Carbon Materials as Catalysts for Decomposition and CO₂ Reforming of Methane: A Review

Beatriz FIDALGO, J. Ángel MENÉNDEZ*

Instituto Nacional del Carbón (CSIC), Apartado 73, 33080 Oviedo, Spain

Abstract: The decomposition and CO₂ reforming of methane, respectively, are promising alternatives to industrial steam methane reforming. In recent years, research has been focused on the development of catalysts that can operate without getting deactivated by carbon deposition, where, in particular, carbon catalysts have shown positive results. In this work, the role of carbon materials in heterogeneous catalysis is assessed and publications on methane decomposition and CO₂ reforming of methane over carbon materials are reviewed. The influence of textural properties (BET surface area and micropore volume, etc.) and oxygen surface groups on the catalytic activity of carbon materials are discussed. In addition, this review examines how activated carbon and carbon black catalysts, which are the most commonly used carbon catalysts, are deactivated. Characteristics of the carbon deposits from methane are discussed and the influence of the reactivity to CO₂ of fresh carbon and carbonaceous deposits for high and steady conversion during CO₂ reforming of CH₄ are also considered.

Key words: carbon catalyst; catalytic activity; decomposition; methane; reforming

CLC number: O643

Document code: A

Nowadays, steam reforming of methane (reaction 1) is the principal process for the production of synthesis gas from natural gas [1–3]. Synthesis gas, or syngas, a mixture of hydrogen and carbon monoxide (H₂ + CO), is used for the production of a large number of chemical products and fuels, including ammonia, H₂ for refineries, and methanol [1]. Current reports on the use of syngas focus on the conversion of natural gas from remote fields into liquid fuels (gas to liquid technology, GTL) and the role that syngas can play in a hydrogen economy [1,4].

The industrial steam reforming process has a number of drawbacks: (i) syngas is produced with a H₂/CO ratio of around 3:1, which is higher than the ratio needed for the synthesis of high value-added by-products; (ii) it is endothermic so a high temperature heat supply is necessary, and a large quantity of CO₂ ranging from 0.35 to 0.42 m³ of CO₂ per m³ of H₂ produced is emitted [5]; and, (iii) to avoid deactivation of the metal catalysts (typically, Ni-based catalysts) by carbonaceous deposits, excess steam must be used at a H₂O/CH₄ ratio of 3 to 4, and operation costs and energy consumption are increased [3]. For these reasons, alternative processes to steam reforming are being investigated. CO₂ reforming of methane, or dry reforming, is a promising option for the conversion of natural gas into syngas [6], while the catalytic decomposition of methane is considered the best process for the production of pure hydrogen [5].

CO and CO₂-free hydrogen can be produced by catalytic decomposition of CH₄ (reaction 2), which would make it possible to reduce emission of CO₂ to as low as 0.05 m³ of CO₂ per m³ of H₂ produced. In addition to hydrogen, carbon is obtained as a by-product, which can be used as feedstock in various processes, such as the production of plastics and in the metallurgical industry [5].

CO₂ reforming of methane (reaction 3) can reduce CO₂ emissions to around 0.2 m³ of CO₂ per m³ of H₂ produced [3,6], and it gives syngas with a lower ratio of H₂/CO of approximately 1:1, which is more suitable for the synthesis of higher hydrocarbons and oxygenated derivatives [7].

The main obstacle to the industrial implementation of CH₄ decomposition and CH₄ reforming with CO₂ is that there are no commercial catalysts that can operate without deactivation due to carbon deposition. However, carbon catalysts have shown good catalytic activity and offer several advantages over metal-based catalysts in the decomposition and CO₂ reforming of methane.

In this work, papers on the decomposition and CO₂ reforming of methane over carbon catalysts are reviewed. The review focuses on the relationship between the physical and chemical properties of the carbon catalysts and their catalytic activity, and the causes of deactivation. The regeneration of the initial carbon catalyst with CO₂ is also consid-

Received 28 August 2010. Accepted 30 September 2010.

*Corresponding author. Tel: +34-985-119090; Fax: +34-985-297662; E-mail: angelmd@incar.csic.es

Foundation item: Supported by Carbuos Metálicos-Air Products Group (Project CEN-2008-1027, Program Ingenio 2010, CDTI).

