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Review

Insight into steam reforming of ethanol to produce hydrogen for fuel cells

Prakash D. Vaidya, Alirio E. Rodrigues*

Laboratory of Separation and Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering,
University of Porto, Porto 4200-465, Portugal

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Abstract

Ethanol can be prepared from agricultural residues and hence is a renewable resource. Its production is simple and cheap and hence steam reforming of ethanol to produce hydrogen for fuel cells is attractive. Process engineering aspects of ethanol steam reforming are discussed here. High temperatures, low pressures and high water-to-ethanol ratios in the feed favor hydrogen production. Ni, Co, Ni/Cu and noble metal (Pd, Pt, Rh)-supported catalysts are promising. Major concerns are fast catalyst coking and formation of by-products such as methane, diethyl ether and acetaldehyde. To overcome these problems, the process should be carried out in a two-layer fixed bed catalytic reactor: at first, ethanol should be dehydrogenated to acetaldehyde in presence of Cu-based catalyst at 573–673 K and then this stream should be passed over a bed containing a mixture of Ni-based catalyst and a chemisorbent at low temperatures around 723 K. The entire process of ethanol steam reforming coupled with selective CO_2 removal by chemisorption will enable production of high-purity H_2 and hence is very promising.

Keywords: Fuel cells; Ethanol; Steam reforming; Hydrogen

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1. Introduction

Hydrogen is produced commercially on a large scale mainly by steam reforming, partial oxidation, coal gasification and electrolysis. Its current worldwide production is around 5×10^{11} N m^3 per year [1]. It is primarily used as a feedstock in the chemical industry, for instance, in the manufacture of ammonia and methanol, and in refinery reprocessing and conversion processes. However, with the environmental regulations becoming more stringent, there is now growing interest in the use of hydrogen as an alternative fuel. Its combustion does not result in any emission other than water vapor (although under certain air/hydrogen ratios, NO_X can also be produced) and hence it is the least polluting fuel that could be used in an internal combustion engine. It can also be used in a fuel cell for the production of electricity for stationary applications and mobile electric vehicle operations.

Fuel cells (FCs) are electrochemical devices that convert the chemical energy of a fuel and an oxidant directly into electricity and heat on a continuous basis. A fuel cell consists of an electrolyte and two electrodes. A fuel such as hydrogen is continuously oxidized at the negative anode while an oxidant such as oxygen is continuously reduced at the positive cathode. The electrochemical reactions take place at the electrodes to produce a direct electric current. FCs use hydrogen as a fuel which results in the formation of water vapor only and thus they provide clean energy. FCs offer high conversion efficiency and hence are promising. The current status of fuel cell technology for mobile and stationary applications has recently been discussed [2].

Among the various types of fuel cells, the proton exchange membrane fuel cells (PEMFCs), the solid oxide fuel cells (SOFCs) and the molten carbonate fuel cells (MCFCs) have attracted considerable interest. SOFCs and MCFCs operate at high temperatures (around 973 K) and are used for stationary power generation. PEMFCs are primarily used for automotive applications. They have a low operating temperature (353 K), high current density and low CO tolerance (10 ppm). They use hydrogen as the fuel and this can be supplied as pure hydrogen. Thus, fuel cell vehicles can be equipped with pressurized hydrogen tanks, thereby ensuring a continuous supply of fuel. Alternately, hydrogen can be stored as a liquid in cryogenic tanks at 20 K. These ways of storing hydrogen are however inconve-

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* Corresponding author. Tel.: +351 22 5081671; fax: +351 22 5081674.
E-mail address: arodrig@fe.up.pt (A.E. Rodrigues).

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Nomenclature

A	ethanol
B	water
C	CO_2
C_A	crude ethanol concentration ($\mathrm{kmol\,m^{-3}}$)
C_i	concentration of species *i* ($\mathrm{kmol\,m^{-3}}$)
D	H_2
E	energy of activation ($\mathrm{kJ\,mol^{-1}}$)
k_0	constant in Eqs. (21) and (22)
K_A	adsorption constant of A ($\mathrm{m^3\,kmol^{-1}}$)
K_P	overall equilibrium constant ($(\mathrm{kmol\,m^{-3}})^4$)
n	order with respect to ethanol
P_{EtOH}	partial pressure of ethanol (atm)
P_{H_2O}	partial pressure of water (atm)
$-r_{EtOH}$	rate of disappearance of ethanol in Eq. (20) ($\mathrm{kmol\,kg_{cat}^{-1}\,s^{-1}}$)
$-r_A$	rate of disappearance of crude ethanol in Eqs. (21) and (22) ($\mathrm{kmol\,kg_{cat}^{-1}\,s^{-1}}$)
R	moles of water per mole of ethanol in feed
T	absolute temperature (K)

nient. Moreover, the use of compressed hydrogen involves safety aspects. Also, there is no proper infrastructure for hydrogen transport and distribution. Therefore, in practice, other hydrogen containing fuels are used.

A number of hydrogen generation routes have been explored [3]. Methanol, ethanol, ammonia, gasoline and natural gas are some possible sources of hydrogen for fuel cells. In addition, petroleum distillates, liquid propane, oil, gasified coal and even gas from landfills and wastewater treatment plants can also be processed to supply hydrogen [4]. For stationary applications, natural gas is the fuel of choice due to its availability and ease in distribution. For automotive applications, gasoline is the most convenient fuel since it can be easily transported. However, PEMFCs are very sensitive to impurities in fuel and have a sulphur specification less than 1 ppm [5]. Gasoline has a 30 ppm sulphur standard in USA while hydrogen from coal gasifiers may contain 100–200 ppm sulphur. Catalytic cracking of ammonia generates a CO_2-free mixture containing 75% hydrogen. However, ammonia is toxic and poses a problem of generating nitrogen oxides during catalytic combustion of the cell effluent [6]. Methanol, which is mainly prepared by syn-gas conversion, has a favorable H:C ratio of 4, is largely distributed and is available in abundance. Moreover, it can be transported and reformed more easily than natural gas. However, its main drawback is its high toxicity. Ethanol is more promising since it is less toxic. It can also be more easily stored and safely handled. Most importantly, it can be produced in large amounts from biomass such as agricultural wastes and forestry residues and hence is a renewable resource, as against methanol and gasoline. This could prove advantageous in tropical countries with a warm climate where there are large plantations of corn and sugarcane. The bio-ethanol thus produced is free from sulphur, which otherwise may poison the fuel cell catalyst. Similarly, it is free from metals as well. Bio-ethanol, which is a dilute aqueous solution containing around 12% (wt.) ethanol, could be directly subjected to steam reforming thereby eliminating one unit operation of distillation required to produce pure ethanol. The entire process could therefore be economically attractive. Above all, ethanol is CO_2 neutral since the CO_2 that is produced in this process is consumed by biomass growth and a closed carbon cycle is operated while the use of methanol and gasoline adds to CO_2 emissions. Thus, the use of ethanol will not contribute to global warming.

