Applied Catalysis A: General 396 (2011) 40–51

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Comparison of metal and carbon catalysts for hydrogen production by methane decomposition

R. Guil-Lopez[a,b,*], J.A. Botas[a], J.L.G. Fierro[b], D.P. Serrano[a,c,**]

[a] Departamento de Tecnología Química y Energética, ESCET, Universidad Rey Juan Carlos, C/Tulipán s/n, 28933-Móstoles, Madrid, Spain
[b] Grupo de Energía y Química Sostenibles, ICP-CSIC, C/Marie Curie 2, Cantoblanco, 28049-Madrid, Spain
[c] IMDEA Energía, C/Tulipán s/n, 28933-Móstoles, Madrid, Spain

ARTICLE INFO

Article history:
Received 22 October 2010
Received in revised form 24 January 2011
Accepted 25 January 2011
Available online 3 February 2011

Keywords:
CO_x-free H_2 production
CH_4 decomposition
Ni-catalysts
Fe-catalysts
Hydrotalcites
Activated carbon
Carbon black
Carbon nanotubes

ABSTRACT

The CO_x-free hydrogen production by decomposition of methane was carried out over metal-free carbons and bulk and supported metal catalysts. Catalysts based on Ni or Fe (oxides, spinels and *ex*-hydrotalcite mixed oxides) and carbon-catalysts of different types (carbon black, activated carbon, carbon nanotubes and graphite) have been used and the performance of both different kinds of catalyst compared in the target reaction, focussing the comparative study on the initial activity and the resistance against deactivation. Catalytic results showed that activity of carbon catalysts is similar to that of the non-prereduced metal catalysts. Carbon blacks, and specifically *vulcan*-type, were found to be most resistant catalysts against deactivation, while the most active ones were nickel catalysts derived from hydrotalcite-like precursors (*ex*-LDH). It was also shown that pre-reduction treatment of nickel precursor to generate the metallic Ni^0 phase before the reaction decreases the threshold temperature to generate hydrogen by about 200 °C.

Along the course of the reaction, nanotubes and nanofibers are formed on the surface of metal catalysts. These carbon structures encapsulate metal particles and deactivate the catalysts. However, when carbons are used as catalysts, the nature of carbon deposits depends largely on the type of carbon material employed as catalyst in the methane decomposition. Thus, the use of carbon blacks and graphite yielded amorphous turbostratic carbon, whereas activated carbons mainly produced carbon, which showed the carbon black structure. Finally, the carbon by-product of the reaction, when carbon nanotubes were used bas catalysts, accumulates in the form of extra layers over the walls of carbon nanotubes thus increasing their wall thickness.

1. Introduction

Hydrogen has long been used in the chemical industry for both oil refining processes such as hydrotreating and hydrocracking and for the production of bulk chemicals such as methanol, ammonia and synthetic hydrocarbons (Fischer–Tropsch synthesis) [1]. Moreover, lately, hydrogen demand has been growing since it appears as a clean energy vector that can be used in fuel cells (FCs) and in internal combustion engines to generate energy with significant improvements in air quality, human health, and climate [2]. Nowadays, the main process for hydrogen production is the catalytic steam reforming of methane (SRM) [2], where the chemistry, production and distribution technologies of methane (CH_4) have already been developed and whose H/C atomic ratio is the highest among the hydrocarbons (H/C = 4 in CH_4) [3]. However, both the growing restrictions in the legislation about CO_2 emissions (the SRM produces as by-product ca. 6 t CO_2/t H_2, and about 9 t CO_2/t H_2 if the contributions of the CO_2 formed by NG combustion to drive the endothermic SRM process and to produce steam are taken into consideration), and the low CO concentration levels in hydrogen stream, required for the hydrogen use in PEM FCs (lower than 10 ppm) [4], are forcing to add new stages to SRM process in order to decrease the concentration levels of both gases in hydrogen stream. Therefore, to decrease the CO_2 emissions, the addition of new CO_2 sequestration, capture and confinement stages are being analyzed [5]. Likewise, to allow the use of SRM hydrogen stream in PEMFC, its purification is required and new subsequent reactions as the preferential oxidation of CO process in hydrogen presence (PROX) are studied [6]. In any case, these additional stages

---

* Corresponding author at: Grupo de Energía y Química Sostenibles, Instituto de Catálisis y Petroleoquímica, CSIC, C/Marie Curie 2, Cantoblanco, 28049-Madrid, Spain. Tel.: +34 915854947; fax: +34 915854760.

