Ethanol steam reforming over bimetallic coated ceramic foams: Effect of reactor configuration and catalytic support

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ABSTRACT

In recent years, hydrogen production from renewable feed-stocks attracts particular attention. Specifically, the steam reforming of biomass-derived bioethanol could provide H_2-rich effluent streams, representing an interesting research field. This study focuses on the development of bimetallic structured catalysts (containing Ni and Pt as active species and supported on ceria and ceria-zirconia) active in Ethanol Steam Reforming (ESR) reaction at low-temperature (300–600 °C) and characterized by improved heat transfer properties. ESR reaction was carried out on ceramic foams and, as a comparison, on powders catalysts. In particular, catalytic tests were carried out on two reactor configurations: catalytic powders were tested in both a tubular and annular reactor; in addition, the tubular configuration was also employed for the structured catalysts. Unsatisfactory results were observed for powders in the tubular reactor while the better thermal management of the annular configuration ensured significantly higher conversions. Moreover, the enhanced thermal conductivity of SiC foams catalysts, tested in the tubular reactor, allowed overcoming heat transfer limitations in an easy reactor geometry, resulting in very good performances. The catalytic behaviour of bimetallic CeO_2 and CeO_2–ZrO_2 based catalysts was also compared and the effect of catalytic support on ethanol conversion and H_2 yield at different space velocities (100,000–400,000 h^{-1}) was investigated. Finally, Pt–Ni/CeO_2–ZrO_2 catalysts, which displayed a more interesting catalytic activity with respect to CeO_2 based samples, were employed for stability tests at 100,000 h^{-1} and 450 °C: products gas distribution was not affected during TOS and total ethanol conversion was recorded for almost 5 h.

Introduction

One of the best ways to reduce oil and natural gas depletion as well as green gas emissions is by encouraging clean energy production. Unlike fossil fuels, hydrogen combustion does not involve the formation of environmental pollutants and this feature, coupled to its abundance in the universe, makes H_2 a suitable fuel to meet future energy supply [1]. Although the

most common technologies for producing hydrogen involve thermo-catalytic processes of natural gas or heavy oils [2], sustainable generation is possible only by using environmentally friendly methods. Widely available and cheap feedstocks, such as biomass, are expected to become preferred sources, in order to reduce energy production costs. However, direct production of hydrogen from biomass through pyrolysis and gasification technologies causes feedstock decomposition, followed by char and tar formation [3]. On the contrary, bioethanol production through hydrolysis and fermentation of biomass and its conversion to hydrogen via steam reforming seems to be a very promising alternative strategy [4–6]. In fact, C_2H_5OH is more advantageous than conventional fuels mainly for the absence of heteroatoms, such as sulphur, and neutrality of process with respect to CO_2 emission, ensuring the closure of carbon cycle [7]. Moreover, the route of feeding bioethanol to a steam reformer is very attractive, mostly due to the deeper knowledge of reforming technologies with respect to other alternative methods for hydrogen production.

Ethanol steam reforming (Eq. (1)) can theoretically provide 6 mol of H_2 per mole of reacted C_2H_5OH:

$$C_2H_5OH + 3H_2O \rightleftarrows 6H_2 + 2CO_2 \qquad \Delta H^0_{298K} = 173.5 \ kJ/mol \qquad (1)$$

However, the reaction system is very complex, resulting in the subsequence of several reactions (Eqs. (1)–(5)); simultaneously, different side-reactions [8,9] could occur (Eqs. (7)–(9)), reducing H_2 yield and selectivity [10,11], and leading to catalyst deactivation.

$$C_2H_5OH \rightleftarrows H_2 + CO + CH_4 \qquad \Delta H^0_{298} = 49 \ kJ/mol \qquad (2)$$

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO \qquad \Delta H^0_{298} = 205 kJ/mol \qquad (3)$$

$$CH_4 + 2H_2O \rightleftarrows 4H_2 + CO_2 \qquad \Delta H^0_{298} = 165 \ kJ/mol \qquad (4)$$

$$CO + H_2O \rightleftarrows H_2 + CO_2 \qquad \Delta H^0_{298} = -41. \ kJ/mol \qquad (5)$$

$$C_2H_5OH \rightleftarrows C_2H_4O + H_2 \qquad \Delta H^0_{298} = 68 \ kJ/mol \qquad (6)$$

$$C_2H_5OH \rightleftarrows C_2H_4 + H_2O \qquad \Delta H^0_{298} = 45 \ kJ/mol \qquad (7)$$

$$C_2H_4 \rightarrow 2C_{(s)} + 2H_2 \qquad \Delta H^0_{298} = -52 \ kJ/mol \qquad (8)$$