The first step in the conversion of ethanol to hydrogen is reforming. This reaction is carried out in the range of temperatures 673–1273 K. Reforming can be either by steam (steam reforming), or by humidified air (partial oxidation reforming), or by a mixture of air and steam (auto-thermal reforming). Here, attention is focussed on the steam reforming reaction. This yields a H_2-rich gas containing CO, which is a poison for PEMFCs. Except for use in high temperature cells, the CO concentration must be reduced to a very low level (around 10 ppm). A water gas shift reactor is therefore used to reduce the CO content of this gas stream. After high temperature and low temperature water gas shift (HTS and LTS), the residual CO is then reduced further to ppm level in a CO preferential oxidation (PROX) reactor [7]. This product gas is then suitable for feeding PEMFCs.

In view of the continuing importance of ethanol as a source of hydrogen for fuel cells, there is a need for a comprehensive review on this topic. Recently, Haryanto et al. [8] have reviewed steam reforming of ethanol, examined the various catalysts reported till date and presented a comparative analysis. They concluded that the ethanol conversion and H_2 production varies greatly with the reaction conditions, the type of catalyst and the method of catalyst preparation. The importance of process engineering related aspects is evident and these need to be discussed at length. This article is aimed at fulfilling this need. It reviews the available literature on catalytic steam reforming of ethanol. All published information on this topic is analyzed and presented in a coherent manner. The role of the catalyst composition and the process conditions in determining product distribution is elucidated. The possible reaction pathways and the kinetic and thermodynamic considerations have also been discussed. The coupling of ethanol steam reforming with selective removal of CO_2 by chemisorption to produce high-purity H_2 at low temperatures has been discussed. It is expected that this will provide an insight into steam reforming of ethanol.

2. Thermodynamic considerations

Thermodynamic aspects of ethanol steam reforming have received a fair amount of attention in the published literature. The reaction is strongly endothermic and produces only H_2 and CO_2 if ethanol reacts in the most desirable way. The basic reaction scheme is as follows:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \quad (\Delta H^\circ_{298} = 174\ \mathrm{kJ\,mol^{-1}}) \tag{1}$$

However, other undesirable products such as CO and CH_4 are also usually formed during reaction. Aupretre et al. [9] have discussed the main reactions in ethanol steam reforming that account for the formation of these by-products:

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2 \quad (\Delta H^\circ_{298} = 256\,\mathrm{kJ\,mol^{-1}}) \tag{2}$$

$$C_2H_5OH + 2H_2 \rightarrow 2CH_4 + H_2O \quad (\Delta H^\circ_{298} = -157\,\mathrm{kJ\,mol^{-1}}) \tag{3}$$

Other reactions that can also occur are: ethanol dehydrogenation to acetaldehyde (4), ethanol dehydration to ethylene (5), ethanol decomposition to CO_2 and CH_4 (6) or CO, CH_4 and H_2 (7).

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \quad (\Delta H^\circ_{298} = 68\,\mathrm{kJ\,mol^{-1}}) \tag{4}$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (\Delta H^\circ_{298} = 45\,\mathrm{kJ\,mol^{-1}}) \tag{5}$$

$$C_2H_5OH \rightarrow \tfrac{1}{2}CO_2 + \tfrac{3}{2}CH_4 \quad (\Delta H^\circ_{298} = -74\,\mathrm{kJ\,mol^{-1}}) \tag{6}$$

$$C_2H_5OH \rightarrow CO + CH_4 + H_2 \quad (\Delta H^\circ_{298} = 49\,\mathrm{kJ\,mol^{-1}}) \tag{7}$$

Acetaldehyde and ethylene are important intermediates that may be formed during reaction even at relatively low temperatures well before the formation of H_2 and CO_x by reactions (1) and (2). In addition, the formation of coke on the surface of the catalyst is also not uncommon. Coke formation may occur as per the following Boudouard reaction:

$$2CO \rightarrow CO_2 + C \quad (\Delta H^\circ_{298} = -171.5\,\mathrm{kJ\,mol^{-1}}) \tag{8}$$

Another possible route for the formation of carbon is through ethylene:

$$C_2H_4 \rightarrow \text{polymers} \rightarrow \text{coke} \tag{9}$$

From the thermodynamic standpoint, since reaction (1) is endothermic and results in increase in number of moles, increasing the temperature and lowering the pressure is in favor of ethanol reforming. At 500 K, steam reforming of ethanol does not occur ($\Delta G > 0$). However, ethanol decomposition can easily occur at this temperature since the value of ΔG is sufficiently negative [10]. In fact, reaction (6) is strongly favored at low temperatures (<473 K).

Garcia and Laborde [11] and Vasudeva et al. [12] have earlier shown that an increase in temperature leads to an increase in the H_2 and CO concentration and a decrease in CH_4 concentration at equilibrium. Garcia and Laborde [11] also found that when compared to methanol steam reforming, higher temperatures and higher water-to-ethanol ratios are needed to obtain the best H_2 production from ethanol. They examined the thermodynamic equilibrium of this system and suggested operation at $T > 650$ K, atmospheric pressure and a water-to-ethanol molar ratio of up to 10 in the feed to maximize H_2 production, minimize the formation of CO and CH_4 and avoid carbon deposition on the catalyst.

Vasudeva et al. [12] found that H_2 yields as high as 5.5 mol/mol of ethanol in the feed can be obtained at equilibrium at temperatures around 773–873 K with water-to-ethanol molar ratios of above 20. They suggested that carbon formation occurs only at low water-to-ethanol ratios (<2) and low temperatures (883 K).

Aupretre et al. [13] have also performed a thermodynamic analysis of the system. They have further shown that an increase in the total pressure leads to a decrease in the H_2 and CO yields while the equilibrium composition in CH_4 increases [14]. However, the entire system of H_2 production and its purification has to be operated under pressure when the CO level is reduced to traces from the H_2-rich gas by using a metallic membrane, for instance, Pd-based membrane. The theoretical production of CH_4 however decreases with a decrease in the water-to-ethanol ratio [6].

