oxide Catalyst Group		
Rh/TiO ₂ ; Rh/SiO ₂ ; Rh/CeO ₂ ; Rh/ZrO ₂ ; Rh/Al ₂ O ₃ ; Rh/MgO; Rh/Al ₂ O ₃ ; Rh/CeO ₂ -ZrO ₂ ; Rh-Au/CeO ₂ ; Rh-Pt/CeO ₂	Rh/CeO ₂ showed good performance for oxidative steam reforming with 100% activity and produced 5 mol H ₂ . ¹⁴ At high Rh loading, Rh/Al ₂ O ₃ was promising for C ₂ H ₅ OH steam reforming. H ₂ yield was 5.5 mol (very close to the stoichiometric coefficient of 6) ^{75,76}	14, 23, 40, 48, 64, 72
Other Catalyst Groups		
Pd/CeO ₂ ; Pt/CeO ₂ ; Au/CeO ₂ ; Pd/Al ₂ O ₃ ; Pt-Pd/CeO ₂ ; Cu/Nb ₂ O ₅ -Al ₂ O ₃ ; Cu-Ni-Al-Zn; NiO-CeO ₂ -ZrO ₂ ; Pd/C; Rh(2,2'-bipyridyl) ₂ Cl; Group VIII (Fe, Ru, Os) [Rh(bipy) ₂]Cl	The performance of these catalysts were inferior compared to the aforementioned catalysts.	23, 39, 47, 50, 54, 59, 62, 63, 77

small amounts of C₂H₄, C₂H₄O, or CH₃COCH₃. Under the reaction conditions of 723 K, atmospheric pressure, a steam:C₂H₅OH molar ratio of 13:1, and a gas hourly space velocity (GHSV) of 22 000 h⁻¹, the ZnO catalyst produced 97.7% H₂ and CO₂, together with molar values of 5.1 for H₂ and 1.7 for CO₂, representing 85% of the stoichiometrical coefficients.⁴⁴ This implies that the ZnO catalyst is extremely selective to the overall steam

reforming reaction of C₂H₅OH. However, no information was available that was associated with the durability of this catalyst.

4.2. Oxide-Supported Metal Catalysts. Among oxide-supported metal catalysts, cobalt/alumina (Co/Al₂O₃) was reported to be a promising catalyst for C₂H₅OH steam reforming.⁵⁸ Co/Al₂O₃ was very selective toward the overall reaction by suppression of methanation of CO and C₂H₅OH decomposition. This catalyst was able to convert 100% of the C₂H₅OH with a H₂ selectivity of ~70%.^{58,80} The H₂ selectivity and product

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compositions are dependent on the preparation method and the precursor of support that was used. With the impregnation method, the H₂ selectivity over Co/Al₂O₃ was 67.3%, whereas with the sol–gel method, the yield selectivity was just 50.7% under the same reaction conditions.⁶⁸ However, Co/Al₂O₃ formed considerable amounts of CH₄ and C₂ compounds (mainly C₂H₄ and C₂H₄O) and produced comparatively small amounts of H₂, deposited a considerable amount of coke, and even progressively decayed after 2–3 h time on stream.^{55,80,81} Al₂O₃ inhibited toward cobalt reduction and the main reaction was the dehydration of C₂H₅OH.⁵⁷ However, increasing the cobalt content by >8% prevented the formation of C₂H₄.⁶⁷

A nickel-supported-on-alumina (Ni/Al₂O₃) catalyst at 673 K converted 100% C₂H₅OH and produced 70 vol % H₂.⁴³ At higher temperatures (>773 K) with a steam:C₂H₅OH molar ratio of 6:1, a Ni/ γ -Al₂O₃ catalyst produced 5.2 mol of H₂ with 91% selectivity toward H₂.⁶⁹ The performance of this catalyst was equivalent to that of Rh/Al₂O₃.⁸² However, Ni/Al₂O₃ deactivated quickly (after a few minutes time on stream), because of coke formation.⁷⁰ The addition of lanthana (La₂O₃) formed a pelleted Ni/(La₂O₃–Al₂O₃) that showed good catalytic performance, in terms of activity and stability for C₂H₅OH steam reforming.⁴⁹ Al₂O₃ promoted dehydration and cracking of C₂H₅OH and produced C₂H₄ (the agent of coking), whereas La₂O₃ promoted the dehydrogenation and cracking of C₂H₅OH.⁴² The selectivity and activity of the Ni/(La₂O₃–Al₂O₃) catalyst was dependent on temperature, and increases in temperature resulted in a decrease in selectivity toward C₂H₄O. At temperatures of >873 K, C₂H₅OH conversion was 100%, H₂ selectivity was ~95%, and the only undesirable product was CH₄. However, Ni/(La₂O₃–Al₂O₃) showed small deactivations during the first 80–100 h of time on stream, in which the conversion decreased from 95% to 90%.⁷⁰

