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Multiscale study of CH_4 pyrolysis: from kinetics to fluidized reactor operation with C-valorization in the steel industry

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Introduction. Catalytic methane pyrolysis ($CH_4 \leftrightarrow 2H_2+C_{(s)}$, $\Delta H°=75$ kJ/mol) is emerging as as a route for CO_x-free hydrogen with solid carbon co-generation. In this work, Fe-Al_2O_3 catalysts were investigated at different scales and reactor configurations. Solid characterization elucidated mechanisms of C-growth and served to assess the potential valorization of spent catalyst in steelmaking as reducing agent for waste iron recovery (Fig1).

Methods. Fe-Al_2O_3 (5-100wt.%Fe) catalysts were prepared by fusion-decomposition from nitrate salts. Pyrolysis tests were performed in thermobalance (TG, 4mg), packed (PBR, 0.75g) and fluidized (FBR, 3.5g) bed reactors, at varying temperature, feed composition, space velocity. Fresh, reduced, spent catalysts were characterized (BET, XRD, SEM, TEM, Raman). The reduction potential of spent catalyst was assessed *via* carbothermal conversion of Fe_xO_y into Fe^0, using waste mill-scale as iron source [1] ($Fe_xO_y+yC_{(s)} \leftrightarrow xFe^0+yCO_{(g)}$).

Results and discussion. From thermogravimetric analyses, the equimolar Fe-Al_2O_3 showed the best performances in terms of activity and C-accumulation capacity. This catalyst was tested in PBR, showing a rapid decrease in CH_4 conversion at increasing CH_4 feed and temperature due to formation of encapsulating-C. Stable operations were demonstrated by reducing the GHSV to 1 NL/h/g_{cat} at 750 °C, achieving the highest C-load of 5 g_C/g_{cat}. A dynamic reactor model was used to derive kinetic expressions for methane pyrolysis and deactivation rate over a wide operating range. Afterwards, pyrolysis tests were carried out in FBR, achieving stable bubbling fluidization regime and enabling longer experiments, spent discharge and post-characterization. The formation of ordered C-nanotubes was observed, leading to a growth in particle size, and reduced density. The spent-materials also exhibited a promising reduction degree (>80%,) and iron recovery ratio, when tested in the carbothermic smelting processes of mill-scale above 1375 °C.

These findings highlight the potential of Fe-Al_2O_3 catalysts to combine high H_2 productivity and C-load, both essential for process commercialization [2]. The resulting C-loaded catalysts could replace iron ore and anthracite in steel industry. Integrating bio-streams as feedstocks would enhance these advantages, producing CO_x-negative H_2 and increasing C-market value.

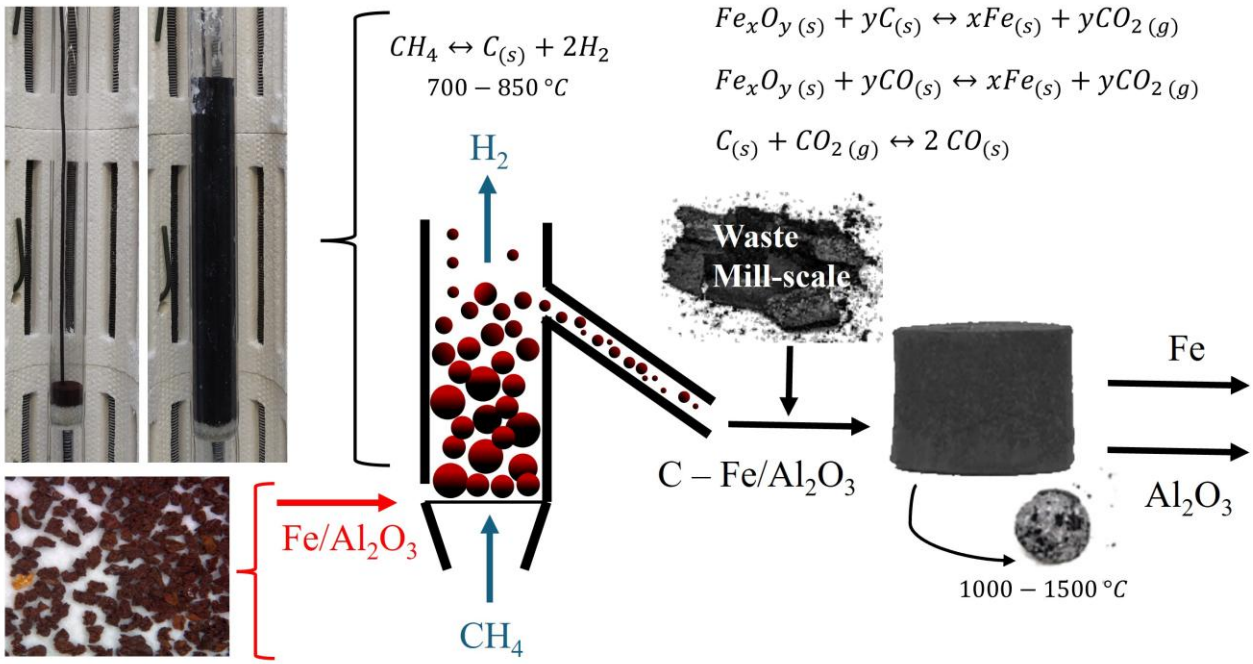

Fig1: Scheme of CH4 pyrolysis in FBR with utilization of spent catalyst for carbothermic reduction of mill-scale

References:

[1] Gianluca Dall'Osto, Davide Mombelli, Sara Scolari, Carlo Mapelli, (2024), Role of the Biogenic Carbon Physicochemical Properties in the Manufacturing and Industrial Transferability of Mill Scale-Based Self-Reducing Briquettes, Metals, 882, https://doi.org/10.3390/met14080882

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