Energetic transition and CO_2 abatement: catalytic methane pyrolysis for hydrogen production

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Highlights

- Innovative synthesis techniques for methane pyrolysis catalysts
- Sample characterization related to catalyst performances
- Activity, durability and kinetic evaluation
- Fluidized bed reactor design for performance improvement

1. Introduction

The combustion of fossil fuels to support today's energy superstructure generates large quantities of pollutant gases and requires a short-term solution. Hydrogen production represents one of the most challenging processes towards a new concept of energetic transition. Despite the classical problems related to storage and transportation of this resource, hydrogen exploitation allows energy production without the emission of greenhouse gases. Steam Methane Reforming (SMR), coal gasification and water electrolysis are the main technologies adopted to produce hydrogen. SMR and gasification are the most widespread and economically advantageous techniques, but they are characterized by high environmental impact. Electrolysis based on renewable sources has low emissions but presents high production costs and a strong dependence on climatic fluctuations. Therefore, it is necessary to develop low-cost techniques based on the exploitation of fossil fuels with a low carbon footprint. Catalytic methane pyrolysis, in this sense, represents one of the most promising technologies for hydrogen production. This process involves the dissociation of the methane molecule into hydrogen and elemental carbon in the presence of a catalyst, leading to the production of the so-called turquoise hydrogen [1]. In this work, the catalytic performance of different iron-based catalysts was studied and a fluidized bed reactor (FBR) for methane pyrolysis was designed, taking into consideration the catalytic kinetics.

2. Methods

Different techniques were employed for the synthesis of iron samples, e.g. Wet-Impregnation (WI) or Solution Combustion Synthesis (SCS), to produce catalysts with different iron loading and textural properties. Several characterization techniques (TPR, XRD, BET, Raman, FESEM, TEM) were carried out in order to evaluate structure, composition and morphology of the produced samples. Time On Stream (TOS) and kinetic tests were performed in order to evaluate the activity, durability and kinetic parameters (order of reaction and activation energy) of the catalysts. All the tests were conducted in a U-tube quartz reactor (filled with 50 mg of sieved catalyst) and inserted in a PID-controlled furnace.

3. Results and discussion

The performances of the catalysts were studied in relation to their structural and morphological properties. XRD and Raman spectroscopy analyses point out the presence of α-Fe_2O_3 in both WI and SCS fresh samples, but the SCS catalysts also contain a mixed Fe-Al oxide, along with amorphous oxides, as illustrated in Figure 1A. Although SCS catalysts have a smaller specific surface area, they contain iron crystallites of reduced size, as detailed in Table 1. Instead, impregnated samples retain part

of the high surface area of the starting alumina. When methane pyrolysis occurs, the iron oxide undergoes a transformation into iron carbide (Fe_3C) due to carbon diffusion into the iron structure. The activity and the kinetic characteristics of the catalysts were studied under various operating conditions. The SCS samples exhibit enhanced activity due to the effective dispersion of iron within the alumina framework, resulting in a higher concentration of active sites compared to the other kinds of catalysts, (see Figure 1C). The kinetic study of the catalysts allowed the determination of the order of the reaction (*n*, variable within the range of 0.5 to 1), the pre-exponential factor k_∞, and the activation energy, E_{act}. These parameters were evaluated through the following power law equation: rate = $k \cdot [C_{CH4}]^n$, with k calculated as $k_\infty \cdot \exp(-E_{act}/RT)$, as indicated in Table 1.

Table 1. Textural and kinetic properties of some of the Fe/Al_2O_3 materials.

Sample	S_{BET} / $m^2\ g^{-1}$	Pore size / nm	Crystal size / nm	k (800 °C) / $m^3\ s^{-1}\ g^{-1}$
Fe/Al_2O_3 - SCS	46.5	0.11	3	$6.8 \cdot 10^{-5}$
Fe/Al_2O_3 - WI	91.8	0.18	27	$1.4 \cdot 10^{-6}$

Kinetic results were employed to design a fluidized bed reactor (FBR) by using a Kunii-Levenspiel method [2]. Deactivation studies were carried out to evaluate the optimal reactor's operating conditions, based on the dependence of activity on catalyst coking (Figure 1B). FBR enhances hydrogen productivity, improves heat and mass transfer, and could be inserted in a closed loop process including a catalyst regeneration section [3].

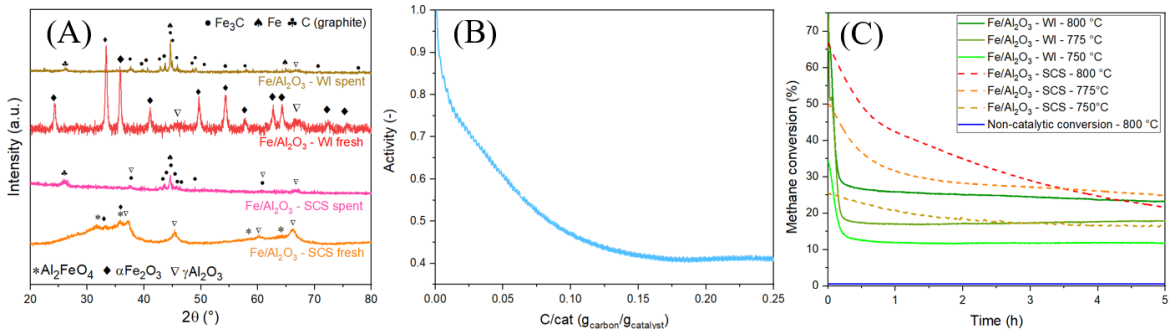

Figure 1. X-ray diffraction (XRD) patterns of some fresh and spent samples (A); SCS catalyst activity profile vs carbon over catalyst mass ratio (B). Methane conversion profiles in TOS tests at different temperature for methane pyrolysis conducted over some WI and SCS catalysts (C).

4. Conclusions

This study focuses on the optimization of iron-based catalysts for methane pyrolysis, but also provides a first evaluation of the environmental impact and industrial-scale scalability of the process, which can give a strong contribution to the energy transition towards the reduction of greenhouse gas emissions.

References

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Keywords

"methane pyrolysis", "iron-based catalysts", "turquoise hydrogen", "fluidized bed reactor design"