Catalytic methane cracking over amorphous and regular structured carbons

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Significance and Relevance

Carbons with amorphous (activated carbons, biochar) and regular structure (Zeolite templated Carbons) are compared for the first time as catalysts for the methane cracking for the selective production of hydrogen. The activity of carbons is not related to inorganic impurities but to surface features, not related to the presence of reducible functional groups, i.e. oxygen-based. The deactivation behavior strongly depend on the carbon type and reaction temperature. Zeolite templated carbons show the highest hydrogen productivity with a good stability.

Introduction and Motivations

Cracking of methane, especially at low temperature, can be considered a promising technology to produce turquoise hydrogen. Nickel-based catalysts are the most investigated, although a rapid deactivation is observed due to the deposition of graphitic carbon[1]. In this concern, catalysis with nanocarbons represents an interesting alternative due to the possibility to promote a carbon-over-carbon growth[2]. Epitaxial growth would make stable the process with the opportunity to produce both hydrogen and high-quality carbons as key products.

Materials and Methods

Two commercial activated carbons, named SICAV SV50 (SICAV S.p.A) and G-BAC (Kureha Group), one biochar (derived from pyrolysis of olive prunings) and one Zeolite Templated Carbon (ZTC), are used as catalysts for methane cracking. Methane cracking is carried out in a lab-scale tubular reactor, feeding a methane/nitrogen feed with a 20 vol.% of methane. The reaction temperature is set at 700 °C, 800 °C or 900 °C and the space velocity is ranged from 240 to 1440 $NL_{CH4}/(h\ kg_{cat})$. Among the investigated materials, the G-BAC activated carbon is characterized by a very low ash content (lower than 500 ppm). ZTC sample is synthesised by chemical vapor deposition/polymerization of ethylene at 800 °C[3].

Results and Discussion

All the samples exhibit a selectivity towards hydrogen close to the unity, under the investigated conditions. The main catalytic results as a function of reaction temperature and gas hourly space velocity are reported in Figure 1. The deactivation behavior strongly depend on both temperature and catalyst type. At 900 °C, a rapid deactivation is observed for biochar, while activated carbons seems to shows a more gradual deactivation, and ZTC is the only sample showing a conversion higher than 10% at the end of the test. Lowering the temperature to 800 °C, deactivation is retarded, albeit biochar slower but completely deactivates during the test. Pre-treatment with hydrogen (results not shown here) does not significantly impacts on the catalytic performances, although the samples show an important hydrogen consumption during temperature programmed reduction measurements. This result indicate that the hydrogen produced during the reaction does not alter the catalytic features, or the reducible functionalities are not responsible for the catalysis.

The temperature of 800 °C is surely the most suitable for hydrogen production, this also favored at lower gas hourly space velocity. Under the optimal conditions, ZTC exhibits the highest hydrogen productivity, which is higher than 700 NL of hydrogen produced for each Nm^3 of methane fed to the reactor, as reported in Figure 2.

Reaction mechanism and the identification of the active sites in carbon-based materials remain open challenges.

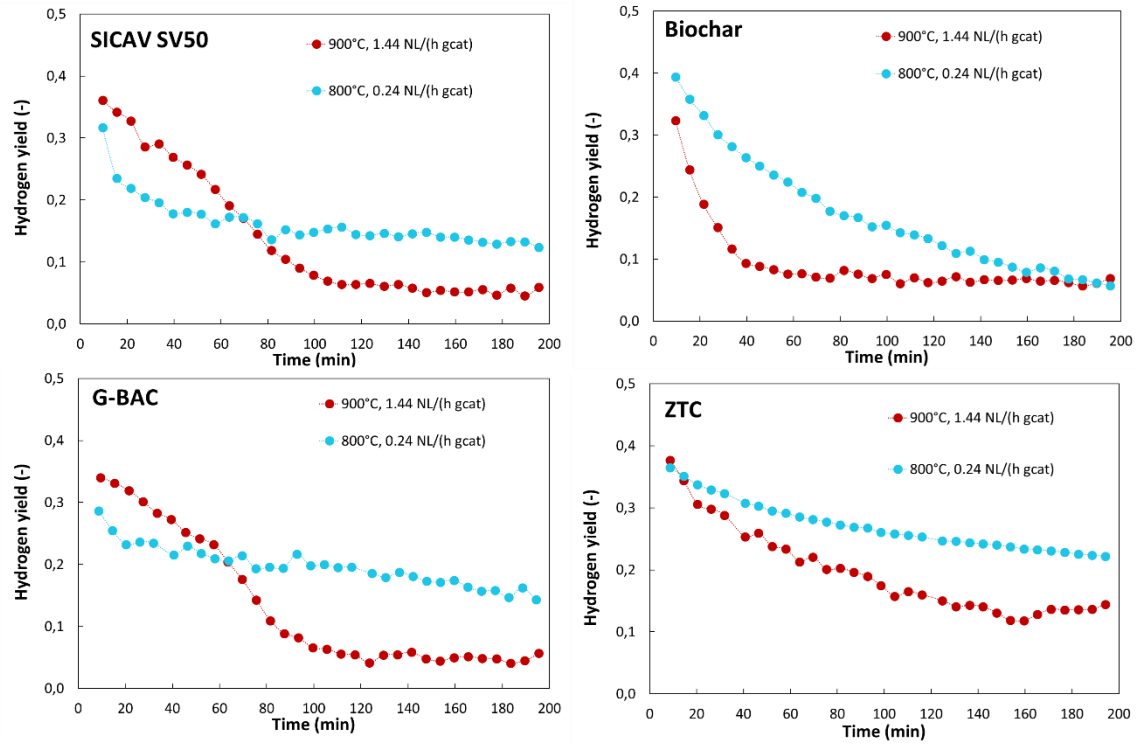

Figure 1 – Time on Stream tests of the investigated materials at different space velocity and temperature.

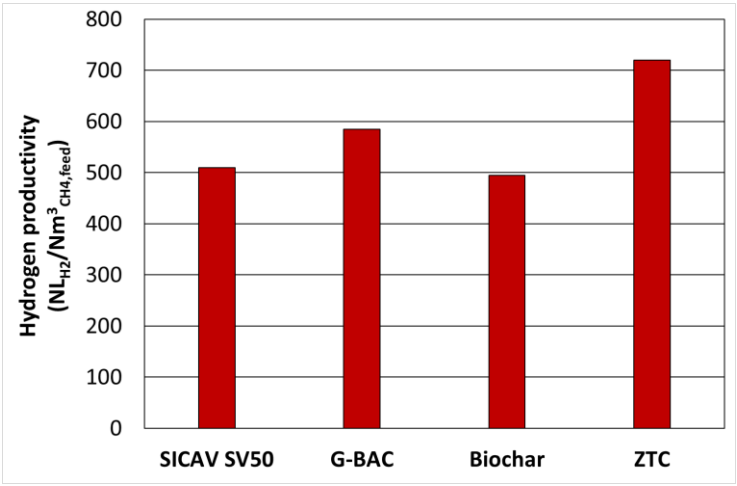

Figure 2 – Hydrogen productivity, 2 h Time-On-Stream, 800 °C and GHSV=240 NL/h/kg.

References

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