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Citation for published version (APA):

Delparish, A., Koc, S., Caglayan, B. S., & Avci, A. K. (2019). Oxidative steam reforming of glycerol to synthesis gas in a microchannel reactor. *Catalysis Today*, 323, 200-208. <https://doi.org/10.1016/j.cattod.2018.03.047>

DOI:

[10.1016/j.cattod.2018.03.047](https://doi.org/10.1016/j.cattod.2018.03.047)

Document status and date:

Published: 15/02/2019

Document Version:

Typeset version in publisher's lay-out, without final page, issue and volume numbers

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Oxidative steam reforming of glycerol to synthesis gas in a microchannel reactor

Amin Delparish^{a,1}, Sinan Koc^a, Burcu Selen Caglayan^b, Ahmet K. Avci^{a,*}

^a Department of Chemical Engineering, Bogazici University, Bebek, 34342, Istanbul, Turkey

^b Advanced Technologies R&D Center, Bogazici University, Bebek, 34342, Istanbul, Turkey

ARTICLE INFO

Keywords:

Glycerol
Synthesis gas
Hydrogen
Microchannel reactor
Rhodium
Oxidative steam reforming

ABSTRACT

Oxidative steam reforming (OSR) of glycerol to synthesis gas (syngas) was studied in a microchannel reactor that involved a thin layer of Rh/Al₂O₃ catalyst coated to the inner wall of a rectangular channel. The effects of reaction temperature (550–700 °C), molar inlet ratios of carbon-to-oxygen (C/O = 0.75, 1.125; C and O: moles of carbon and oxygen atoms at the inlet, respectively) and steam-to-carbon (S/C = 3–5) and microchannel reactor configuration on product distribution and syngas composition were investigated. In all experiments, complete, coke-free conversion of glycerol to gaseous carbon containing species was observed. The only exception was seen at 550 °C and C/O = 1.125 that led to 93% glycerol conversion and solid carbon deposition, the latter being verified by XPS and Raman spectroscopy analyses. Decrease in C/O from 1.125 to 0.75 promoted oxidation of H₂, CO, CH₄, C₂H₄, C₂H₆ and other carbon containing species on the catalyst surface, with the magnitude of promotion being increased notably with temperature. Despite O₂-enriched feeding, Rh remained at metallic state as revealed by XPS characterization of the spent samples. Lowering C/O also elevated yields of CO₂ and steam, the latter which drove water-gas shift (WGS), an important side reaction that affected product distribution on Rh/Al₂O₃ in favor of H₂. Yields of C₁–C₂ hydrocarbons decreased at higher temperatures and at lower C/O and S/C ratios due to their consumption via total oxidation and steam reforming routes, respectively. Microchannel reactor packed with particulate form of catalyst gave yields of CO₂ and H₂ lower and yields of CO and C₁–C₂ hydrocarbons higher than those obtained in the coated configuration under identical conditions. These findings seemed to correlate with the extents of oxidation reactions and WGS, which were believed to vary mainly with different heat transport characteristics of the reactor schemes. H₂/CO ratios close to the ideal value of 1 for Fischer-Tropsch synthesis were obtained at 700 °C, S/C = 3–4 and C/O = 1.125.

1. Introduction

Increasing concerns about global warming caused by the consumption of fossil fuels together with the economic and technical issues regarding their exploration and production have facilitated efforts related to research, development and commercialization of fuels derived from renewable feedstocks. Among a number of such renewable fuels, biodiesel is receiving increased commercial interest due to its properties that make it compatible with the existing diesel engines and allow its direct blending with the conventional diesel fuel [1]. As a result, biodiesel market has been showing an annual growth rate of ~23% since 2005 [2].

Biodiesel is conventionally synthesized via transesterification of animal-based or vegetable oils in the presence of an alcohol (methanol

or ethanol) and a catalyst such as potassium hydroxide [3,4]. This route gives a biodiesel-rich product mixture including ~10% glycerol by weight as a by-product. Considering the increasing demand on and throughput of biodiesel, transesterification stoichiometry causes formation of glycerol in quantities that notably exceed the volumes needed by industry [4]. Unless valorized into value-added chemicals, excess glycerol is expected to have adverse effects on the production cost of biodiesel. In this respect, conversion of glycerol into syngas (H₂ + CO) becomes a promising option as it offers the potential of lowering the dependence on natural gas, the conventional, non-renewable feedstock of syngas [3–5]. Moreover, syngas obtained from glycerol can be converted either into methanol on-site to be used back in biodiesel production or into synthetic hydrocarbons via Fischer-Tropsch (FT) synthesis [3,4].

* Corresponding author.

E-mail address: avciahme@boun.edu.tr (A.K. Avci).

¹ Present address: Laboratory of Chemical Reactor Engineering, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands.

<https://doi.org/10.1016/j.cattod.2018.03.047>

Received 28 January 2018; Received in revised form 20 March 2018; Accepted 25 March 2018
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Owing to the distributed nature of its feedstocks, biodiesel synthesis is usually characterized by decentralized production at small throughputs. Such a production scheme calls for the need of processing units that can be set-up and operated at any location, and can operate with small minimum economic capacities. These requirements are possible by process intensification that allows continuous, profitable operation of the processing units at capacities which conventional counterparts can handle only at excessive production costs [6,7]. Implementation of a structured architecture involving parallel flow paths having characteristic dimensions below $\sim 10^{-3}$ m is a commonly accepted approach for the intensification of two or three phase catalytic reactors [8]. The resulting units, called microchannel reactors, involve a thin ($< \sim 10^{-4}$ m thick), porous layer of catalyst coated to the inner walls of the cylindrical, square or rectangular shaped channels that are precisely machined onto substrates usually made of thermally conductive metals [7–9]. Besides providing a significant volumetric intensification (i.e. surface area-to-volume ratios $\sim 10^2$ m²/m³ higher than those of conventional units), microchannel reactors offer high heat and mass transfer rates allowing efficient utilization of the catalyst bed. Ease of scalability simply by numbering-up the channels in accordance with the desired capacity, possibility of installation into remote production sites (such as offshore oil rigs) and inherent safety due to reduced inventory of reactive species are other benefits of microchannel reactors [8,9].

