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Enhancing Pt-Ni/CeO_2 performances for ethanol reforming by catalyst supporting on high surface silica

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ABSTRACT

In this paper, bimetallic Pt-Ni/CeO_2 catalysts supported over mesoporous silica were employed for ethanol reforming in the low-temperature range. In particular, catalyst behaviour was investigated under a $H_2O/C_2H_5OH/N_2$ as well as H_2O/C_2H_5OH/AIR mixture between 300 and 600 °C at different space velocities (10000–30000 h^{-1}). Ethanol conversion, for both steam (ESR) and oxidative steam reforming (OSR) reactions, was not affected by contact time decrease at $T > 480$ °C while at lower temperatures, the space velocity growth led to reduced C_2H_5OH conversion, more pronounced when tests were performed without O_2 co-feeding. Moreover, the catalysts showed high resistance to deactivation during reforming tests at 500 °C and 20000 h^{-1}: the improvement of active species dispersion, as a consequence of catalyst formulation enrichment by SiO_2 addition, resulted in lower carbon selectivity with respect to the SiO_2-free sample. However, the higher extent of coke gasification reaction for OSR further increased catalyst stability and total ethanol conversion was recorded for almost 3500 min, 1000 min more than ESR case.

1. Introduction

Nowadays, the development of new technologies for clean energy generation is becoming an urgent need. In this scenario, hydrogen for fuel cells applications emerges as a very promising energetic vector. Hydrogen can be produced from a variety of primary energy sources: methanol [1], ethanol, ammonia, gasoline and natural gas are some possible feedstocks for H_2 generation. 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 [2].

At present, the great part of the hydrogen comes from fossil fuel-based processes. In particular, natural gas steam reforming is the most important route for H_2 production [3–6]. However, this source is a kind of fossil fuel, and its usage fails to provide a proper solution to deal with the huge amount of carbon dioxide emissions during the reforming processes. In addition, the use of fossil fuels for secondary energy production is non-sustainable. As a result, there is a growing interest in the search for effective alternatives to produce renewable hydrogen cleanly and safely.

Among the various feedstocks, ethanol is very attractive as a renewable source for hydrogen production thanks to its following features: it has a relatively high hydrogen content; it is available, it is non-toxic; it is easy to carry, storage and handle; it can be produced renewably by fermentation of biomass; it is a clean fuel; it doesn't contain sulphur compounds and heavy metals [7,8]. In addition, when employed as raw material for the steam reforming reaction, bioethanol provides a further benefit: since bioethanol mixtures also contain water, the very expensive ethanol concentration steps may be avoided.

Bioethanol can be catalytically converted to H_2 through steam reforming and the main interest towards this process arises from the benefit of combining high H_2 yields to a renewable source produced though a mature technology [9].

$$C_2H_5OH + 3H_2O \leftrightarrow 6H_2 + 2CO_2 \qquad \Delta H^{\circ}_{298} = 173.5\,\text{kJ/mol} \tag{1}$$

In the global reaction of ethanol steam reforming, ethanol reacts with water, both in gaseous state in an endothermic reaction, with the production of carbon dioxide and hydrogen, as shown in Eq. (1) [10].

However, this reaction can lead to a complex equilibrium involving several reactions and giving off numerous by-products including carbon monoxide, methane, ethylene, acetaldehyde, and coke. The main steps are the ethanol decomposition (Eq. (2)) in a mixture of H_2, CO and CH_4, followed by a methane steam reforming (Eq. (3)) and the water gas shift reaction (WGS, Eq. (4)) [11,12].

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$$C_2H_5OH \leftrightarrow H_2 + CO + CH_4 \quad \Delta H^{\circ}_{298} = 49\text{kJ/mol} \tag{2}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H^{\circ}_{298} = 165\text{kJ/mol} \tag{3}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta H^{\circ}_{298} = -41\text{kJ/mol} \tag{4}$$

$$C_2H_5OH \leftrightarrow C_2H_4O + H_2 \quad \Delta H^{\circ}_{298} = 68\text{kJ/mol} \tag{5}$$

$$C_2H_5OH \leftrightarrow C_2H_4 + H_2O \quad \Delta H^{\circ}_{298} = 45\text{kJ/mol} \tag{6}$$

$$C_2H_4 \rightarrow polymers \rightarrow coke \tag{7}$$

$$CH_4 \leftrightarrow C_{(s)} + 2H_2 \quad \Delta H^{\circ}_{298} = 75\text{kJ/mol} \tag{8}$$

$$2CO \leftrightarrow C_{(s)} + CO_2 \quad \Delta H^{\circ}_{298} = -171\text{kJ/mol} \tag{9}$$

However, C_2H_5OH can be either dehydrogenated to acetaldehyde (Eq. (5)), which, in turn, can react with steam yielding hydrogen and carbon oxides or dehydrated to ethylene (Eq. (6)) [13,14]. Dehydration reactions, followed by ethylene polymerization (Eq. (7)), CH_4 decomposition (Eq. (8)) and Boudouard reaction (Eq. (9)) are the main pathways responsible for coke precursors formation [15]. Despite the steam reforming endothermicity (Eq. (1)), the choice of performing the reaction at $T < 600$ °C result from both economical (relevant heat duties [16]) and technical requirements (fuel cells operating at $T < 100$ °C tolerate very low CO levels[17,18]).

