



Catalytic stability of a Ni-Catalyst towards biogas reforming in the presence of deactivating trace compounds



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ABSTRACT

Trace compounds contained in the produced biogas range from tens to thousands of ppm(v) and the gas cleaning is crucial, as much as it is important the investigation of the trace compounds impact on the reforming section and on the SOFC performance. The catalytic stability of a Ni-catalyst towards biogas reforming in the presence of three types of deactivating compounds (sulfur, siloxanes and aromatic compounds) was investigated. When the biogas is composed of a methane to carbon dioxide ratio >1 under the tested operating conditions, the Ni catalyst stability is achieved. A Ni/Al₂O₃ catalyst appears suitable for the steam reforming of biogas including contaminants, under the operative conditions adopted. On the contrary, the effect of a biogas stream with composition CH₄/CO₂ = 50/50 vol % is much more harmful under steam reforming conditions both in terms of activity and stability. This result was due to CO₂-promoted Boudouard reaction that leads to extensive carbon formation on the catalyst surface. Under this condition, sulfur and D5 compounds in the biogas have a significant impact on the longevity of the Ni catalyst. Hence, carbon formation rate is affected by the degree of catalyst poisoning due to adsorption and/or deposition of other species on catalytic sites.

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1. Introduction

Biogas coming from the anaerobic digestion of organic waste covers a crucial role regarding landfilling and pollutant reduction, matter recovery and energy production. Putrescible waste can derive from the domestic urban organic waste, agricultural waste, manure and sludge collected in wastewater treatment plants. Biogas consists of CH₄ (45–70 vol %), CO₂ (30–50 vol %), N₂ (<5 vol %), O₂ (0–3 vol %) and a wide variety of trace compounds. The type and quantity of trace compounds depend on waste treated [1–4]. In fact, trace compounds found in landfill biogas and from digestion of organic wastes are completely different [1,5]. Landfill gas quality is widely varying depending on the degradation status of the land-filled material as well as moisture and temperature conditions, all of which may vary considerably in different parts of the landfill body [5]. The higher amount of aromatic compounds found in landfill biogas compared to sewage or farm biogases is often associated

with older waste even though elevated levels of aromatic compounds have also been measured in urban waste disposal bins [6–8]. The main trace compound contained in a biogas from the anaerobic digestion of organic wastes – both from WWTPs or municipal organic waste – is hydrogen sulfide (H₂S) [1,5,9]. The H₂S concentration can range from 10 to thousands of ppm(v), and it is a function of the organic waste, digester temperature and pre-treatments process adopted to improve the methane yield [1,10]. Some pre-treatments can be adopted during the biogas production to reduce the sulfur content in the biogas, such as processes with metal oxides. Other processes are implemented outside the digester, mainly processes that adopt the physical adsorption solution to abate trace concentration [3,8,11–17]. Among energy generators, SOFCs are silent systems, with low emissions and high electrical and thermal efficiency. These systems can produce energy in a distributed way and they can be adopted in the next future to reduce the energy dependency from fossil fuels with high efficiency [8,18,19]. The cleaning process of biogas results to be mandatory in order to reduce the trace contaminants to achieve SOFC requirements [3,12,13,15,19–21]. A SOFC co-generator fed by biogas needs a reforming process to produce a more suitable gas mixture

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Nomenclature

ASR	Area Specific Resistance
CEM	Controlled Evaporator Mixer
DIR	Direct Internal Reforming
EIS	Electrochemical Impedance Spectroscopy
FID	chromatography-Flame Ionization Detector
FU	Fuel Utilization
GC	Gas Chromatography
GHSV	Gas Hourly Space Velocity
LSCF	Lanthanum Strontium Cobalt Ferrite
OFMSW	Organic Fraction Municipal Solid Waste
ppb(v)	parts per billion by volume
ppm(v)	parts per million by volume
SEM	Scanning Electron Microscope
SOFC	Solid Oxide Fuel Cell
TAR	dark brown or black viscous liquid of hydrocarbons
TCD	gas chromatography-Thermal Conductivity Detector
TEM	Transmission Electron Microscope
TPB	Three Phase Boundary
WWTP	Waste Water Treatment plant
YSZ	Yttria-Stabilized Zirconia

rich in hydrogen and carbon monoxide content, electrochemically suitable for the SOFC [22,23].

