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Rh catalysts for syngas production via dry reforming and partial oxidation of biogas

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Highlights

- Rh catalysts showed good catalytic performance and stability even at high space velocities.
- The calcination step is detrimental to the catalysts' activity in dry reforming.
- Adding O_2 in the system enhances CH_4 conversion in biogas-to-syngas valorization.

1. Introduction

Biogas production has significantly raised in the recent years due to the increased treatment through anaerobic digestion of different organic wastes such as urban and municipal organic solid residues, sewage sludge derived from wastewater treatment plants and manure from different livestock breeding. Biogas is a gas mixture mainly composed of CH_4 and CO_2, though other compounds can be present in minor proportions, including N_2, H_2S, and NH_3, among others. There are different alternatives for the valorization of this gas, including the transformation into syngas ($CO + H_2$), which makes it possible to valorize simultaneously CH_4 and CO_2 [1]. Syngas is a valued intermediate product in the industry, constituting the feedstock of numerous industrial processes for producing a variety of chemicals, commodities and synthetic fuels.

Methane dry reforming processes for syngas production have been widely studied in the literature using Ni catalysts, due to their high activity and moderate cost. However, Ni catalysts suffer from severe deactivation by carbon deposition. An alternative is the development of noble metal-based catalysts, such as Rh and Pt, which present the advantages of a much higher catalytic activity and superior resistance to coking [2]. In order to overcome the difficulties associated to the dry reforming processes, as the strongly endothermic nature of the reaction and the catalysts deactivation, a combination of the methane dry reforming with the partial oxidation reaction has been proposed in the literature, usually named as combined reforming or oxy-CO_2 reforming, with very promising results recently reported using Rh-based catalysts [3].

The general objective of this work is the development of suitable catalysts for syngas production from biogas through the combination of dry reforming and partial oxidation processes using Rh/Al_2O_3 catalysts having a relatively low Rh content. The specific objectives were the study of the effect of the catalysts' preparation method, catalysts support nature and the effect of the addition of O_2 in the feeding on the catalytic activity and stability, especially the effect exerted on methane conversion and on the CO and H_2 yields over time.

2. Methods

0.5 % Rh/Al_2O_3 catalysts were prepared by the incipient wetness impregnation technique. The solids were dried at 105 °C (catalyst named Rh prep), and some of them were calcined at 750 °C for 6 h (Rh calc). A 0.5 % Rh/Al_2O_3 commercial catalyst (Johnson Matthey) was also tested and used as reference (Rh com) to compare the catalytic results. These catalysts were characterized by means of different techniques, including N_2 adsorption, temperature-programmed-reduction (TPR), CO pulse chemisorption and X-ray diffraction (XRD).

The catalysts were tested in a fixed-bed tubular quartz reactor (8 mm of internal diameter) at atmospheric pressure. On-line gas analysis system consisted on a gas chromatograph equipped with a thermal conductivity detector (TCD). The catalytic tests were carried out at 700 °C, with different O_2/CH_4 molar ratios between 0 and 0.45 and using two gas hourly space velocities (GHSV): 30 and 150 N L $CH_4/(g_{cat}\cdot h)$. A synthetic gas mixture composed of 54 % CH_4, 40 % CO_2 and 6 % N_2 was used as feedstock, adding synthetic air (21% O_2) to the gas feeding line in those cases where the partial oxidation reaction was included.

3. Results and discussion

Firstly, the effect of catalyst calcination on the catalytic activity was studied under dry reforming conditions (O_2/CH_4 = 0). Figure 1 shows the evolution of methane conversion over the reaction time and the thermodynamic equilibrium calculated by simulation (calculated using HYSYS software and represented in in the figures as horizontal lines). The commercial catalyst tested at 30 N L $CH_4/(g_{cat}\cdot h)$ yielded values for methane conversion close to that of the maximum imposed by the thermodynamic equilibrium at the studied conditions. The catalytic activity of the different catalysts was compared at 150 N L $CH_4/(g_{cat}\cdot h)$. It can be observed that the catalyst calcination has a detrimental effect on the reaction performance, whereas the prepared catalyst tested without a previous calcination, had a superior performance, remarkably providing better results than the commercial sample throughout.

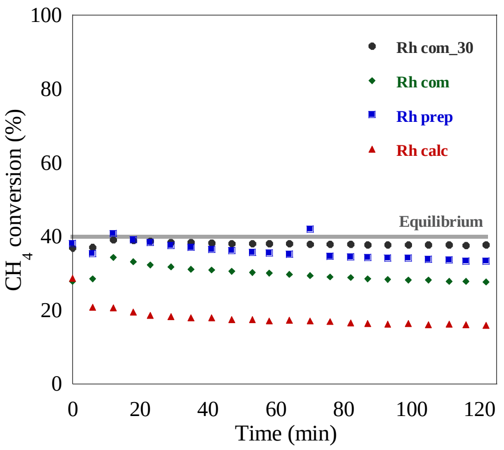

Figure 1. Effect of catalyst calcination on the reaction performance.

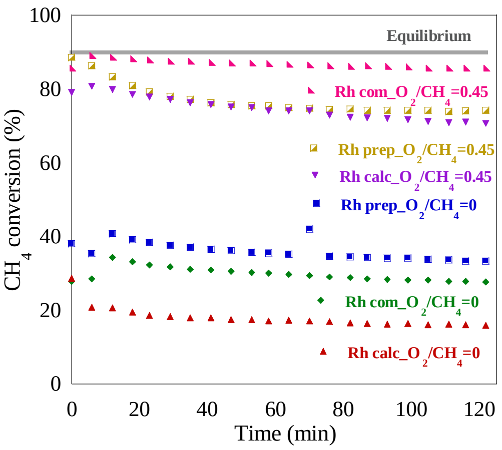

Figure 2. Effect of O_2 addition on methane conversion.

The influence of adding O_2 on the gas feed was also studied at 150 N L $CH_4/(g_{cat}\cdot h)$. Figure 2 shows the evolution of methane conversion over time under dry reforming and oxy-CO_2 reforming (O_2/CH_4 = 0.45) conditions. It is also shown the thermodynamic equilibrium corresponding to the latter conditions. It can be observed a positive effect of the addition of O_2 on the catalytic activity in all cases, with a notable increase in methane conversions, as well as in the corresponding H_2 yields and H_2/CO molar ratios (not depicted). Interestingly, catalyst calcination does not exert any appreciable effect under oxy-CO_2 reforming conditions.

4. Conclusions

High methane conversions can be achieved in the combined reforming of biogas to syngas using Rh-based catalysts under relatively high space velocities. The addition of O_2 to the feed is beneficial, causing an increase on methane conversion achieved. All the studied catalysts showed a very good catalytic performance and stability under oxy-CO_2 reforming conditions, though calcination of the impregnated precursor was detrimental on the catalytic activity under dry reforming conditions.

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Keywords

Biogas reforming, syngas, oxy-CO_2 reforming, Rh catalysts.