** Corresponding author at: Departamento de Tecnología Química y Energética, ESCET, Universidad Rey Juan Carlos, C/ Tulipán s/n, 28933-Móstoles, Madrid, Spain. Tel.: +34 916647450; fax: +34 914887068.

E-mail addresses: rut.guil@icp.csic.es (R. Guil-Lopez), david.serrano@urjc.es (D.P. Serrano).

0926-860X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2011.01.036

determine to a large extent the cost of the hydrogen produced by SRM process, decreasing the economical and environmental competitiveness of the SRM process, which opens the possibility to obtain hydrogen by other processes.

An attractive alternative route for SRM with additional stages to produce CO_x-free H_2 involves the moderately endothermic catalytic methane decomposition process ($DeCH_4$) [3,5,7–10]:

$$CH_4(g) \rightarrow 2H_2(g) + C(s) \quad \Delta H^{\circ}_{298} = 74.9\,\mathrm{kJ/mol}(CH_4) \tag{1}$$

Analyses of the economical and environmental viability of the $DeCH_4$ process to produce hydrogen free of CO (ideal for its use in the PEMFC) and CO_2 (decreasing the CO_2 total emission of the hydrogen production process) have been carried out [5,7,8,10]. In this sense, no CO or CO_2 is co-produced with hydrogen during this reaction, according to Eq. (1). Nevertheless, traces of CO or CO_2 can be detected in the hydrogen stream at the beginning of the reaction [11], where oxygen may come from the oxygenated groups in the surface of the starting catalysts, and consequently, this CO_x production is limited and it is observed as a few amount (as traces of less than 1% of yield during the first minutes of the reaction). The carbon atom of the methane molecule forms the only by-product of this reaction: solid carbon material, which can be co-produced in large amounts (more than 0.27 kg C/$m^3{}_{STP}$ H_2 according to Eq. (1)). Therefore, produced carbon (C_{prod}) application can be a key factor to consolidate $DeCH_4$ technology to obtain hydrogen [8]. The carbon applications depend on their morphologies and properties, which are determined by the characteristics of carbon materials [12–15]. Therefore, the morphology and nature of C_{prod} must be analyzed in the studies of the H_2 production from $DeCH_4$ reaction. However, this carbon production during the $DeCH_4$ process can cause reactor plugging problems. Fixed-bed reactor is the usual option employed in this process [3,9], although C_{prod} deposits plug the reactor, stopping the process [11]. The best option to carry out the large-scale development of this $DeCH_4$ process seems to be the use of a fluidized-bed reactor [7,8,12], which avoids reactor plugging problems caused by the C_{prod} deposits [8,16–18], delaying the inevitable catalyst deactivation [13,16–19]. Nevertheless, to increase the knowledge of the process, engineering problems involved in the use of a fluidized-bed reactor make the analysis to understand the process difficult. In this sense, the thermobalance reactor allows to accumulate carbon deposits without reactor plugging problems, while continuously measuring the weight increase produced by C_{prod} deposits [20–22]. This experimental set-up provides not only a simple way to continuously monitor the hydrogen production but also allows work as a differential reactor, in which by selecting appropriate operating conditions, the reaction rates measured can be considered as true intrinsic rates of the $DeCH_4$ process [20]. In summary, the use of a thermobalance reactor allows: (i), to study the resistance against the deactivation of the catalysts, while a huge amount of carbon is by-produced, (ii), to follow the reaction development with a continuous monitoring of the H_2 produced; and (iii), to study the initial behaviour of the catalysts at a really short time at the beginning of the reaction.