Attractive characteristics of microchannel reactors are highly compatible with the requirements of glycerol-to-syngas conversion, which involves simultaneous reaction of glycerol, O₂ and H₂O vapor on a catalyst at temperatures above ~ 500 °C via the following overall reaction [3]:

In this route, known as oxidative steam reforming (OSR) or auto-thermal reforming (ATR), syngas composition can be adjusted by regulating the amounts of H₂O and O₂ in the feed. Besides promoting syngas production, presence of O₂ at the inlet also suppresses solid carbon (C_(s)) formation, which can take place via the following possible reactions under conditions of glycerol reforming:

In addition to the formation/removal of C_(s), water-gas shift (WGS - Reaction (6)), oxidation and steam/CO₂ reforming of CH₄ (Reactions (7)–(9), respectively) and of higher hydrocarbons that are produced during the complex network of glycerol breakdown [10] are other reactions that affect product distribution:

As summarized in a number of comprehensive reviews [3,4], studies regarding catalytic OSR/ATR of glycerol in the literature are focused mostly on development and testing of precious (Rh, Ru, Pt, Ir) and non-precious (Ni, Co) metal-based catalysts for obtaining increased glycerol conversions and syngas yields without carbon formation. In the majority of these studies, catalysts in particulate form are randomly packed in tubes to obtain the so-called packed-bed reactor configuration. However, it is known from previous studies that the reactor type,

which dictates the geometric form of the catalyst bed, affects catalytic performance via modified transport rates. For example, comparison of the particulate form of a Ni-based catalyst with its counterpart that is wash-coated on the channels of a metal monolith in the context of CH₄ steam reforming showed that the latter form gave notable increase in catalytic activity due to improved transport rates [11]. Testing of the same reaction on coated and particulate forms of a Rh-based catalyst under identical conditions showed higher volumetric productivity in the former [12,13]. Similar outcomes are reported for non-oxidative and oxidative CH₄ steam reforming on coated and particulate forms of alumina supported Pt, Ni, Rh and Ru catalysts [14–16]. Potential benefits of the structured (i.e. monolith or microchannel) reactors involving wash-coated form of the catalyst for glycerol reforming is addressed only in a limited number of studies. Liu et al. [17] tested monolithic Pt and Rh/Pt catalysts coated as single and double layers, respectively, for glycerol ATR carried out at 300–700 °C, S/C = 0.4–1.5, C/O = 1.67–2.5 and gas hourly space velocity (GHSV) = 1.5×10^4 h⁻¹, and concluded near-complete glycerol conversion and near-equilibrium product concentrations with negligible coking. Similar monolithic configurations were used to ensure transport resistance free investigation of the kinetics of glycerol ATR which was found to have an activation energy of ~ 131 kJ/mol [18]. Liu and Lin [19,20] studied glycerol ATR on coated forms of LaMnO₃ and LaNiO₃ perovskites in monolith reactors and found that the latter favored H₂ production, which was possible on LaMnO₃ by Pt promotion to give $\sim 60\%$ and $\sim 40\%$ selectivity towards H₂ and CO, respectively. Use of structured reactors for glycerol ATR was also studied by Sadykov et al. [21,22]. The authors tested Ni-Ru catalyst integrated to a metallic substrate with high thermal conductivity, and observed near equilibrium syngas yields with no transport resistances. They also emphasized the importance of optimizing the amount of O₂ in the feed for improving catalyst stability via reduced coking [22]. Oxidative conversion of glycerol in the absence and presence of inlet H₂O vapor was studied at 900–1200 °C and C/O = 0.8–1.6 in a different catalyst geometry dictated by α -Al₂O₃ foam on which Rh-Ce/ γ -Al₂O₃ was wash-coated [23]. The findings showed selectivities up to $\sim 80\%$ for CO and $\sim 56\%$ for H₂, the latter which increased up to 79% upon addition of H₂O vapor into the feed to obtain S/C = 4.5. The possibility of adjusting syngas composition via respective amounts of H₂O vapor and O₂ at the inlet was also reported by Rennard et al. [24] on similar foam structures coated with Pt. Koc and Avci [25] studied glycerol reforming in the absence and presence of O₂ in the feed on Ni/Al₂O₃ coated to FeCrAlY substrates. Although it was loaded with less catalyst and run at contact times in the order of 10^{-2} s, the resulting microchannel reactor delivered catalyst productivities that were significantly higher than those obtained in a packed-bed reactor. Moreover, in accordance with the previous findings [17,22,24], O₂ in the feed helped regulating coke formation and product distribution. Similarly, Bobadilla et al. [26,27] reported superiority of Ni-based metallic monoliths in terms of highly active and stable H₂ production by glycerol steam reforming. The authors emphasized that strong interaction between the catalyst particles and the washcoated alumina layer improved functionality of the monolithic catalyst.

Owing to the benefits of structured reactors and catalyst geometries on glycerol reforming, the present work aims to carry out parametric investigation of glycerol OSR run in a microchannel reactor with a coated or packed bed of Rh/Al₂O₃ catalyst. In this context, the effects of reaction temperature, molar inlet C/O (atomic carbon/atomic oxygen) and S/C (steam/atomic carbon) ratios on glycerol conversion and product yields are studied. Moreover, configuration of the microchannel reactor is investigated as an additional parameter for its possible impacts on the response of the catalyst. In addition to the activity tests, X-ray Photoelectron Spectroscopy and Raman Spectroscopy characterizations of the fresh (i.e. reduced) and 5 h spent Rh/Al₂O₃ catalysts are carried out to provide insight into the possible changes on the catalyst surface driven by different reaction temperatures and O₂

amounts in the feed.

2. Experimental

2.1. Catalyst synthesis and the microchannel reactors

2 wt.% Rh/Al₂O₃ catalysts were prepared using incipient-to-wetness impregnation method. The support was chosen as δ -Al₂O₃ as it was capable of providing both high surface area (82 m²/g) and high thermal stability [28]. To prepare the support, γ -Al₂O₃ was dried at 150 °C for 120 min and calcined at 900 °C for 240 min. Rh precursor (Rh(NO₃)₃, Sigma-Aldrich) was impregnated over the support by a MasterFlex computerized-drive peristaltic pump under vacuum conditions to obtain a homogeneous slurry of catalyst. The resulting slurry was mixed ultrasonically for 90 min under vacuum, dried in an oven at 120 °C for 960 min, and consequently calcined in a muffle furnace under air at 600 °C for 180 min. The catalysts were applied to glycerol reforming in the context of coated and packed microchannel reactor configurations. Other than the particle size of alumina support, preparation procedures of the Rh/Al₂O₃ catalysts used in different reactor configurations were the same. Alumina (γ -Al₂O₃, Alfa Aesar, purity: 99%) with particle size of 3×10^{-6} m was used in the preparation of the catalyst involved in the coated configuration. While, to avoid pressure drop in the packed scheme, catalyst preparation was started with γ -Al₂O₃ having a particle diameter (d_p) range of 180–255 $\times 10^{-6}$ m, which was shown to be free of intraparticle diffusion limitations in the previous studies [28].

