

Microwave catalytic reactors for methane revalorization.

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Highlights

- A custom-designed monomodal MW applicator is presented.
- Non-oxidative methane coupling reactions are selected.
- Zeolites and iron-based catalysts are tested for conventional and MW heating.
- Selectivity of end-products varies under conventional and MW heating conditions.

1. Introduction

Natural gas is currently being considered as one of the most promising alternatives to crude oil for the production of chemical feedstocks of interest for the petrochemical industry to fabricate polymer and other advanced materials [1-2]. In contrast to crude oil, shale gas and natural gas appear as abundant, environmentally sustainable and less expensive sources for energy and chemical production in the near future. Since methane is the main component in these gas complex mixtures, the proper activation and selectivity enhancement of this molecule towards added-value chemical precursors remains as a remarkable challenge of great interest since the severe reaction conditions required for its activation are likely to cause degradation of the reaction products (C₂₊ hydrocarbons) [1-2]. In the frame of the H2020 European Project ADREM (Adaptable Reactors for Resource- and Energy-efficient Methane Valorization) [3], this work focuses on the evaluation and comparison of performances of conventional reactors and microwave catalytic cavities. The concept behind the development of a novel microwave cavity relies on the temperature gradient expected between the locally heated catalytic bed and the less-heated gas phase. This temperature gradient would prevent the primary byproducts to evolve into undesired byproducts in secondary reactions occurring at high temperatures. Herein, the non-oxidative coupling of methane (MNOC) towards hydrocarbons (essentially ethylene, benzene and naphthalene) is evaluated and monitored in terms of methane conversion and selectivity to end-products.

2. Methods

A cylindrically-shaped monomodal cavity was designed and constructed. The cavity dimensions (105 mm diameter and 85 mm height) were selected since the resonant mode TE₁₁₁ meets the typical 2.45 GHz frequency employed in industrial applications. The cavity hosts and heats up 1.5 cm high x 1.0 cm diameter catalytic samples (either in powder or supported on monoliths) under uniform electric field. The samples are confined within non-absorbing quartz tubes and heated by a 115 W MW generator with frequency span auto-tuning to control the heating rate and the sample temperature. Thermal and digital cameras, as well as a pyrometer are attached to the lateral cavity holes to measure the temperature distribution along the sample and its appearance. Supported catalysts such Mo/ZSM-5, Fe/CNTs or Fe/SiO₂ were heated up to reaction temperatures (700°C – 1000°C) without noticeable hotspots and low surface temperature gradients (< 100 °C). The change in the dielectric material properties as a result of the formation of coke could be controlled by the auto-tuning cavity keeping a constant reaction temperature along the time on stream.

3. Results and discussion

Different catalytic samples based on Mo-ZSM5 systems with different Si:Al ratios were evaluated under conventional and microwave heating conditions. Remarkably, some specific Si:Al ratios enabled a more effective and homogeneous heating under MW than others. Moreover, a major selectivity towards benzene production was achieved under MW, probably caused by the gas-solid temperature gradient that prevents and

retards the formation of C10+ hydrocarbons that typically act as seeds for coke formation. Likewise, the use of other catalytic systems based on iron, completely changed the selectivity towards hydrogen production. In this regard, the selection of CNTs, an extremely good MW absorber support enabled a very energy-efficient system to reach high reaction temperatures with extremely low consumption costs. This result further reinforced the versatility of MW cavities to tune the selectivity of products and save energy in comparison with conventional reactors operated at high temperatures (i.e. $T > 700\text{ }^{\circ}\text{C}$).

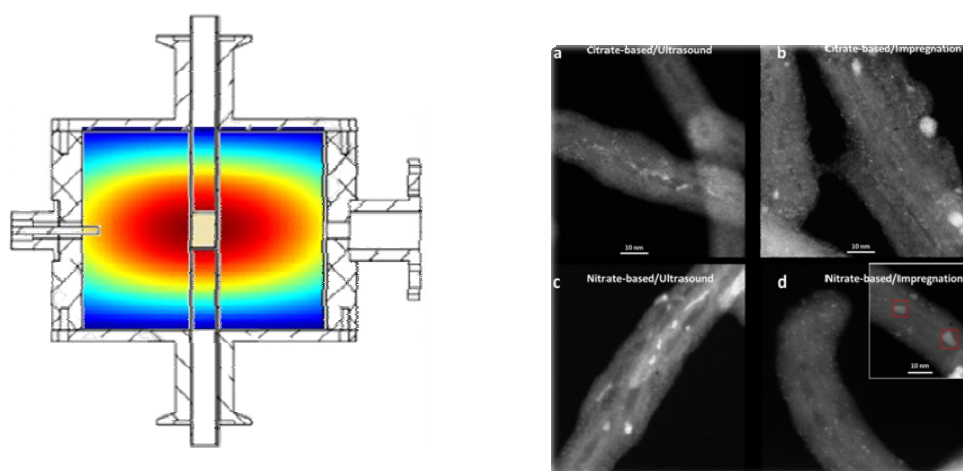


Figure 1. (Left) Scheme of the side-view MW reactor including the EM field simulation the central position of the catalytic bed in the maximum heating spot; (Right) Selection of representative TEM images corresponding to Fe-CNTs samples prepared by impregnation methods that are efficiently heated under MW for hydrogen production.

4. Conclusions

The design of novel MW cavities that maximize the matching capacity of the electromagnetic irradiation source with the catalytic materials is shown as a very promising alternative to activate methane and revalorize it into highly demanded chemical precursors. Moreover, the selective heating provided by MW heating combined with a proper selection of catalysts and supports can enhance the selectivity towards certain end-products.

References

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Keywords

Microwaves; Gas-Solid Temperature Gradient; Methane; Revalorization.