Fuel Processing Technology 169 (2018) 207–216

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Optimum operating conditions in ethanol steam reforming over a Ni/La_2O_3-αAl_2O_3 catalyst in a fluidized bed reactor

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ARTICLE INFO

Keywords:
Ethanol
Hydrogen production
Steam reforming
Fluidized reactor

ABSTRACT

This manuscript analyzes the steam reforming of ethanol (SRE) over a Ni/La_2O_3-αAl_2O_3 catalyst in a fluidized bed reactor under a wide range of operating conditions (500–650 °C, space time up to 0.35 $g_{catalyst}h/g_{EtOH}$, and steam/ethanol (S/E) molar ratio in the feed between 3 and 9) in order to select optimum conditions for maximizing H_2 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_4 reforming and reverse WGS reactions are also promoted, so that the yield of H_2 and CO increases, that of CH_4 decreases and the one of CO_2 remains almost constant with temperature. The increase in S/E molar ratio increases H_2 yield, but attenuates the rate of some reactions involved in the process. 600 °C, a space time of 0.35 $g_{catalyst}h/g_{EtOH}$ and S/E = 6 are suitable conditions for maximizing ethanol conversion (100%) and H_2 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_2 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_2 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_2O) 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:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \qquad \Delta H_{298}{}^0 = 173.3 \text{ kJ/mol} \qquad (1)$$

The use of steam/ethanol (S/E) molar ratio in the feed above the stoichiometric value (S/E = 3) improves H_2 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_2 yield. Among the secondary reactions, the following are considered [9–11]:

Ethanol dehydrogenation: $C_2H_5OH \leftrightarrow C_2H_4O + H_2$ (2)

Ethanol dehydration: $C_2H_5OH \rightarrow C_2H_4 + H_2O$ (3)

Ethanol decomposition: $C_2H_5OH \rightarrow H_2 + CO + CH_4$ (4)

Acetic acid formation: $C_2H_5OH + H_2O \rightarrow CH_3COOH + 2H_2$ (5)

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http://dx.doi.org/10.1016/j.fuproc.2017.10.003
Received 5 April 2017; Received in revised form 6 September 2017; Accepted 5 October 2017

$$\textit{Acetone formation}: 2\ C_2H_5OH \rightarrow CH_3COCH_3 + CO + H_2 \tag{6}$$

$$\textit{Acetone steam reforming}: CH_3COCH_3 + 2H_2O \rightarrow 3CO + 5H_2 \tag{7}$$

$$\textit{Acetic acid steam reforming}: CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2 \tag{8}$$

$$\textit{Incomplete ethanol reforming}: C_2H_5OH + H_2O \rightarrow CH_4 + 2H_2 + CO_2 \tag{9}$$

$$\textit{Acetaldehyde decomposition}: C_2H_4O \rightarrow CH_4 + CO \tag{10}$$

$$\textit{Acetaldehyde reforming}: C_2H_4O + H_2O \rightarrow 2CO + 3H_2 \tag{11}$$

$$C_2H_4O + 3H_2O \rightarrow 2CO_2 + 5H_2 \tag{12}$$

$$\textit{Water Gas Shift reaction}: CO + H_2O \leftrightarrow H_2 + CO_2 \tag{13}$$

$$\textit{Methane steam reforming (reverse to methanation of CO and } CO_2\text{)}: CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{14}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \tag{15}$$

$$\textit{Ethylene steam reforming}: C_2H_4 + 2H_2O \rightarrow 4H_2 + 2CO \tag{16}$$

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):

$$\textit{Ethylene polymerization}: C_2H_4 \rightarrow \text{polymers} \rightarrow C \tag{17}$$

$$\textit{Boudouard reaction}: 2CO \leftrightarrow C + CO_2 \tag{18}$$

$$\textit{Methane decomposition}: CH_4 \rightarrow 2H_2 + C \tag{19}$$

$$\textit{Coke gasification}: C + H_2O \rightarrow CO + H_2 \tag{20}$$

Due to the complexity of the reaction scheme, the yield and selectivity of 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 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 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_2 and $Ni/\alpha\text{-}Al_2O_3$ catalysts prepared by incipient wetness impregnation, which is due to a higher Ni content leading to a significant agglomeration of metal crystals.

$\gamma\text{-}Al_2O_3$ 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_2O_3, which facilitates the reduction of Ni^{+2} species to Ni^0 [26,27]. However, Ca contents above 5 wt% increase Ni active particle size, which causes a lower 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 $\gamma\text{-}Al_2O_3$ caused similar results to those obtained by doping with CaO [28–30]. Nevertheless, the doping of the support ZrO_2 with CaO did not affect Ni reducibility and hindered coke deposition [31]. Furthermore, the addition of La_2O_3 provides stability to Ni/Al_2O_3 catalyst by lowering coke formation rate [32–34]. In a previous work, a $Ni/La_2O_3\text{-}\alpha Al_2O_3$ 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 $Ni/La_2O_3\text{-}\alpha Al_2O_3$ catalyst in the SRE process, in order to determine the conditions maximizing ethanol conversion and 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 $Ni/La_2O_3\text{-}\alpha Al_2O_3$ 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_2O_3) determined in a previous work [25]. It has been proven that once calcined at 550 °C fSor 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_2–He flow (10 vol% H_2). 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_{BET}) and porous structure, by N_2 adsorption – desorption in a Quantacrome Autosorb IQ2 in physisorption mode; metal surface area and dispersion, by H_2 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_2O_3 to $\alpha\text{-}Al_2O_3$ support had a minor unfavorable effect on the physical and metal properties of

Table 1
Physical and chemical properties of $Ni/La_2O_3\text{–}\alpha Al_2O_3$ catalyst.

Technique	Property	Results
N_2 physisorption	S_{BET} (m^2/g)	35
ICP	Ni (%)	8.8
	La (%)	6.8
H_2 chemisorption	Metal dispersion (%)	4.7
	Metal active surface (m^2/g)	3.1
XRD	Crystal size (Å), $2\theta = 52°$	106