



## Research article

# Optimum operating conditions in ethanol steam reforming over a Ni/La<sub>2</sub>O<sub>3</sub>-αAl<sub>2</sub>O<sub>3</sub> catalyst in a fluidized bed reactor



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## ABSTRACT

This manuscript analyzes the steam reforming of ethanol (SRE) over a Ni/La<sub>2</sub>O<sub>3</sub>-αAl<sub>2</sub>O<sub>3</sub> catalyst in a fluidized bed reactor under a wide range of operating conditions (500–650 °C, space time up to 0.35 g<sub>catalyst</sub>h/g<sub>EtOH</sub>, and steam/ethanol (S/E) molar ratio in the feed between 3 and 9) in order to select optimum conditions for maximizing H<sub>2</sub> production. The significance the individual reactions in the reaction mechanism have on products distribution and the role of the catalyst in the extent of these reactions has also been analyzed. Blank runs (without catalyst) have been performed to test the contribution of thermal routes to this mechanism. Ethylene and acetaldehyde are intermediate products in the kinetic scheme, whose presence is only observed when ethanol conversion is not full. The increase in temperature enhances the reforming and decomposition of ethanol and acetaldehyde and, when the catalyst is used, CH<sub>4</sub> reforming and reverse WGS reactions are also promoted, so that the yield of H<sub>2</sub> and CO increases, that of CH<sub>4</sub> decreases and the one of CO<sub>2</sub> remains almost constant with temperature. The increase in S/E molar ratio increases H<sub>2</sub> yield, but attenuates the rate of some reactions involved in the process. 600 °C, a space time of 0.35 g<sub>catalyst</sub>h/g<sub>EtOH</sub> and S/E = 6 are suitable conditions for maximizing ethanol conversion (100%) and H<sub>2</sub> yield (82%) with high catalyst stability.

## 1. Introduction

The foreseen 30% growth in worldwide energy demand for 2040, together with the increasing social awareness concerning the negative consequences of the use of fossil fuels, have boosted the development of technologies for maximizing energy production from renewable sources, so that 37% of power generation will be from renewable resources in 2040, compared to 23% today [1]. Among these, biorefinery technologies aimed at converting different biomass types into chemicals and fuels have a relevant role [2], and the reforming of biomass derived oxygenates has gained an important strategic interest because of the increasing demand of H<sub>2</sub> for use as a fuel, and as raw material in petrochemical industry and agrochemistry [3].

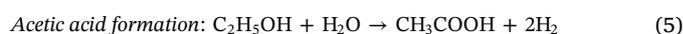
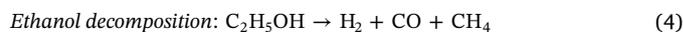
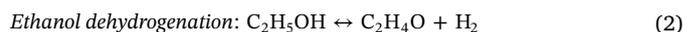
Among biomass derived oxygenates, bio-ethanol has great interest as raw material for producing H<sub>2</sub> by reforming [4,5], mainly due to the good perspectives for its production from lignocellulosic biomass, with a forecasted increase from the current 270 L/t biomass to 400 L/t biomass in 2030, as a result of the advance in the technology of enzymatic hydrolysis-fermentation [6]. Moreover, the steam reforming (SR) of bio-ethanol (~86% H<sub>2</sub>O) avoids the high cost required for its

dehydration (estimated at 50% of the total product cost [7]) in order to be used as a fuel (dehydrated ethanol).