$$2CO \rightarrow C_{(s)} + CO_2 \qquad \Delta H^0_{298} = -171 \ kJ/mol \qquad (9)$$
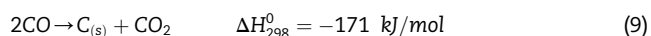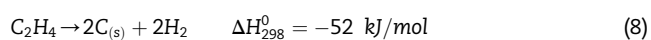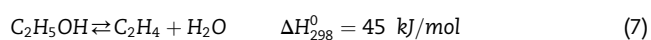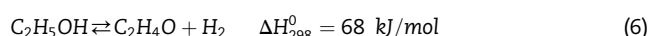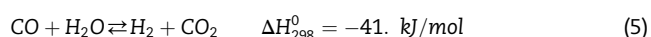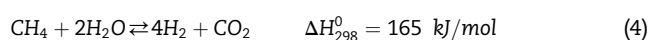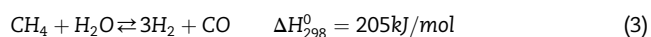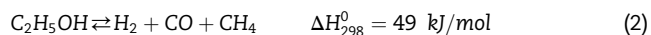
In order to maximize hydrogen production efficiency, proper operating conditions (temperature, pressure, feeding and dilution ratios) have to be selected. As reported in Eq. (1), the ethanol steam reforming reaction is endothermic, and results in a mole number increasing; thus, the reaction is thermodynamically promoted at high operating temperature and low pressure. On the contrary, due to the Water-Gas Shift reaction (WGS) equilibrium (Eq. (5)), to operate at too high temperature, could result in a not-negligible carbon monoxide production, limiting the possibility of feeding the reforming mixture to a fuel cell, since amounts of CO higher than 10 ppm are responsible for PEMFCs poisoning [12]. In addition, increasing temperatures impact significantly on hydrogen

production costs, both in term of operating and plant charges. Accordingly, the chance of performing ethanol steam reforming in the low temperature range appears particularly interesting. However, acetaldehyde and ethylene formation (Eqs. (6) and (7)) are favoured at relatively low temperatures and also CO dissociation to form coke (Eq. (9)) easily occurs [9]. From the thermodynamic standpoint, the choice of optimal feeding conditions (water to ethanol molar ratios higher than 3) allows avoiding coke formation [13]. Moreover, low reaction temperature may negatively effect on reaction kinetics, resulting in a too slow reaction system. A proper choice of catalytic formulations can result in a selective reaction rate increasing, that in turn drives the system to a better byproducts selectivity and hydrogen yield. In addition, due to the highly endothermic nature of the ESR reaction, the heat transfer rate from the heating medium to the catalytic system is one of the most crucial issues for the process; therefore, the role of thermal support properties requires further investigation.

Several authors studied ethanol steam reforming on oxides-supported noble and non-noble metals based catalysts [14–20]. Among non-noble metals, selected on the basis of their lower cost with respect to noble ones, cobalt and nickel showed the highest activity towards ethanol steam reforming [21]. Ni based catalysts exhibited a relevant ability in promoting C—C bonds breaking and hydrogenation/dehydrogenation reactions [22], while Co based catalysts are interesting for their low generation of CH_4 as by-product and coke [23]. However, the interaction of active species with catalytic supports rather than others is responsible for different performances, in terms of both activity and selectivity. To that end, if Ni is dispersed on Al_2O_3, especially in the low temperature range, dehydration reactions, followed by polymeric carbonate species formation, occurred [24]. On the contrary, by supporting Ni on rare earth oxides decreasing carbon formation rates were observed [25]. Ni/CeO_2 catalysts were shown to be very active towards ESR: nickel sites promote ethanol adsorption on the catalytic surface, while CeO_2 ensures water decomposition, allowing OH groups releasing, which are involved in CO_2 and H_2 formation. Moreover, high water-to-ethanol molar ratios avoid catalyst's deactivation due to the coke deposition on the catalytic surface, as only the production of filamentous carbon was favoured [26]. Stoichiometric feeding conditions are also sufficient for obtaining relevant H_2 selectivity and a very low concentration of carbon monoxide [27]. The ESR promotion related to CeO_2 supports can be improved by adding proper dopants. In particular, for CeO_2—ZrO_2 based nickel catalysts, the effect of different metal loads was evaluated, showing a considerable amount of hydrogen also at low Ni percentages, probably due to the smaller particle metal size that promoted the metal-support interactions [28]. The combination of CeO_2 and ZrO_2 was also shown to promote ethanol reforming over Co based catalysts [29]. Moreover, the investigations on Co/CeO_2 catalysts highlighted that the surface basification through calcium doping could be a possible route for increasing the catalytic resistance to coke formation [30].

Catalytic activity of noble metals was also analysed in depth [31–33]. Rhodium based catalysts were found to be very useful in reducing ethylene and acetaldehyde formation [34].