Fishtik et al. [15] found that for temperatures at or above 700–800 K and for high water-to-ethanol ratios, the desired reaction of ethanol steam reforming is predominant and the formation of CO and CH_4 is minimized. At high temperatures (>1073 K), the equilibrium H_2 selectivity is nearly 100% [16]. However, the use of a water-to-ethanol ratio higher than stoichiometry results in increased enthalpy needs for water evaporation.

In a more recent study, Mas et al. [17] suggested that while high temperatures and high water-to-ethanol ratios favor H_2 production, low temperatures and high water-to-ethanol ratios are suitable to minimize CO formation. At a water-to-ethanol molar ratio of 3, temperatures higher than 500 K are required to avoid coke formation.

Freni et al. [18] carried out a thermodynamic analysis of the ethanol–water system as applied to an MCFC and suggested that a high water-to-ethanol ratio in the feed reduced the yield of undesirable products such as CO, CH_4 and carbon. In another study, Thoephilus [19] reported a H_2 yield of nearly 100% at 1000 K, atmospheric pressure and a water-to-ethanol molar ratio of 5.

3. Catalysts for steam reforming of ethanol

The steam reforming of ethanol over Ni, Co, Ni/Cu and noble metals (Pd, Pt, Rh) has been extensively studied. The greatest concern lies in developing an active catalyst that inhibits coke formation and CO production. We now take an overview of the published literature.

3.1. Supported cobalt catalysts

Earlier, Co-based catalysts were deemed as appropriate systems for steam reforming of ethanol. Llorca et al. [20,21] proposed the use of ZnO-supported Co catalysts in steam reforming of ethanol. The use of $Co(CO)_8$ as precursor produced a highly stable catalyst that enabled the production of CO-free H_2 at low temperatures (623 K). They concluded that the method of catalyst preparation affected its performance and structural characteristics.

Haga et al. [22] studied the catalytic properties of Co among other metals and found that selectivity to H_2 was in the order Co > Ni > Rh > Pt, Ru, Cu. In another study, they found that the supports vastly influenced the properties of Co catalysts [10]. The formation of H_2 decreased in the order: $Co/Al_2O_3 > Co/ZrO_2 > Co/MgO > Co/SiO_2 > Co/C$. The Co/Al_2O_3 catalyst exhibited the highest selectivity to H_2 (67% at 673 K) by suppressing methanation of CO and decomposition of ethanol. Similarly, Cavallaro et al. [23] found that Co/MgO is more resistant to coke formation than Co/Al_2O_3 at 923 K.

Kaddouri and Mazzocchia [24] reported high catalytic activity of Co/SiO_2 and Co/Al_2O_3 for steam reforming of ethanol and concluded that the product distribution was dependent on both the nature of the support and the method of catalyst preparation, thereby suggesting metal–support interaction. Batista et al. [25] studied ethanol steam reforming over Co/Al_2O_3 and Co/SiO_2. The catalysts showed average conversion higher than 70% at 673 K. The metal loading influenced ethanol conversion and product distribution.

3.2. Noble metal catalysts

Steam reforming of ethanol over Rh-based catalysts has earlier been studied. Frusteri et al. [26] investigated the performance of MgO-supported metal catalysts and reported that H_2 could be efficiently produced from ethanol over Rh/MgO at 923 K. The activity of the catalysts reduced in the order Rh > Co > Ni > Pd. Rh/MgO was most resistant to coke formation. They proposed a reaction mechanism for ethanol steam reforming (Fig. 1). As per this scheme, ethanol is first dehydrogenated to acetaldehyde which subsequently decomposes to CH_4 and CO. These lead to the formation of H_2 and CO_2 by steam reforming and water gas shift (WGS) reactions. Thus, the exit stream composition is governed by CH_4 steam reforming and WGS reactions.

Cavallaro et al. [27] studied ethanol reforming over Rh/Al_2O_3 at 923 K and found that less coke was formed and the catalyst was more stable in presence of O_2. They suggested the occurrence of several reactions: acetaldehyde formed by dehydrogenation of ethanol is decomposed to CH_4 and CO (10) or undergoes steam reforming (11).

$$CH_3CHO \rightarrow CH_4 + CO \tag{10}$$

$$CH_3CHO + H_2O \rightarrow 2CO + 3H_2 \tag{11}$$

Water reforms the C_1 products to hydrogen.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (\Delta H^\circ_{298} = 205\,\mathrm{kJ\,mol^{-1}}) \tag{12}$$

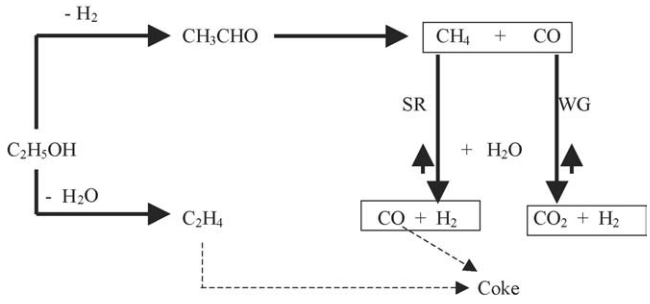

Fig. 1. Reaction mechanism for steam reforming of ethanol.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (\Delta H^\circ_{298} = -41.2\,\mathrm{kJ\,mol^{-1}}) \tag{13}$$

In addition, the following reactions occur when O_2 is present:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \tag{14}$$

$$C_2H_5OH + \tfrac{1}{2}O_2 \rightarrow CH_3CHO + H_2O \tag{15}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{16}$$

$$C + O_2 \rightarrow CO_2 \tag{17}$$

Fierro et al. [4] reported high activity and selectivity to H_2 production of Rh/Al_2O_3 catalyst in bio-ethanol oxidative steam reforming. In addition, the catalyst was highly stable. Cavallaro [28] also studied this reaction over Rh/Al_2O_3 and found that coke formation could be prevented at high temperatures by sufficiently large amounts of Rh and strong excess of water. At 973 K, only C_1 products were present in the exit stream. Aupretre et al. [14] studied ethanol steam reforming over Rh/Al_2O_3 under pressure (1.1 MPa). They reported that the nature of the metal precursor salt, metal loading and the reaction conditions influenced the performance of the catalyst.

