



Regeneration study of Ni/hydroxyapatite spent catalyst from dry reforming

Bruna Rego de Vasconcelos*, Doan Pham Minh, P. Sharrock, A. Nzihou

Université de Toulouse, Mines Albi, UMR CNRS 5302, Centre RAPSODEE, Campus Jarlard, F-81013 Albi cedex 09, France

ARTICLE INFO

Keywords:

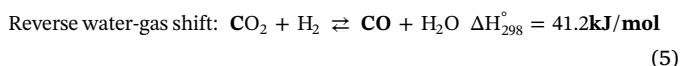
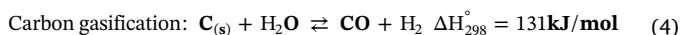
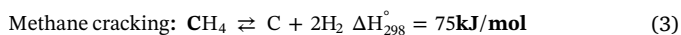
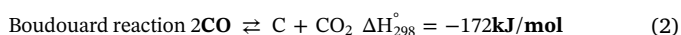
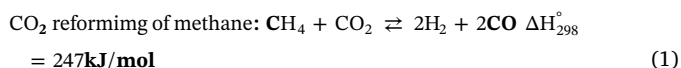
hydroxyapatite
dry reforming of methane
nickel catalyst
syngas
catalyst regeneration

ABSTRACT

In the present work, the regeneration of a spent nickel hydroxyapatite-based catalyst (Ni/Ca-HA1.5) used in dry reforming of methane (DRM) was investigated. Three successive cycles of DRM/regeneration were performed. Two different gasifying agents were tested for the regeneration step: air and carbon dioxide (21%CO₂/N₂). The aim was to evaluate the ability of regeneration of the catalyst under different atmospheres. The regeneration was performed *in situ* at 700 °C under 70 mL/min of gasifying agent. Reproducible results were obtained between each cycle for the two atmospheres tested and only a small irreversible deactivation was noticed. Several characterizations (SEM, TEM, TPR, XRD) of the fresh and spent catalysts allowed proving that the irreversible deactivation was provoked by densification of nickel particles and core-shell carbon formation. Despite the slight decrease in reactants' conversions, selectivity to syngas was around 80–90% during the three cycles of DRM/regeneration with both atmospheres and no changes in the selectivity were observed. The results proved that the Ni/Ca-HA1.5 catalyst could be easily regenerated under different atmospheres and make it competitive for dry reforming of methane.

1. Introduction

Carbon dioxide (CO₂) reforming of methane (CH₄) (Eq. (1)) has gained increasing attention due to the conversion of two main greenhouse gases into syngas (mixture of hydrogen and carbon monoxide), which can further be used in the production of energy and of high-value added chemicals [1–3]. Nickel-based catalysts have been extensively investigated for this process due to its high catalytic activity in this reaction. However, they undergo severe deactivation due to catalyst sintering under the high temperatures required for the reaction and mostly due to coke deposition over the active sites of the catalyst [4,5]. In fact, many parallel reactions occur along with the dry reforming reaction (DRM) (Eq. (2)–(5)) and coke can originate from many of these reactions (Eq. (2)–(4)).



So, in the past few years, many studies have focused on the improvement of the physico-chemical properties of the catalysts and on the optimization of the reaction conditions in order to obtain high catalytic conversion and stability during long periods of time [6]. They include the use of basic promoters, of supports with oxygen storage capacity, the combination of different transition metals, the optimization of preparation pathways of the catalysts etc [7–19]. Also, temperature, pressure, reactants ratio and type of reactor have been investigated [10,20,21].

Nevertheless, the capacity of regeneration of the catalysts is also an important parameter. The regeneration process allows cleaning the coke deposit from the surface and the pores of the catalyst without destroying or modifying the structure of the catalyst [7]. This aspect has economic and environmental impact. In fact, the costs of regeneration should remain lower than the costs of obtaining fresh catalysts [7]. Moreover, regenerating the catalyst instead of disposing it as solid waste is an environmentally friendly option since the spent catalyst can form toxic metal compounds in the environment [22]. So, regeneration studies of spent catalysts have also been conducted aiming to re-use the deactivated catalysts.

Vicerich et al. [23] investigated the regeneration with oxygen diluted in nitrogen at 450–550 °C of the PtReIn/Al₂O₃ catalyst used in cyclohexane dehydrogenation and cyclopentane hydrogenolysis. They showed that the regeneration process could fully recover the activity of the spent catalyst. Wu et al. [15] showed that the regeneration at 300 °C

* Corresponding author. Bruna Rêgo de Vasconcelos, Ecole des Mines d'Albi-Carmaux, 81000 Albi France.
E-mail addresses: bregodev@mines-albi.fr, bregodev@gmail.com (B. Rego de Vasconcelos).

