



Ethanol steam reforming for hydrogen production: Latest and effective catalyst modification strategies to minimize carbonaceous deactivation



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ARTICLE INFO

Keywords:

Carbon deposit
Catalyst deactivation
Ethanol steam reforming
Hydrogen

ABSTRACT

Hydrogen is being contemplated as the future fuel in view of the abundant availability of hydrogen bearing substances in nature, its high energy content (120.7 kJ/g), and its combustion without creating any environmental pollution. Pollution free sources for hydrogen generation and efficient conversion to useful energy are the two important factors controlling the development of hydrogen economy. Out of various liquid hydrogen sources, ethanol is a sustainable candidate because of its renewable nature, increasing availability, biodegradable nature, low toxicity, and ease of transport. It can be easily converted to a hydrogen rich mixture through catalytic steam reforming process. Further, ethanol steam reforming (ESR) is thermodynamically feasible and does not cause catalyst poisoning due to complete absence of S-impurities. However, the carbonaceous deposition during ESR is still an issue to make it sustainable for hydrogen generation. This review contains all parallel possible reactions besides the desired reactions, which can promote carbonaceous deposition over catalyst surface with respect to temperature. The role of operating conditions such as water and ethanol feed ratio and temperature with carbon generation were interrelated. The characterization of different carbon forms synthesized during ESR and the possible role of active catalyst into carbon synthesis mechanism was also considered. The contribution of precursor used for catalyst preparation, the role of active metals, the interaction between active metals for bimetallic catalyst, different kind of support prominently studied for ESR and their structural behaviors were also correlated. This review makes an attempt to critically summarize the recent strategies used to reduce the carbonaceous deactivation of catalyst during ESR on the basis of available literature survey. The focus of the review is catalyst deactivation due to carbonaceous deposition during reforming and possible strategies used to control the deactivation process during ESR.

1. Introduction

Energy crisis, global warming, climate change and need for sustainable development have aroused global interest in developing renewable energy sources [1]. Under such a scenario researchers look forward to hydrogen as the future energy for transportation, fuel cells and power stations [2–7]. The comparative study of technical and environmental issues between fossils fuels and hydrogen energy reveals hydrogen economy as an absolute solution for our planet from environmental challenges [8]. There are several pathways of hydrogen production such as electrolysis, photolysis and thermo-lysis of water, biological reactions, gasification and pyrolysis of biomass, steam reforming and partial oxidation of hydrocarbons [9,10]. Recently, photocatalytic production of hydrogen from ethanol has also gained impetus [11,12]. However, excessive requirement of electricity makes

electrochemical process expensive and also, photolysis of water is highly expensive owing to requirement of expensive electrodes. Biological methods are also reported but they suffer from a lower rate of hydrogen generation. These drawbacks make thermo chemical method a feasible pathway for hydrogen generation sustainably [13,14]. All over the world, 50% feedstocks of natural gases are used for hydrogen production via steam reforming which is not a renewable source [4]. Other feeds such as glycerol; methanol, and ethanol have also been used for the steam reforming to produce hydrogen. Among these ethanol steam reforming (ESR) using an appropriate catalyst shows the most efficient way of renewable hydrogen production [15] as represented by the following overall stoichiometric equation:



Various types of catalysts such as noble metals [16–23] (Pt, Pd, Rh,

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Au and Ru), transition metals (Cu, Co and Ni) as well as the combinations of both [24–27] have been used to catalyze the ESR reaction. However, these catalysts get deactivated due to carbonaceous deposits formed as the byproduct during ESR reaction (described later under reaction mechanism). Up to 1990s only a few papers discussed the catalytic steam reforming of ethanol [28–30], whereas, in the last two decades a lot of work has been done on the modification strategies to minimize carbon formation during ESR.

In catalytic steam reforming of ethanol, noble metal catalysts show high activity and selectivity for hydrogen production with negligible or no coke formation [16,17,21,27,31–35]. However, noble metal catalysts are not cost effective [36]. In periodic table, among non-noble metal catalyst Cu, Ni and Co are reported to be most active metals for ESR [37]. Therefore, these metals have been widely studied on several supports such as Al₂O₃, SiO₂, ZrO₂ and CeO₂ [38]. Large volumes of work have been reported on the deactivation of non-noble metal catalysts by carbonaceous deposition during ESR [39–45]. The deposition of carbonaceous materials on their surface is still a major challenge. In this regard, the oxidative steam reforming of ethanol on non-noble catalyst [46] is a good approach for hydrogen production though the carbonaceous deposition is comparatively lower than ESR, but the overall yield of hydrogen per mole of ethanol is also lower [47]. Modification of non-noble catalysts using an appropriate approach to minimize the catalyst deactivation by carbonaceous deposition is being projected as a useful way to produce hydrogen.