Breen et al. [29] studied a range of oxide-supported metal catalysts for reforming of ethanol–water mixtures. They found that Al_2O_3-supported catalysts promote dehydration of ethanol to ethylene and the order of activity of metals for such catalysts is Rh > Pd > Ni = Pt. However, with CeO_2/ZrO_2-supported catalysts, ethylene is not formed and the order of activity at higher temperatures is Pt ≥ Rh > Pd. They showed that by using a combination of CeO_2/ZrO_2-supported metal catalysts with alumina support, ethylene formation does not inhibit steam reforming at high temperatures. Diagne et al. [30] showed that up to 5.7 mol H_2 can be produced per mol ethanol at 623–723 K on Rh/CeO_2–ZrO_2 in presence of excess of water. Other studies also suggest that Rh-based catalysts are promising [31,32].

There is scarce information in the literature on Pt-based catalysts. Navarro et al. [33] studied oxidative reforming of ethanol over a Pt/Al_2O_3 catalyst modified by Ce and La. The presence of Ce as an additive was found to be beneficial for hydrogen production. The presence of La however did not promote ethanol conversion. When both Ce and La were present on the support, poorer catalyst behavior was observed due to lower Pt–Ce interaction with respect to La-free ceria–alumina support.

Few studies on Pd catalyzed steam reforming of ethanol have also been reported earlier. Goula et al. [34] studied steam reforming of bio-ethanol over a commercial Pd/Al_2O_3 catalyst and reported 95% selectivity to hydrogen at 923 K. Ethanol conversion was 100% even at low temperatures (573–623 K). In another such study on Pd/Al_2O_3, these researchers reported that CO concentration was minimum at 723 K and the amount of coke formed was negligible even at stoichiometric water-to-ethanol ratios [35].

Galvita et al. [36] studied ethanol decomposition over a Pd catalyst supported on a porous carbonaceous material in presence of steam in the range of temperatures 603–633 K. The catalyst was found to have high activity and stability. Frusteri et al. [26] however observed that a Pd/MgO catalyst drastically deactivated during reaction due to metal sintering at 923 K. Coke formation on Pd/MgO occurred at a higher rate than on MgO-supported Rh, Ni and Co catalysts.

Liguras et al. [37] studied Ru-catalyzed steam reforming of ethanol in the range of temperatures 873–1123 K. There was a marked increase in conversion of ethanol and selectivity to H_2 over Ru/Al_2O_3 with an increase in the Ru content. At a high Ru loading (5 wt.%), the performance of Ru was comparable to Rh. The catalyst was stable and had activity and selectivity higher than Ru/MgO and Ru/TiO_2. Fierro et al. [4] showed that the order of performance of alumina-supported noble metal catalysts (5% metal loading) for bio-ethanol oxidative steam reforming at 973 K was $Pt < Pd \ll Ru < Rh$.

3.3. Ni-supported catalysts

The performance of various Ni-supported catalysts is summarized in Table 1. Comas et al. [38] studied steam reforming of ethanol over Ni/Al_2O_3 in the range of temperatures 573–773 K and did not find any evidence of the water gas shift reaction occurring over Ni. They proposed a reaction scheme for ethanol reforming on Ni-based catalyst at 773 K. As per this scheme, acetaldehyde and ethylene formed as intermediates during reaction produce CO, CO_2, CH_4 and H_2 as the final products by steam reforming while the effluent gas composition is determined by methane steam reforming:

$$CH_3CHO + H_2O \rightarrow CO_2 + CH_4 + H_2 \quad (\Delta H^\circ_{298} = -55.8\,\mathrm{kJ\,mol^{-1}}) \tag{18}$$

$$C_2H_4 + 2H_2O \rightarrow CO_2 + CH_4 + 2H_2 \quad (\Delta H^\circ_{298} = -36.9\,\mathrm{kJ\,mol^{-1}}) \tag{19}$$

Frusteri et al. [26] reported high H_2 selectivity (>95%) at a space velocity $4 \times 10^4\,\mathrm{h^{-1}}$ over Ni/MgO at MCFC operating conditions (923 K). The performance of alkali-doped Ni/MgO catalysts on bio-ethanol steam reforming was also studied [39]. The addition of Li and K enhanced the catalyst stability mainly by depressing Ni sintering. Freni et al. [40] found that Ni/MgO exhibited high activity and selectivity to H_2 than Co/MgO due to the lower tendency of Ni to oxidize during reaction and to promote methanation of CO and decomposition of ethanol.

Fatsikostas et al. [41,42] showed that Ni/La_2O_3 exhibited high activity and stability in steam reforming of ethanol to hydrogen. This was attributed to the formation of lanthanum oxycarbonate species ($La_2O_2CO_3$), which reacts with the surface carbon deposited during reaction and prevents deactivation. In another study, Fatsikostas and Verykios [43] studied ethanol reforming over Ni catalysts supported on γ-Al_2O_3, La_2O_3 and La_2O_3/γ-Al_2O_3. The impregnation of Al_2O_3 with La_2O_3 reduced carbon deposition. The presence of La_2O_3 on the catalyst, high water-to-ethanol ratios and high temperatures offered high resistance to carbon deposition.

Sun et al. [44] studied steam reforming of ethanol over Ni-supported catalysts at lower temperatures (523–623 K). The catalytic activity, stability and selectivity of H_2 formation reduced in the order $Ni/La_2O_3 > Ni/Y_2O_3 > Ni/Al_2O_3$. A kinetic study revealed that the reaction was first order with respect to ethanol. In another kinetic study over Ni/Al_2O_3, Therdthianwong et al. [45] proposed the following rate expression for ethanol steam reforming at 673 K and atmospheric pressure:

$$-r_{\mathrm{EtOH}} = 77.8(P_{\mathrm{EtOH}})^{2.52}(P_{\mathrm{H_2O}})^{7} \tag{20}$$

where $0.0003 < P_{\mathrm{EtOH}} < 0.0508$ atm, $0.7094 < P_{\mathrm{H_2O}} < 0.9371$ atm, $-r_{\mathrm{EtOH}}$ has the units $\mathrm{kmol\,kg_{cat}^{-1}\,s^{-1}}$ and the reaction rate constant is expressed as $\mathrm{kmol\,kg_{cat}^{-1}\,s^{-1}\,atm^{-9.52}}$. The various kinetic studies over Ni-based catalysts are listed in Table 2.