<http://dx.doi.org/10.1016/j.cattod.2017.05.092>

Received 26 February 2017; Received in revised form 19 May 2017; Accepted 29 May 2017
0920-5861/ © 2017 Elsevier B.V. All rights reserved.

of the $\text{Rh}_{0.1}\text{Ni}_{1.0}/\text{BN}$ catalyst could remove the carbon deposit and reactivate the catalyst, but a small decrease in the activity was observed. Simson et al. [24] investigated the regeneration of a Pt/Rh catalyst after steam reforming of an ethanol/gasoline mixture. They showed that thermal treatment under air could fully restore the performance of the catalyst. However, after regeneration, their catalyst deactivated more quickly than the fresh one. Similarly, Sanchez et al. [25] reported that the catalytic performance of their reforming catalyst could be recovered by air combustion of the coke deposits but its selectivity to H_2 quickly decreased.

Most of the literature reports on catalyst regeneration are related to the combustion of coke with air due to its availability. Also, the mechanism of carbon species oxidation by O_2 has been widely investigated. There are many references in the literature to carbon bulk diffusion through the metal particle, oxygen spillover and redox mechanism [26]. However, coke deposits can be eliminated not only by O_2 but also by different gasifying agents, such as steam and CO_2 [27]. There are only few studies that investigated the effect of other gasifying agents such as CO_2 on the regeneration of catalysts [28] and the mechanism of carbon removal by these gases is not yet well known [26].

Hydroxyapatite has been investigated as catalyst support in many different reactions such as water gas shift [29], partial oxidation of methane [30], steam reforming of glycerol [31] etc. In fact, hydroxyapatite can undergo substitutions in its crystal lattice, which may favor the incorporation of an active phase to the catalyst [32,33]. Also, this material present high chemical and thermal stability, it has very low solubility in water and it does not sinter at temperatures lower than $700\text{ }^\circ\text{C}$ [34,35]. Moreover, it presents basic sites that can reversibly adsorb carbon dioxide and help coke removal [36]. Despite all these advantages, only few works has been published using hydroxyapatite as catalyst for dry reforming of methane reaction. We have previously demonstrated that hydroxyapatite-based catalysts were performing for dry reforming of methane reaction [37,38]. So, in the present work, Ni/hydroxyapatite catalyst was investigated in CO_2 reforming of CH_4 reaction, with a focus on the regeneration process of the deactivated catalyst. The effect of gasifying agent on the re-use of the catalyst was also investigated by using two different gasifying agents: air and carbon dioxide. CO_2 was used in this work because it is one of the reactants of DRM and the reaction between CO_2 and solid carbon (Boudouard reaction, Eq. (2)) produces CO, which is one of the products of DRM. Also, the basic properties of the hydroxyapatite could favor the CO_2 adsorption and consequently, solid carbon ($\text{C}_{(s)}$) gasification. The objective of this work was to evaluate the reproducibility of the performance of the Ni/hydroxyapatite catalyst under several reaction/regeneration cycles and under different regeneration atmospheres.

2. Materials and methods

2.1. Catalyst preparation

The hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) support used in this work was provided by PRAYON. Besides coke deposition, one of the reasons for catalyst deactivation is the support sintering [7]. So, as in this work the DRM reaction is performed at mild temperature ($700\text{ }^\circ\text{C}$), the hydroxyapatite support was previously sintered at $1000\text{ }^\circ\text{C}$ for 5 h at $10\text{ }^\circ\text{C}/\text{min}$ to ensure support stability during the catalytic tests and to avoid later catalyst deactivation by support sintering. The catalyst was prepared by incipient wetness impregnation method by impregnating the support with an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fisher Scientific, > 98 wt%). The amount of nickel on the catalyst was 5.7 wt%. Then the catalyst was dried at $105\text{ }^\circ\text{C}$ overnight. The catalyst was referred to as Ni/Ca-HA1_S. In order to obtain more precise characterization results of nickel particles on the catalyst during the reaction, a calcination step under air at $500\text{ }^\circ\text{C}$ was performed for two hours before XRD, SEM and TEM analyses.

2.2. Dry reforming of methane

The dry reforming of methane was carried out in a fixed-bed tubular reactor with inner diameter of 8 mm 300 mg of the catalyst was diluted 2 times with inert alumina powder to improve heat exchange inside the catalyst bed. The same alumina was used to place the catalyst at the center of the reactor. The pressure drop in the reactor was 1.6 bar. The temperature of the reaction was controlled by a thermocouple placed at the center of the catalyst bed. The catalyst was reduced *in situ* at $700\text{ }^\circ\text{C}$ for 2 h under $4\%\text{H}_2/\text{N}_2$ flow ($70\text{ mL}/\text{min}$). Then, DRM was carried out for 30 h at $700\text{ }^\circ\text{C}$ with a WHSV of $15882\text{ mL h}^{-1}\text{ g}_{\text{cat}}^{-1}$ with a synthetic gas mixture containing 20% of CH_4 , 20% of CO_2 and 60% of N_2 (volume percentage). A silica gel tube was used as water trap at the reactor outlet. Quantification of the water produced during the reaction was made by mass difference of this water trap. Also, a gas counter was used for the measurement of the total gas flow rate at the reactor outlet. The measure of the total gas flow rate at the reactor outlet allowed taking into account the change in the total number of moles between reactants and products to calculate the composition at the reactor outlet. Gas products were analyzed by a $\mu\text{-GC A3000}$ (Agilent) equipped with a thermal conductivity detector (TCD).