English edition available online at ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

ered in the case of CO₂ reforming of methane.

1 Carbon materials in heterogeneous catalysis

The physical and chemical properties of carbon materials, mainly porosity and surface chemistry, make them suitable for application in many catalytic processes. Traditionally, carbon materials have been used as supports for catalysts in heterogeneous catalytic processes, although their use as catalysts on their own is becoming more and more common [8–11].

Although several carbon materials have been tested, activated carbon catalysts and carbon blacks are the most commonly used carbon supports [10,12]. The typically large surface area and high porosity of activated carbon catalysts favour the dispersion of the active phase over the support and increase its resistance to sintering when the quantity of metal loaded is low. The pore size distribution can also be adjusted to suit the requirements of each reaction. The surface chemistry of carbon catalysts also influences their performance as catalyst supports, especially during the synthesis stage. Carbon materials are normally hydrophobic and they usually show a low affinity towards polar solvents, such as water, and a high affinity towards non-polar solvents, such as acetone. Although their hydrophobic nature may affect the dispersion of the active phase over the carbon support, the surface chemistry of carbon materials can easily be modified, for example by oxidation, to increase their hydrophilicity to favour ionic exchange. Apart from an easily tailorable porous structure and surface chemistry, carbon materials have other advantages [10]: (i) metals on the support can be easily reduced; (ii) the carbon structure is resistant to acids and bases; (iii) the structure is stable to high temperatures (even above 750 °C); (iv) porous carbon catalysts can be prepared in different physical forms (as granules, cloth, fibers, pellets, etc.); (v) the active phase can be easily recovered; and, (vi) the cost of carbon supports is usually lower than that of conventional supports, such as alumina and silica. Nevertheless, carbon supports have some disadvantages, such as, they can be easily gasified, which makes them difficult to use in hydrogenation and oxidation reactions [11], and their reproducibility can be poor, esp. activated carbon catalysts, since different batches of the same material can have varying ash content.

Carbon supported metal catalysts are employed in a number of applications including hydrosulfurization of petroleum, hydrodenitrogenation, dehydrohalogenation, hydrogenation of CO, hydrogenation of halogenated nitroaromatics compounds and nitrocompounds, hydrogenation of unsaturated fatty acids, hydrogenation of alkenes and alkynes, oxidation of organic compounds and organic pollutants, and for fuel cells [9–12].

As well as acting as catalyst supports, carbon materials themselves can be used as catalysts for different heterogeneous reactions [13]. At the end of the 1960s, Coughlin [14] suggested that the catalytic activity and selectivity of carbon catalysts was related to their electric properties. Carbon materials can exhibit the properties of a conductor, semi-conductor or insulator, depending on the methods of pre-treatment and preparation. By applying the right treatment, the catalytic properties of carbon can be adjusted to suit a specific application. Thermal and graphitization treatments would favour metallic behaviour; oxidation would tend to localize π -electrons and lead to semiconductivity; and other treatments can result in highly disordered carbon with an insulator-type behaviour. Moreover, in view of the strong electronic anisotropy of graphitic carbon, a broad spectrum of crystalline properties can be possible within a given carbon catalyst, which may explain the poor selectivity that is sometimes observed with carbon catalysts.

Later on, the catalytic activity of carbon materials came to be associated with their surface area and surface groups, mainly oxygen surface groups [9, 10, 13]. When carbon is used as catalyst instead of as support, a large surface area and a good pore size distribution do not necessarily give high catalytic activity. The surface chemistry may determine catalytic activity. The ash composition may also influence the catalytic properties of carbon catalysts [10].

Most of the reactions that are catalyzed by carbon catalysts can be classified into one of the following groups: (i) oxidation-reduction; (ii) hydrogenation-dehydrogenation; (iii) combination with halogens; and (iv) decomposition. There are also examples of the catalysis of dehydration, isomerisation and polymerisation reactions [11,13,14]. Some of the reactions catalyzed by carbon catalysts are summarized in Table 1.

