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Syngas production by steam and oxy-steam reforming of biogas on monolith-supported CeO₂-based catalysts

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ABSTRACT

In this study, the syngas production by steam reforming (SR) and oxy-steam reforming (OSR) of clean biogas over cordierite monoliths (400 cpsi) lined with Ni, Rh, or Pt on CeO₂ catalyst was deeply investigated. Structured catalysts were prepared by using an alternative method to traditional washcoating based on the combination of the solution combustion synthesis (SCS) with the wetness impregnation (WI) technique. TEM and SEM analysis were used to study the morphology of the catalytic layer and to determine its thickness, while the quality of the coating in terms of adhesion on the monolith was evaluated by ultrasonic treatment in isopropyl alcohol solution. The performance and the stability of the structured catalysts were investigated at different process parameters, namely temperature (700–900 °C), steam-to-carbon (S/C = 1–5) and oxygen-to-carbon (O/C = 0.1–0.2) molar ratios, and weight space velocity (WSV = 30,000–250,000 NmL g_{cat}⁻¹ h⁻¹). The SCS + WI deposition method allowed obtaining a uniform and thin coated layer with high mechanical strength. The following order of activity was exploited: Rh > Pt > Ni for biogas SR and Rh > Pt ≈ Ni for biogas OSR. The Rh-based catalyst exhibited higher activity and long-lasting stability towards biogas SR and OSR reactions for syngas production.

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Introduction

Increasing of energy demand, limited fossil resources, dependence on crude oil, as well as environmental problems

are important challenges for our society. The need of a deep transformation of the world's energy production is, of course, already widely recognized in the context of the growing concern about global climate change. Starting from this background, fuels obtained from renewable resources (waste

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List of abbreviations, acronyms and symbols

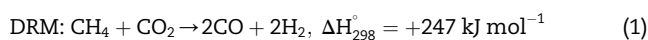
DRM	Dry reforming of methane
X_{CO_2}	Carbon dioxide Conversion
SRM	Steam reforming of Methane
O/C	Oxygen-to-carbon molar ratio (O_2/CH_4)
OSR	Oxy steam reforming
PROX	Preferential Oxidation
PSA	Pressure Swing Absorption
S/C	Steam-to-carbon molar ratio (H_2O/CH_4)
SCS	Solution combustion synthesis
SR	Steam reforming
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TRM	Tri-reforming of methane
TOS	Time On Stream
WGS	Water gas shift
WI	Wetness impregnation
X_{CH_4}	Methane conversion
X_{CO_4}	Carbon dioxide conversion
XRD	X-Ray Diffraction
WHSV	Weight Hourly Space Velocity ($g_{gas} g_{cat}^{-1} h^{-1}$)
WSV	Weight Hourly Space Velocity (NmL $g_{cat}^{-1} h^{-1}$)

and biomass) can meet existing and growing energy requirements [1,2]. Biomass is an attractive renewable energy source: because of the high CO_2 recycling, energy generation from biomass does not increase CO_2 emissions [3,4].

In this regard, the European Union (EU) has introduced some specific legislative instruments to promote the integration of renewable resources within the European energy system [5,6]. In particular, biogas is becoming one of the most popular renewable fuels obtained from biomass belonging to several sectors, ranging from agro-industrial to zootechnical [7,8]. Thus, biogas is a valid fuel for reducing the consumption of fossil fuels and the emissions of greenhouse gases. The composition of biogas strongly depends on the initial substrate. Biogas mainly contains methane and carbon dioxide, whose concentrations range between 50 and 75 vol% CH_4 and 25–45 vol% CO_2 . Other minor components are: H_2O (2–7 vol% at 20–40 °C), N_2 (2 vol %), H_2 (less than 1 vol%) and traces of siloxanes, H_2S , NH_3 , O_2 , and halides [9].

The most used technologies for energy generation from biogas (gas turbines and internal combustion engines) are characterized by low electrical conversion (18–25%), serious environmental emissions and high levels of noise [10,11]. Nevertheless, a more sustainable use of biogas consists in the production of bio-methane by purification and upgrading processes [12,13], or syngas by reforming routes after biogas purification to eliminate components as siloxanes, H_2S , NH_3 , O_2 , and halides [12–15]. Furthermore, syngas obtained from biogas reforming processes can be used for the synthesis of valuable chemicals [16,17] or to produce combined heat and energy also at low power range (5–20 kW_{el}) with high temperature fuel cells [18–26].

The reforming of biogas is essentially CO_2 reforming of CH_4 , also known as dry reforming of methane (DRM):



In DRM, high temperatures are needed to obtain high conversion levels, resulting in a high energy requirement. Moreover, carbon deposition over the catalyst surface is one of the main drawback of this process that limits the industrial application [27,28]. In addition, concerning the catalyst, the metallic phase and the support can sinter with further deterioration of the catalytic activity [29,30].

The endothermic steam reforming of methane (SRM) is the widespread chemical process used to transform CH_4 into H_2 -rich gas stream:

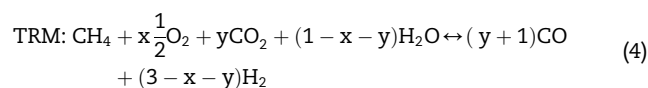


The steam reforming (SR) process can be used to produce syngas from biogas and, in comparison with DRM, it produces higher H_2 yields [31]. Indeed, the presence of steam favors the water gas shift (WGS) equilibrium, increasing the H_2 content in the syngas.

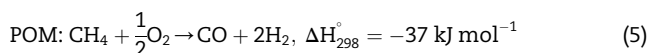


The use of an excess of steam limits carbon formation. Thus, SR requires a steam-to-carbon (S/C) molar ratio more than 3 times of the stoichiometry. However, considering the endothermic nature of SMR, external heat sources are necessary with a resulting reduction of the process efficiency [20,32].

Recently, the tri-reforming of methane (TRM) emerges as a new catalytic process [33,34] for the production of syngas with an appropriate H_2/CO molar ratio:



The process involves a combination of DRM, partial oxidation of methane (POM), and SRM in a single step.



Typically, TRM requires CH_4 (or natural gas) and CO_2 as reagents. CO_2 comes without separation step directly from the exhaust gasses of electric power plants fed by fossil fuels [33–35]. The presence of steam contributes to reduce carbon deposition, while the endothermic reforming reactions can be compensated by adding O_2 , achieving a possible overall thermo-neutral balance of the reactions [36–38]. Moreover, the combination of O_2 and H_2O allows an easy adjustment of the H_2/CO molar ratio to optimize the efficiency of the downstream processes. TRM can be successfully used for the biogas reforming to produce syngas. When biogas is the starting primary fuel together with oxygen and steam, the process can also be referred as oxy-steam reforming (OSR) of biogas. Fig. 1 shows a general scheme of the biogas pathways based on syngas production by reforming processes.

Suitable catalysts for the reforming of biogas must be able to convert CH_4 and CO_2 efficiently in the presence of H_2O for SR or H_2O and O_2 for OSR. Biogas reforming catalysts range from noble metals (Rh, Ru, Pt and Pd) to base metals (mainly

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