The catalytic steam reforming of ethanol is a heterogeneous gas-solid catalyzed reaction and involves the following transfer processes: diffusion of the reactants from the bulk gas phase to the catalyst surface, intraparticle diffusion followed by chemi-

Table 1
The performance of Ni-supported catalysts in steam reforming of ethanol

Catalyst	Temperature (K)	Feed		R (mol/mol)	Initial EtOH Conversion (%)	H_2 selectivity (%)	Space time ($\mathrm{g\,s\,cm^{-3}}$)	Reference
		EtOH (%)	Inerts (%)					
Ni/Al_2O_3	773	1.7	80	1–6	100	91[a]	0.06	[38]
Ni/MgO	923	8	24	8.4	100	>95[b]		[26]
Ni/MgO and Li, Na, K	923	8	24	8.4	100	>95[b]		[39]
Ni/MgO	923	8	24	8.4	100	90[b]		[40]
Ni/La_2O_3	>873	9	63	3	100	>90[b]	0.0375	[41]
Ni/La_2O_3	1023	9	63	3	100	>90[b]	0.0375	[42]
Ni/Al_2O_3					>90			
Ni/YSZ					92			
Ni/MgO					80			
Ni/Y_2O_3	593			3	93.1	53.2[c]	5.4	[44]
Ni/La_2O_3					99.5	48.5		
Ni/Al_2O_3					90.1	44		
Ni/ZnO	923			8	100	95[b]		[50]

[a] $H_2\ \text{selectivity} = \dfrac{\text{mol/h of } H_2 \text{ produced}}{3[(\text{mol/h of EtOH})_{\text{in}} - (\text{mol/h of EtOH})_{\text{out}}] + [(\text{mol/h of } H_2O)_{\text{in}} - (\text{mol/h of } H_2O)_{\text{out}}]}$.

[b] Selectivity is defined as the ratio of the moles of H_2 to the consumed moles of ethanol, as per stoichiometry.

[c] Selectivity is expressed as mol% of gaseous products.

Table 2
Kinetics of steam reforming of ethanol over Ni-based catalysts

Catalyst	Temperature (K)	Rate constant	Order w.r.t. ethanol	Order w.r.t. steam	E (kJ mol^{-1})	Investigators
Ni/Al_2O_3	673	77.8 kmol kg_{cat}^{-1} s^{-1} $atm^{-9.52}$	2.52	7		Therdthianwong et al. [45]
Ni/Y_2O_3	403	2.95×10^{-3} m^3 kg_{cat}^{-1} s^{-1}	1		7.04	Sun et al. [44]
Ni/Al_2O_3		2.32×10^{-3} m^3 kg_{cat}^{-1} s^{-1}	1		16.88	
Ni/La_2O_3		19.1×10^{-3} m^3 kg_{cat}^{-1} s^{-1}	1		1.87	
Ni/Al_2O_3	593–793		0.43		4.41	Akande [48]
Cu-plated Raney nickel	523–573		1		149	Morgenstern and Fornango [5]

cal reaction at the active centres and diffusion of the products. Any of these mass transfer processes (external or internal) can influence the rates of reaction. The high discrepancy and low values of the energy of activation presented in Table 2 confirm this fact. Marino et al. [46] have observed the presence of diffusional resistances even at temperatures as low as 573 K and using catalyst particles in the size range 125–177 μm, thereby suggesting the high rates of ethanol dehydrogenation in presence of Cu. Further, the diminution of these diffusional resistances decreased the selectivity of intermediary compounds such as acetaldehyde.

Akande et al. [47] studied reforming of crude ethanol over Ni/Al_2O_3 catalysts. Akande [48] suggested a power law model for crude ethanol reforming in the range of temperatures 593–793 K. Thus the rate could be expressed as

$$-r_A = k_0\, e^{-E/RT} C_A^n \tag{21}$$

where '$-r_A$' is in kmol kg_{cat}^{-1} s^{-1}, 'k_0' is in kmol$^{0.57}$ $(m^3)^{0.43}$ kg_{cat}^{-1} s^{-1}, 'C_A' is crude ethanol concentration in kmol m^{-3}, 'n' denotes order with respect to ethanol and T is temperature in K. The order with respect to ethanol was found to be 0.43 while the energy of activation 'E' was found to be 4.41 kJ mol^{-1}.

Aboudheir et al. [49] also reported an Eley Rideal type kinetic model for catalytic reforming of crude ethanol over Ni/Al_2O_3 for temperatures in the range 593–793 K, assuming dissociation of adsorbed crude ethanol as the rate-determining step:

$$-r_A = \frac{k_0\, e^{-E/RT}(C_A - C_C^2 C_D^6 / K_P C_B^3)}{(1 + K_A C_A)^2} \tag{22}$$

where '$-r_A$' is the rate of disappearance of crude ethanol in kmol kg_{cat}^{-1} s^{-1}, 'k_0' is in m^3 kg_{cat}^{-1} s^{-1}, 'A' = ethanol, 'B' = water, 'C' = CO_2, 'D' = H_2, 'C_i' denotes concentration of species 'i' in kmol m^{-3}, 'K_P' denotes the overall equilibrium constant in (kmol m^{-3})^4, K_A denotes the adsorption constant of A in m^3 kmol^{-1}.

Yang et al. [50] studied steam reforming of ethanol over a Ni/ZnO catalyst and found that the catalyst was more selective to H_2 than Ni/La_2O_3, Ni/MgO and Ni/Al_2O_3. Ethanol was completely converted at temperatures above 603 K and the selectivity to H_2 was around 95% at 923 K at a space velocity of 5 h^{-1}.

Freni et al. [51] studied reforming of ethanol in a two-layer fixed bed reactor wherein ethanol was first converted to acetaldehyde over Cu/SiO_2 at 643 K and this was later converted to a H_2-rich mixture over Ni/MgO at 923 K. This type of reactor prevented coke formation and provided hydrogen yields close to equilibrium.

3.4. Modified Ni catalysts

Fierro et al. [4] found that a Ni–Cu/SiO_2 catalyst is more active and selective towards H_2 production in bio-ethanol oxidative steam reforming than Ni/SiO_2 which rapidly deactivates due to coke formation. In previous studies, these researchers presented optimization of oxidative reforming of ethanol over Ni–Cu/SiO_2 [52,53].