FeCrAl plates (Goodfellow Cambridge Ltd.) with dimensions of 2×10^{-3} m $\times$ 5×10^{-3} m $\times$ 2×10^{-2} m, were heat-treated in a muffle furnace under air at 900 °C for 120 min to enhance the adhesion of the coated plates by forming a native alumina layer on the plates [29,30]. The plates were then rasped carefully on their edges, coated with Rh/Al₂O₃ and fit into the cylindrical housing to obtain a catalytic microchannel with of dimensions of 7.5×10^{-4} m (H) $\times$ 4×10^{-3} m (W) $\times$ 2×10^{-2} m (L) (Fig. 1a and b). The 310-grade stainless steel cylindrical housing having a diameter of 1.9×10^{-2} m and a length of 3.0×10^{-2} m was manufactured by wire electro discharge machining (EDM) technique. Integration of the catalyst with the FeCrAl plate involved blade coating of the slurry with water-to-catalyst powder ratio of 5:1 to reach 35–40 mg of slurry per cm² of plate surface. The coated plate was then dried at 120 °C for 960 min and calcined in a muffle furnace under air at 600 °C for 180 min, resulting in a mechanically stable catalytic layer with mass and thickness of ~ 20 mg and $\sim 5 \times 10^{-5}$ m, respectively (Fig. 1a). To configure the packed microchannel shown in Fig. 1c, heat-treated, but uncoated plate was first inserted into the housing. The resulting channel was filled with 20 mg of Rh/Al₂O₃ which was diluted and mixed with δ -Al₂O₃ to obtain a bed height ($L = 2 \times 10^{-2}$ m) to particle diameter ratio (between 78 and 111, based on the d_p range) sufficient to exceed the criterion (L/d_p

$d_p > 50$) for minimizing axial dispersion effects [8].

2.2. Reaction tests and characterization studies

Glycerol OSR experiments were conducted at atmospheric pressure in a down-flow 2×10^{-2} m ID and 8×10^{-1} m long cylindrical quartz reactor tube in which the housing, either with coated or particulate catalyst, was placed (Fig. 1b and c, respectively). Coated plate or packed catalyst/diluent mixture was immobilized by quartz wool packing on both ends of the microchannel. The housing and quartz reactor tube were designed such that the annulus-shaped gap between the housing and tube was blocked after expansion of the housing at reaction temperatures, minimizing the flow of any bypass stream [14–16]. Quartz tube also involved a ring at its midpoint, which was used to support the housing and ensure its stationary position. In addition, physical overlap between the quartz ring and the housing closed the path for the slip of any bypass flow [14–16]. The tube, with the catalyst loaded microchannel, was placed inside a furnace (Protherm PZF 12/50/500) with three zones, each of which was PID controlled to ± 1.0 °C via K-type thermocouples and was finally connected to the upstream and downstream sections which involved equipments for precisely controlled gas/liquid feeding and product analysis, respectively.

The experiments were aimed to investigate the effects of temperature (550–700 °C), steam-to-carbon ratio ($S/C = 3$ –5) and carbon-to-oxygen ratio ($C/O = 0.75$ and 1.125) at a weight-hourly space velocity (WHSV) of 4.8×10^3 NmL/g_{cat} min. In all experiments, inlet flow rate of glycerol vapor and total inlet flow rate were set at 3 and 96 NmL/min, respectively. Default values of S/C and C/O were 5 and 1.125, respectively, and changed only at time of studying their individual effects. Prior to the reaction tests, 40 NmL/min H₂ flow was passed over the catalyst at 800 °C for 120 min to ensure reduction of the active phase to its metallic state. A Shimadzu LC-20AD HPLC pump was utilized to feed the deionized water and glycerol (Sigma-Aldrich, 99.5%) mixture into the reaction system with constant and pulse-free flow. The gaseous species, N₂ (used as make-up gas), O₂ and H₂ (all supplied by Linde with purities above 99.99%), were carried separately from pressurized storage cylinders to the system by Bronkhorst F-201CV series digital mass flow controllers. The feed which was composed of the gaseous species (O₂ and N₂) and liquid glycerol-water mixture was directly sprayed into the quartz reactor tube located within the three-zone furnace by means of a 1/16 in. OD 316 stainless steel injection tubing. In order to ensure complete evaporation of glycerol and water upon their spraying, tip of the injection tubing was located in the middle of the first zone which was controlled to 310 °C. Each of the zones were 0.2 m long and the quartz tube was positioned such that the catalyst loaded housing would be in the middle of the second zone which was controlled to the pertinent reaction temperature.

Fig. 1. (a) Top views of the blank stainless steel housing manufactured by EDM and the FeCrAl plate coated with Rh/Al₂O₃ catalyst, (b) coated configuration obtained by insertion of the catalyst coated plate into the housing, (c) packed configuration obtained by placing catalyst and inert particles into the empty microchannel generated upon insertion of the uncoated plate into the housing.

Fig. 2. XP spectra of Rh 3d region for fresh (reduced) and spent catalyst samples tested at different reaction temperatures with a feed mixture involving C/O equal to (a) 0.75 and (b) 1.125 (S/C = 5, WHSV = 4.8×10^3 NmL/g_{cat} min).

Temperature of the first zone was controlled to 310 °C to prevent condensation on the walls of quartz tube. The product stream leaving the reactor was passed through two cold traps for the removal of condensable species (e.g. steam and, if exists, unconverted glycerol). After the cold traps, species remaining in the gas phase were directed to two on-line gas chromatography (GC) units connected in parallel. N₂, H₂, CO and CH₄ were detected and analyzed by a Shimadzu GC-2014 unit equipped with a Molecular Sieve 5A packed column and a thermal conductivity detector (TCD) involving 25 NmL/min Ar (Linde, purity > 99.99%) carrier gas flow. Amounts of CO₂, C₂H₄ and C₂H₆, together with N₂ and CH₄ were quantified by a Shimadzu GC-8A unit, equipped with a 80–100 mesh size Porapak Q packed column and a TCD involving 25 NmL/min He (Linde, purity > 99.99%) carrier gas flow. Sample injection to both GC units was realized by gas sampling valves, each of which was equipped with a 1 mL sample loop. Product sampling and analysis were started 30 min after the onset of the reaction, and continued periodically at every 45 min. The results reported in Section 3 were based on the arithmetic average of the results of product analysis carried out between 120th and 300th min of the experiments where the reaction continued in a steady pattern. Despite the presence of oxidative conditions, exothermic temperature rise was not observed and isothermal conditions were satisfied in the tests due to small reactant flow rates and catalyst loadings, and presence of metallic housing that helped in immediate suppression of any possible hot-spots. This behavior was in alignment with the previous studies that involved similar catalytic microchannel reactor configurations for oxidative conversion of methane [16,31]. Moreover, in both coated and packed microchannel configurations pressure drop remained negligible, which was confirmed by the pulse-free flow of the reactor effluent stream that was monitored by means of a soap-bubble meter. In addition to the catalytic experiments, additional tests without catalysts were carried out to provide insight into the significance of any homogeneous reactions. The so-called blank experiments were conducted at C/O = 1.125, S/C = 3, 5, and at 700 °C, the highest temperature in the experimental plan, to magnify the impact of non-catalytic phenomena on glycerol conversion and product distribution. The experimental setup, whose capability of reproducing the results was demonstrated previously for microchannel enabled methane steam reforming [14], delivered a high

degree of repeatability (< ~2% difference between the successive measurements) under glycerol OSR conditions.

