



Improved stability of Ni/Al₂O₃ catalysts by effect of promoters (La₂O₃, CeO₂) for ethanol steam-reforming reaction



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ARTICLE INFO

Article history:

Received 31 January 2015

Received in revised form 22 April 2015

Accepted 23 April 2015

Available online 6 June 2015

Keywords:

Hydrogen production

Ethanol steam reforming

Ni catalysts

Metal oxide promoters, Catalyst stability

ABSTRACT

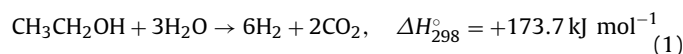
Ni-based catalysts supported on γ -Al₂O₃ modified by La₂O₃ and CeO₂ promoters were prepared in the present work. The objective was to study the promotional effect of addition of 15 wt% La₂O₃ and different CeO₂ contents on stability of Ni/Al₂O₃ catalysts for ethanol steam-reforming reaction. The physical chemical characteristics of the catalysts, activity and the carbon deposition on the catalyst surface were carried out by TEM, NH₃-TPD, XRD, TPR, XPS, DRIFT, TPO-TG and Raman. The stability of Ni/ γ -Al₂O₃ was effectively improved by addition of 15 wt% La₂O₃ and 10 wt% CeO₂ as the carbon deposition rate was reduced 72% compared with catalyst supported on bare alumina. The role of promoters was to decrease the selectivity to ethylene by reduction of strong Lewis acid sites of γ -Al₂O₃ and the removing carbon deposits during reaction, through both lanthanum oxycarbonate formations from La₂O₃ as the higher amount of mobile lattice oxygen induced by the CeO₂ promoter. This catalyst showed good results of selectivity to H₂, no presence of C₂ intermediates above 723 K and it was stable up to 48 h of time-on-stream at 773 K. In addition, it was possible to recover part of the original catalyst activity after a reactivation process, in order to remove some carbon deposits as potential causes of deactivation.

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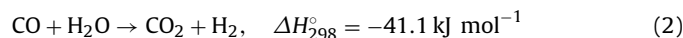
1. Introduction

Nowadays, most of the energy we use comes from fossil fuels—a non-renewable energy source. Our dependence on fossil fuels as energy sources has been caused serious environmental problems, *i.e.* air pollutants and greenhouse gas emissions, and natural resource depletion. Molecular hydrogen (H₂) is a potential energy carrier in the clean energy-based economy and is currently produced in large quantities by natural gas steam reforming, mainly to meet the demands of certain chemical processes, such as the refinery (hydrotreating and hydrocracking) and ammonia synthesis. Nevertheless, the clean and non-polluting characteristics of H₂ as a fuel depend on the process, the raw material and the source of energy employed for its production. In this context, ethanol is very attractive for the production of hydrogen due to its wide availability since this can be produced from several biomass sources, its relative low cost and the high H₂ production capacity of the process per molecule of ethanol reformed [1,2]. Steam reforming

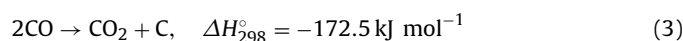
(SR) is the most interesting process for obtaining hydrogen from ethanol, because it generates the highest hydrogen yield at temperatures lower than those required for the steam reforming of other fuels. The overall ethanol steam-reforming (ESR) reaction could be stoichiometrically represented as follow:



From the thermodynamic view, since ESR is endothermic and results in an increase in the number of moles, increasing the temperature and lowering the pressure is in favor of ethanol reforming [3]. However, high temperature (>973 K) of ESR shifts the equilibrium of the water gas-shift (WGS) reaction (Eq. (2)) toward the formation of CO, which dictates further costly purification steps in order to remove CO.

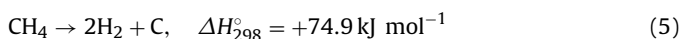


Moreover, carbon monoxide can undergo the Boudouard reaction (Eq. (3)), that is one of the main reactions responsible for coke formation [4].



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In addition, steam-reforming reaction produces a wide range of undesirable by-products such as CH_3COCH_3 , CH_3CHO , C_2H_4 , CH_4 , etc. [5] and undesired reactions which contribute to catalyst deactivation by coke formation (Eqs. (4) and (5)):



Development of suitable catalysts which are able to produce a H_2 -rich stream with very low CO concentration at medium or low temperature and stable over time is still a challenge [6]. Different catalysts, including supported metals (Ni [7–12] and Co [13,14]), supported noble metals [2] and bimetallic catalysts [15–17] have been studied for the ESR. Among transition metals, Ni has been widely used as active phase for ethanol-reforming reactions because to its high C–C and O–H bond-breaking activity [18], its relatively low cost and its known participation in the WGS reaction [19]. It is generally accepted that the chemical nature of the support may strongly affect the products distribution and catalyst stability during SRE. Among oxide supports, alumina-based supports are often used in reforming catalysts because of their mechanical and chemical resistance under reaction conditions and the possibility that it offers to control the surface area and pore size distribution. Nevertheless, the use of Al_2O_3 as support promotes catalysts deactivation by deposition of carbon from ethylene intermediate produced *via* dehydration reactions of ethanol on acid sites of the support. Taking into account the deactivation process, due to carbon deposition on the catalysts surface during the SRE reaction, oxidative steam reforming (OSR) is an effective route for producing hydrogen from ethanol because it can attenuate coke deposition [20–23]. The major drawback of OSR is decrease the yield of H_2 due to its oxidation.