Among the metal-oxide catalysts studied (which are listed in Table 2), Co/ZnO showed the best performance, in terms of activity, selectivity to H₂, and stability. Although Al₂O₃ inhibited cobalt reduction, ZnO promoted it.⁵⁷ At 723 K, the Co/ZnO catalyst was able to convert C₂H₅OH completely, with a H₂ selectivity of ~80% or even 90% after 50 h time on stream. Increasing the GHSV from 2300 h⁻¹ to 22 000 h⁻¹ reduced the undesired byproducts (such as CH₄, C₂H₂, C₃H₆, and CH₃CHO) but increased H₂ selectivity without reducing the degree of conversion.⁸¹ Co/ZnO characteristics were influenced by the cobalt precursor and pretreatment. With the Co(NO₃)₂ precursor and calcination, the catalyst produced a considerable amount of C₂H₂, C₃H₆, and CH₃CHO, as well as Me₂CO, with a H₂ selectivity of 62%.⁶⁵ With calcination followed by a reduction process, the catalyst became active (100% conversion at 623 K and a H₂ selectivity of 73%) without C₂ and C₃ species and the formation of only small amounts of CH₄. Using Co₂(CO)₈ as a cobalt precursor also resulted in better performance, with a C₂H₅OH conversion of 100% and a

H₂ selectivity of 73%, with the production of 5.51 mol of H₂, 1.87 mol of CO₂ (92% of stoichiometric coefficient) with no C₂ or C₃ species produced, and only small amounts of CH₄. The catalyst also did not produce any CO. The aforementioned stoichiometry suggests that Co/ZnO catalyst promotes the C₂H₅OH steam reforming reaction via the H₂ and CO₂ pathway (reaction 1).⁴¹ However, Co/ZnO showed a considerable amount of carbon deposition after the reaction.⁶⁵ This caused deactivation of the cobalt catalysts. The deactivation rate was dependent on the support used and the temperature.⁸¹ The addition of 0.98 wt % of sodium to the Co/ZnO catalyst improved the catalytic performance, in terms of the H₂ yield and stability, compared to unpromoted catalyst.⁴¹

4.3. Rh-oxides Catalyst. Rhodium (Rh)-supported-on-oxide catalysts are promising catalysts for C₂H₅OH steam reforming, among the noble metals. Frusteri⁴⁶ reported that a Rh/MgO catalyst was able to convert 100% of C₂H₅OH. However, it was also noticed that Rh/MgO produced significant amounts of CH₄ (10%). This implies that this catalyst is active in C₂H₄O decomposition and WGS reactions or CO_x methanation and is not active in the C₂H₅OH steam reforming reaction. Another drawback of Rh/MgO is coke formation, although at a low rate (<1 mg C/g_{cat}·h).

Another rhodium-based catalyst that showed potential for C₂H₅OH steam reforming is Rh/CeO₂. Although Toth⁴⁸ found that the activity of Rh/CeO₂ was lower than that of Rh/Al₂O₃, Aupretre et al.⁸² reported that the H₂ yield on Rh/CeO₂ was higher than that on Rh/Al₂O₃ at 873 K. Deluga et al.¹⁴ reported that Rh/CeO₂ was more stable and showed greater WGS activity than the noble metal alone. Furthermore, Rh/CeO₂ was good for oxidative reforming and converted >95% of C₂H₅OH for all C/O compositions with no significant deactivation. However, this catalyst produced significant amounts of CO.⁴⁸