Eqs. (10) and (11) defined glycerol conversion and product yield, both of which were used as metrics for monitoring catalytic performance:

$$\text{Glycerol conversion} = 100 \times (\text{moles of carbon in gaseous products} / (3 \times \text{moles of glycerol in the feed})) \quad (10)$$

$$\text{Yield of product } i = \text{moles of species } i \text{ in gaseous products} / \text{moles of glycerol fed} \quad (11)$$

Glycerol conversion was calculated on dry basis via carbon containing species in the gaseous product stream detected via GC analysis (CO, CO₂, CH₄, C₂H₄ and C₂H₆). Thermodynamic analysis calculations carried out under the reaction conditions predicted that generation of other hydrocarbons were highly suppressed and their total molar composition remained below 1% [25]. Therefore, hydrocarbons other than CH₄, C₂H₄ and C₂H₆ were ignored in the formulation of Eq. (10). Moreover, C_(s) species, whose formation was assumed to be unlikely under OSR conditions, were not considered in the formulation of Eq. (10).

In addition to the microreactor tests, samples of reduced Rh/Al₂O₃ before the reaction and after testing at C/O = 0.75 and 1.125 under the complete temperature range (550, 600, 650 and 700 °C) were comparatively analyzed by X-ray Photoelectron Spectroscopy (XPS) by using Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer. All binding energies were referenced to the 484.8 eV C1s line. Data analysis was performed by Thermo Advantage software; the peak intensities were estimated by calculating the integral of each peak, after subtraction of the S-shaped Shirley-type background, and by fitting the curve to a combination of Lorentzian (30%) and Gaussian (70%) lines. Spent catalyst samples highlighted by XPS for possible existence of C_(s) species were further analyzed by Raman spectroscopy via a Renishaw inVia Raman microscope with the following operation parameters: 532 nm 100 mW diode laser as the excitation source; laser intensity of ~5 mW; 10 s acquisition time; a total of 5 accumulations per spectrum. Before measurements, Raman spectrum was calibrated by using a silicon wafer peak at 520 cm⁻¹. All the samples were analyzed under atmospheric

condition without pre-treatment with the defocusing technique.

3. Results and discussion

3.1. Catalyst characterization

The surface state of Rh species was investigated performing deconvolution analysis to Rh 3d XP spectra of the freshly reduced and spent catalyst samples. The two peaks appeared in the Rh 3d spectra of all the studied catalyst samples shown in Fig. 2 at around 307.3 and 312 eV, separated by 4.7 eV, were attributed to the Rh 3d_{5/2} and Rh 3d_{3/2} spin-orbit components, respectively, of the Rh⁰ phase, that indicated the metallic nature of the catalyst surface [32–34].

XPS analysis was also used to understand the possible existence of C_(s) species on the spent catalyst samples. The Rh 3d spectrum of the catalyst sample tested at 550 °C with C/O = 1.125 was found to have lower intensity and was slightly shifted to higher binding energies compared to the Rh 3d spectra of other spent samples. In order to interpret this observation, which could be attributed to possible coke deposition on the surface of the catalyst tested at 550 °C with C/O = 1.125, deconvolution analysis was carried out on the general spectra of the spent catalyst samples to predict percentage of the carbon containing species on the catalyst surface. The results, presented in Fig. 3, revealed negligible existence of carbon containing species on the surface of all samples except the one spent at 550 °C and C/O = 1.125. Considering that this condition was the only one that caused incomplete (93%) glycerol conversion (Section 3.2), the related sample was further investigated by Raman spectroscopy for the structural analysis of the catalyst surface. Raman spectrum given in Fig. 4 confirmed presence of C_(s) species, showed a D band, associated with the disordered structural mode of crystalline carbon species, and a G band, corresponded to the graphitic carbon with high degree of symmetry, at around 1350 and 1580 cm⁻¹, respectively. The relative intensity/area of D and G bands (I_D/I_G) gave information about the degree of crystallinity and was very useful while characterizing coke since the average coke crystallite size (L_a) could be calculated based on Tuinstra–Koenig correlation, L_a (nm) = k/(I_D/I_G), where constant k is 4.4 nm [35,36]. The estimated (I_D/I_G) and L_a values were 1.2 and 3.6 nm, respectively. In addition to these two peaks, another one centered at 1450 cm⁻¹, was detected (Fig. 4). This peak could possibly be attributed to a statistical distribution of amorphous carbon on the interstitial position of the graphitic islands [37] and to structural defects of the clusters [35,36]. Apart from the specific behavior noted at 550 °C and C/O = 1.125, the findings presented in Figs. 2 and 3 together with the Raman spectroscopy analyses carried out for the rest of the spent samples confirmed the validity of the assumption of neglecting formation of C_(s) species under oxidative conditions.

Fig. 3. Percentage of carbon containing species on the surface of the spent catalyst samples tested at different reaction temperatures with a feed mixture involving C/O equal to (a) 0.75 and (b) 1.125 (S/C = 5, WHSV = 4.8×10^3 NmL/g_{cat} min).

Fig. 4. Raman spectrum of the spent catalyst sample tested at 550 °C and C/O = 1.125 (S/C = 5, WHSV = 4.8×10^3 NmL/g_{cat} min).

3.2. Effect of temperature and C/O

The effects of reaction temperature and O₂ concentration in the feed mixture were studied by carrying out experiments at 550, 600, 650 and 700 °C with inlet C/O ratios of 0.75 and 1.125 at each temperature. During these studies, S/C and WHSV were kept constant at 5 and 4.8×10^3 NmL/g_{cat} min, respectively.

In all experiments, complete conversion of glycerol into gaseous carbon containing species (Eq. (10)) was observed. The only exception was noted at 550 °C and C/O = 1.125 that gave glycerol conversion of 93%. These findings were related to the degree of oxidation of C_(s) species that formed during thermally induced breakdown of glycerol. In contrast with their existence on Rh/Al₂O₃ surface at 550 °C and C/O = 1.125, C_(s) species were completely oxidized into carbon oxides (i.e. CO and CO₂) in the rest of the experiments. This argument was confirmed by Raman and XPS analyses, both of which also pointed out deposition of C_(s) species only at 550 °C and C/O = 1.125 (Section 3.1).