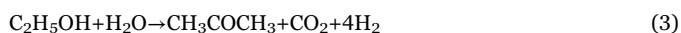
The growth of carbon on the surface of catalyst is determined by the structure of hydrocarbons [48] (CH₄/C₂H₆/C₂H₄) resulting as byproducts during ESR. Thus, the carbon source as well as catalyst composition play a major role in the rate of carbon deposition and its development. The rate of carbon deposition gets accelerated at high temperature [49]. The support as well as metal and support interface are the major sites for carbon deposition [50].

Recently, in reviews on hydrogen production via ESR, a very brief account of catalyst deactivation has been reported [51–53]. Although, there is no review paper solely devoted to noble metal or non-noble metal catalysts as modification strategies to minimize carbon formation during ESR. Therefore, on the basis of a critical review of the previous literature, an attempt has been made for the first time to summarize sustainable catalyst formulation in reference to their stability as well as ESR efficiency for renewable hydrogen production emphasizing non noble cost effective catalysts.

2. Reaction mechanism of ESR and carbon formation

Steam reforming of ethanol may comprise several other simultaneous reactions along with the hydrogen producing reactions. A few of these result in the generation of unwanted products [54–56]. These unwanted products are formed by dehydrogenation (Eq. (2)), decomposition (Eq. (4)), dehydration (Eq. (8)), hydrogenolysis (Eq. (6)), and aldolic condensation followed by dehydrogenation (Eq. (3)) of ethanol itself. Acetaldehyde on decarbonylation [57] also produces CH₄ and CO (Eq. (7)). Ethane can be the major product over a selective catalyst which facilitates ethanol adsorption (leading to diethyl ether formation) followed by hydrogenation (Eq. (5)) [22,58,59]. The reaction network can be written as follows:

Hydrogen producing:



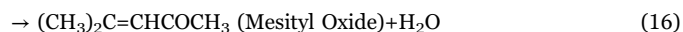
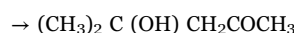
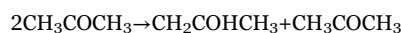
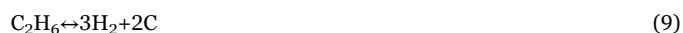
Hydrogen Consuming:



Other reactions:



The intermediate reactions during ESR and liable for the carbon deposition on the catalyst surface are as follows [60].



The reactions (Eqs. (2)–(8)) suggest that saturated, unsaturated hydrocarbons or both can be produced simultaneously during ESR. The dehydrogenation, dehydration, polymerization and decomposition reactions of different byproducts (Eqs. (9)–(16)) are able to generate different forms of carbon. The unsaturated hydrocarbon, C₂H₄ formed after ethanol dehydration, gets polymerized to coke [61] on the surface of catalyst (Eq. (10)). But the presence of π- bonds in the structure makes them easily disruptive in nature. In a recent review [51], it was pointed out that the decomposition of C₂H₄ occurred at higher temperature but contradicting experimental results showed that even at the lower temperature (> 200 °C), the decomposition of C₂H₄ (Eq. (11)) occurred efficiently [62]. Lower temperature hindered the carbon crystallization during deposition of carbon on the metal surface especially in presence of carburizing gases because of highly intense C–C bond.

Saturated hydrocarbon such as CH₄ is highly stable and its thermal decomposition (Eq. (12)) occurs at temperature > 1173 K [63]. On decomposition, CH₄ is able to generate three kinds of surface carbonaceous species. Firstly, the carbidic species which is highly reactive (hydrogenable at temperature ≈ 323 K) and is formed by methane dissociation [48]. It acts as an intermediate in the filamentous carbon growth [54]. During ESR, Co and Cu (over TiO₂ and SiO₂) did not form carbide species but Ni and Fe may form this precursor [64,65]. The spectroscopic study during hydrogenation of carbidic carbon by He et al. found that carbon on Ni (100) needs lower decomposition temperature than Ni (111) surface. They suggested that the different form of Ni surfaces (100) and (111) may affect the local structure of CH_x species growth and so thermal stability may be different [66]. However, nickel carbide is not stable and is easy to decompose into metallic as well as graphite form of nickel at high (> 873 K) temperature [67]. Secondly, amorphous carbon that is less reactive is formed by polymerization of carbidic carbon. It helps to form carbon whisker. Thirdly, the graphite carbon is hydrogenable at temperature around 673 K and has different reactivity for oxidation and hydrogenation.

The study over Ni (111) catalyst revealed that carbide formation either in the isolated or string form on the terrace site took place without island formation for C₂H₄. But the growth of carbide formation

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