Rhodium supported on alumina (Rh/Al₂O₃) also showed good performance for C₂H₅OH steam reforming. Aupretre⁸² noted that Rh/Al₂O₃ was better than other metal-supported-on-alumina catalysts (M/Al₂O₃, where M = Pt, Pd, Ru, Cu, Zn, and Fe). It was also found that Rh/Al₂O₃ showed the highest activity among rhodium supported on oxide (Rh/oxides) catalysts (in which oxides = CeO₂, TiO₂, ZrO₂, MgO, and SiO₂).⁴⁸ However, the performance of this catalyst is greatly influenced by the rhodium loading. At low rhodium loading (0.5 wt %), this catalyst suffers from deactivation and produces CH₄.^{40,70} Cavallaro and co-workers^{75,76} reported that, on oxidative steam reforming, the formation of coke at a rate of 0.27 mg/g_{cat}·h was also observed over this catalyst. The coke formation is attributable to the polymerization processes of CH_x species formed during reaction. The addition of a small amount of O₂ (0.4 vol %) in the feed gas significantly decreased the catalyst deactivation but promoted metal sintering. Toth⁴⁸ also mentioned that one of the main products of C₂H₅OH steam reforming over Rh/Al₂O₃ was C₂H₄, and its formation rate increased with time on stream. Cavallaro⁴⁰ offered a reaction pattern over Rh/Al₂O₃. First, the C₂H₅OH is converted to C₂H₄ by dehydrogenation or to C₂H₄O by dehydrogenation. Next, the C₂H₄O undergoes decarbonylation to form CH₄ and CO. Finally, the CH₄

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Table 3. Selected Best-Performing Catalysts in the Steam Reforming of Ethanol

catalyst rank	temp, T (K)	Performance		comments
		ethanol conversion (%)	H ₂ selectivity (%)	
Co–ZnO	573–723	100	85	Llorca ⁸¹ found ZnO to be the best for C ₂ H ₅ OH steam reforming. ZnO catalyst produces 5.51 mol H ₂ and 1.87 mol CO ₂ , which attributes to 85% of stoichiometrical coefficients ^{41,44,45,57}
ZnO	573–723	100	85	Llorca et al. ⁴⁴ stated that ZnO (or as a supporter for Co) was the best catalyst for steam reforming of C ₂ H ₅ OH among other oxides. The working temperature of this catalyst was relatively low (i.e., 623 K). At 100% C ₂ H ₅ OH conversion, selectivity toward H ₂ was ~73%.
Rh/Al ₂ O ₃	723–923	100	92	This catalyst had good activity and durability without coke formation. ^{40,84} Breen et al. ⁸⁵ showed that Rh/Al ₂ O ₃ was more active than Pd/Al ₂ O ₃ , Ni/Al ₂ O ₃ , or Pt/Al ₂ O ₃ . Auprete et al. ⁸⁶ added that a rhodium catalyst derived from a chlorinated metal precursor was better. However, Toth ⁴⁸ stated that C ₂ H ₄ formation occurred, which may have caused coke formation.
Rh/CeO ₂	573–1073	100	>100 ^a	Rh/CeO ₂ performed well in oxidative steam reforming. ¹⁴
Ni/La ₂ O ₃ –Al ₂ O ₃	573–1073	100	> 90	This catalyst showed high activity and selectivity but suffered deactivation during the first 80–100 h on stream. ^{42,49}

^a Not considering both water and ethanol in the selectivity calculation.

undergoes steam reforming, followed by the shift reaction of the CO. Furthermore, the excess water was able to prevent coking, even after several working hours. The C₂H₄O was decarbonylated by the rhodium to form CH₄ and CO, whereas C₂H₄ was converted to C₁ species by steam reforming. The coke prevention on an acid support (Al₂O₃) was also observed when the process was conducted at high temperatures. At low rhodium loading, the possibility of application of this catalyst for C₂H₅OH steam reforming was questionable, because Al₂O₃ showed catalytic activity for the production of C₂H₄.⁸³

