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Syngas production by means of biogas catalytic partial oxidation and dry reforming using Rh-based catalysts

Ainara Moral^a, Inés Reyero^{a,b}, Carmen Alfaro^a, Fernando Bimbela^{a,b,*}, Luis M. Gandía^{a,b}^a Grupo de Reactores Químicos y Biorreactores, Departamento de Química Aplicada, Universidad Pública de Navarra, Edificio de los Acebos, Campus de Arrosadía, 31006 Pamplona, Spain^b Institute for Advanced Materials (InaMat), Universidad Pública de Navarra, Campus de Arrosadía, 31006 Pamplona, Spain

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ABSTRACT

The catalytic oxy-CO₂ reforming of biogas (a combination of partial oxidation and dry reforming reactions) was studied with various Rh-based catalysts prepared in the laboratory using different supports: γ -Al₂O₃, SiO₂ and CeO₂. Their performance was compared to a commercial Rh/Al₂O₃ catalyst serving as reference. Different O₂/CH₄ ratios were studied: 0 (dry reforming), 0.10, 0.20 and 0.45. In all cases, both laboratory-prepared and commercial Rh/Al₂O₃ catalysts clearly outperformed the others, including a Pt commercial catalyst tested under dry reforming conditions. It could be established that the catalytic performance of the Rh-based catalysts prepared by impregnation on different supports had the following decreasing order: Rh/Al₂O₃ > Rh/SiO₂ > Rh/CeO₂. Equilibrium conditions could be achieved through 2 h of dry reforming of biogas at 700 °C using the Rh commercial catalyst at gas hourly space velocities (GHSV) of 30 N L CH₄/(g_{cat}·h). Higher GHSV values (150 and 300 N L CH₄/(g_{cat}·h)) resulted in a slow decay of the activity over time, more accentuated at the most severe space velocity condition. However, the decrease in methane conversion and H₂ yield was milder when oxy-CO₂ reforming conditions were used. Adding O₂ to the reactor feed was proven beneficial, enhancing initial and overall CH₄ conversions as well as hydrogen yields, which followed an increasing trend with increasing O₂/CH₄ ratios in all cases. The characterization of the spent samples under dry reforming conditions revealed the presence of carbon deposits of predominantly polymeric nature, though co-existing with other types of coke. These promising results pave the path for developing highly active and stable catalytic formulations for producing syngas by means of oxy-CO₂ reforming of biogas with Rh-based catalysts.

1. Introduction

Significant efforts are being directed nowadays toward finding alternatives that could restrain the climate change, owing to the awareness raised at last by governmental bodies and policymakers from most of the nations all over the world, as reflect the agreements established in the last COP21 and COP22 climate summits. Particularly, it is of utmost importance to seek for technologies that could convert two of the main product gases responsible for the greenhouse effect, namely methane and carbon dioxide, avoiding their massive release into the atmosphere as a result of human activity, which has been ongoing for many decades now.

Different methane-rich gas streams can be found, both of natural and anthropogenic origin. Natural gas exploitation has gained increased interest in recent years, as a result of the new developments in oil extraction techniques such as hydraulic fracturing. Interestingly, nat-

ural gas can help mitigate global warming in the transition from coal conversion full-scale technologies to renewables [1]. Indeed, CO₂ emissions related to electric power generation have drastically decreased in the U.S.A. during the last decade.

On the other hand, the amount of wastes and residues generated by our highly developed societies has led to the need for implementing technologies and processes that can help valorizing as much as possible from these troublesome materials, aiming at ambitious “zero-waste” targets (or else, waste minimization, which could be more realistic) while obtaining value added products, including renewable-based methane-rich product gas streams. In this sense, waste management technologies based on the anaerobic digestion of different residual streams such as municipal solid wastes in landfills, cattle manure and urban wastewaters have played a significant role in the last decades, which allow to obtain a methane-rich gas usually called raw biogas.