Dependence of the yields of products of glycerol OSR on C/O at 550, 600, 650 and 700 °C was presented in Fig. 5a–d. Regardless of the reaction temperature, yield of CO₂ increased whereas those of H₂, CH₄, C₂H₄ and C₂H₆ decreased upon changing C/O from 1.125 to 0.75. The same change also caused reduction in the percentage of carbon containing species on the catalyst surface at all temperatures predicted by the XPS analysis (Fig. 3). Considering that CO₂ was a primary product of total oxidation, increased amounts of inlet O₂ seemed to promote oxidative conversion of H₂, C₁–C₂ hydrocarbons and other carbon containing surface species. Possibility of this route became stronger by the inherently high activity of Rh/Al₂O₃ towards total oxidation of light hydrocarbons that was reported in previous studies [31,38].

Changes in product yields with temperature were found to follow patterns that somewhat depended on C/O ratio. At C/O = 0.75, yields of H₂ and CO₂ decreased upon increasing temperature from 550 to 600 °C. An opposite trend, however, was observed for both species in the range of 600–700 °C, with the increase first being limited to 0.12 mol/mol glycerol fed between 600 and 650 °C, and then became significant (i.e. 0.67 mol H₂ and 0.92 mol CO₂ per mol glycerol fed) above 650 °C (Fig. 5a–d). Temperature response of CO yield was found to be just the opposite of those of H₂ and CO₂ in terms of trend, but similar to them in terms of numerical difference. These findings pointed

Fig. 5. Product yields obtained with feed mixtures involving C/O = 0.75 and 1.125 at reaction temperatures of (a) 550 °C, (b) 600 °C, (c) 650 °C and (d) 700 °C (S/C = 5, WHSV = 4.8×10^3 NmL/g_{cat} min).

out the impact of WGS (Reaction (6)) in differing characteristics. Product distribution between 550 and 600 °C seemed to be dictated by reverse WGS, which is endothermic and thermodynamically favored with temperature. However, between 600 and 650 °C, promotion of WGS was likely to occur as a result of additional steam supply from oxidation of some of the H₂ present in the reaction medium. The resulting steam, together with its supply at the inlet, was believed to overcome the opposing thermodynamic effect of temperature. This argument was supported by the fact that at lower concentrations of inlet O₂ (i.e. at lower extent of oxidation at C/O = 1.125 that produced less steam) product yields remained almost unchanged in the range of 600–650 °C.

The role of oxidation of H₂, together with CO, CH₄ and other combustible species became more significant above 650 °C. This argument could be supported by comparing changes in the product yields in the 650–700 °C range for two different C/O values. At C/O = 1.125, changes in the yields of H₂, CO₂ and CO were determined as 0.85, 0.76 and -0.71 mol/mol glycerol fed, respectively, upon 50 °C increase in temperature. The responses were measured to be 0.67, 0.92 and -0.85 for H₂, CO₂ and CO, respectively at C/O = 0.75 (Fig. 5a–d). Higher changes in CO and CO₂ yields and limited increase in H₂ yield at C/O = 0.75 pointed out oxidation of CO and H₂ into CO₂. In addition, changes in CH₄ yield (-0.05 and -0.03 moles/mol glycerol fed at C/O = 0.75 and 1.125, respectively) in the same temperature range also indicated promotion of CH₄ removal in O₂-rich conditions. Besides oxidation, WGS and hydrocarbon reforming induced by the steam generated via oxidation were the other possible routes that simultaneously shaped up product distribution above 650 °C.

In addition to the catalytic experiments, complete glycerol conversion was also obtained in the blank test carried out at 700 °C. Even though this observation suggested that conversion occurred via homogeneous reactions, the use of catalyst caused substantial changes in product yields (Fig. 5d). The results clearly showed that in the presence of Rh/Al₂O₃, yields of H₂ and CO₂ were higher but that of CO was lower than the counterparts measured in the absence of the catalyst. These trends were in good accordance with the stoichiometry of WGS (Reaction (6)), which acted as a catalytic side reaction. Such a particular effect of catalyst on product mixture in glycerol reforming was also reported in the literature [25,26]. Comparison of the blank and

catalytic tests also showed that yield of CH₄ decreased on Rh/Al₂O₃ (Fig. 5d). In other words, CH₄ that formed during breakdown of glycerol [10,39] was decomposed catalytically most likely via its oxidation and steam reforming (Reactions (7) and (8), respectively), as Rh/Al₂O₃ was reported to be highly active for both reactions [38,40]. Reforming of CH₄ with CO₂ (Reaction (9)), on the other hand, was not taken into account as its rate was reported to be notably smaller than that of Reaction (8) in the presence of steam in the feed [41]. These arguments were also valid for interpreting the changes in the yields of C₂H₄ and C₂H₆ measured upon use of catalyst.

3.3. Effect of S/C

In order to investigate the effect of amount of steam in the feed, experiments were conducted in the S/C range of 3–5 at two different temperatures, namely 550 °C and 700 °C. In all experiments C/O and WHSV were kept constant at 1.125 and 4.8×10^3 NmL/g_{cat} min, respectively.

The results presented in Fig. 6a and b showed that, at both temperatures yields of H₂ and CO₂ increased, whereas those of CO decreased upon changing S/C from 3 to 5. As mentioned in Section 3.2 this trend could be attributed to WGS (Reaction (6)) which was thermodynamically and kinetically favored at higher amounts of inlet steam to transform CO into H₂ and CO₂. Significance of WGS could also be observed from the comparison of the outcomes of blank and catalytic tests carried out at 700 °C and S/C = 3 (Fig. 6b). As the comparison was carried out at the lowest S/C, it could be expected that the impact of WGS would be more pronounced at higher concentrations of steam in the feed. In all of the experiments including the blank test, complete glycerol conversion was obtained. It could therefore be stated that the catalyst did not affect conversion but changed the product distribution in favor of H₂.