The steam reforming of ethanol (SRE) is an endothermic process that proceeds at relatively low temperatures (between 300 and 800 °C), with the following stoichiometry:

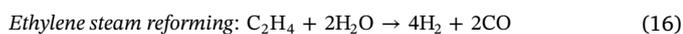
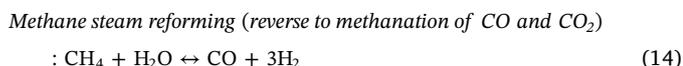
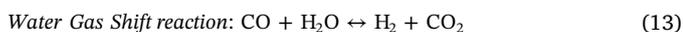
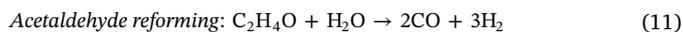
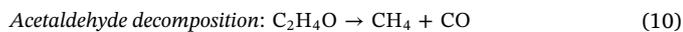
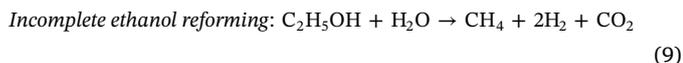
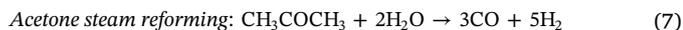


The use of steam/ethanol (S/E) molar ratio in the feed above the stoichiometric value (S/E = 3) improves H<sub>2</sub> selectivity and attenuates deactivation by coke deposition [8]. Nevertheless, the reaction mechanism is complex due to secondary reactions that take place in parallel to the steam reforming reaction and generate intermediate products and by-products, thus reducing H<sub>2</sub> yield. Among the secondary reactions, the following are considered [9–11]:

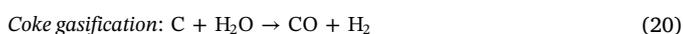
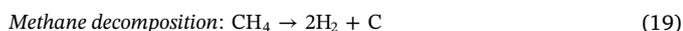
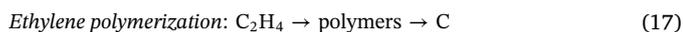


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Other reactions take also place, but they are not relevant for products distribution, although they contribute to catalyst deactivation by formation or elimination (by gasification) of coke (C):



Due to the complexity of the reaction scheme, the yield and selectivity of  $\text{H}_2$  is highly affected by reaction conditions (temperature, S/E molar ratio and space time), as well as by catalyst composition. Consequently, the industrial viability of the SRE process requires the development of highly active and selective catalysts for  $\text{H}_2$  formation (minimize secondary reactions), which are stable and hardly affected by coke formation. With this objective in mind, several reviews have analyzed the use of catalysts with both noble and non-noble metals supported on different oxides [9,12–15]. Noble metal catalysts, especially Rh based catalysts, are highly active and selective for SRE [16,17], but their practical applications are limited by their high cost. Among the non-noble catalysts, those based on Ni and Co are the most studied due to their high C–C bond breakage activity [18–23].

Furthermore, it is well established that an increase in metal content in Ni based catalysts improves ethanol conversion, but does not guarantee a higher  $\text{H}_2$  selectivity. Thus, Han et al. [24] determined an optimum content of 15 wt% Ni for a catalyst prepared by sol-gel technique, which showed a high Ni dispersion and resistance to coke deposition. Gayubo et al. [25] reported an optimum content of 10 wt% Ni in Ni/SiO<sub>2</sub> and Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts prepared by incipient wetness impregnation, which is due to a higher Ni content leading to a significant agglomeration of metal crystals.

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> has been widely used as support because of its high thermal and mechanical stability, together with a high specific surface area, which also improves the dispersion of the active phase. Nevertheless, its acidity promotes ethanol dehydration reaction and, as a result, coke deposition via ethylene, which causes a rapid deactivation of the catalyst. Consequently, several methods have been studied for the neutralization of its acidity. The addition of basic additives, such as CaO, lowers the support acidity and weakens the interaction between Ni and Al<sub>2</sub>O<sub>3</sub>, which facilitates the reduction of Ni<sup>+2</sup> species to Ni<sup>0</sup> [26,27]. However, Ca contents above 5 wt% increase Ni active particle size, which causes a lower  $\text{H}_2$  yield [27] and promotes the formation of encapsulating coke responsible for the rapid deactivation of the catalyst [26]. The addition of MgO to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> caused similar results to those obtained by doping with CaO [28–30]. Nevertheless, the doping of the