Marino et al. [46,54–56] reported that Cu/Ni/K/γ-Al_2O_3 catalyst exhibited acceptable activity, stability and selectivity to hydrogen at 573 K. A reaction network that accounted for the formation of acetic acid and diethyl ether during reaction was proposed [55]:

$$C_2H_5OH + H_2O \rightarrow C_2H_4O_2 + 2H_2 \tag{23}$$

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \tag{24}$$

In this system, Cu is the active agent and promotes fast ethanol dehydrogenation to acetaldehyde, Ni promotes C—C bond rupture of acetaldehyde to produce CH_4 and CO and increases hydrogen selectivity while K neutralizes acidic sites of γ-Al_2O_3, avoids formation of products such as ethylene and diethyl ether and improves the general performance of the catalyst. Marino et al. [56] have reported the formation of CuNiAl hydrotalcite type compounds during catalyst preparation. The addition of Ni favored the formation of these compounds thereby suggesting metal–support interaction.

Velu et al. [57,58] have used Cu–Ni–Zn–Al mixed metal oxide catalysts in oxidative steam reforming of bio-ethanol. They found that the dehydrogenation of ethanol to acetaldehyde is favored by Cu-rich catalysts while the introduction of Ni leads to C—C bond rupture producing CO, CO_2 and CH_4.

Luengo et al. [59] reported ethanol reforming over Ni/Cu/Cr/Al_2O_3 catalyst at 573–823 K and suggested that the catalytic effect was more pronounced at lower temperatures. Morgenstern and Fornango [5] showed that Cu-plated Raney nickel is an active and stable catalyst for low temperature steam reforming of ethanol (523–573 K). Methanation was not observed but WGS activity was very poor. The kinetics were modeled by a sequence of two first order reactions: dehydrogenation of ethanol to acetaldehyde (E_{act} = 149 kJ mol^{-1}) and decarbonylation of acetaldehyde.

Kugai et al. [60] studied oxidative steam reforming of ethanol over a bimetallic Rh–Ni/CeO_2 catalyst at low temperatures (<723 K) to produce a H_2-rich gas. The presence of O_2 enabled complete conversion of ethanol even at low temperatures (648 K) and reduced the selectivity to CO.

3.5. *Cu-based catalysts*

Cu-based catalysts have received particular attention. The methanol reforming system for industrial H_2 production uses Cu/ZnO/Al_2O_3 catalyst. Cavallaro and Freni [61] investigated steam reforming of ethanol over CuO/ZnO/Al_2O_3 and found that the catalyst exhibited good activity with CO, CO_2 and H_2 as the main products above 630 K.

The steam reforming of ethanol over CuO/CeO_2 to produce acetone and hydrogen has also been studied [62]. The formation of acetone could be described by following reaction:

$$2C_2H_5OH + H_2O \rightarrow CH_3COCH_3 + CO_2 + 4H_2 \quad (25)$$

Amphlett et al. [63] suggested that CuO/ZnO, CuO/SiO_2, CuO/Cr_2O_3 or CuO/NiO/SiO_2 might prove promising for reforming of ethanol–water mixtures at 623–723 K. Machado et al. [64] studied the performance of Cu/Nb_2O_5 and Cu/Nb_2O_5/Al_2O_3 catalysts in ethanol steam reforming. The dispersion of Nb_2O_5 on Al_2O_3 improved catalyst action.

4. Discussion and overview

From the fore goings, it is clear that the catalyst activity and product distribution over supported metal catalysts depend on the type of metal precursor used, metal content, presence of additives, type of support and method of catalyst preparation. With this realization, the role of nature of the catalyst in governing product distribution is discussed.

4.1. *Active metal components*

Several possible reactions can occur when an ethanol–water mixture is in contact with a catalyst at high temperature. The behavior of each metal can be explained considering its activity towards specific reactions involved in the reaction mechanism. Haryanto et al. [8] have discussed the various reaction pathways over metal catalysts and suggested that different catalysts induce different ways to produce hydrogen. Knowledge of the type of ethanol–metal interaction is therefore of prime importance for a thorough understanding of the process. Studies on the reactions of ethanol over various metal surfaces indicate that ethanol is adsorbed as an ethoxide species [65,66]. On Rh and Ni metals, the adsorbed ethoxide species forms an oxametallacycle intermediate, which favors the C—C bond cleavage effectively. In addition, the reaction also proceeds through the formation of acetaldehyde intermediate which undergoes C—C bond rupture [60].

Diagne et al. [30] have presented the following elementary steps of ethanol decomposition to describe the complete process ((a): adsorbed):

$$CH_3CH_2OH \rightarrow CH_3CH_2O(a) + H(a) \quad (26)$$

$$CH_3CH_2O(a) \rightarrow (a)CH_2{-}CH_2O(a) + H(a) \quad (27)$$

$$(a)CH_2{-}CH_2O(a) \rightarrow CH_4(g) + CO(g) \quad (28)$$

$$CH_4(g) + H_2O(a) \rightarrow 3H_2(g) + CO(g) \quad (29)$$

$$2CO + 2H_2O \rightarrow 2CO_2 + 2H_2 \quad (30)$$

$$2H(a) \rightarrow H_2(g) \quad (31)$$

Rh abstracts H from the CH_3-group leading to the stable oxametallacycle intermediate ((a) CH_2—CH_2O(a)). Thus, Rh has a unique effect in the decomposition pathway of the ethoxy species.

Idriss [67] also has presented the various reactions occurring with ethanol on metal surfaces and suggested that Rh is the most suitable compound to break the C—C bond to produce H_2 from ethanol. Rh is known to activate the C—H bonds as well [65]. It is significantly more active and selective compared to Pt, Pd and Ru catalysts of similar metal loading [4]. However, it is rare and prohibitively expensive. Additionally, it has limited water gas shift (WGS) activity [68]. In comparison, Pt has relatively higher WGS activity. Pt also has good thermal stability. Ru is another versatile catalyst having high activity in steam reforming of hydrocarbons. Among Ru, Pd, Pt and Rh, Ru is the cheapest and hence a catalyst based on Ru is expected to be far less expensive. We have in our laboratory found that Ru is active in the ethanol dehydration reaction leading to the formation of ethylene. It is however possible to enhance the activity and stability of Ru-based catalysts and suppress carbon deposition by the addition of suitable promoters.