Biogas can be converted to synthesis gas either by dry reforming or by a combination of dry and steam reforming using appropriate catalysts [24–27]. Since the CH₄ to CO₂ (molar) ratio in biogas is about 1.5, dry reforming alone can lead to significant carbon deposition within the reactor [24,28,29]. Therefore, it is desirable to mix biogas with steam for reforming and generally, the H₂O to CH₄ ratio (S/C) is maintained at 2 to avoid any coke formation [22,23,30]. Besides carbon deposition issues, the presence of impurities has a tremendous effect on the performance of the catalyst. Among these, the most studied contaminant for catalytic steam reforming is sulfur, in the form of H₂S, which leads to an almost total deactivation of the catalyst [31–33]. Catalyst poisoning occurs due to the strong adsorption of sulfur or other impurities on active sites, promoting by poisoning-metal electron affinity; this consequently, blocks or alters the adsorptivity of the other species [34,35]. Overall, the saturation coverage of sulfur and other species (silicon compounds) depends on the operating temperature, metal loading, and the partial pressure of reacting gasses. Catalysts with lower metal loading lose activity at a faster rate compared to catalysts with higher metal loading [36,37].

Moreover, the presence of higher molecular weight hydrocarbons (C_nH_m such as ethane, propane, etc.) and aromatic compounds (benzene, toluene, etc.) can significantly affect the formation of carbon species and thus the effectiveness of the catalyst [38,39]. The formation of carbon on the catalyst under steam reforming conditions may take place mostly through cracking of hydrocarbons and aromatic compounds as well as the Boudouard reaction. In this way, researchers [40,41] determined the coking tendency for steam reforming of methane in the presence of C2 and C3 hydrocarbons over a Ni catalyst, and an increasing of coking with carbon number was noted especially in the presence of olefin species. D'Angeli et al. [42] have also shown that coke formation increases with the molecular weight of the feed and that the deactivation rates during steam-reforming of ethane and propane over Ni/MgO were higher compared to methane.

Although poisoning of Ni in the presence of H₂S or hydrocarbons is well known, combined effects of H₂S with other contaminants – which are the typical case of biogas – are lacking in the literature. Hence, the main objectives of our research are:

- i) to investigate the catalytic stability of a Ni-catalyst towards biogas reforming in the presence of three types of deactivating compounds (H₂S, higher hydrocarbons, and siloxane compounds) either alone or combined;
- ii) to analyze the catalytic performances when different biogas compositions are used;
- iii) to evaluate reforming options to increase catalyst lifetime and/or reduce the reformer operating temperature;
- iv) to find the best performance regarding carbon deposition and voltage stability in an SOFC single cell fed with a mixture that simulates the direct internal reforming of biogas;
- v) to investigate the SOFC performance fed by biogas with different trace compounds, starting from sulfur compounds (H₂S) to continue with the addition of siloxanes (D4) and aromatic compounds (C₇H₈).

The novelty of the paper, from the catalytic point of view, can be identified mainly on two aspects. The first aspect is related to the combined effect of biogas contaminants on Ni catalytic stability; while the second one is the performance evaluation of biogas contaminants depending on biogas stream composition in terms of CH₄/CO₂ inlet ratio.

2. Experimental

2.1. Catalytic experiments on the reformer Ni catalyst

Catalytic experiments were carried out in a quartz fixed-bed reactor (i.d. = 4 mm; h_{bed} = 2.0–4.0 cm) at 1073 K and atmospheric pressure. 0.2 g of commercial Ni/Al₂O₃ reforming catalyst [22,28,43]. The operative temperature in the reactor was assured by three thermocouples located in different zones of the catalytic bed. Before each test run, catalysts were reduced in-situ at T = 1073 K for 1.5 h under hydrogen flow (100 cc/min).

The flow rates of biogas (CH₄+CO₂) and poisoning species (H₂S, hydrocarbons, and siloxane) were controlled by Brooks Instruments mass flow meters. In particular, the following poisoning concentrations ranges were added in the reactant mixture: i) H₂S = 0.4–1 ppm(v), ii) Decamethylcyclopentasiloxane (D5-siloxane, C₁₀H₃₀O₅Si₅ = 0.5–1 ppm(v) and iii) hydrocarbons mixture = 200–800 ppm(v).

Carbon formation during experiments was estimated by using a CHSN-O Carlo Erba elementary analysis instrument, while a PHILIPS CM12 Transmission Electron Microscope (TEM) provided with a high-resolution camera was used to analyze the morphology of both fresh and spent Ni catalysts. A field emission Scanning Electron Microscope (SEM) equipped with EDAX microprobe (Philips XL30 S FEG) was used to carry out qualitative and quantitative analysis of solid compounds (i.e., SiO₂) on the powders of spent Ni catalysts.

2.2. Electrochemical characterization of SOFC single cells

Single SOFC cells were tested with simulated biogas to investigate the effects of direct internal reforming and fuel contamination on the electrochemical performance of the fuel cell.

The laboratory test station is designed to test the planar SOFCs. A schematic diagram of the test rig is provided in Fig. 1. The test rig includes an oven, in which ceramic housings holding the planar cell are placed. Moreover includes a gas mixing and distribution

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