support ZrO<sub>2</sub> with CaO did not affect Ni reducibility and hindered coke deposition [31]. Furthermore, the addition of La<sub>2</sub>O<sub>3</sub> provides stability to Ni/Al<sub>2</sub>O<sub>3</sub> catalyst by lowering coke formation rate [32–34]. In a previous work, a Ni/La<sub>2</sub>O<sub>3</sub>- $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst used in the SRE reaction achieved an equilibration state subsequent to a reaction-regeneration cycle (consisting in the steam reforming at 700 °C followed by coke combustion with air at 550 °C), which allowed attaining a reproducible performance in successive reaction-regeneration cycles [35].

In view of this background, this work analyzes the effect operating conditions (temperature, S/E molar ratio and space time) have on the behavior of an equilibrated Ni/La<sub>2</sub>O<sub>3</sub>- $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst in the SRE process, in order to determine the conditions maximizing ethanol conversion and  $\text{H}_2$  yield. The study covers a wide range of operating conditions, including those for kinetic regime control (a limited extent of the individual reactions) in order to get information on the nature of the reaction intermediates. Moreover, the significance individual reactions of the complex reaction mechanism (Eqs. 1–16) have on product distribution has also been analyzed, which has allowed establishing an original kinetic scheme accounting for the significance of individual reactions under the conditions studied. With the aim of assessing the contribution of the thermal reaction steps to the overall scheme, blank runs (without catalyst) have also been performed. Moreover, catalyst stability has been approached by means of long duration runs (200 h), as it is an essential aspect for larger scale applications. A Ni/La<sub>2</sub>O<sub>3</sub>- $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst subjected to thermal equilibration treatment [35] has the additional interest that the results are reproducible when successive reaction-regeneration cycles are carried out. The fluidized bed reactor is also interesting for ensuring bed temperature homogeneity because, in addition to controlling this variable, it also has good perspectives for scaling-up.

## 2. Experimental section

### 2.1. Catalyst preparation

The catalyst was prepared by incipient wetness impregnation method [36], and with a composition (nominal contents of 10 wt% Ni and 9 wt% La<sub>2</sub>O<sub>3</sub>) determined in a previous work [25]. It has been proven that once calcined at 550 °C for 2 h in air, and subsequent to an equilibration treatment, the catalyst achieves a reproducible kinetic behavior in reaction-regeneration cycles [35]. Prior to the kinetic runs the catalyst was reduced in situ at 700 °C for 2 h by using a H<sub>2</sub>-He flow (10 vol% H<sub>2</sub>). The properties (Table 1) have been determined as follows: composition, by inductively coupled plasma and atomic emission spectroscopy (ICP-AES) in a Thermo X7-II spectrometer; surface area ( $S_{\text{BET}}$ ) and porous structure, by N<sub>2</sub> adsorption – desorption in a Quantacrome Autosorb IQ2 in physisorption mode; metal surface area and dispersion, by H<sub>2</sub> chemisorption in a Quantacrome Autosorb IQ2. The metal content in the catalyst is very close to the nominal value, which confirms that the preparation method by incipient wet impregnation is suitable. A comparison of the physical and metallic properties of Ni catalysts with different supports and their effect on the kinetic performance in the SRE reaction has already been studied by the authors [25]. It was proven that the addition of La<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support had a minor unfavorable effect on the physical and metal properties of

**Table 1**  
Physical and chemical properties of Ni/La<sub>2</sub>O<sub>3</sub>- $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

Technique	Property	Results
N <sub>2</sub> physisorption ICP	$S_{\text{BET}}$ (m <sup>2</sup> /g)	35
	Ni (%)	8.8
	La (%)	6.8
H <sub>2</sub> chemisorption	Metal dispersion (%)	4.7
	Metal active surface (m <sup>2</sup> /g)	3.1
XRD	Crystal size (Å), 2 $\theta$ = 52°	106

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