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Catalytic conversion of methane over a biomass char for hydrogen production: deactivation and regeneration by steam gasification

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ABSTRACT

CH_4 decomposition over a wood char was investigated as an alternative green catalyst to produce hydrogen from hydrocarbons. Pyrolytic carbon (pyrocarbon) deposition leads to apparent deactivation of the catalyst by pore-mouth plugging. The activity of the carbon bed and its available surface area are easily restored by H_2O gasification. The used char with pyrocarbon deposition was even found to be more reactive to gasification than the fresh char used in our conditions. This finding was highlighted by: (i) determination of gasification reaction extents by steam, (ii) temperature-programmed oxidation (TPO) of the fresh, used and reactivated chars and (iii) TPO under differential scanning calorimetry of these chars and demineralised chars. High-resolution transmission electron microscope (HRTEM) analysis of the chars showed different multiscale organisation of the carbon materials (disordered and graphitic mesoporous nanostructures). The fast regeneration of the used char could be attributed to the catalytic effect of the minerals present in the char that are reduced under our conditions of CH_4 conversion. The predominant oxidation of the pyrocarbon compared to the char during its regeneration is evidenced through differential annealing (at 1800 °C) followed by XRD analysis. The oxidation of pyrocarbon is faster than the oxidation of the weakly reactive mesoporous carbon in char as shown by the HRTEM analysis. Consequently, wood char is an effective, easy to regenerate and cheap catalyst for converting hydrocarbons (CH_4 or tar) into syngas.

1. Introduction

Thermal decomposition of methane over various kinds of catalysts is now accepted as a serious alternative route for producing hydrogen and simultaneous carbon sequestration or carbon nanotubes production [1–4]. Methane conversion was shown to occur at much lower temperatures and with increased kinetics using metal catalysts like iron, cobalt and nickel [5–8]. However, metals are sensitive to sulphur poisoning and are prone to carbidisation, and consequently quickly deactivate. The use of carbon-based catalysts has thus been suggested for overcoming these problems [9,10]. The catalytic properties of carbon-based material on hydrocarbons conversion is known for a long time [11–13]. The char might be an interesting catalyst for methane or tar conversion during biomass or coal gasification [12–15]. Several kinds of carbonaceous materials, such as activated carbons, carbon blacks or ordered mesoporous carbons, have been tested for the catalytic decomposition of methane [16–33]. The defects present on the graphene layers' edges are the main active sites for methane conversion over carbon catalysts [17,24,27].

One of the main obstacles for methane or tar decomposition is the regeneration of the carbon catalyst by oxidation. Deactivation is indeed induced by deposition of pyrolytic carbon (pyrocarbon) and resultant pores mouth blocking [17,21,24,26]. Pinilla et al. [22] concluded that "the regeneration conditions should be chosen according to the properties of the deposited carbon and not to the ones of the initial catalyst", but there is still a strong lack in understanding the properties of the deposited carbon.

The mechanisms of pyrocarbon formation are still controversial and were mainly studied on "clean" carbon surfaces such as graphitised carbon blacks (as Graphon) or carbon fibre [34–39]. To our knowledge, the formation of pyrocarbon onto disordered

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carbon such as activated char remains poorly understood. Moreover, the conditions of high methane conversion for producing hydrogen are very different from those of carbon vapour deposition, because, in the latter case, a low rate of conversion is looked for in order to reach a high degree of pore filling [35,40]. As noticed by Muradov et al. [17]: "it is not clear if carbon atoms formed from methane build upon the existing hexagon layer of the carbon catalyst, or they give rise to a new carbon crystallite."

The regeneration of activated carbons by stepwise oxidation of the deposited pyrolytic carbon has been studied by Muradov et al. [41] using steam, by Pinilla et al. [22] in a fluidised bed reactor and Abbas and Wan Daud [30] in thermobalance using carbon dioxide. The catalytic activity of lignite-based chars loaded with pyrocarbon was almost restored after 0.5 h in steam at 950 °C [41]. By contrast, a low reactivity of the deposited carbon on a CG Norit carbon submitted to CO_2 was observed [22]. The atomic structure of the deposited carbon onto different kinds of carbon-based catalyst has been studied by Guil-Lopez et al. [8], but the regeneration properties of the carbon-based catalysts are not yet understood.

As far as the authors know, and despite the high number of works dealing with the reactivity of carbonaceous catalysts for methane decomposition [16–33], the reactivity of a wood char coated by a pyrocarbon deposit after CH_4 conversion has not been studied so far. No investigation about the regeneration by steam gasification of a wood char after pyrocarbon deposition has been reported.

In a previous paper [24], we have focused on the concurrent deposition of pyrocarbon and activation of a wood char bed. It was shown that a methane conversion degree higher than 60% can be maintained at 1000 °C, provided that the BET surface area is also maintained through oxidation by steam and carbon dioxide. However, the stepwise regeneration of the wood char was not investigated. The kinetics of methane decomposition was described in a second paper, in which Knudsen diffusion in micropores was shown to become the mechanism controlling methane conversion rate in a microporous carbon [25].

