International Journal of Environmental Research and Development.
ISSN 2249-3131 Volume 4, Number 3 (2014), pp. 203-212

http://www.ripublication.com/ijerd.htm

Steam Reforming of Ethanol: Production of Renewable Hydrogen

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Abstract

Abnormal growth of population and development enormously increases energy demand. In present scenario utilization of fossils fuels to meet this demand is not enough and also leads to pollution, global warming, climate change as well as natural disaster. Therefore, hydrogen as energy carrier is a major option on these prospects as it is non-polluting and renewable. The renewable hydrogen energy can be generated through ethanol steam reforming (ESR), a thermo-chemical method. Steam reforming is most widely used to generate hydrogen not only with nonrenewable fossil fuels (Coal, natural gas, petroleum) but also with renewable raw materials such as ethanol. In last two decades research interest in the area of catalytic steam reforming of ethanol has been increased.

Ethanol contains higher number of hydrogen per molecule as compared to water, methanol and methane. During steam reforming of ethanol, catalyst plays a major role in the productivity and selectivity of generated gas. In the present paper, literature survey of noble (Pt, Pd, Rh and Ru) as well as non noble metals (Cu, Ni, Ir and Co) catalysts were accomplished. Study depicts that the different kinds of catalyst compositions of noble metal were reported as highly efficient whereas, the few nanosized non noble metal catalysts can be comparable to them, especially with respect to productivity and selectivity of hydrogen. An extensive research work over non noble metal catalysts is required to make ethanol steam reforming cheaper and efficient.

Keywords: Ethanol steam reforming, Catalyst, Renewable hydrogen.

1. Introduction

Renewable energy resources have shown a peculiar attention at present global scenario owing to abnormal growth of population and development which leads to progressive depletion of conventional fossil fuels (coal, petroleum, natural gas). Among renewable energy resources, hydrogen (H_2) is considered as an important energy carrier for the future as it is abundantly available and contains the maximum energy per unit of weight (120.7kJ g^{-1}) of presently known fuels (Rostrup Nielsen, 2002, Nishiguchi et al, 2005). Production of renewable hydrogen energy comprises thermo-chemical, electrochemical, photo-biological and photo-electrochemical methods. Among thermo-chemical technologies, steam reforming is most widely used to generate H_2 not only with nonrenewable fossil fuels (Coal, natural gas, and petroleum) but also with renewable raw materials such as ethanol. In India large amount of molasses as by product from sugar industry can be reformed to renewable hydrogen. Molasses besides the renewable source of ethanol, it is advantageous as carbon lean fuel and non hazardous over other conventional fossil fuels. Ethanol steam reforming (ESR) is an endothermic reaction (Bilal and Jackson, 2012) and thus it requires heat energy to generate hydrogen (eq1). The major challenge is to minimize the heat energy. Catalysts play a significant role in minimizing the heat energy (Basagiannis et al, 2008, Ciambelli et al, 2010).

$$C_2H_5OH + 3H_2O \xrightarrow[200\text{-}800^0C]{\text{Catalyst}} 2CO_2 + 6H_2 \qquad \Delta H_{298} = +174 \text{ kj mol}^{-1} \qquad (1)$$

Meng et.al (2007) reviewed the technological developments in bio-ethanol steam reforming for hydrogen production, with an emphasis on catalyst development. Recently, Mattos et al (2012) reviewed reaction mechanism and catalyst deactivation for ESR. The aim of this review is to update the development regarding reaction characteristics and different types of catalysts used for ESR emphasizing summary at a glance in a tabular form. This review paper will be helpful to the scientist working in the field of ESR.

2. Reaction Mechanism

During ESR ethanol, it-self on decomposition (eq2), hydrogenolysis (eq3), dehydration (eq4) and dehydrogenation (eq5) get converted into intermediate carbonaceous products such as CH_4, CO, C_2H_4, CH_3COCH_3 and C_2H_4O. Ethanol can also form acetone through aldol condensation, followed by dehydrogenation (eq6).

$$C_2H_5OH \rightarrow CH_4 + CO + H_2 \qquad (2)$$

$$C_2H_5OH + 2H_2 \rightarrow 2CH_4 + H_2O \qquad (3)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad (4)$$

$$C_2H_5OH \rightarrow C_2H_4O + H_2 \qquad (5)$$

$$2\ C_2H_5OH + H_2O \rightarrow CH_3COCH_3 + CO_2 + 4H_2 \qquad (6)$$

Furthermore, acetaldehyde on decomposition (eq7) and CO (eq8) as well as CO_2 (eq9) on hydrogenation gets converted into CH_4.

$$C_2H_4O \rightarrow CH_4 + CO \quad (7)$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (8)$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (9)$$

Among these intermediate products CO produce hydrogen via water gas shift reaction (eq10) whereas CH_4 generates hydrogen not only through steam reforming (eq11) but also by means of dry reforming reaction (eq12).