Ni is the catalyst of choice in hydrogenation and dehydrogenation reactions due to its high activity and low cost. Ni-based catalysts have high steam reforming activity. Pure Ni causes bond breaking of ethanol in the following order: O—H, –CH_2–, C—C and –CH_3 [69,70]. Additives such as Cu, Cr or K further enhance the performance of Ni [46,54–56,59]. The electronic enrichment of Ni due to presence of an alkali may possibly modify the interaction between the adsorbed reaction intermediates and the metal phase [39]. However, Ni has limited WGS activity [38,71]. Ni possesses hydrogenation activity and hence it may help in combining adsorbed H atoms on the catalyst surface to form molecular hydrogen [60].

Although Cu has limited steam reforming activity, it is a good dehydrogenation catalyst [72,73]. Cu has high WGS activity. Ni addition to Cu/Ni/K/γ-Al_2O_3 catalyst favored ethanol gasification, increased the gas yield and reduced acetaldehyde and acetic acid production [55]. The presence of Ni favored the segregation of Cu^{2+} ions to the catalyst surface. Marino et al. [46] proposed a probable reaction mechanism over Cu–Ni catalysts and identified the role of each metal. The mechanism in the absence of water which involved Cu and Ni sites was as follows:

$$CH_3CH_2OH + \sigma_{Cu} \rightarrow CH_3CH_2OH^* \quad (32)$$

$$CH_3CH_2OH^* \rightarrow CH_3CHO + H_2 + \sigma_{Cu} \quad (33)$$

$$CH_3CH_2OH + \sigma_{Ni} \rightarrow CH_3CH_2OH^{**} \quad (34)$$

$$CH_3CH_2OH^{**} \rightarrow CH_3CHO^{**} + H_2 \quad (35)$$

$$CH_3CHO^{**} \rightarrow CH_4 + CO + \sigma_{Ni} \quad (36)$$

$$CH_3CHO^{**} \rightarrow CH_3CHO + \sigma_{Ni} \quad (37)$$

The dissociative adsorption of water through a redox mechanism, which occurred only over Cu sites, was also proposed to explain the effect of presence of water on product distribution.

Co-based catalysts have exhibited good performance for H_2 production in steam reforming of ethanol [20–22]. However, supported Co catalysts are adversely affected by metal sintering and surface Co oxidation and hence are not suitable for use at high temperatures [40].

4.2. Catalyst supports

Metals alone may not assist hydrogen production significantly [74–76]. So performance of metal catalysts could be improved using supports. The nature of the support also plays a key role in determining the selectivity to H_2. Choice of the support is hence crucial. Duprez et al. [77] have earlier proposed a bi-functional mechanism for the alkylated aromatics selective reforming reaction where the hydrocarbon to be reformed would be activated on the metal particle while the water would be activated on the support as hydroxyl groups. In agreement with this mechanism, Aupretre et al. [71] have shown that oxide supports with high OH group surface mobility promote the steam reforming reaction of ethanol. Aupretre et al. [9] have discussed the role of supports in steam reforming. Supports may promote the migration of OH groups towards the metal particles, catalyze the reforming reaction or stabilize the metal particles at high temperature under steam. Llorca et al. [78] have discussed performance of various oxides in ethanol reforming.

Al_2O_3 is commonly used as a support in the steam reforming reaction. However, it is acidic and promotes dehydration of ethanol to ethylene, which in turn polymerizes to form coke on the catalyst surface. In contrast, MgO is basic. The highly active Rh catalysts act independently of the support (Al_2O_3 or MgO) as far as coke formation is concerned. However, the less active Co catalyst is more selective and stable when supported on MgO than on Al_2O_3 [23]. Freni et al. [40] reported modest amounts of coke formation over Ni/MgO and attributed it to the inhibition of ethanol dehydration to ethylene and to the electronic enrichment of supported Ni, which in turn promotes a stronger interaction of Ni atoms with electron-acceptor intermediates.

ZnO also has basic characteristics. In addition, unlike γ-Al_2O_3 and MgO, it also has redox properties. Like MgO, it promotes dehydrogenation to acetaldehyde. The redox properties of ZnO then aid steam reforming [78]. The catalytic performance and stability of Ni is enhanced when supported on La_2O_3, compared to Al_2O_3, YSZ and MgO [42]. La_2O_3 does not possess any acidic sites and promotes dehydrogenation to acetaldehyde.

CeO_2 is also basic and has redox properties. It has oxygen storage capacity and hence its presence improves resistance to coke deposition. It also promotes the action of precious metals. For instance, the addition of CeO_2 to Pt prevents sintering of Pt metal particles and ensures high dispersion of Pt over CeO_2 [33]. CeO_2 is also active in the WGS reaction [79]. ZrO_2 has both acidic and basic properties and is thermally stable. Addition of ZrO_2 to CeO_2 significantly increases its oxygen storage action, redox properties and thermal resistance. Srinivas et al. [80] studied steam reforming of bio-ethanol over $NiO/CeO_2/ZrO_2$ catalysts and found that the catalyst was stable for more than 500 h without deactivation. Bergamaschi et al. [81] showed that Ni–Cu/ZrO_2 catalyst exhibits high activity for ethanol steam reforming with 100% conversion of ethanol and 60% selectivity to H_2 at 823 K.

4.3. Catalyst stability

The two factors that largely govern the stability of the catalyst are coke formation and metal sintering. The high temperatures used during reaction, the high reactivity of ethanol and its low thermal stability mainly lead to coke formation. Coke can be formed due to polymerization of ethylene formed during ethanol dehydration, or from the Boudouard reaction, or from the decomposition of methane. It destroys the catalyst structure and deteriorates its activity. The rate of carbon formation can be substantially suppressed using noble metals, which is ascribed to a smaller dissolution of carbon in to these metals [82]. While acidic supports such as γ-Al_2O_3 favor dehydration, coke formation occurs to a less extent on basic supports such as MgO. The presence of suitable promoters such as K can neutralize the acidic sites of γ-Al_2O_3, thereby reducing coke formation [55]. The impregnation of Al_2O_3 with La_2O_3 reduces carbon deposition [43]. The presence of oxygen reduces coke formation drastically possibly due to combustion of carbonaceous species formed during reaction [27,53]. However, this may lead to the formation of hot-spots, thereby resulting in an increase in the metal particle size. This in turn leads to a decrease in the metal active surface and hence the catalyst activity. Higher the metal sintering, higher is the catalyst deactivation. Metal sintering in Ni and Co catalysts is mainly due to presence of excess of water in the reaction system. Aupretre et al. [9] studied Rh catalyzed ethanol reforming using MgAl-based spinels deposited on alumina. When compared with the alumina based catalysts, the spinel-supported catalysts exhibited slightly higher basicity while the surface acidity was strongly reduced. The spinel layer also improved the stability of Rh particles upon reaction.

