Promoting behavior of yttrium over nickel supported on alumina-yttria catalysts in the ethanol steam reforming reaction

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ABSTRACT

The effect of different amounts of Y_2O_3 (5%wt, 10%wt and 15%wt) on the characteristics of nickel supported over mixed non-crystalline $Al_2O_3-Y_2O_3$ was investigated. These materials were tested in ethanol steam reforming reaction. Prior to reaction, the materials were characterized by N_2 adsorption, X-ray diffraction, temperature programmed reduction, temperature programmed desorption of ammonia (NH_3-TPD), and Nuclear Magnetic Resonance. As the yttrium content in the catalytic support increased, nickel started to reduce at lower temperatures and for high yttrium loading (10%wt and 15%wt) an increase in hydrogen uptake was observed. NH_3-TPD showed that yttrium presence decreased the total acidity of alumina and also lowered the strength of the acid sites. The influences of the water to ethanol molar ratio and of the weight gas hourly space velocity on the reaction were also investigated. Yttrium containing systems decrease the presence of C_2 compounds in the exhaust gases and show less formation of CO. After activity test, yttrium containing catalysts seem to present less carbon deposits than the nickel supported on pure alumina catalyst.

Introduction

Clean-energy alternatives are undeniably becoming a vital need for modern society to sustain its current lifestyle and at the same time to substantially reduce its overall carbon footprint. To address these concerns, one of the most promising alternatives is the use of hydrogen as fuel, since it burns without emitting environmental pollutants and when produced from raw materials obtained from renewable sources (bioethanol), the whole process becomes part of a closed loop in the CO_2 life cycle [1]. Additionally, hydrogen can be used in highly efficient devices, such as fuel cells (FCs). However, commercial development of both FCs and hydrogen is affected by their interdependence, as low temperature FCs

require pure hydrogen to operate and small scale hydrogen production, distribution and transport, is not yet cost effective. In this regard, ethanol steam reforming (ESR) is an attractive option for producing hydrogen, as it is low-priced and is based on technology currently available. However, this process involves a complex set of reactions with about a dozen potential products, affecting hydrogen purity and production efficiency.

The thermodynamics of the ESR have been studied by several researchers [2–5], concluding that the reaction is thermodynamically feasible at temperatures above 673 K. A water-ethanol molar ratio equal or beyond 3:1 results in higher hydrogen production and ethanol conversion, whereas pressure seems to have no effect on the reforming reaction. These authors used different approaches to predict the composition in the equilibrium for the ESR reaction, and the theoretical results still presented differences when compared with experimental results. This may be associated to the fact that different catalyst induces different pathways and, therefore, the selection of a suitable catalyst plays a crucial role in the ESR for hydrogen production. Active catalysts should maximize hydrogen selectivity and inhibit coke formation as well as CO production.

Noble metals (Pt, Pd, Rh and Ru) [6–10] and transition metal based catalysts (Ni and Co) have been used extensively in ESR. Although noble metals have high conversion and resistance to coke deposition, their limited availability and high cost hinder their application at a commercial scale. Ni is widely used as a low-cost non-noble metal catalyst in industry for a number of chemical reaction processes. For ethanol reforming, Ni also works well as it favors C–C bond rupture. However it presents deactivation by carbon deposition and sintering of the active phase [11–14].

The nature of the catalytic support is essential in the performance of Ni catalysts in ESR, because it affects the dispersion and stability of the metal. These interactions may favor the selectivity of some reactions. Alumina has been widely used as support for catalysts in ESR, but its acidic nature promotes an ethanol dehydration reaction, which leads to the formation of ethylene and its subsequent polymerization to coke [13,14]. Besides Al_2O_3, other oxides have been studied as supports for Ni catalysts. Sun et al. [15] compared the catalytic activity of Ni/Y_2O_3, Ni/La_2O_3, and Ni/Al_2O_3 for hydrogen production by ESR and found that the catalytic activity and stability decreased in the following order: $Ni/La_2O_3 > Ni/Y_2O_3 > Ni/Al_2O_3$. Nonetheless the selectivity of hydrogen was higher for Ni/Y_2O_3 which is consistent with the order of crystal grain sizes in the three catalysts. Other authors suggest that incorporating dopants to Al_2O_3 could prevent the carbon formation and enhance catalyst stability in ESR. Sanchez et al. [13], found that the presence of MgO and ZrO_2 decreases the acidity of Al_2O_3 and modifies the degree of interaction with Ni, while the addition of lanthana enhances the nickel dispersion and also leads to nickel phases partly covered by La_2O_3. Addition of La_2O_3 and CeO_2 to the catalysts prevented the formation of carbon filaments, which are responsible for the changes in product selectivity with reaction time. K. Elias et al. [16], added CaO by impregnation and co-precipitation methods to diminish the acidity of Ni/Al_2O_3 catalyst, and they found that the impregnation method was more efficient, but that it also promoted an undesired increase in methane selectivity.