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (10)$$
$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad 11)$$
$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (12)$$

However, the importance of every reaction is governed by the reaction operating conditions such as Steam/Ethanol (S/E) ratio, temperature, residence time and most importantly the selection of catalyst. The effect of operating parameters on distribution of product during ESR was thermodynamically (Garcia and Laborde, 1991, Mas et al, 2006) as well as experimentally (Fatsikostas and Verykios, 2004, Vizcaino et al, 2007) reported at several literatures. Therefore, during ESR along with H_2 several other gases such as CO, CH_4, and CO_2 are produced. In this prospects where ultimate goal is energy generation selectivity of hydrogen is a major characteristic.

The study of ESR over supported metal catalysts in the temperature range (873-1073K) by Liguras et. al (2003) suggested that at higher temperature conversion of ethanol as well as selectivity of CO, CO_2 and H_2 get increased (Liguras et al, 2003). At higher temperature reverse water gas shift reaction is only responsible reaction to lower down the H_2 yield (Lima et al, 2009). The theoretical calculation by Rabenstein et. al reveals relation between temperature and water to ethanol feed ratio. The molar feed ratio of ethanol and water higher than 4 at reaction temperature range (823-923K) able to produce more than 4 moles of H_2 (Rabenstein and Hacker, 2008). Selectivity of H_2 is increased considerably with increase in S/E molar ratio (Comas et al, 2004).

3. Catalysts for Ethanol Steam Reforming

ESR was reported over noble metals (Pt,Pd,Rh,Ru), non noble metals (Ir,Cu,Co,Ni), metal oxides, mixed metal oxides, hydrotalcite, spinel and perovskite catalysts as summarized at a glance in Table 1. Among non-noble metal catalyst Cu, Ni, Ir and Co were reported as most active metals (Duan and Senkan 2005). The nature of metal and support contributes the selection of path for hydrogen generation. Highly acidic nature of support facilitate dehydration (Fajardo and Probst, 2006) of ethanol whereas basic nature (La_2O_3,MgO,SiO_2) (Dominguez et al. 2010) or addition of promoters (alkali and alkaline earth metals) which reduce acidity (Hou et al, 2003), hinders dehydration and deactivation of catalysts by carbonaceous deposition. Among noble metal catalysts study of Liguras et. al (2003) shows the selectivity of H_2 over γ-Al_2O_3 support in the order as Rh >> Pt > Ru ≈ Pd. High activity and selectivity of Rh for ESR was also supported by work of Aupretre et. al.(2002). Ru is inactive over γ-Al_2O_3 with lower than 5% loading but it shows 100% ethanol conversion with high selectivity over CeO_2/YSZ support on 2% loading (Ramos et al, 2012). The study reported by Frusteri et al (2004) over MgO support for Rh (3%) and Pd (3%) shows inferior activity as

compared to Ni (21%) over similar support. Rh leads to methane formation during ESR and has relatively low efficiency as compared to Ni and Co for the SR of methane. The higher capability of nickel to break C-C and O-H bond and hydrogenation, leading to molecular hydrogen formation makes it a best option for ESR. Furthermore addition of alkali and alkaline earth metals effects the interaction between metal and adsorbed species (Elias et al, 2013). Cobalt also shows higher activity for ESR but sintering at high temperature is major issues. Metallic cobalt sites are dynamic for ethanol decarbonylation and dehydrogenation reactions promoted by Co^{2+} leads to formation of acetaldehyde species (Hyman and Vohs 2011). Machocki et al. (2010) has reported the best ethanol conversion (100%) and H_2 (92.6%) selectivity over nanosized CeO_2 support at lower temperature.

Table 1: Literature review at a glance for ESR: Conversion and hydrogen selectivity of catalysts.

Catalyst		**Reaction Condition**		**Ethanol Conversion (%)**	**Hydrogen selectivity (%)**	**References**
Metal load (%)	**Support**	**S/E**	**Temp(K)**			
Noble		3	1073	100	96	(Liguras et al, 2003)
Rh (2)	γ-Al_2O_3					
Rh (3)	MgO	8.5	923	99	91	(Cavallaro et al,2003)
Rh (1)	CeO_2	3	723	Above 90	82	(Frusteri et al, 2004)
Rh (2)	CeO_2	8	723	100	69	(Erdohelyi et al, 2006)
Rh (2)	ZrO_2	8	723	100	70.3	(Diagne et al, 2004)
Rh (2)	CeO_2- ZrO_2 (Ce/Zr = 1)	8	723	100	70.3	(Diagne et al, 2002)
Ru (5)	γ-Al_2O_3	3	1073	100	96	(Liguras et al, 2003)
Ru (1)	CeO_2	3	723	Above 90	57	(Erdohelyi et al, 2006)
Pt (2.5) Ru (1)	γ-Al_2O_3	10	823	100	100	(Koh et al, 2008)
Pt (1)	γ-Al_2O_3	3	1073	100	96	(Liguras et al, 2003)
Pt (0.5)	γ-Al_2O_3	4	613	95	40	(Basagiannis et al, 2008)
Pt (1)	CeO_2	3	573	100	39	(Ciambelli et al, 2010)