The improvement of the ESR, it is frequently reported in the literature by Al_2O_3 modification with addition of alkali metals, rare earths oxides and other basic oxides, which decrease the acidity, enhance the oxygen mobility, improve the metal dispersion and prevent the sintering of the metal sites [10,24]. Among used modifiers, La_2O_3 is known to be an excellent formulation as support and promoter for stability of Ni-based catalysts, which is attributed to scavenging of coke deposition by lanthanum oxycarbonate species that are developed on the top of Ni particles or at the Ni–La interface [10,25]. Likewise, CeO_2 has also shown excellent results in catalyst stability as it favors the coke gasification and WGS reaction due to its capacity to store, release and transport oxygen. Additionally, CeO_2 improves the redox reversibility of metallic phase and has been observed that can prevent the loss of surface area of bare alumina and the sintering the metallic species during the thermal treatment [26–28].

The aim of this paper was to study the promotional effect of addition of 15 wt% La_2O_3 and different CeO_2 contents on stability of Ni/ Al_2O_3 catalysts for ESR reaction. $\gamma\text{-Al}_2\text{O}_3$ support was modified with both promoters in order to search a synergistic effect between the two promoters, since both have shown excellent results individually on stability [24,29–33]. With this objective, it was evaluated the effect of promoters on the physical chemical characteristics, H_2 selectivity and stability of the catalyst in the reaction of steam reforming of ethanol at mild temperature (773 K).

2. Experimental

2.1. Catalyst preparation

Supports were prepared by successive wet impregnation of inorganic precursors of La_2O_3 and CeO_2 in the order: $\text{La}_2\text{O}_3\text{-}x\text{CeO}_2\text{-}\gamma\text{-Al}_2\text{O}_3\text{-}x\text{CeO}_2\text{-}\gamma\text{Al}_2\text{O}_3$ supports were prepared by impregnation of $\gamma\text{-Al}_2\text{O}_3$ (Glider $S_{\text{BET}} = 189 \text{ m}^2 \text{ g}^{-1}$) with the

appropriate amount of an aqueous solution of cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9% Merck) under stirring for 4 h at room temperature, to obtain solids containing 5, 10 and 15 wt% CeO_2 . After impregnation, the supports were dried at 373 K for 0.5 h and finally calcined at 923 K for 6 h under static air. La_2O_3 (15 wt%) was introduced into $x\text{CeO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$ and bare $\gamma\text{-Al}_2\text{O}_3$ supports using an aqueous solution of lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9% Merck) as precursor. Supported Ni catalysts were prepared by impregnation on supports with aqueous solutions of nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.9% Merck) using a similar protocol to the one used for support preparation, to obtain catalysts with 10 wt% Ni. The calcination was performed over dried samples under dynamic air (30 mL min^{-1}) at 773 K for 4 h at a heating rate of 10 K min^{-1} . The samples were designated as Ni/L(X)CA where C = CeO_2 , L = La_2O_3 and A = $\gamma\text{-Al}_2\text{O}_3$ (X = 0, 5, 10 or 15 wt%). The solids were reduced prior characterization or catalytic evaluation in H_2 flow (30 mL min^{-1}) at 923 K for 1.5 h.

2.2. Catalyst characterization

The specific area and porosity were obtained from nitrogen adsorption–desorption isotherms at 77 K performed in an automatic Micromeritics apparatus Model ASAP 2010 on samples previously outgassed at 393 K for 2 h under N_2 flow. The BET surface areas were calculated using a linear section of the BET plot based on IUPAC parameters. Pore-size distributions were calculated from the N_2 adsorption branch using the Barrett–Joyner–Halenda model (BJH). Metal dispersion was measured by H_2 pulse chemisorptions on a Micromeritics ASAP 2100 unit. Prior to the pulse chemisorption experiments, all samples were reduced under *in situ* H_2 for 1.5 h at 923 K. Subsequently, in order to remove hydrogen chemisorbed, vacuum was performed for 1 h at 623 K. Then, the systems were brought to room temperature and hydrogen isotherms were carried out. To calculate metal dispersion, adsorption stoichiometry of $\text{H}/\text{M} = 1$ was assumed. Particle size was determined by TEM micrographs obtained in a Jeol Model JEM-1200 EXII System. Samples were dispersed on carbon grids after sonicating the samples in H_2O :ethanol (50:50) for 0.5 h. Up to 300 individual metal particles were counted for each catalyst, and the surface area-weighted mean Ni diameter (d_p) was calculated using the following equation:

$$d_p = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}$$

where n_i is the number of particles and d_i is the diameter. The size limit for detecting the N_i particles on the samples was *ca.* 1 nm.

Total acidity was evaluated by temperature-programmed desorption of ammonia ($\text{NH}_3\text{-TPD}$). Samples (100 mg) were reduced *ex situ* at 923 K in H_2 flow (30 mL min^{-1}) for 1.5 h just before analysis. Prior to NH_3 adsorption, the supports were pre-treated under He flow at 383 K up to baseline stabilization and subsequently were ammonia-saturated at 383 K using NH_3 pulses. Once saturated surface, weakly adsorbed NH_3 was removed by flowing He at 383 K for 0.5 h. Subsequently, the systems were cooled down to room temperature and desorption were carried out using a linear heating rate for 10 K min^{-1} from 383 to 1073 K. TPD curves were recorded by a TCD. All desorption profiles were normalized per gram of catalyst.

X-ray diffraction (XRD) patterns were recorded on supports and reduced catalysts using a Bruker diffractometer Model D4 Endeavor and nickel filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) under constant instrument parameters. The test was carried out at 40 mV and 20 mA over Bragg angles between 5° and 90° . A rate of 0.02 s

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