Iron catalyst for CH_4 pyrolysis: characterizing C formation to understand catalyst deactivation

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Significance and Relevance

Methane pyrolysis represents a potential route to H_2 production with direct sequestration of solid C. Iron-based catalysts are active and robust, but the increasing accumulation of carbon is accompanied by rapid loss of activity. Yet, maximizing the C-capacity is a key factor behind process development. This work examines Fe/Al_2O_3 catalysts at high Fe load and investigates the compositional effects, the role of reduction, the transformations that follow the incipient and extensive formation of C to better elucidate the carbon build-up chemism and obtain rational guidelines to scale-up and industrialization.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis; H_2 storage and transportation, green H_2 production, hydrogen vectors
Preferred presentation: Oral preferred

Introduction and Motivations

Catalytic methane pyrolysis ($CH_4 \rightarrow 2\ H_2 + C$, $\Delta H° = 75.6$kJ/mol) to produce CO_x-free hydrogen is receiving more and more attention as a solution to meet the goals of decarbonization. Temperatures above 1000°C are needed with C-based catalysts or in thermal processes, but the use of metal-based catalysts (as Fe, Ni, and Co) allows to obtain appreciable methane conversions in the range of 700-900°C. Due to the still severe temperatures, active catalysts also call for proper textual properties [1].

In this work, iron-based catalysts with Al_2O_3 as a textural promoter have been prepared, characterized, and tested in methane pyrolysis. The research focus has been on the chemism of C-formation from Fe/Fe_3C to better understand the deactivation law and the overall C-load capacity. Besides, the final morphology and reactivity of the spent catalyst were characterized, in view of the open final destiny, which might involve C-valorization and/or underground storage.

Materials and Methods

Fe/Al_2O_3 catalysts with variable Fe/Al molar ratios were prepared by the fusion-decomposition (FD) method, after Pinilla et al.[2]: iron nitrate and aluminum nitrate are mixed and calcined at 350°C for 1 h, to promote the thermal decomposition of nitrates, and subsequently to 450°C for 8 h, to promote the formation of their respective oxides. Catalysts were also reduced according to the suggested procedure, with a maximum reduction temperature of 550°C to preserve the Fe-surface.

Experiments of catalytic CH_4 pyrolysis were carried out in thermobalance under temperature ramp (TG/MS, catalyst load 5 mg), but also in packed bed reactor (catalyst load 0.75 g) and in fluidized reactor (catalyst load = 3-5 g). Fresh, reduced and C-loaded catalysts were characterized by BET, XRD, (HR)-SEM, HR-TEM, TPR, and TPO.

Results and Discussion

The results herein reported focus on the 1:1=Fe:Al molar ratio, since this formulation was especially active and prone to high C-loading. The surface area amounted to about 100 m^2/g_{cat}; XRD highlighted a well-defined crystal structure, mainly associated with hematite phase (Fig. 1A, fresh catalyst). In conventional H_2-TPR, two major reduction stages were seen below 600°C and were ascribed to $Fe_2O_3 \rightarrow Fe_3O_4$, and $Fe_3O_4 \rightarrow FeO \rightarrow Fe^0$ transformations. At 900-1000°C a minor and broad H_2 consumption was ascribed to the reduction of $FeAl_2O_4$, resulting from the reactions between Fe_3O_4, FeO, Fe^0, and Al_2O_3. However, the reduction protocol (used in the reactor) up to 550°C with hold in pure H_2 was effective in obtaining Fe^0; indeed, H_2-TPR after such reduction process showed that only a minor high temperature consumption of H_2 related to the iron aluminate occurs.

The formation of metallic α-Fe and $FeAl_2O_4$ is evident in the XRD pattern, with an estimated Fe-size of 30 nm (Fig. 1A, reduced samples). FESEM and TEM images of fresh catalyst reveal flat islands of Al_2O_3 over which iron is dispersed; the presence of α-Fe and $FeAl_2O_4$ in the reduced sample is confirmed by the calculation of the interplanar distance. In the TG/MS experiment (Fig. 1B), the initial reduction phase is consistent with the TPR studies. Once CH_4 is added, an increase of the sample weight is observed due to the C formation and accumulation following the pyrolysis reaction (Fig. 1B). The weight gain (i.e. the reaction rate) is very high at the beginning, then it declines with time and C-load. The heterogeneous morphology of the catalysts where Fe aggregates are readily accessible might be the key behind the capability to grow C-structures that greatly exceed the pore volume.