Increasing the rhodium loading improved the performance of Rh/Al₂O₃ for C₂H₅OH steam reforming. Freni⁸³ reported that 5 wt % Rh/Al₂O₃ converted 100% of C₂H₅OH at a temperature of 923 K, pressure of 0.16 MPa, steam:C₂H₅OH molar ratio of 8.4:1, and GHSV of 37 500 h⁻¹. In full thermodynamic equilibrium conditions, the 5 wt % Rh/Al₂O₃ catalyst fully converted C₂H₅OH with no yield of C₂H₄ or C₂H₄O. Cavallaro and co-workers^{75,76} observed that, at GHSV = 5000–80 000 h⁻¹, Rh/Al₂O₃ converted 100% of C₂H₅OH. At low GHSV (5000 h⁻¹), Rh/Al₂O₃ yielded 5.5 mol of H₂ per mol of C₂H₅OH (92% of the stoichiometric coefficient). They observed that⁵⁵ 5 wt % Rh/Al₂O₃ at a temperature of 923 K and a pressure of 1.0 bar showed a great selectivity to C₁ compounds at high space velocity (GHSV up to 300 000 h⁻¹). Long-term experiments demonstrated that these characteristics remained constant with time. Finally, the 5 wt % rhodium catalyst showed no coke formation.

4.4. Other Catalysts. Some other catalysts that have been used for the C₂H₅OH steam reforming reaction include Pd/CeO₂, Pt/CeO₂, Au/CeO₂, Pd/Al₂O₃, Pt–Pd/CeO₂, Cu/Nb₂O₅–Al₂O₃, Cu–Ni–Al–Zn, NiO–CeO₂–ZrO₂, Pd/C, Rh(2,2'-bipyridyl)₂Cl, and Group VIII (Fe, Ru, Os)[Rh(bipy)₂Cl].^{23,39,47,50,54,59,62,63,77} However, the performance of these catalysts is inferior, compared to all the aforementioned catalysts.

It can be summarized that, generally, steam reforming of C₂H₅OH works well at temperatures of >773 K.

(83) Freni, S. Rh-Based Catalysts for Indirect Internal Reforming Ethanol Applications in Molten Carbonate Fuel Cells. *J. Power Sources* **2001**, *94* (1), 14–19.

Most of the studies referenced in Table 2 show that the majority of the reactions occur under atmospheric pressure conditions. To achieve complete conversion, the mole number of water must be higher than that of C₂H₅OH, and a H₂O:C₂H₅OH molar ratio of 3:1 generally was used. The amount of catalyst load was also important and was greatly influenced by the type and size of the reactor; however, catalyst loads of 50 and 100 mg were noted to be more frequent. Other conditions involved gas flow rate and GHSV. Although gas flow rates greatly varied from 10 mL/min to 4000 mL/min, flow rates in the range of 100–300 mL/min were frequently used. Similarly, the GHSV values also widely varied, from 5000 h⁻¹ to 300 000 h⁻¹, but generally were in the range of 40 000–100 000 h⁻¹.

Good catalysts are characterized by being efficient and having wide ranges of operating temperatures, high selectivity toward H₂, and low selectivity toward byproduct compounds, in addition to being durable, resistant toward shock, nonpyrophoric (no degradation upon exposure to air), and cost-effective. Table 3 lists a few promising catalysts that perform well for the C₂H₅OH reforming reaction to produce H₂. These catalysts are grouped based on their activity (in terms of conversion), selectivity toward H₂, and coking potential.

As observed in the aforementioned discussion, most catalysts for C₂H₅OH steam reforming also produce CO where the WGS reaction is required for the full H₂-producing reaction to occur. Table 4 lists selected catalysts that performed the combined HTS/LTS–WGS reaction satisfactorily. These catalysts were chosen mainly based on their activity and their selectivity toward WGS reaction and stability. Platinum supported on CeO₂ or TiO₂, as well as gold supported on CeO₂ or Fe₂O₃, performed well in this reaction. Ru/ZrO₂ and Cu/CeO₂ were less costly alternatives. For the conventional

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(85) Breen, J. P.; Burch, R.; Coleman, H. M. Metal-Catalysed Steam Reforming of Ethanol in the Production of Hydrogen for Fuel Cell Applications. *Appl. Catal., B* **2002**, *39* (1), 65–74.