Yttrium-based materials have also been investigated by some researchers as support or promoter in catalytic reforming reactions. L. Sun et al. [17] used a $Ni/\gamma-Al_2O_3-Y_2O_3$ catalyst on the autothermal reforming of methane and suggest that adding Y_2O_3 might increase the oxygen mobility in the catalysts, thus increasing catalytic activity by enhancing the reducibility of the catalysts. Furthermore, they found that the addition of Y_2O_3 prevented Ni sintering and carbon deposition. Santos et al. [18] investigated the addition of Y_2O_3 to $Ni/\alpha-Al_2O_3$ catalyst on the autothermal reforming of methane, and they found an increase in the activity and stability of the Ni catalyst over $Y_2O_3/\alpha-Al_2O_3$ when compared to Ni supported on pure Al_2O_3. M. H. Youn et al. [19] studied Ni catalysts over $Me-ZrO_2$ (where Me refers to the metal oxide associated to Zr, Y, La, Ca, and Mg) to produce hydrogen by auto-thermal reforming of ethanol, and they reported that Ni catalyst supported on yttria-stabilized zirconia showed the best catalytic performance by improving the resistance against carbon deposition and enhancing the structural stability of mesoporous zirconia. Le Valant et al. [20] studied the influence of the addition of Ni on the catalytic behavior of a $Rh/Y_2O_3-Al_2O_3$ catalyst on the ESR reaction by adding impurities in the feed to emulate the composition of raw bioethanol. The authors concluded that the presence of yttrium oxide and nickel reinforces the amount of weak Lewis acid sites, thus preventing the catalyst deactivation by carbonaceous deposits. The addition of nickel modifies the metallic phase by increasing the rhodium accessibility and stabilizing the rhodium particles. Moreover, the authors suggest that the presence of the nickel aluminate at the support surface prevented the loss of rhodium by diffusion in the support bulk. H. Ma et al. [21] prepared $Ni/Y_2O_3-Al_2O_3$ catalysts with different molar ratios by co-precipitation, and they found that different mole ratios of Y and Al in the composite support could have a beneficial effect between active phase and support, since the catalyst $Ni/Y_2O_3-Al_2O_3$ performed well with a high water/ethanol ratio (13:1) and low temperature (723 K).

The aforementioned studies present yttrium oxide as a good alternative to improve the catalytic stability of Ni/Al_2O_3 for reforming reactions. Nevertheless, the effect of different amounts of Y_2O_3 in $Y_2O_3-Al_2O_3$ as Ni support in the ESR reaction is still unclear. The aim of this research is to elucidate the promoting behavior of yttrium in $Ni/Al_2O_3-Y_2O_3$ catalysts and analyze their catalytic performance in the ethanol steam reforming reaction.

Experimental

Preparation of catalysts

$Al_2O_3-Y_2O_3$ oxides were prepared by the sol–gel method using as precursors aluminum tri-sec-butoxide [Al [OCH(CH$_3$) C$_2$H$_5$]$_3$ (97% Aldrich)] and yttrium (III) nitrate hexahydrate [Y(NO$_3$)$_3$·6H$_2$O (99.8% Aldrich)]. The synthesis method is similar to the one described in our previous paper [22]. The molar ratios for the synthesis were 80/30/0.2/1 iso-propyl alcohol/water/acid/alcoxide, with the appropriate amount of