Catalytic reforming of biogas in a microwave-heated reactor

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Highlights

- Fast, efficient and selective heating with microwaves.
- High and stable catalytic activity.
- Coking resistant material.

1. Introduction

Process intensification and use of renewable resources for the production of chemicals and fuels can have a significant impact on climate change.

Catalytic dry reforming of methane allows to convert two greenhouse gases into syngas, but presents several drawbacks like high endothermicity, catalyst deactivation due to coking and sintering that limit its application in industry [1]. The use of microwave heating could help to overcome part of these limitations by providing a new and more efficient way to deliver the heat to the catalyst.

The use of microwave heating in catalysis is relatively recent, this technique brings a number of advantages, allowing an extremely efficient and fast direct heating of the entire volume of a selected material [2], without a direct contact between the catalyst and the heating source. However, the use of microwave heating in this field still remains limited: the property of matter to absorb microwaves depends mainly on its dielectric properties, which in turn depends on a wide range of parameters such as temperature, purity, frequency of microwaves [3].

2. Methods

There are two sides in which the current research can be divided: the synthesis of nickel-based catalysts (and their characterization) and the heating and catalytic tests of them.

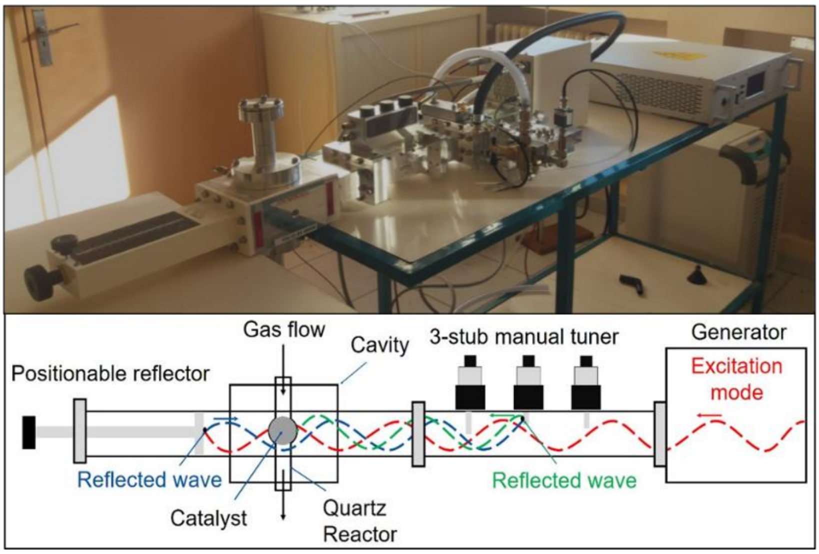

Figure 1. Photo and operative scheme of the microwave oven.

Nickel nitrate is deposited on porous silicon carbide (a good microwave absorber) by wet impregnation, followed by calcination in air. After the synthesis, the catalysts undergo a series of characterizations, like RX diffractometry, measurement of SSA by the BET method, chemical analysis and thermogravimetric analysis. These measurements are repeated before and after heating / catalytic tests to detect any changes in the material as a result of the experiments.

The testing is carried out on two test benches, with the catalyst in a fixed bed reactor made of quartz: the first in which the materials are heated by means of a classic electrically-heated furnace, while in the second **(**fig. 1), the samples are heated by microwaves. Both setups are designed with a line for reagents and a bypass line to pre-treat the samples, in both cases the output mixture is analyzed using a μ-GC.

The tests are carried out in the same way for the two benches, with the first one serving as a reference to monitor any differences in the results obtained using the microwave bench.

The catalytic tests comprise two steps: a pre-treatment of the sample with a flow of H_2 at 650°C to reduce the catalyst into the active metallic form, subsequently the dry reforming experiment is studied at different temperatures between 700/850°C using CO_2 and CH_4 (ratio 3:1), diluted with N_2 and He (µ-GC's internal standards).

Temperature measurement are done by using thermocouple in the electric furnace setup, while for the microwave setup, temperature is monitored with a pyrometer and an IR-camera.

3. Results and discussion

The most challenging task during the microwave experiments is the monitoring of the temperature. It is not possible, as with the electric furnace, to rely on an internal thermocouple, since the presence of a metallic device could perturbate the flow of the electro-magnetic radiation. To overcome this problem, the microwave cavity of our setup was suitably machined to create a slit in which an IR camera could be placed to monitor the temperature along the reactor. Furthermore, it is also difficult to achieve a homogeneous absorption of the microwaves along the reactor, through some heating tests with different types of SiC and different filling strategies to place it inside the cavity, we found out that a homogeneous mixture of SiC and Ni/SiC is ideal to achieve a homogeneous temperature inside the cavity during the catalytic experiments (fig.2).

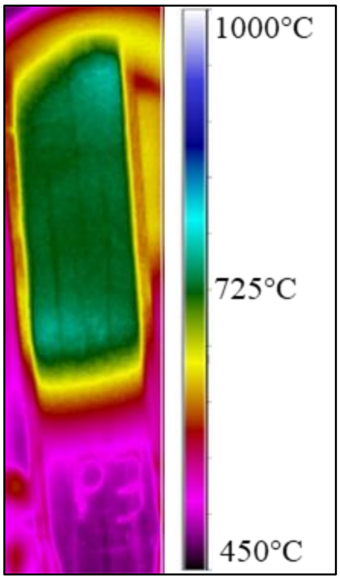

Figure 2. Temperature distribution inside the reactor during the catalytic reforming experiment with microwave heating

We compared then the catalytic performances of our material at the same conditions with the electric furnace and the MW heating. In a 1-hour long experiment in both cases no sign of deactivation has been noticed, the average conversion of CO_2 and CH_4 for the experiment with MW-heating was respectively 50% and 70%, while with the electric furnace the gas conversion was 10% for both gasses.

Additionally, TGA under air of the spent catalyst shows a very small mass loss (<4%), this can be explained by considering a very limited coke formation on the catalysts during the reforming experiments.

4. Conclusions

We have compared methane dry reforming in both an electrically and microwave heated fixed bed reactor over Ni/SiC. Temperature monitoring with IR camera of the quartz reactor shows that we achieved an uniform temperature distribution during the reforming experiments. The comparison of the two sets of experiments (electric furnace vs microwave oven) shows an improved performace of the catalytic perfomances of the Ni/SiC, very likely due to a much more efficient and selective delivery of the heat. In the end, post treatment TGA indicate that the prepared catalysts have an high resistance to the coke formation at the reaction conditions. All these initial experiments prove the efficiency of the microwaves as an alternative mean to provide the necessary heat to perform the wanted reaction, without the cons of the classic thermal heating (large thermal gradients, large loss of heat, non-selective heating).

References

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Keywords
“Biogas reforming”, “Microwave catalysis”, “Carbon dioxide”, “Ni/SiC”