(86) Auprêtre, F.; Descorme, C.; Duprez, D. Hydrogen Production for Fuel Cell from the Catalytic Ethanol Steam Reforming. *Top. Catal.* **2004**, *30*–31.

Table 4. Selected Best-Performing Catalysts for the Combined HTS/LTS–WGS Reaction

catalyst	temp, T (K)	CO conversion (%)	others	comments
Ru/ZrO ₂	523–573	96	100% selectivity	Goerke et al. ⁸⁷ reported that this catalyst was able to reduce the CO content by >95%. Even with selective oxidation, CO content could be reduced with a conversion of >99%.
Pt/CeO ₂	827	95	stable	Pt-ceria is nonpyrophoric, stable, and has a low selectivity toward CH ₄ . This catalyst was able to reach 95% activity. Methanation conversion was reported to be negligible with maximum CO conversion. ⁷⁸
Cu/CeO ₂	723	~93	stable	This catalyst showed high activity (93% CO conversion) and stability at 450 °C in CO ₂ -rich and H ₂ -rich gas streams. CO ₂ , which became problematic for iron-based catalysts (because of its poisoning effects) does not present severe inhibition with this catalyst. ⁸⁸
Pt/TiO ₂	423–723	>95		Panagiotopoulou and Kondarides ⁸⁹ reported this catalyst was better among the other noble-metal/TiO ₂ catalysts. Its activity increased with the amount of metal loading and reached >95%.
Au/CeO ₂	473–623	>95	stable	Preparation methods and gold loading greatly influence catalytic performances. Deposition–precipitation with 3–5 wt % gold loading yielded a catalyst that had high activity and was stable for WGS reaction over a wide range of temperatures. ^{90–93}
Au/Fe ₂ O ₃	423–623	97 (average)		Hua et al. ⁹⁴ reported that 8%Au/Fe ₂ O ₃ dried at 398 K and calcined at 423 K showed high activity for WGS reaction (CO conversion of ~98%) over a wide range of temperatures (423–623 K)

two-stage LTS and HTS process, Fe/Cr₂O₃ and Cu/ZnO, respectively, are the catalysts that are still used commercially.

5. Conclusions

Different catalysts have been used for the steam reforming of ethanol (C₂H₅OH). Depending on the type

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(88) Stephanopoulos, M. F.; Meldon, J.; Qi, X. *Water-Gas Shift with Integrated Hydrogen Separation*; U.S. Department of Energy (DOE): Washington, DC, September 1, 2000–August 31, 2001.

(89) Panagiotopoulou, P.; Kondarides, D. I. Effect of Morphological Characteristics of TiO₂-Supported Noble Metal Catalysts on their Activity for the Water-Gas Shift Reaction. *J. Catal.* **2004**, *225*, 327–336.

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(92) Andreeva, D.; Idakiev, V.; Tabakova, T.; Ilieva, L.; Falaras, P.; Bourlinos, A.; Travlos, A. Low-Temperature Water-Gas Shift Reaction over Au/CeO₂ Catalysts. *Catal. Today* **2002**, *72*(1–2), 51–57.

of catalysts, reaction conditions, and the catalyst preparation method, the C₂H₅OH conversion and H₂ production vary greatly. It was determined that Co/ZnO, ZnO, Rh/Al₂O₃, Rh/CeO₂, and Ni/La₂O₃–Al₂O₃ performed the best for the steam reforming of C₂H₅OH. Because many catalysts produce CO as a byproduct in the C₂H₅OH steam reforming process, water-gas-shift (WGS) catalysts also have an important role in the overall reforming process. Recent research has focused more on the combined low-temperature shift/high-temperature shift (LTS/HTS) reaction. The study found that Ru/ZrO₂, Pt/CeO₂, Cu/CeO₂, Pt/TiO₂, Au/CeO₂, and Au/Fe₂O₃ performed best in the combined LTS/HTS reaction. Still, for commercial applications, Cu/ZnO is used for the LTS reaction, whereas Fe/Cr₂O₃ is used for the HTS reaction.

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