2 Carbon materials as catalysts for methane decomposition

The use of carbon catalysts for CH₄ decomposition offers certain advantages over metal-based catalysts [8,15,16]: (i) low cost, availability, and durability; (ii) high temperature resistance; (iii) tolerance to sulphur and other potentially harmful impurities; (iv) no metal carbides are formed; (v) the hydrogen is not contaminated with carbon oxides; (vi) no need for the regeneration of the catalyst by burning carbon off the catalyst surface; (vii) production of a possible marketable carbon byproduct; and (viii) mitigation of CO₂ emission.

Methane decomposition over carbon catalysts has been extensively studied in the last decade. In general, research has been focused on the influence of the operating conditions (space velocity, temperature...) on CH₄ conversion

Table 1 Reactions catalyzed by carbon catalysts (adapted from Refs. [10,11,14])

General classification	Example
Oxidation-reduction	$\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3$
	$\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2$
	$2\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{S}_2 + 2\text{H}_2\text{O}$
	$\text{C}_6\text{H}_5\text{C}_2\text{H}_5 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{C}_2\text{H}_3 + \text{H}_2\text{O}$
	toxin oxidation (creatinine) oxidation of industrial effluents (oxalic acid)
Hydrogenation-dehydrogenation	$\text{RX} + \text{H}_2 \rightarrow \text{RH} + \text{HX}$ ($\text{X} = \text{Cl}, \text{Br}$)
	$\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2$
	$\text{CH}_3\text{CHOHCH}_3 \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2$
Combination with halogens	$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$
	$\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$ (phosgene)
	$\text{C}_2\text{H}_4 + 5\text{Cl}_2 \rightarrow \text{C}_2\text{Cl}_6 + 4\text{HCl}$
	$\text{SO}_2 + \text{Cl}_2 \rightarrow \text{SO}_2\text{Cl}_2$
	$\text{C}_6\text{H}_5\text{CH}_3 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{HCl}$
Decomposition	$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
	$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$
Dehydration, isomerization, and polymerisation	$\text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO}$
	$3\text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$
	$\alpha\text{-olefines} \rightarrow \text{poly}(\alpha\text{-olefines})$ $\alpha\text{-oxime} \rightarrow \beta\text{-oxime}$

[17–23], and on the relationship between the catalytic activity of carbon catalysts and their physical and chemical properties [8,15,17,21,24–33]. Authors have also proposed kinetic expressions and mechanisms for the CH₄ decomposition reaction over carbon materials [16,17,20,22,24,28, 34]. Although the catalytic activities of activated carbon and carbon black catalysts have been the main objective of these studies, the activities of materials such as char, soot, graphite, diamond powder, carbon nanotubes or fullerene have also been evaluated [8,15,19,26,30,31,34,35].

Muradov [36] was one of the first authors to suggest employing carbon as catalyst for CH₄ decomposition. In an experiment involving the decomposition of CH₄ over alumina, Muradov found that surface deposits of carbon catalyzed the reaction. As can be seen in Fig. 1, the initial catalytic activity of alumina was low but after 20 min the rate of CH₄ decomposition increased due to the presence of carbon deposits, which made the process autocatalytic until it decreased back to a steady value.

Later, the same research group studied the decomposition of methane over different carbon catalysts [8,15]. Activated carbon materials, carbon black materials, graphite materials, carbon nanotubes, fullerenes and synthetic diamond powder were compared. It was reported that the different catalytic activities of the carbon materials may be due to differences in origin, surface area, presence of oxygenated surface groups, crystal structure, or the presence of surface energetic abnormalities. Taking into account the results obtained by different research groups, it can be concluded that acti-

Fig. 1. Thermal decomposition of methane over activated alumina at 850 °C. Reprinted from Ref. [36] with permission from ACS Publications.

vated carbon catalysts, independently of the surface area, origin or activation method, have high initial catalytic activity but became rapidly deactivated [8,15,18,20,23,24,37,38], whereas carbon black catalysts show a lower but steadier activity [21,22,28,31–33]. Serrano et al. [30] found that mesoporous carbon catalysts, with a large surface area and a controlled porous structure, can present both high initial catalytic activity and high resistance to deactivation. Most of the more structurally ordered carbon catalysts showed negligible catalytic activity. Figure 2 compares the different CH₄ conversion profiles obtained over several carbon materials, mainly activated carbon and carbon black catalysts.