* Corresponding author at: Grupo de Reactores Químicos y Biorreactores, Departamento de Química Aplicada, Universidad Pública de Navarra, Edificio de los Acebos, Campus de Arrosadía, 31006 Pamplona, Spain.

E-mail address: fernando.bimbela@unavarra.es (F. Bimbela).

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Biogas is a product gas mixture mainly composed of CH₄ and CO₂, though having other impurities and product gases, the concentration of which can vary significantly depending on the starting raw material [2] and other factors, namely the bacteria responsible for the anaerobic fermentation of these substrates [3]. After suitable conditioning this gas presents various energy applications, being one of the most usual its application for heat and power generation by means of direct combustion of the raw biogas [4].

Nonetheless, there is an increasing interest in finding other possibilities for the valorization of the raw landfill biogas produced, such as its use as raw material in the production of alternative, sustainable and environmentally friendly biofuels as well as valuable chemicals of industrial relevance. There are different alternatives for conditioning and upgrading raw landfill biogas aiming at a further use as raw material for producing biofuels and/or chemicals. The most developed way implies an enrichment of the gas stream on its methane content, by means of different conditioning and purification technologies [5,6]. However, there are other alternatives, including the transformation of biogas into syngas that could lead to the development of promising valorization technologies. Of these, the production of syngas via dry reforming processes has been widely proposed in the literature, because of the straightforward utilization of both major constituents from raw biogas (CH₄ and CO₂). Typically, the process is carried out using Ni-based catalysts, which have been extensively researched in the literature, as evidenced in recent reviews [7,8]. These catalysts suffer from severe deactivation by carbon deposition and numerous efforts have been devoted to enhancing their resistance to coking.

The other approach in the dry reforming of methane (DRM) from biogas is the development of catalysts based on noble metals, which have also constituted a matter of significant research studies, as magnificently reviewed by Spivey and co-workers recently [9,10]. The former references reflect the advantages of choosing noble metals instead of transition metals, namely their superior performance in terms of intrinsic activity and resistance to coking, thus outperforming catalysts based on nickel and other transition metals such as cobalt or iron in terms of stability [8,9].

As accurately signaled in the excellent reviews by Kawi et al. [8] and Kumar et al. [10], there are interesting alternative strategies for performing the DRM reaction that could help overcoming its inherent complications associated: the strongly endothermic nature of the reaction and the catalyst deactivation. In this regard, the “combined reforming” processes aim at coupling DRM with steam reforming (by adding H₂O) and/or partial oxidation (by adding O₂). The former is typically known as “bi-reforming” whereas the latter is usually named as “oxy-CO₂ reforming”, while some authors have already gone one step beyond and proposed intricate “tri-reforming” reactions by simultaneously adding H₂O and O₂ to the biogas mixture [11]. These strategies are highly beneficial for various reasons, namely, high flexibility as a result of the feasibility of tuning the produced syngas H₂/CO ratios to a certain extent, reduction of carbon formation (hence mitigating catalyst deactivation), high methane conversions as well as very high selectivity to H₂ and CO. Furthermore, oxy-CO₂ poses additional advantages such as reducing the energy requirements of the process. Ultimately, autothermal operation of the reactor is technically feasible but safety issues regarding the presence of oxygen have limited its scalability to date. Nevertheless, some studies have proven the beneficial effects of adding a little oxygen in terms of alleviating coke formation [12,13]. Such an approach may be very attractive when carbon deposition on the catalyst surface is moderate through long time-on-stream periods and with active phases that do not become easily reoxidized.

It is in this context where catalytic formulations based on noble metals such as rhodium or platinum lead by far other more conventional approaches based on nickel or other transition metals. Naturally, when discussing the use of noble metals in catalytic formulations, the issue of their high cost and limited availability is inevitably brought into spotlight, and it is the main reason why the scale-up of the process

is hindered [9,10]. It is therefore necessary to bear this in mind when proposing the development of new catalysts based on noble metals, and a rational utilization of the active metal is a must. Hence more efforts must be directed toward finding new catalysts that can achieve similar levels of activity and stability against deactivation while significantly decreasing the loading of noble metal on the catalyst.