5. Process considerations

The following issues need to be addressed from process engineering point of view: (1) reforming should preferably be carried out at low temperatures and atmospheric pressures to reduce the operating costs; (2) the catalyst should provide high selectivity to H_2 and inhibit CO formation, the formation of by-products such as methane, acetaldehyde and diethyl ether should be minimum; (3) the catalyst must resist coke formation which reduces the number of active sites and hence the reaction rates; (4) the catalyst should not be poisoned by impurities found in the ethanol–water mixtures formed during biomass fermentation; (5) the H_2-rich mixture should be purified further to remove CO formed during reaction for meeting PEMFC specifications.

Catalyst coking strongly depends on the reaction conditions and the properties of the catalyst. Ethylene is a known coke precursor and carbon formation is primarily attributed to its presence in the product stream. However, coke formation can be prevented if ethanol is instead dehydrogenated to acetaldehyde, which has a very low coking activity. Acetaldehyde thus formed can then be subjected to steam reforming. The effectiveness of Cu in dehydrogenation reactions is no novelty. Freni et al. [51] studied steam reforming of ethanol over Cu/SiO_2 and found that at temperatures in the range 573–723 K, ethanol conversion was 100% and acetaldehyde and H_2 were the major reaction products. Traces of methane and CO were also detected. Thus, they concluded that at these temperatures, the ethanol dehydrogenation reaction is predominant. These results are in agreement with other previous studies [72,73]. At higher temperatures (>773 K), ethylene formation was observed and the selectivity to ethylene increased with increasing temperatures thereby suggesting that the dehydration reaction also takes place at such high temperatures. Nishiguchi et al. [62] reported almost selective dehydrogenation of ethanol to acetaldehyde and H_2 over CuO and CuO/SiO_2 in the range of temperatures 473–673 K. Steam reforming of ethanol over CuO/CeO_2 at 533 K also led to the formation of acetaldehyde and hydrogen. From the fore goings, it is clear that ethanol can be almost selectively converted to acetaldehyde over Cu-based catalysts at low temperatures. Ni which has high activity in steam reforming will then promote C—C bond rupture in acetaldehyde.

The steam reforming process should therefore be carried out in a two-layer fixed bed catalytic reactor. A schematic diagram of this proposed process is shown in Fig. 2. An ethanol–water mixture should be passed at 573–673 K over the first layer made of Cu-based catalyst thereby converting ethanol to acetaldehyde.

$$C_2H_5OH \rightarrow CH_3CHO + H_2$$

Ethylene formation can be prevented by working at such low temperatures thereby reducing catalyst coking. Acetaldehyde thus formed may decompose to CH_4 and CO or may undergo steam reforming as per the following reactions:

$$CH_3CHO \rightarrow CH_4 + CO$$

$$CH_3CHO + H_2O \rightarrow 2CO + 3H_2$$

$$CH_3CHO + H_2O \rightarrow CO_2 + CH_4 + H_2$$

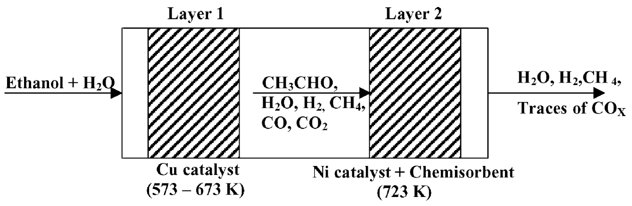

Fig. 2. Proposed two-layer fixed bed reactor for ethanol steam reforming.

The following other reactions may also occur:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$$

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$$

However, it is expected that ethanol dehydrogenation reaction will be much faster than the ethanol steam reforming reaction. Thus, this mixture primarily consisting of acetaldehyde and H_2, excess of water and small amounts of CH_4, CO_2 and CO should then be fed to the second layer made of a mixture of Ni-based catalyst and a chemisorbent. In presence of Ni, the residual acetaldehyde will undergo steam reforming even at low temperatures (around 723 K). The methane steam reforming reaction will however be thermodynamically controlled:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

The chemisorbent selectively removes CO_2 formed during reaction. The WGS reaction is reversible and hence the equilibrium shifts to the right and favors the formation of H_2 and CO_2 as products at lower temperatures.

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The selective removal of CO_2 from the product stream by chemisorption further enables production of high-purity H_2 at low temperatures along with methane and traces of CO. Further purification by methanation or preferential oxidation should not be necessary. The chemisorbent can then be periodically regenerated by pressure swing adsorption. It should however be noted that the presence of an adsorbent implies a transient operation.

The entire process of ethanol steam reforming coupled with selective CO_2 removal by chemisorption is very promising. In comparison, high temperatures are needed for obtaining high ethanol conversions in conventional steam reforming in a fixed bed reactor packed with the catalyst alone and further purification is necessary. Hufton et al. [83] have earlier demonstrated the use of such a sorption enhanced reaction process to produce H_2 from methane steam reforming.

6. Conclusions

In the present review, catalytic steam reforming of ethanol for H_2 production is discussed in-depth. The effects of process variables such as temperature, pressure and the water-to-ethanol molar ratio in the feed on the H_2 yield at equilibrium are discussed. An overview of previous studies using Ni, Co, Ni/Cu and noble metals (Pt, Pd, Rh) is given. The catalyst performance characteristics suggest strong metal–support interaction. The reaction pathway is complex and a number of undesirable side reactions occur thereby affecting the selectivity to H_2. Catalyst coking is mainly due to the formation of ethylene by ethanol dehydration. The use of a two-layer fixed bed reactor is therefore promising: At low temperatures, ethanol should first be converted by dehydrogenation over Cu into acetaldehyde which has a lower coking activity. The resulting mixture can then be passed at low temperatures around 723 K over a bed containing a mixture of Ni catalyst and a chemisorbent. While Ni will be active in steam reforming of acetaldehyde thus formed, the selective removal of CO_2 from the product mixture by chemisorption will enable production of H_2-rich streams that can be fed to a PEMFC.

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