

Kinetic behaviour of commercial catalysts for methane reforming in ethanol steam reforming process

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Abstract

Ethanol steam reforming has been studied in a fluidized bed (in order to ensure bed isothermicity) on commercial catalysts for methane reforming. The results allow analyzing the effect of temperature (in 300–700 °C range), and both metal and support nature on the reaction indices (ethanol conversion, yields and selectivities to H₂ and byproducts (CO₂, CO, CH₄ and C₂H₄O)). Special attention has been paid to catalysts' stability by comparing the evolution of the reaction indices with time on stream at 500 °C (minimum CO formation) and 700 °C (minimum deactivation by coke deposition). Although they provide a slightly lower H₂ yield, the results evidence a good behaviour of Ni based catalysts, indicating that they are an interesting alternative of more expensive Rh based ones.

Key words

ethanol steam reforming; hydrogen; commercial catalyst; selectivity; deactivation

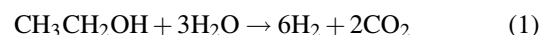
1. Introduction

The technological development of hydrolysis-fermentation of lignocellulosic biomass explains that second generation bioethanol is considered to be an alternative source to oil for the production of automotive fuels and petrochemicals [1–3] and to fulfill the increasing demand of H₂ for use as fuel and raw materials in the hydroprocessing units in refineries.

Viikari et al. [4] review the aspects concerning the decrease in lignocellulosic bioethanol production costs, with their estimation being in 0.41–0.57 euro/L range in the EU and in 0.24–0.34 euro/L range in the USA, which is encouraging for the viability of its valorization at industrial scale in a near future. Moreover, bioethanol is a more attractive raw materials for use in fuel cell hydrogen production, which provides higher electrical and thermal efficiency in solid oxide fuel cell (SOFC) than other renewable fuels, such as biogas and glycerol [5].

The steam reforming of bioethanol (SRE) is an attractive route to obtain H₂, as it avoids the energy-demanding water separation processes needed for upgrading bioethanol as a fuel

or in its valorisation following other routes. The reaction takes place with the following stoichiometry:



Several undesired reactions also take place, which diminish H₂ yield, give way to the formation of byproducts in the reaction medium (CO, CH₄, acetaldehyde, ethylene) and contribute to catalyst deactivation by coke deposition from these byproducts. These reactions include: ethanol dehydrogenation to acetaldehyde, ethanol decomposition to CO+CH₄ and H₂, ethanol dehydration to ethylene (which is considered as one of the main responsible for coke formation by intermediate oligomers), acetaldehyde decomposition to CO and CH₄, which in turn contribute to H₂ formation by water-gas shift reaction (WGS) and reforming reaction, respectively, Boudouard reaction, CO and CO₂ methanation reactions, methane decomposition to carbon and H₂ [6–8].

Catalyst deactivation by coke is one of the main problems in SRE reaction and its attenuation requires operation to be carried out at a sufficiently high temperature for the main reactions reforming ethanol, intermediate compounds and byproducts, such as CH₄. Moreover, given that a cata-

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lysts with a good balance between activity, selectivity to H₂ and stability is required, numerous metallic functions have been tested, such as transition metals (Ni, Co) and noble metals (Pt, Pd, Rh), as well as bimetallic alloys, which have been supported on different materials (Al₂O₃, SiO₂, MgO, ZnO, TiO₂, CeO₂) [9–16].

This paper deals with the kinetic behaviour of methane steam reforming (SRM) commercial catalysts which are used in SRE reaction, in 300–700 °C range and in an isothermal fluidized-bed reactor (in order to ensure bed isothermicity in the experimental runs). The results are a basis for the subsequent studies involving the adaptation of catalysts prepared in the laboratory to industrial scale, bearing in mind that the fluidized bed has suitable features for large-scale operation. Ni and Rh based catalysts have been studied as alternatives, given that catalysts cost is a key factor for the viability of the industrial implementation of SRE reaction.