Catalysts at different C-loads were obtained also from pyrolysis tests in packed bed and fluidized bed reactors. Importantly, a generalized deactivation law was deduced from the kinetic analysis of the CH_4 pyrolysis tests, such that the catalyst activity is uniquely dependent on the specific C-load and on temperature. We expect thus that the characterization of spent catalysts obtained from very different reacting and reactor conditions (but same temperature) and largely varying C-load provide a pathway through the surface transformations. XRD of spent catalysts showed that iron is present mainly as Fe_3C, and the initial α-Fe decreases in intensity as the reaction proceeds (i.e. as the C loading increases); at the same time the reflex attributed to graphitic carbon grows. $FeAl_2O_4$ is not long present, probably reduced to Fe^0 by carbon. FESEM and TEM confirmed the presence of Fe_3C and ordered C structures with a tubular structure (i.e. nanotubes, $d_{average}$ 50nm ca.); Raman spectra also suggested a highly ordered structural morphology for the carbon (I_G/I_D ratio > 2).

It is inferred that C structures are formed by precipitation from the C-soluble Fe_3C phase, while the residual Fe content governs the actual rate of reaction. The mechanism of Fe deactivation thus would pass through its progressive conversion and desegregation into Fe_3C particles. Fe aggregate size of the initial reduced catalyst might play an important role, which is currently under investigation by the analysis of the effect of Fe load and preparation procedures.

Regeneration experiments were carried out on the spent catalysts. Gasification tests showed that O_2 can react with solid C at 340°C, suggesting accessibility of Fe/Fe_3C sites despite significant C coverage; similarly, CO_2 gasified solid C (reverse Boudouard reaction) at 630°C, aligning with typical non-noble metal catalyst activity like dry reforming. Instead, steam gasification tests required around 740°C for solid C conversion, with high rates suggesting a higher activation energy compared to CO_2 gasification.

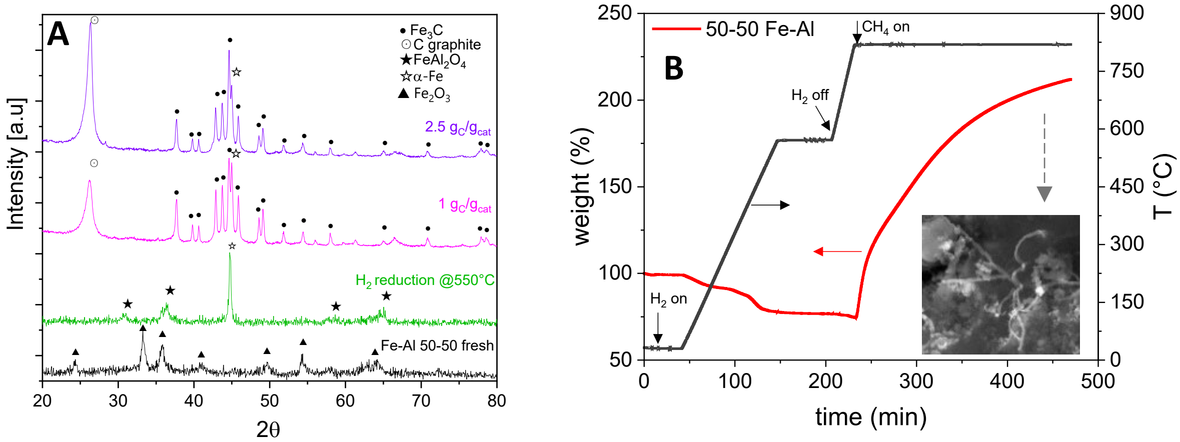

Figure 1 A) XRD pattern of fresh, H_2 reduced, spent catalyst; B) TG/MS analysis of reduction and CH_4 pyrolysis over fresh catalyst with SEM image of spent catalyst.

References

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2. J.L. Pinilla, R. Utrilla, R.K. Karn, I. Suelves, M.J. Lázaro, R. Moliner, A.B. García, J.N. Rouzaud, *International Journal of Hydrogen Energy* **2011**, 36, 7832-7843