Catalytic cracking of methane over carbon-based catalysts

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This study compares carbons with amorphous structures (activated carbons, biochar) and ordered structures (Zeolite Templated Carbons, ZTC) for the first time as catalysts in methane cracking aimed at selective hydrogen production. The catalytic activity is attributed to surface characteristics rather than inorganic impurities or reducible oxygen-based functional groups. Catalyst deactivation behavior varies significantly with carbon type and reaction temperature. ZTC exhibits the highest hydrogen productivity and stable performance.

Low-temperature methane cracking is a promising route for producing turquoise hydrogen. While nickel-based catalysts are widely studied, their rapid deactivation from graphitic carbon deposition limits their effectiveness. Nanocarbon-based catalysts offer a compelling alternative by enabling carbon-over-carbon growth, potentially leading to a more stable process and the co-production of hydrogen and valuable carbon materials.

The catalysts used include commercial activated carbons, biochar from pyrolyzed olive prunings, and ZTC synthesized via chemical vapor deposition of ethylene at 800 °C. Methane cracking experiments were conducted in a lab-scale tubular reactor using a methane/nitrogen mixture (20 vol.% CH_4). Reactions were carried out at 700 °C, 800 °C, and 900 °C with gas hourly space velocities (GHSV) between 240 and 1440 $NL_{CH_4}/(h \cdot kg_{cat})$.

All catalysts demonstrated near-unity hydrogen selectivity. Catalyst performance varied with temperature and type. At 900 °C, biochar rapidly deactivated, activated carbons showed gradual deactivation, and ZTC maintained over 10% methane conversion. At 800 °C, deactivation was delayed; biochar deactivated completely, while ZTC remained stable. Hydrogen pre-treatment had minimal impact on catalytic activity, although significant hydrogen uptake during temperature-programmed reduction was observed. This suggests that reducible surface functionalities do not play a major catalytic role.

The optimal temperature for hydrogen production was found to be 800 °C, especially at lower GHSV. Under these conditions, ZTC achieved the highest hydrogen productivity, exceeding 700 NL of hydrogen per Nm^3 of methane fed, highlighting its potential for efficient hydrogen production.

ZTC outperforms other carbon-based catalysts in methane cracking due to its structured surface and stability. Although the exact active sites and reaction mechanisms in carbon-based catalysts are not yet fully understood, ZTC presents a promising path for sustainable hydrogen production.

Keywords: *heterogenous catalysis, methane cracking, nanostructured carbons.*