Interestingly, despite Rh-based catalysts showing very good performances in the partial oxidation of methane with very good selectivity to syngas at relatively low temperatures as shown, among others, in the works by the groups of A. Holmen [14–16], E. Ruckenstein [17,18], P. Forzatti [19–22] and L. Schmidt [23,24], the literature concerning the oxy-CO₂ reforming of methane-rich gas streams is almost inexistent. Choudhary et al. reviewed the state of the art of different oxy-methane reforming reactions, including oxy-CO₂ reforming [25]. Only two works considered Rh-based catalysts for the combined reforming of methane. Cimino et al. studied the autothermal CO₂ reforming of methane using Rh-LaCoO₃ supported on structured cordierite monolithic catalysts [26], while Tsyganok et al. analyzed the combined partial oxidation and dry reforming of methane over Ru-, Rh- and Pt-based catalysts supported on hydrotalcites-derived Mg-Al mixed oxides [27]. The tests were carried out at 1 atm and 850 °C, using an O₂/CH₄ molar ratio of 0.46 and a space velocity of 79 N L CH₄/(g_{cat}·h). The authors reported the absence of carbonaceous deposits during 5 h time-on-stream, and both Ru- and Rh-based catalysts yielded very high activities throughout.

Thus, the present work aims at preliminarily exploring an alternative route for landfill biogas valorization into syngas through a catalytic reforming process in the presence of oxygen. The development of suitable catalysts for the process based on Rh as active metal will be carried out aiming at achieving a H₂-rich syngas that could serve as raw material for the production of synthetic fuels and chemicals. For the sake of comparison two commercial Rh and Pt catalysts supported on Al₂O₃ will be tested as references. The latter has been selected so as to compare the activity of Rh and Pt, considering the relatively higher number of works using Pt-based catalysts under oxy-CO₂ reforming conditions [27–30]. Ultimately the overall goal of this research is developing highly active and stable catalysts that can be effective in the oxy-CO₂ reforming of biogas.

2. Experimental

2.1. Catalysts preparation and physicochemical characterization

Five different catalysts were selected for this study. Two of them were commercial 0.5 wt. % Pt/Al₂O₃ and 0.5 wt. % Rh/Al₂O₃ (Johnson Matthey). The other three catalysts were prepared in the laboratory.

0.5 wt. % Rh/Al₂O₃ and 0.5 wt. % Rh/SiO₂ were prepared by the incipient wetness impregnation technique. The “as-received” beads of γ-Al₂O₃ (Spheralite 505, Procatalyse) and SiO₂ (Kali-Chemie) were grinded to get the starting supports in powder form. The solids were sieved so as to have a particle size distribution ranged between 100 and 200 μm, and preconditioned by calcination at 750 °C during 6 h under air atmosphere before the impregnation step.

A 0.5 wt. % Rh/CeO₂ catalyst was developed in a two-step process. Firstly, the ceria support was obtained from Ce (III) nitrate by precipitation of the hydroxide at increasing pH followed by ageing, drying and calcination at 750 °C. Afterwards, the active metal was deposited by means of incipient wetness impregnation and subsequent recalcination. All the necessary chemicals and metal precursors for the syntheses carried out were purchased in the form of high purity commercial reagents (Sigma-Aldrich or Acros Organics). The Rh precursor salt was a Rh (III) nitrate solution containing 10% (w/v) Rh in 20–25 wt. % nitric acid purchased to Acros Organics.

Fresh samples in powder form were characterized under different techniques, including N₂ adsorption-desorption, temperature-programmed reduction (TPR) and CO pulse chemisorption. In addition,

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