Changes in the yield of CH₄ provided some insight into the possible side reactions running during OSR. The results presented in Fig. 6b also revealed positive correlation of CH₄ yield with S/C at 700 °C. Considering the fact that C/O remained constant, slightly higher CH₄ yields detected under steam-rich conditions could possibly be explained by limited inhibition of Reaction (8) with steam. This argument was in alignment with the previous outcomes that confirmed limited impact of

Fig. 6. Product yields obtained with feed mixtures involving S/C = 3, 4 and 5 at reaction temperatures of (a) 550 °C and (b) 700 °C (C/O = 1.125, WHSV = 4.8×10^3 NmL/g_{cat} min).

partial pressure of steam on the rate of CH₄ steam reforming on Rh-based catalysts [42,43]. Limited and non-monotonic effects of steam concentration on the rate of CH₄ steam reforming were also reported for Ni-based catalysts in the literature [44]. In contrast with the trend at 700 °C, CH₄ yield remained almost unaffected by S/C at 550 °C (Fig. 6a). The magnified impact of steam at 700 °C could therefore be used as another evidence pointing out a kinetic effect.

Responses of the yields of carbon oxides against changes in S/C were found to depend on temperature. For example, CO₂ yield increased by ~31% and ~52%, whereas CO yield decreased by ~19% and ~25% upon increasing S/C from 3 to 5 at 550 °C and 700 °C, respectively (Fig. 6a and b). This trend might be explained by the increased extent of oxidation of the carbon containing species on catalyst surface into CO with temperature, and the post conversion of the resulting CO into CO₂ by WGS that was promoted with S/C as discussed above. This possible route might have been accompanied either by the oxidation of the surface species directly into CO₂ or by their gasification with steam. Regardless of the route, promotion of removal of carbon containing surface species with temperature was confirmed by the outcomes of XPS analyses (Fig. 3). Even though the final status of all scenarios involved co-production of CO₂ and H₂, changes in H₂ yield against S/C were found to be almost the same at both temperatures (i.e. ~26% and ~23% at 550 °C and 700 °C, respectively), which were in contrast with the responses of CO₂ production. This outcome might be explained by the consumption of some of the H₂ via oxidation. Once produced, CO₂ stayed in the product mixture, as reverse WGS was suppressed and dry reforming could provide only negligible conversion of CO₂ under steam-rich conditions [41].

3.4. Effect of microchannel reactor configuration

In order to investigate the possible effects of microchannel reactor configuration on product distribution, comparative experiments were carried out on coated and packed microchannel geometries at 550 and 700 °C (Fig. 7a and b, respectively). In all experiments C/O, S/C and WHSV were kept constant at 1.125, 5 and 4.8×10^3 NmL/g_{cat} min,

respectively.

The results showed that at both temperatures, yields of H₂ and CO₂ obtained for coated configuration were notably higher than those measured for the packed one, which favored existence of CO and C₁-C₂ hydrocarbons in the product mixture (Fig. 7a and b). Moreover, changes in the yields obtained in different configurations became magnified with temperature. At 700 °C, yields of H₂ and CO₂ increased by 0.83 and 0.37 mol/mol glycerol fed, respectively, upon the use of coated microchannel (Fig. 7b). However, the changes measured at 550 °C against reactor configuration were 0.42 and 0.27 mol/mol glycerol fed for H₂ and CO₂, respectively (Fig. 7a). Similar changes in trends were observed also for CH₄, C₂H₄ and C₂H₆. These findings could be related to the improved heat transfer rates offered by the coated microchannel reactors [11–16]. Due to its direct contact with the Fe-CrAl plate, heat transport on the thin ($< 10^{-4}$ m thick) catalyst layer was inherently fast that favored its effective utilization via uniform temperature distribution. This characteristic feature was thought to be responsible for increasing the extent of catalytic oxidation of C₁-C₂ hydrocarbons into CO₂ and H₂O, the latter which, together with the inlet steam, promoted WGS to elevate H₂ yield. On the other hand, inherently low heat transfer rates associated with the presence of voids within the bed of catalyst and diluent particles [15,16], seemed to suppress oxidation and subsequent yields of H₂ and CO₂ in packed microchannel configuration. As the differences between the reactor specific heat transport rates got reduced with temperature, reactor type turned out to have less impact on product yields obtained at 550 °C (Fig. 7a).

3.5. Syngas composition

The effect of S/C on syngas composition (H₂/CO ratio) was presented in Fig. 8a. H₂/CO ratio increased with both S/C and temperature. Moreover, setting OSR conditions to 700 °C and S/C = 3–4 was found to deliver H₂/CO = 0.9–1.2, which was very close to 1, the ideal syngas composition for FT synthesis [45]. This finding also demonstrated the possibility of syngas manufacturing with lower requirements

Fig. 7. Product yields obtained in coated and packed microchannel reactor configurations at (a) 550 °C and (b) 700 °C (S/C = 5, C/O = 1.125, WHSV = 4.8×10^3 NmL/g_{cat} min).

Fig. 8. Synthesis gas composition obtained as functions of (a) S/C at 550 and 700 °C, and (b) C/O at 550, 600, 650 and 700 °C.

of inlet steam, whose production calls for the need of high energy inputs and operating expenses. Upon further increase of S/C to 5, product mixture became more abundant with H₂ (i.e. H₂/CO ~ 1.5), which was desired for fuel cell applications [46]. The clear trends demonstrated in Fig. 8a showed that product stream was tunable towards desired H₂/CO ratio, which could be achieved by suitably setting the conditions including temperature, S/C and C/O.

The effect of amount of O₂ in the feed on H₂/CO ratio was shown in Fig. 8b. Syngas compositions resulting from a feed stream with C/O = 1.125 exceeded those obtained with C/O = 0.75 at all temperatures due to the particular dependency of H₂ and CO yields on inlet O₂ quantity and temperature as explained in Section 3.2. In addition to tuning S/C, keeping it at 5 but setting C/O = 0.75 also delivered a near ideal syngas ratio of 1.1 at 700 °C (Fig. 8b). However, this option would require higher amounts of inlet steam and O₂, and eventually increase the cost of syngas production due to the high costs associated with air separation. Moreover, at larger scales, intense O₂ feeding would elevate concerns and related measures regarding process safety and equipment maintenance, as they become more susceptible to corrosion in O₂-rich atmospheres. Consequently, tuning C/O at 1.125 and S/C between 3 and 4 at 700 °C seemed promising for obtaining syngas from glycerol OSR at H₂/CO ~ 1 with reduced CO₂ content and operating expenses.