2. Experimental

2.1. Catalysts

Five commercial reforming catalysts have been supplied by Süd Chemie (G90 and G117), BASF (SG9301 and SG9402) and Fuel Cell Materials (Rh/ZDC), with the following formulations: G90 (NiO, CaAl₃O₄, Al₂O₃), G117 (NiO, MgO), SG9301 (NiO, CaO, La₂O₃, Al₂O₃), SG9402 (NiO, CaO, Al₂O₃), Rh/ZDC (Rh, CeO₂, ZrO₂). More detailed information on the composition of these catalysts cannot be provided due to a confidentiality agreement. In order to be used in the fluidized reactor, the catalysts provided by Süd Chemie and BASF (which are supplied as rings) were previously ground and sieved to 150–250 μm range. Rh/ZDC catalyst (supplied as powder) was pressed, ground and sieved to the same size, which is suitable for use in the fluidized reactor. As stated in the confidentiality agreement, composition and chemical properties of these catalysts were not measured.

The physical properties (Table 1) were determined by N₂ adsorption-desorption in a Micromeritics ASAP 2010C and Hg porosimetry in a Micromeritics Autopore 9220. The Micromeritics ASAP 2010C was also used for the analysis of the metallic surface by H₂ chemisorption. Rh/ZDC commercial catalyst (with CeO₂ and ZrO₂ as support) had high values of BET surface area and pore volume, and the values of both properties were very low for the rest of the catalysts.

Table 1. Metal content and physical properties of commercial catalysts used for SRE

Catalysts	Metal content ^a (wt%)	S _{BET} (m ² /g)	V _{pore} (cm ³ /g)	d _{pore} (Å)
Rh/ZDC	2	76	0.28	127
SG9301	10–15	21	0.07	162
SG9402	11–13	26	0.06	135
G90	>1	19	0.04	122
G117	5	8	0.02	149

^a Provided by the supplier

2.2. Reaction conditions and equipment for reaction and product analysis

The kinetic runs were carried out in automated reaction equipment (Microactivity Reference from PID Eng & Tech) provided with an isothermal fluidized-bed reactor (22 mm of internal diameter and total length of 460 mm) connected on-line to a gas chromatograph (Agilent Micro-GC 3000) for product analysis [17]. The hydrodynamic properties of the bed were improved by mixing the catalyst (particle size between 150 and 250 μm) with an inert solid (CSi, particle size between 60 and 90 μm) at a catalyst/inert ratio of 1 : 4. The Micro-GC was provided with four modules for analyzing: (1) permanent gases; (2) oxygenates, light olefins (C₂–C₃) and water; (3) C₂–C₆ hydrocarbons; (4) C₆–C₁₂ hydrocarbons and oxygenate compounds. The compounds were quantified and identified using calibration standards of known concentration. The balance of atoms (C, H, O) was closed in all the runs above 98%.

The kinetic runs were performed under the following operating conditions: 300–700 °C; pressure, 1.2 bar; ethanol partial pressure in the feed (diluted in He), 0.11 bar; steam/ethanol molar ratio, 6; space time, 0.14 g_{cat}·h·g_{ethanol}⁻¹; time on stream, up to 50 h. These operating conditions were selected on the basis of a previous study [18] for delimiting the proper ranges of operating variables to obtain kinetic results and attain a stable fluidization regime. As proven in this previous paper, a steam/ethanol ratio higher than 6 was not interesting because the improvement in H₂ was low and the energy cost was excessive.

3. Results and discussion

3.1. Kinetic behaviour of the catalysts at zero time on stream

The following reaction indices have been defined in order to quantify the kinetic behaviour of the catalysts:

Ethanol conversion:

$$X = \frac{F_{E,0} - F_E}{F_{E,0}} \quad (2)$$

where, $F_{E,0}$ and F_E are the molar flow rates of ethanol at the reactor inlet and outlet, respectively.

Yield of H₂:

$$Y_{H_2} = \frac{F_{H_2}}{6F_{E,0}} \quad (3)$$

where, F_{H_2} is the molar flow rate of H₂ at the reactor outlet.

Selectivity to i product (H₂, CO₂, CO, CH₄ and C₂H₄O):

$$S_i = \frac{F_i}{\nu_i(F_{E,0} - F_E)} \quad (4)$$

where, F_i is the molar flow rate of i product at the reactor outlet and ν_i is the corresponding stoichiometric coefficient by assuming the independent formation from ethanol: $\nu_i = 6$ for H₂, 2 for CO₂, CO and CH₄, 1 for C₂H₄O (acetaldehyde, which was formed by ethanol dehydrogenation and whose

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