On the other hand, a further reduction of the energetic costs for H_2 production via ethanol reforming may be achieved by adding oxygen/air to the reacting mixture. Oxidative steam reforming (OSR), which is a combination of steam reforming and partial oxidation, provides a reasonable method to minimize the external heat requirements [5,19–21]. Moreover, the oxygen co-feeding is expected to reduce catalyst deactivation phenomena, due to the promotion of coke oxidation reactions to carbon oxides. However, it's worthwhile noting that the presence of oxygen may also affect H_2 productivity and the reasonable compromise between thermal sustainment and hydrogen selectivity can be reached by properly modulating the O_2/C_2H_5OH ratio [22,23]. The ethanol reforming reaction can be generally written as reported in Eq. (10), where, for x = 0, it is possible to include the steam reforming case.

$$C_2H_5OH + (3-2x)\,H_2O \leftrightarrow (6-2x)\ H_2 + 2CO_2 \quad 0 \le x \le 0.6 \tag{10}$$

The choice of H_2O/C_2H_5OH and O_2/C_2H_5OH ratios equal to 1.8 and 0.6, respectively, may assure the thermal neutrality to the reaction (at 298 K $\Delta H^{\circ}_{298} = 4.4$ kJ/mol) [24]. In fact, it is obvious that, for realising the thermal neutral conditions, the dependence of enthalpy from both temperature and feeding conditions has to be studied. Thermodynamic analysis, carried out by the method of Gibbs free energy minimization, shows that, for a fixed O_2/EtOH ratio, the equilibrium temperature of $\Delta H = 0$ increases with the decrease of H_2O/EtOH ratio, and for a fixed H_2O/EtOH ratio, the equilibrium temperature increases with the increase of O_2/EtOH ratio [25]. Fig. 1 shows the trend of specific enthalpy of reaction as a function of temperature and x, also accounting for the ESR case, which demonstrates that at 500 °C and x = 0.4 (for a steam to ethanol molar ratio of 4) the system reaches autothermal conditions. In addition, it is mandatory to point out that oxygen co-feeding can make the reaction pathway more complex and other reactions, including ethanol, methane, acetaldehyde, carbon monoxide and hydrogen oxidations may take place [26]. Moreover, relative high temperatures can also promote dry reforming reaction of methane.

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \quad \Delta H^{\circ}_{298} = 247\text{kJ/mol} \tag{11}$$

Therefore, in order to perform steam reforming and oxidative steam reforming as efficiently as possible, the selection of highly active and selective catalysts represents a key issue.

Noble as well as non-noble metals were extensively reported as suitable active species for both ESR and OSR [27–29]. However, recently, bimetallic catalysts have gained increasing interest due to their capability of exploiting the synergy related to both the metals, which may result in enhanced catalytic activity, selectivity and stability. For example, Palma et al. [30] evaluated the performances of monometallic Pt/CeO_2 and Ni/CeO_2 catalysts, finding by-products formation (C_3H_6O) in the first case and uncompleted ethanol conversion over the latter sample. Conversely, bimetallic catalysts achieved the highest performances in terms of both H_2 yield and stability. Palma et al. [31] also found that Pt-Ni catalysts supported over CeO_2 are able to assure total ethanol conversion in the low-temperature range (300–600 °C) and a good agreement with thermodynamic predictions. Moreover, Divins et al. [32] showed that $RhPd/CeO_2$ catalysts are suitable for achieving high efficiency in C—C bonds breaking and CO conversion through WGS. The very promising performances of CeO_2 based catalysts are ascribable to the oxygen storage and release capacity of this oxide [33], which promote C_2H_5OH and H_2O dissociation as well as CO and coke precursors oxidation [34]. Concerning SiO_2 based catalysts, the strong interaction of Ni with the support in $CuNi/SiO_2$ catalysts was responsible for an improvement of C—C bond rupture and ethanol conversion at $T < 400$ °C [35].

The employment of rare earth metal based oxides was successful also for oxidative steam reforming process [28,36,37]. Kugai et al. [38] observed that OSR over $Rh\text{-}Ni/CeO_2$ catalysts the noble metals play a crucial role for C—C and C—H bond cleavage while Ni favoured WGS reaction. In the case of bimetallic CoRh and CoRu catalysts supported over SiO_2, the presence of noble metals assured an improvement in the cobalt phase stabilization, thus achieving higher resistance to deactivation than monometallic samples [39].

The present work is focused on the study of activity and stability of bimetallic $Pt\text{-}Ni/CeO_2$ catalysts supported on mesoporous SiO_2 with very high specific area for both steam and oxidative steam reforming in the low-temperature range. In fact, it is well known that the physiochemical properties of supports may significantly affect the catalyst performances and, in particular, high surface area oxides allow a greater dispersion of the metal active phases [40,41] and SiO_2 addition was aimed at improving the catalytic behaviour of previously studied $Pt\text{-}Ni/CeO_2$ samples [16]. Catalyst activity was investigated between 300 and 600 °C at different space velocity (10000, 20000 and 30000 h^{-1}): the agreement of product distribution with thermodynamic predictions was not affected by contact time decrease at $T > 480$ °C in the presence (C_2H_5OH:H_2O:O_2: = 1:4:0.5) as well as in the absence of oxygen (C_2H_5OH:H_2O = 1:4). Moreover, O_2 addition assured a relevant improvement of catalyst stability, due to the higher extent of coke gasification reaction which resulted in total ethanol conversion for almost 57 h at 500 °C and GHSV = 20000 h^{-1}.

2. Experimental

2.1. Catalyst preparation and characterization

The bimetallic catalysts were prepared by wet impregnation. Before preparation, SiO_2 gel powder (Aldrich, mean pore size 60 Å) was calcined in air at 600 °C for 3 h (dT/dt = 10 °C/min) in a muffle furnace.

The impregnation procedure started with the salt precursor dissolution in bi-distilled water at ambient temperature: $Ce(NO_3)_3{*}6H_2O$, $Ni(NO_3)_2{*}6H_2O$ and $PtCl_4$, supplied by Strem, were selected as CeO_2, Ni and Pt precursors, respectively. Once dispersed SiO_2 in the aqueous