Methane and carbon dioxide conversion and products selectivity were calculated as follows:

$$\text{CH}_4\text{conversion}(\%) = (\dot{Q}_{(\text{CH}_4)_{\text{in}}} - \dot{Q}_{(\text{CH}_4)_{\text{out}}})/(\dot{Q}_{(\text{CH}_4)_{\text{in}}}) \times 100 \quad (6)$$

$$\text{CO}_2\text{conversion}(\%) = (\dot{Q}_{(\text{CO}_2)_{\text{in}}} - \dot{Q}_{(\text{CO}_2)_{\text{out}}})/(\dot{Q}_{(\text{CO}_2)_{\text{in}}}) \times 100 \quad (7)$$

$$\text{H}_2\text{Oselectivity}(\%) = (\dot{Q}_{\text{O}(\text{H}_2\text{Oproduced})})/(\dot{Q}_{\text{O}(\text{CO}_2\text{consummed})}) \times 100 \quad (8)$$

$$\text{COselectivity}(\%) = (\dot{Q}_{\text{O}(\text{COproduced})})/(\dot{Q}_{\text{O}(\text{CO}_2\text{consummed})}) \times 100 \quad (9)$$

$$\text{H}_2\text{selectivity}(\%) = (\dot{Q}_{\text{H}(\text{H}_2\text{produced})})/(\dot{Q}_{\text{H}(\text{CH}_4\text{consummed})}) \times 100 \quad (10)$$

$$\text{C}_{(s)}\text{selectivity}(\%) = (\dot{Q}_{\text{C}_{(s)}(\text{out})})/(\dot{Q}_{\text{C}(\text{CH}_4\text{consummed})} + \dot{Q}_{\text{C}(\text{CO}_2\text{consummed})}) \times 100 \quad (11)$$

where $\dot{Q}_{(\text{CH}_4)_{\text{in}}}$ and $\dot{Q}_{(\text{CH}_4)_{\text{out}}}$: methane molar flow rate (mmol h^{-1}) at the reactor inlet and outlet; $\dot{Q}_{(\text{CO}_2)_{\text{in}}}$ and $\dot{Q}_{(\text{CO}_2)_{\text{out}}}$: carbon dioxide flow rate (mmol h^{-1}) at the reactor inlet and outlet; $\dot{Q}_{\text{O}(\text{H}_2\text{Oproduced})}$: atomic oxygen flow rate (mmol h^{-1}) at the reactor outlet (under H_2O form); $\dot{Q}_{\text{O}(\text{CO}_2\text{consummed})}$: atomic oxygen flow rate (mmol h^{-1}) (under form of CO_2 consumed); $\dot{Q}_{\text{O}(\text{COproduced})}$: atomic oxygen flow rate (mmol h^{-1}) at the reactor outlet (under CO form); $\dot{Q}_{\text{H}(\text{H}_2\text{produced})}$: atomic hydrogen flow rate (mmol h^{-1}) at the reactor outlet (under H_2 form); $\dot{Q}_{\text{H}(\text{CH}_4\text{consummed})}$: atomic hydrogen flow rate (mmol h^{-1}) (under form of CH_4 consumed); $\dot{Q}_{\text{C}_{(s)}(\text{out})}$: solid carbon flow rate at the outlet of the reactor deduced from mass balance.

The reaction/regeneration cycles were carried out as follows:

a) Activation of the catalyst at $700\text{ }^\circ\text{C}$ under $4\%\text{H}_2/\text{N}_2$ was performed for 2 h. The dry reforming reaction was carried out at $700\text{ }^\circ\text{C}$ for 30 h as previously explained. After the reaction, the reactive gases were switched with air. The temperature was kept at $700\text{ }^\circ\text{C}$ and $70\text{ mL}/\text{min}$ of air flowed through the catalyst for 1h30 min. During the regeneration process, the concentration of CO_2 resulting from the oxidation of coke was monitored by a gas chromatography.

b) Activation of the catalyst at $700\text{ }^\circ\text{C}$ under $4\%\text{H}_2/\text{N}_2$ was performed for 2 h. The dry reforming reaction was carried out at $700\text{ }^\circ\text{C}$ for 30 h as previously explained. After the reaction, the reactive gases were switched to a gas mixture containing 21% of CO_2 and 79% of N_2 (volume percentage). The temperature was kept at $700\text{ }^\circ\text{C}$ and $70\text{ mL}/\text{min}$ of the gas mixture flowed through the catalyst for 1h30 min. During the regeneration process, the concentration of CO resulting from the oxidation of coke was monitored by gas chromatography.

Three cycles of DRM/regeneration for both gasifying agents were performed to test the regeneration capacity of the hydroxyapatite catalyst under different atmospheres.

Download English Version:

<https://daneshyari.com/en/article/6504294>

Download Persian Version:

<https://daneshyari.com/article/6504294>

[Daneshyari.com](https://daneshyari.com)