4. Conclusions

The aim of this study was to carry out parametric investigation of syngas production by glycerol OSR in a Rh/Al₂O₃ coated microchannel reactor. The effects of feed composition, reaction temperature and microchannel reactor configuration were investigated. Glycerol was consumed completely in all conditions except at 550 °C, C/O = 1.125 and S/C = 5, at which conversion was observed to be 93%. XPS and Raman spectroscopy characterization of the spent catalyst samples indicated coke deposition at the condition that gave incomplete conversion, whereas no coking was detected in the rest of the operating conditions. XPS analysis of the fresh and spent samples also showed that Rh remained at reduced state under all conditions. Temperature affected product distribution via increasing the extent of oxidation of combustible species in the product mixture. This effect became more pronounced when C/O was reduced from 1.125 to 0.75. WGS, whose existence was negligible in the blank tests but became significant in the presence of Rh/Al₂O₃, played important role in elevating yields of H₂ and CO₂ due to the additional steam formation via total oxidation at higher temperatures and lower C/O ratios. Promotion of WGS in the presence of steam was verified by reducing S/C from 5 to 4 and from 4 to 3, both of which led to monotonically decreasing yields of H₂ and CO₂, and increasing yield of CO. Amounts of CH₄, C₂H₄ and C₂H₆ in the product mixture were reduced by increasing temperature and decreasing S/C and C/O ratios, all of which led to their consumption via

total oxidation and steam reforming reactions. Tuning the glycerol OSR conditions to 700 °C, S/C = 3–4 and C/O = 1.125 delivered syngas with H₂/CO = 0.9–1.2, which was compatible with FT synthesis conditions. Evolution of the desired syngas specifications at lower requirements of steam and oxygen, both of which necessitate high manufacturing costs, was noted as an additional benefit. Apart from operating conditions, configuration of the microchannel reactor affected product distribution. Under identical conditions, microchannel reactor packed with particulate form of catalyst gave yields of CO₂ and H₂ lower and yields of CO and C₁–C₂ hydrocarbons higher than those obtained in the coated configuration. These findings seemed to correlate with the extents of oxidation reactions and WGS, which were thought to depend mainly on the heat transfer rates associated with the particular reactor scheme.

Acknowledgements

This work was supported by TUBITAK [grant numbers 113M962 and 117M163] and by Bogazici University Research Fund [grant number 13880].

References

- [1] J.V. Gerpen, Biodiesel processing and production, *Fuel Process. Technol.* 86 (2005) 1097–1107.
- [2] R.L. Naylor, M.M. Higgins, The political economy of biodiesel in an era of low oil prices, *Renew. Sust. Energ. Rev.* 77 (2017) 695–705.
- [3] Y.-C. Lin, Catalytic valorization of glycerol to hydrogen and syngas, *Int. J. Hydrogen Energy* 38 (2013) 2678–2700.
- [4] C.A. Schwengber, H.J. Alves, R.A. Schaffner, F.A. da Silva, R. Sequinel, V.R. Bach, R.J. Ferracin, Overview of glycerol reforming for hydrogen production, *Renew. Sust. Energ. Rev.* 58 (2016) 259–266.
- [5] J.M. Silva, M.A. Soria, L.M. Madeira, Challenges and strategies for optimization of glycerol steam reforming process, *Renew. Sust. Energ. Rev.* 42 (2015) 1187–1213.
- [6] J.B. Powell, Application of multiphase reaction engineering and process intensification to the challenges of sustainable future energy and chemicals, *Chem. Eng. Sci.* 157 (2017) 15–25.
- [7] A. Delparish, A.K. Avci, Intensified catalytic reactors for Fischer-Tropsch synthesis and for reforming of renewable fuels to hydrogen and synthesis gas, *Fuel Process. Technol.* 151 (2016) 72–100.
- [8] Z.I. Onsan, A.K. Avci, *Multiphase Catalytic Reactors: Theory, Design, Manufacturing, and Applications*, Wiley, Hoboken, New Jersey, 2016.
- [9] G. Kolb, Review: Microstructured reactors for distributed and renewable production of fuels and electrical energy, *Chem. Eng. Process. Process Intensif.* 65 (2013) 1–44.
- [10] T. Valliyappan, N.N. Bakhshi, A.K. Dalai, Pyrolysis of glycerol for the production of hydrogen or syn gas, *Bioresour. Technol.* 99 (2008) 4476–4483.
- [11] J.-H. Ryu, K.-Y. Lee, H. La, H.-J. Kim, J.-I. Yang, H. Jung, Ni catalyst wash-coated on metal monolith with enhanced heat-transfer capability for steam reforming, *J. Power Sources* 171 (2007) 499–505.
- [12] A.Y. Tonkovich, S. Perry, Y. Wang, D. Qiu, T. LaPlante, W.A. Rogers, Microchannel process technology for compact methane steam reforming, *Chem. Eng. Sci.* 59 (2004) 4819–4824.
- [13] Y. Wang, Y.H. Chin, R.T. Rozmiarek, B.R. Johnson, Y. Gao, J. Watson, A.Y.L. Tonkovich, D.P. Vander Wiel, Highly active and stable Rh/MgOAl₂O₃ catalysts for methane steam reforming, *Catal. Today* 98 (2004) 575–581.
- [14] M. Karakaya, S. Keskin, A.K. Avci, Parametric study of methane steam reforming to

