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The nature of the deposited carbon at methane cracking over a nickel loaded wood-char

La nature du carbone déposé à la suite de la réaction de craquage du méthane sur un char de biomasse chargé en nickel

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ABSTRACT

The catalytic properties of raw biomass chars and Ni-loaded biomass chars prepared at a high-heating-rate were assessed in the methane decomposition reaction. The raw chars exhibited a moderated catalytic activity in methane cracking while the Ni-loaded chars showed a catalytic activity 10 times higher than the raw chars. The deposited carbon was a highly ordered one as evidenced by XRD, Raman analysis and oxygen reactivity tests. The activation energy in the combustion reaction was estimated to be 300 kJ/mol. These results indicate that biomass char can be an effective low-cost and active support for metal impregnation to be used in catalytic cracking of hydrocarbons for hydrogen production.

Mots-clés:
Char de biomasse
Imprégnation de nickel
Craquage du méthane
Réactivité du char
Caractérisation du char

RÉSUMÉ

Les propriétés catalytiques des chars de biomasse, dopés ou non au nickel et préparés par pyrolyze rapide à haute température, ont été évalués dans la réaction de décomposition du méthane. Les chars non dopés présentent une activité catalytique modérée dans la réaction de craquage du méthane, tandis que ceux dopés en nickel ont montré une activité catalytique 10 fois plus élevée. Le carbone déposé sur le char dopé était très ordonné, comme en témoignent les analyses DRX et Raman ainsi que les tests de réactivité à l'oxygène. L'énergie d'activation de la réaction de combustion a été estimée à 300 kJ/mol. Ces résultats indiquent que le char de biomasse représente un support catalytique à faible coût et efficace pour l'imprégnation de métaux utilisé dans le craquage catalytique d'hydrocarbures pour la production d'hydrogène.

1. Introduction

Methane can be decomposed into carbon and hydrogen according to the moderately endothermic reaction:

$$CH_4 \rightarrow 2H_2 + C(s)\ \Delta H = +75.6\ \text{kJ/mol} \quad (1)$$

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Due to the strong C–H bonds, non-catalytic thermal cracking of methane requires temperatures higher than 1200 °C to obtain a reasonable yield. Using a catalyst allows to reduce markedly the temperature. Commonly used catalysts are metal based and carbon based ones [1]. Ni and Fe based catalysts are widely used and exhibit very good activities in methane decomposition. The performance of a catalyst depends on the nature of the support. Common metal supports are alumina, SiO_2, metal oxides and zeolites[2].

Carbonaceous catalysts have also been tested in methane decomposition. These materials are less expensive, have a higher temperature resistance and are tolerant to sulfur and other harmful impurities that cause deactivation in metal based catalysts. A wide range of carbonaceous materials for catalytic application in methane decomposition was investigated in the literature [3–5]. The focus is mainly on activated carbons (manufactured from different carbon-based sources) and carbon blacks due to their good activities and stabilities over time.

For instance, Muradov et al. [3] investigated the catalytic activity of various carbon based materials such as activated carbon, carbon black, glassy carbon, acetylene black, graphite, diamond powder, CNT and fullerene. The authors found that there is a linear correlation between the initial methane decomposition rate and the specific surface area of the carbon material. This linear relationship is only valid in the surface area range of 5–1200 m^2/g. The authors stated that the catalytic activity of carbon is rather related to its level of structural ordering. The less ordered are the carbons, the most efficient they are for methane decomposition. Thus activated carbons and carbon blacks (amorphous, micro-crystalline) are more efficient for methane catalytic decomposition than graphite, diamond and carbon nanotubes (highly ordered carbons).

Commercial activated carbons (ACs) can also be used as active supports for metal catalysts such as nickel which leads to a net increase in the catalytic activity of the material [6,7]. For instance, Sarada et al. [7] studied the methane decomposition over Ni-loaded coconut shell activated carbon. AC samples were impregnated with an acetone solution containing Ni-nitrate. The authors showed that the performance of the catalyst depends on the loading amount of Ni and its particle size. Decomposition tests were performed for 4 h and showed that the optimal loading of nickel that ensures the best stability and maximum accumulated carbon along cracking (7.92 g C/g Ni) was 23% of Ni in AC.

Biomass chars can also be used as catalysts in methane cracking [8–10]. However, the raw char does not exhibit a sustained activity and is rapidly deactivated by pore blocking due to carbon deposition [11]. Klinghoffer et al. [9] reported maximum deposited carbon amounts of 0.05–0.2 g/g of char, for pine char obtained after gasification with steam and CO_2 at different conversion levels, which is a quite low activity.

Biomass chars can be loaded with Nickel for an enhanced catalytic activity in methane cracking. This can be done on the char or before the pyrolysis reaction by impregnating the parent biomass. Nickel wet impregnation on woody materials leads to a very good dispersion of the metal in the wood and in the char after the pyrolysis reaction [12]. Impregnation of the parent biomass has the advantage of providing an intimate contact of the nickel with the biomass during the pyrolysis, which modifies the pyrolysis reaction mechanisms, reducing tars via cracking reactions and enhancing the production of light gases [13,14]. For instance, Blin et al. [14] reported an increase in H_2 production of around 260% for a nickel-impregnated wood compared to a pyrolysis test without catalyst. The resulting char containing highly dispersed nickel particles can be used in catalytic cracking of hydrocarbons.

To the best of the knowledge of the authors, nickel-loaded activated carbons or biomass chars used for methane cracking are commonly prepared by a dry mixing or a wet impregnation of the chars. We chose, in the present study, to impregnate the parent material so as to maximize the light gas production during pyrolysis and to obtain a good dispersion of the metal in the final char as proposed by Blin et al. [12,14].

This study focuses on the final Ni-containing chars. Besides the evolution of the catalytic activity in methane cracking, we followed the nickel fate during the three reactions of pyrolysis, methane cracking and combustion. We also looked closely on the deposited carbon structural properties and reactivity.

2. Materials and methods

2.1. Parent wood sample impregnation

Biomass samples are beech wood-chips provided by SPPS Company (France). Raw samples were initially sieved. Biomass particles having sizes in the range of 4–5 mm and thickness of about 1 mm were selected to perform the pyrolysis experiments. Proximate and ultimate analyses of the biomass samples are presented in Table 1. The results are given on a dry basis. The moisture content of the wood-chips was estimated to be 10% ± 1%. Ni-loaded woodchips were prepared following a wet impregnation method [12]. A load of 20 g of wood-chips was impregnated with 200 mL of nickel nitrate aqueous solution (1 mol Ni/l) prepared with $Ni(NO_3)_2\,6H_2O$ (Sigma Aldrich, 99% purity). At low pH values, H^+ protons compete with Nickel for adsorption on the functional groups. For that reason the pH of the solution was continuously adjusted in the range of 6.5–7 with an ammonia solution (1M). Wood impregnation was carried out for 3 days at room temperature (293 K) and under magnetic stirring. The impregnated wood chips were afterward filtered, washed with 500 mL of deionized water and dried at 323 K for 24 h.

2.2. Nickel identification and quantification

The nickel content in the dried impregnated wood sample was determined by optical emission spectrometry

Table 1
Proximate and ultimate analysis of the beech wood-chips (wt.% on dry basis).

	Proximate analysis			Ultimate analysis				
	VM	Ash	FC	C	H	O	N	Ni
Raw-wood	88.1	0.4	11.5	46.1	5.5	47.9	0.1	0
Ni-wood	–	3.0	–	42.0	5.4	51.8	0.8	2.9