The objective of the present work is to study the stepwise deactivation and regeneration of a wood char and to go deeper into the mechanisms of deactivated char regeneration, especially through the following techniques: temperature-programmed oxidation (TPO), high-resolution transmission electron microscopy (HRTEM) and differential annealing followed by XRD analysis.

2. Material and methods

2.1. Materials and experimental set-up

Experimental device and materials were already presented in a previous paper [24]. Only the salient points are briefly presented here.

Wood char was obtained from the pyrolysis of pinewood in a pyrolysis screw reactor (CIRAD Pyrotar facility [42]). The heating rate was about 20 °C min^{-1} up to the final temperature of 750 °C. After pyrolysis, the resultant char was sieved in order to collect the granulometric fractions ranging from 0.2 to 0.4 mm. These particles were next heated half an hour in nitrogen at 1000 °C. After such a heat treatment, any modification of the resultant material was then expected to be only due to the subsequent catalytic process and not to thermally induced char devolatilisation. A demineralised wood char was also produced by pyrolysing a wood that was first demineralised by HCl (0.05 M in methanol, during 48 h). This wood char has a lower content in mineral matters and hence should have a lower catalytic effect of minerals during the char formation. More details about preparation and characterisation of the wood chars can be found elsewhere [24].

CH_4 and N_2 flow rates were controlled by two mass regulators (Brooks Instrument, Veenendaal, The Netherlands). Demineralised H_2O was injected with a syringe pump (Avantec, Illkirch, France) in a vaporisation chamber set at 250 °C and flushed by the CH_4/N_2 mixture. The resultant gas composition was: CH_4 14 mol%, H_2O 30 or 0 mol%, N_2 QS, with a total gas flow of 430 N mL min^{-1}. In all cases (H_2O injected or not), the CH_4 mole fraction was maintained constant by adjusting the N_2 flow rate. Gases and steam were injected through a heated line (250 °C) into the char bed. The bed of wood char was placed inside a vertical quartz tubular reactor heated by an electric oven to 1000 °C. The bed of carbon particles was supported by a plate of sintered silica, and the (nickel-based) thermocouple used for controlling the temperature was systematically removed before the thermocatalytic experiments. At the outlet of the reactor, the gases (CH_4, CO, N_2 and H_2) were analysed with a micro-gas chromatograph (μGC) equipped with two columns (5A molecular sieve and Poraplot Q) and two thermal conductivity detectors (Varian, Palo Alto, CA, USA).

The space time was defined as $m_{char}/(Q \times 10^3)$, m_{char} being the mass of the char bed (g) and Q the total gas flow rate (L min^{-1}) at the temperature of the reactor. Following the suggestion by Lee et al. [18], a reference space time was defined as the one corresponding to the initial bed weight. As a first approximation, gas expansion (below 15% in the case of CH_4/H_2O mixture) was neglected. In this paper, reference space time was set at 3.3 min g L^{-1} for all methane conversion experiments. All methane conversion experiments were conducted at 1000 °C. At the end of the experiments, the char was flushed and cooled under N_2 flow.

Blank experiments conducted with an empty reactor (to study gas-phase reaction) and with silica instead of char were previously presented to demonstrate the catalytic effect of char on methane conversion under our conditions [24]. Moreover, gas-phase conversion of methane have been previously studied in details [43].

2.2. Analysis of the carbonaceous materials

Surface area and porosity were determined from the corresponding nitrogen adsorption–desorption isotherms obtained at −196 °C with an automatic instrument (ASAP 2020, Micromeritics). The samples were previously outgassed at 523 K for several hours. The surface areas were measured by the Brunauer–Emmet–Teller (BET) calculation method [44] applied to the adsorption branch of the isotherms. The micropore volume, V_{DR}, corresponding to pores narrower than 2 nm, was calculated according to the Dubinin–Radushkevitch (DR) method [45]. The total pore volume, sometimes referred to as the so-called Gurvitch volume $V_{0.99}$, was defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure $p/p_0 = 0.99$ [46]. The Gurvitch volume is assumed to be the sum of micropore plus mesopore volumes. The mesopore volume, V_{meso}, was calculated as the difference between $V_{0.99}$ and V_{DR}.

Fourier-transform infrared spectroscopy and temperature-programmed desorption analyses for the determination of functional surface groups were previously reported [24]. Few differences in the surface chemistry were evidenced between wood char samples before and after deactivation or gasification. Such a finding should be related to the experimental difficulty of quenching carbon samples reacting at 1000 °C. At this temperature, the rate of decomposition of surface functions, especially the oxygenated ones, is very high, and what was measured after cooling might not be representative of the surface chemistry existing during the thermocatalytic experiments. Nevertheless, the relation between surface functions concentration and methane conversion will be discussed in this paper by means of CO analyses at the outlet of the reactor during stepwise H_2O feeding.