- syngas in a catalytic microchannel reactor, *Appl. Catal. A Gen.* 411 (2012) 114–122.
- [15] E. Simsek, A.K. Avci, Z.I. Onsan, Investigation of catalyst performance and micro-structured reactor configuration for syngas production by methane steam reforming, *Catal. Today* 178 (2011) 157–163.
 - [16] E. Simsek, M. Karakaya, A.K. Avci, Z.I. Onsan, Oxidative steam reforming of methane to synthesis gas in microchannel reactors, *Int. J. Hydrogen Energy* 38 (2013) 870–878.
 - [17] Y. Liu, R. Farrauto, A. Lawal, Autothermal reforming of glycerol in a dual layer monolith catalyst, *Chem. Eng. Sci.* 89 (2013) 31–39.
 - [18] Y. Liu, A. Lawal, Kinetic study of autothermal reforming of glycerol in a dual layer monolith catalyst, *Chem. Eng. Process. Process Intensif.* 95 (2015) 276–283.
 - [19] S.-K. Liu, Y.-C. Lin, Autothermal partial oxidation of glycerol to syngas over Pt-, LaMnO₃-, and Pt/LaMnO₃-coated monoliths, *Ind. Eng. Chem. Res.* 51 (2012) 16278–16287.
 - [20] S.-K. Liu, Y.-C. Lin, Generation of syngas through autothermal partial oxidation of glycerol over LaMnO₃- and LaNiO₃-coated monoliths, *Catal. Today* 237 (2014) 62–70.
 - [21] V. Sadykov, N. Mezentseva, Y. Fedorova, A. Lukashevich, V. Pelipenko, V. Kuzmin, M. Simonov, A. Ishchenko, Z. Vostrikov, L. Bobrova, E. Sadoyskaya, V. Muzykantov, A. Zadesenets, O. Smorygo, A.C. Roger, K. Parkhomenko, Structured catalysts for steam/autothermal reforming of biofuels on heat-conducting substrates: Design and performance, *Catal. Today* 251 (2015) 19–27.
 - [22] V. Sadykov, N. Mezentseva, M. Simonov, E. Smal, M. Arapova, S. Pavlova, Y. Fedorova, O. Chub, L. Bobrova, V. Kuzmin, A. Ishchenko, T. Krieger, A.C. Roger, K. Parkhomenko, C. Mirodatos, O. Smorygo, J. Ross, Structured nanocomposite catalysts of biofuels transformation into syngas and hydrogen: Design and performance, *Int. J. Hydrogen Energy* 40 (2015) 7511–7522.
 - [23] P.J. Dauenhauer, J.R. Salge, L.D. Schmidt, Renewable hydrogen by autothermal steam reforming of volatile carbohydrates, *J. Catal.* 244 (2006) 238–247.
 - [24] D.C. Rennard, J.S. Kruger, L.D. Schmidt, Autothermal catalytic partial oxidation of glycerol to syngas and to non-equilibrium products, *ChemSusChem* 2 (2009) 89–98.
 - [25] S. Koc, A.K. Avci, Reforming of glycerol to hydrogen over Ni-based catalysts in a microchannel reactor, *Fuel Process. Technol.* 156 (2017) 357–365.
 - [26] L.F. Bobadilla, A. Álvarez, M.I. Domínguez, F. Romero-Sarria, M.A. Centeno, M. Montes, J.A. Odriozola, Influence of the shape of Ni catalysts in the glycerol steam reforming, *Appl. Catal. B Environ.* 123–124 (2012) 379–390.
 - [27] L.F. Bobadilla, V. Blay, A. Álvarez, M.I. Domínguez, F. Romero-Sarria, M.A. Centeno, J.A. Odriozola, Intensifying glycerol steam reforming on a monolith catalyst: A reaction kinetic model, *Chem. Eng. J.* 306 (2016) 933–941.
 - [28] A.K. Avci, D.L. Trimm, A.E. Aksoylu, Z.I. Onsan, Hydrogen production by steam reforming of n-butane over supported Ni and Pt-Ni catalysts, *Appl. Catal. A Gen.* 258 (2004) 235–240.
 - [29] I. Aartun, T. Gjervan, H. Venvik, O. Görke, P. Pfeifer, M. Fathi, A. Holmen, K. Schubert, Catalytic conversion of propane to hydrogen in microstructured reactors, *Chem. Eng. J.* 101 (2004) 93–99.
 - [30] I. Aartun, B. Silberova, H. Venvik, P. Pfeifer, O. Görke, K. Schubert, A. Holmen, Hydrogen production from propane in Rh-impregnated metallic microchannel reactors and alumina foams, *Catal. Today* 105 (2005) 469–478.
 - [31] I. Sen, A.K. Avci, Exhaust gas reforming of methane in a catalytic microchannel reactor, *Ind. Eng. Chem. Res.* 53 (2014) 1760–1767.
 - [32] P.Y. Sheng, W.W. Chiu, A. Yee, S.J. Morrison, H. Idriss, Hydrogen production from ethanol over bimetallic Rh-M/CeO₂ (M = Pd or Pt), *Catal. Today* 129 (2007) 313–321.
 - [33] M.C. Campa, G. Ferraris, D. Gazzoli, I. Pettiti, D. Pietrogiacomini, Rhodium supported on tetragonal or monoclinic ZrO₂ as catalyst for the partial oxidation of methane, *Appl. Catal. B Environ.* 142–143 (2013) 423–431.
 - [34] U. Izquierdo, M. Wichert, V.L. Barrio, G. Kolb, Sustainable syngas production from ethylene glycol reforming processes using Rh-based catalysts in microreactors, *Appl. Catal. B Environ.* 152–153 (2014) 19–27.
 - [35] M. Ibáñez, B. Valle, J. Bilbao, A.G. Gayubo, P. Castaño, Effect of operating conditions on the coke nature and HZSM-5 catalysts deactivation in the transformation of crude bio-oil into hydrocarbons, *Catal. Today* 195 (2012) 106–113.
 - [36] P. Castaño, G. Elordi, M. Olazar, A.T. Aguayo, B. Pawelec, J. Bilbao, Insights into the coke deposited on HZSM-5, H β and HY zeolites during the cracking of polyethylene, *Appl. Catal. B Environ.* 104 (2011) 91–100.
 - [37] A. Lazzarini, A. Piovano, R. Pellegrini, G. Leofanti, G. Agostini, S. Rudic, M.R. Chierotti, R. Gobetto, A. Battiato, G. Spoto, A. Zecchina, C. Lamberti, E. Groppo, A comprehensive approach to investigate the structural and surface properties of activated carbons and related Pd-based catalysts, *Catal. Sci. Technol.* 6 (2016) 4910–4922.
 - [38] A. Donazzi, A. Beretta, G. Groppi, P. Forzatti, Catalytic partial oxidation of methane over a 4% Rh/ α -Al₂O₃ catalyst: Part I: Kinetic study in annular reactor, *J. Catal.* 255 (2008) 241–258.
 - [39] W. Wang, Thermodynamic analysis of glycerol partial oxidation for hydrogen production, *Fuel Process. Technol.* 91 (2010) 1401–1408.
 - [40] J.R. Rostrup-Nielsen, Steam reforming, in: G. Ertl, H. Knozinger, F. Schüth, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, Wiley-VCH, Weinheim, 2008pp. 2882–2905.
 - [41] J.R. Rostrup-Nielsen, J.H.B. Hansen, CO₂-Reforming of methane over transition metals, *J. Catal.* 144 (1993) 38–49.
 - [42] M. Maestri, D.G. Vlachos, A. Beretta, G. Groppi, E. Tronconi, Steam and dry reforming of methane on Rh: Microkinetic analysis and hierarchy of kinetic models, *J. Catal.* 259 (2008) 211–222.
 - [43] J.G. Jakobsen, M. Jakobsen, I. Chorkendorff, J. Sehested, Methane steam reforming kinetics for a rhodium-based catalyst, *Catal. Lett.* 140 (2010) 90–97.
 - [44] S.S.E.H. Elnashaie, A.M. Adris, A.S. Al-Ubaid, M.A. Soliman, On the non-monotonic behaviour of methane—steam reforming kinetics, *Chem. Eng. Sci.* 45 (1990) 491–501.
 - [45] D. Pakhare, J. Spivey, A review of dry (CO₂) reforming of methane over noble metal catalysts, *Chem. Soc. Rev.* 43 (2014) 7813–7837.
 - [46] O. Tan, E. Masalaci, Z.I. Onsan, A.K. Avci, Design of a methane processing system producing high-purity hydrogen, *Int. J. Hydrogen Energy* 33 (2008) 5516–5526.