There are mainly two kinds of materials capable of catalyzing $DeCH_4$ to produce hydrogen: (i), metal catalysts; and (ii), carbon materials. Traditionally, the aim of $DeCH_4$ reaction has been to produce carbon materials, nowadays, mainly carbon nanofibers (H_2 as by-product). The most usual catalysts to produce C-nanofibers are Ni or Fe-based catalysts [17,19,20,23,24]. Mild reaction conditions must be used to favour the growth of C-nanofibers [23], even though H_2 is produced at low rates and low conversion levels. The metal catalyst deactivation is caused by the coverage of the metal active centres by C_{prod} deposits. When the process is finish, either the Ni-catalyst is destroyed, and subsequently, removed, while C-nanofibers without harmful Ni-impurities are recovered [25], or deactivated Ni-catalyst is separated from C-nanofibers and subsequently, the Ni-catalyst is recovered and re-activated. Consequently, non-expensive and non-stabilized Ni or Fe supported catalysts seem to be the best choice for large-scale production of carbon nanotubes at low cost [26]. However, when the aim of the $DeCH_4$ process is the H_2 production, high conversion is pursued and the metal catalyst is usually recovered. Therefore, metal catalysts must be stabilised into mixed oxides matrices [11,19,21,27] in order to guarantee the stability of the active centres during the consecutive cycles of reaction-deactivation-regeneration [11,21]. The mixed oxides derived from calcined hydrotalcite-like precursors (coded hereafter as *ex*-LDH) fulfill all conditions to stabilize the active centres [11,19]. Moreover, the particular structure and properties of LDH allow modulating the *ex*-LDH catalyst properties with the incorporation of modifying cations, which increase the catalysts performance [28]. As it commented before, the presence of harmful Ni in C_{prod} limits its applications. Consequently, when the metal catalyst is based on Ni, the separation of C-nanofibers and deactivated Ni-catalysts must be carried out [21]. The partial separation of C-nanofibers and deactivated Ni-catalysts can be favoured using a fluidized-bed reactor [17–19], and subsequently, the deactivated recovered Ni-catalysts must be reactivated, producing a lower amount of CO_x by the combustion of remaining carbon deposits. On the other hand, Muradov analyzed the energetic and economical factors to develop the $DeCH_4$ reaction using carbon materials as catalysts [8]. Carbons are non-expensive commercial catalysts and they are more resistant than metal ones, and no catalyst regeneration is needed [8,9,28]. Specific studies about the activity of activated carbons [29], carbon blacks [16], or new synthetic carbon materials [30,31] have been developed. Likewise, comparative studies of different types of carbons in $DeCH_4$ reaction have been carried out [32,33]. It has been shown that microporous carbons become deactivated by blockage of their micropore network [30,33] whereas the mesoporous carbons show good resistance toward deactivation [30,34].

Nevertheless, to the best of our knowledge, comparative studies with similar reaction conditions about advantages and drawbacks of the use of metals or carbons as catalysts in CH_4 decomposition have not been reported yet. Accordingly, this work was undertaken with the aim to compare the performance of metal catalysts (Ni and Fe based) with different carbon catalysts. Therefore, this study has been focused on the amount of hydrogen produced, the temperature at which H_2 starts to be produced (threshold temperature, T_{th}), and on the morphology and properties of produced carbons.

2. Experimental

2.1. Catalysts

Two types of catalysts were tested in the DeCH4 reaction: (a), metal-based; and (b), carbon materials. The representative metal based catalysts were chosen to cover the main range of metal catalysts used in this reaction. Six Ni-based catalysts were considered: commercial bulk nickel oxide (coded as NiO-com, from *Aldrich*), NiO supported on SiO_2 and on Al_2O_3 (coded Ni/SiO_2 and Ni/Al_2O_3, respectively), Ni–Al spinel (coded Ni-spinel) and two NiMgAl-mixed oxides from hydrotalcite-like materials (Ni-*ex* LDHs) with different metal loading. In addition, two commercial bulk iron oxides, hematite (Fe_2O_3-hem from *Aldrich*) and magnetite (Fe_3O_4-mag from *Manuel Riesgo S.L.*), were used as metal-catalysts too.

Two Ni-supported catalysts (23 wt%) were prepared by incipient wetness impregnation method on SiO_2 (commercial amorphous SiO_2 from *Rhodia* calcined at 500 °C) and on Al_2O_3 (commercial γ-Al_2O_3 from *Merck* calcined at 500 °C). An appropriate quantity