Pt (1.5)	CeO_2- ZrO_2 (Ce/Zr = 4)	10	823	100	88	(Chen et al, 2008)
Pd (1)	γ-Al_2O_3	3	1073	55	50	(Liguras et al, 2003)
Pd (5)	γ-Al_2O_3	3	923	100	95	(Goula et al, 2004)
Rh_6Pt_2	La_2O_3	7	973	100	78	(Cobo et al, 2013)
Ru	CeO_2/YSZ	5	853	100	86.6	(Ramos et al, 2012)
Non noble						
Ni (7) Ni/ Ce (7/10) Ni/Zr (7/10)	SiO_2	3.7	873	97.1 100 100	82.6 84.4 82.5	(Calles et al, 2010)
Cu(2) Ni (7) Mg (10)	SiO_2	7.4	873	100	84.8	(Carrero et al, 2010)
Co (1)	V_2O_5 ZnO La_2O_3 CeO_2 Sm_2O_3	13	723	100 100 85 93.7 85.9	53.5 71.3 63.1 69.6 64.7	(Llorca et al, 2002)
ZnO (30) ZnO (50) ZnO (70) ZnO	SiO_2 SiO_2 SiO_2 -	12	773	91.8 92.0 92.3 91.7	57.0 51.4 61.0 58.6	(Seker, 2008)
Ir (2)	CeO_2	3.2	923	100	75	(Zhang et al, 2008)
Ir (2)	$Ce_{0.9}Pr_{0.1}O_2$	3	773	100	72	(Wang et al, 2011)
Co (52)(molar ratio)	Zn =18 Al=30	3	823	100	83	(Busca et al, 2010)
Co(20)	CeO_2	3	873	100	66	(Lovon et al, 2012)
Co	CeO_2-N ZrO_2-N Ce/ZrO_2-N Ce/ZrO_2-M	5.5	693	100	92.6 85.0 91.9 91.5	(Machocki et al, 2010)
Ni-Cu (3)	ZrO_2	-	873	100	84	(Sharma et al, 2013)
Ni(4) Zr(6) (30)	MCM-48	1	1023	95	85	(Lee et al, 2013)

Ni(10) Ga(30) Mg(30)	Zeolite Y	3	973	100	87	(Kwak et al, 2011)
Hydrotalcite	-	6	923	100	64.9	(Li et al, 2010)
NiMg6					64.1	
NiMg8						
Co (10)	-	-	923	100	71	(Contreras et al, 2008)
NiFe 1	-	6	773	100	80	(Abello et al, 2013)
Co/Mg/Al 1/2/1	-	4	773	100	69.5	(Espinal et al, 2012)
$Zn_{0.58}Ni_{0.42}[Al_{0.44}Co_{0.56}]_2O$	-	6	823	100	90	(Li et al, 2010)
Spinel		6	823	100	45	(Muroyama et al, 2010)
$NiAl_2O_4$	-					
Perovskite						
$Cu/Ni/La_2O_3$	-	-	563	100	37	(Liu et al, 2013)
$LaNiO_3$	-	13	573	100	70	(Lin et al, 2013)
Mixed metal oxides						
$Pt_{0.5}Co_{10}$	/ZnO	4	598	100	73.2	(Chiou et al, 2013)

4. Discussion

The literature survey as mentioned above depicts that among noble metal catalysts the conversion of ethanol reported as 100% and selectivity was near to 99% depending upon type of support and loading of metal. However γ-Al_2O_3 support was reported as highly active in terms of selectivity for different noble metals catalyst but optimum loading of metals is not same. Among non noble metal catalysts Co is reported as highly active, showing 100% ethanol conversion over nano sized CeO_2 with 93% hydrogen selectivity. Few non noble metals also show 100% ethanol conversion over other supports at low temperature but selectivity of hydrogen is relatively low. The different kinds of perovskite, hydrotalcite and spinel type catalysts show improvement of activity, ethanol conversion and stability, but low H_2 selectivity. Synergistic effect between metals has improved catalyst activity as reported by work over bimetallic catalysts. Overall, non noble metal has significant capability for the conversion of ethanol but selectivity especially at lower temperature is still a matter of concern. Therefore, detailed research work over non noble metal catalysts for ESR is required to make it cost effective.

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