Intensifying glycerol steam reforming on a monolith catalyst: A reaction kinetic model

L.F. Bobadilla [a], V. Blay [b], A. Álvarez [a,1], M.I. Domínguez [a], F. Romero-Sarria [a], M.A. Centeno [a,*],
J.A. Odriozola [a]

[a] Instituto de Ciencia de Materiales de Sevilla, Universidad de Sevilla-Consejo Superior de Investigaciones Científicas, Avenida Américo Vespucio s/n, 41092 Sevilla, Spain
[b] Instituto de Tecnología Química (UPV-CSIC), Universitat Politècnica de València, Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022 Valencia, Spain

HIGHLIGHTS

- A stable and selective monolith catalyst was designed.
- A heterogeneous kinetic model based on a sequential scheme was proposed.
- Unexpected behavior was found for certain parameter values.

GRAPHICAL ABSTRACT
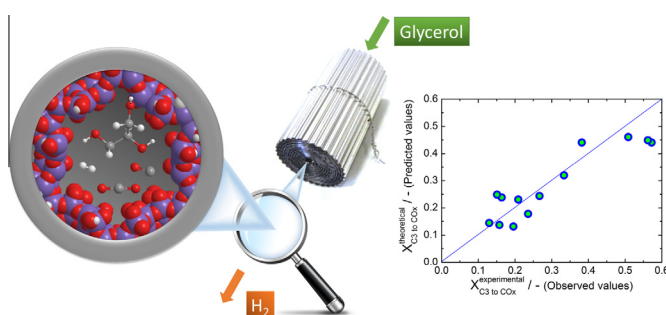
ABSTRACT

In this work, a structured monolithic catalyst has been tested under a wide range of conditions (partial pressure, residence time, temperature and time-on-stream), with the aim of modeling its kinetic behavior and assessing its economic and upscaling potential. We have developed a sequential model to help us interpret both main trends and salient features. Unexpected behavior was found for certain parameter values, which led us to consider kinetic parasitic effects such as mass or heat transfer limitations. By independently invoking these effects, a conciliatory view of the results observed could not be reached. A combined explanation may prove successful, although overfitting could not be ruled out at this point. More importantly, however, the observed salient features of this stable and selective monolith catalyst may hold potential for process intensification of glycerol steam reforming, thus contributing to a more sustainable industry.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, biodiesel has attracted a considerable attention worldwide as an alternative renewable fuel to replace traditional petroleum diesel product because of limited reserves of traditional fossil resources, the instabilities of crude oil price and the concerns over greenhouse gases emissions [1,2]. During the production of biodiesel by catalytic transesterification reaction from vegetable oils or animal fats, a large amount of glycerol is formed as byproduct. As a result of the increased biodiesel production during the last years, a saturated market for glycerol has provoked an expected fall in glycerol prices; therefore, finding effective and economical ways for conversion of glycerol into useful products is necessary. Recent studies have suggested that an attractive idea would be to produce hydrogen from glycerol via catalytic reforming processes, thus adding value to the glycerol surplus [3,4].

Nomenclature

d	monolith external diameter/cm
Ea	activation energy/kJ mol^{-1}
F	molar flow/mol s^{-1}
GHSV	gas hourly space velocity (total flow, 0 °C, 1 atm)/h^{-1}
k	kinetic constant/mol s^{-1} m^{-3} atm^{-1} or mol s^{-1} m^{-3} atm^{-2}
K$_P$	equilibrium constant/-
L	monolith length/cm
p	partial pressure/atm
P	total pressure/atm
r	reaction rate/mol s^{-1} m^{-3}
R	universal gases constant/J mol^{-1} K^{-1}
T	temperature/°C
κ	modified global heat transfer coefficient/cm^{-3}

V	monolith volume/cm^3
Γ	approach to equilibrium/-
τ	space time/s

Subscripts

j	jth component
0	initial
A	lump A
B	lump B
d	thermal decomposition
G	glycerol
r	steam reforming
WGS	water gas shift

Glycerol steam reforming (SR) has been demonstrated to be an effective method for hydrogen production with high selectivity, and it can be performed in gas or aqueous phase depending on the reaction conditions, mainly temperature and pressure [5]. Steam reforming, although highly endothermic, is preferable since the low pressure favours selectivity to hydrogen. Nickel is the most used active metal for glycerol steam reforming because of its good activity for C-C, C-O and C-H bond cleavage, as well as for its ability to remove the adsorbed CO by water gas shift (WGS) reaction [6–17]. In addition to their optimal performance, Ni-based catalysts are preferred due to the low cost and high availability. However, the suppression of coke deposition to enhance catalytic stability still remains a major challenge. Different studies have suggested that the combination of basic promoters (Mg, Ce) and a group IV alloying element such as Sn favors coke-resistance of Ni catalysts in the SR of hydrocarbons [18–21]. Typically these additives help to avoid carbon deposition and enhance their catalytic stability.

In a previous paper [22], we demonstrated that a Ni-based monolith catalyst is very active and stable for hydrogen production by glycerol steam reforming. Coke formation was not observed in the monolith catalyst thanks to the strong interaction between the catalyst particles and the alumina layer in the monolith. The utilization of metallic monolith catalysts in practical applications is very important to control the heat and mass transport properties since the majority of catalytic reactions depend on heat transfer, fluid dynamics, and surface reaction kinetics. In addition to this, metallic monoliths are excellent models for the initial studies of microchannel reactors in which coupled endo- and exothermic reactions are used for controlling the process selectivity [23].

Concerning the reactor modeling, several studies on the kinetics and the reaction mechanism for glycerol steam reforming have been carried out in the last ten years [14,24–27]. However, most of the reported kinetics are based on power-law models and refer to powdered catalysts. To the best of our knowledge, there are only two works published very recently that describe a kinetic model for glycerol steam reforming using a wall-coated catalytic microchannel [28] and a kinetic study of autothermal reforming of glycerol in a dual layer monolith catalyst [29], respectively. Liu et al. found that the reaction rate of glycerol reforming was not limited by mass transfer within the catalyst washcoated layer and the surface reaction was the rate controlling step Langmuir-Hinshelwood kinetics considering non-dissociative adsorption of glycerol and dissociative adsorption of steam were proposed to describe the autothermal reforming of glycerol in this dual layer monolith catalyst [29].

This work involves a detailed study with the aim of understanding the kinetic behavior of the well-performing Ni-based monolith catalyst under a wider range of conditions (partial pressure, residence time, temperature and time-on-stream), looking out for potential upscaling. We anticipate that unusual effects were found in this study, which we attempted to rationalize based on the data at hand and prior knowledge. These results may well deserve additional work, as they hold promise for improved economics at commercial scale.

2. Experimental

2.1. Synthesis of NiSn/CeO$_2$-MgO/Al$_2$O$_3$ catalyst

NiSn/CeO$_2$-MgO/Al$_2$O$_3$ catalyst was prepared by the impregnation method using a synthesis procedure previously reported [19,22]. Spherical pellets of γ-Al$_2$O$_3$ (*Spheralite SCS505*) with 2.5 mm diameter were milled in a high-energy ball mill in order to obtain γ-Al$_2$O$_3$ with a particle size of 7–8 μm, which was used as support to prepare the catalyst used in this study. All the precursors were impregnated simultaneously on the alumina support with an aqueous solution containing appropriate quantities of Mg(NO$_3$)$_2$·6H$_2$O (Sigma-Aldrich), Ce(NO$_3$)$_3$·6H$_2$O (Fluka), Ni(NO$_3$)$_2$·6H$_2$O (Panreac) and SnCl$_2$ anhydrous (Fluka), followed by drying overnight at 120 °C and final calcination in air at 700 °C for 12 h. The nominal metal loading was 26 wt% with a Ni-to-Sn atomic ratio equal to 6.

2.2. Metallic monolith manufacture

Metallic sheets of AluChrom YHf® with 50 μm thickness (Goodfellow) were used as substrates for preparation of the metallic monolith. Cylindrical monoliths were prepared by rolling flat and corrugated foils alternatively around a spindle (L = 30 mm, d = 16 mm, V = 6 cm^3, cell density 170 cells/cm^2), following the steps presented in Fig. 1. This geometry was optimized previously to ensure a more efficient heat and mass transfer [30–32], as will be discussed below. The metallic monolith was thermally pre-treated in air at 900 °C for 22 h in order to generate an adherent α-Al$_2$O$_3$ layer [33]. This treatment ensures a good adherence of the catalyst to the metallic substrate.

2.3. Washcoating process

The first requirement for an effective washcoating process is obtaining stable slurries. In order to achieve a uniform coating of the metallic substrate it is necessary to prepare the slurry controlling the parameters affecting its stability, such as particle size of