Numerous factors have been proposed as the reason(s) for the catalytic activity of carbon catalysts: BET specific surface area, oxygenated surface groups, crystallinity, and surface defects. In general, most of the interpretations of the catalytic activity of carbon catalysts are consistent. However, there may be some controversy arising from the comparison of carbon materials obtained from different precursors, different methods of preparation, etc. [27].

Figure 3 illustrates the relationship between the characteristics of carbon catalysts and their catalytic activity. Various authors [8,16,20,37] found that there is no direct connection between the BET surface area of activated carbon catalysts and their initial catalytic activity. In the case of carbon materials other than activated carbon, Muradov et al. [8,15] observed that the initial rates of CH₄ decomposition over various carbon black catalysts were linearly correlated with their BET surface area, whereas Bai et al. [34] using a char as catalyst and Lee et al. [22] using carbon black catalysts did not find such a relationship.

Most authors argue that there is no direct relationship between the surface area of a carbon and its initial activity since only part of the BET surface area is active. In other words, the number of active centres is not proportional to the BET surface area. However, Dufour et al. [26] believed

Fig. 2. Methane decomposition over activated carbon catalysts and fullerene soot (a) and carbon black catalysts and carbon nanotubes (b). Reprinted from Ref. [15] with permission from Elsevier.

Fig. 3. Initial rate of methane decomposition as a function of the BET surface area. (a) Activated carbon catalysts (Reprinted from Ref. [20] with permission from IJHE); (b) Carbon black catalysts (Reprinted from Ref. [15] with permission from Elsevier).

that the absence of any relationship is due to diffusion limitation on methane inside the micropores. Muradov et al. [8] concluded that the active centres for methane decomposition are high energy sites (HES), such as surface defects, dislocations, vacancies, low-coordination sites, and other energetic abnormalities. A lower degree of crystallinity gave a larger number of HES, and therefore, a higher catalytic activity. Thus the catalytic activities of amorphous carbon catalysts, such as activated carbon and carbon black catalysts, were better than the activities of more ordered carbon catalysts. Serrano et al. [31] also stated that although there may be a correlation between the catalytic activity of a carbon and its specific surface area, it was neither linear nor decisive. They believed that the catalytic activity of a carbon depends on the concentration of surface defects on the carbon surface rather than on the surface area; however, a large number of defects is usually related to a large specific surface area. Chen et al. [25] asserted that defects are due to

the decomposition of oxygen surface groups, and this gave unsaturated atoms of carbon that can react with the CH₄. Moliner et al. [21,28,29,32,33] also found that the initial catalytic activities of activated carbon and carbon black catalysts were proportional to the concentration of oxygen surface groups, mainly the groups that desorbed as CO in TPD experiments.

Figure 4(a) shows that various activated carbon and carbon black catalysts gave a good correlation between the initial rate of CH₄ decomposition, defined as the mass of deposited carbon with respect to the initial mass of carbonaceous catalyst, and the concentration of oxygen surface groups desorbed as CO. However, the presence of oxygenated groups that can be desorbed as CO₂ did not correlate well with the initial CH₄ decomposition rate. Two different mechanisms were proposed: (i) the direct reaction of CH₄ molecules with the oxygenated groups, and (ii) the activation of CH₄ on the active centres formed from the decompo-

Fig. 4. Influence of surface chemistry on the initial catalytic activity of different carbon catalysts for methane decomposition. (a) Initial rate of CH₄ decomposition vs. concentration of oxygen surface groups that desorb as CO and CO₂ in TPD experiments (Reprinted from Ref. [33] with permission from Elsevier); (b) Relationship between the threshold temperature and percentage of oxygen groups on the catalyst surface determined by XPS (Reprinted from Ref. [31] with permission from Elsevier).

sition of the surface groups. Other authors found neither a relationship between oxygenated groups and initial catalytic activity [26,31] nor any effect exerted by the surface groups on the production of H₂ from CH₄ [8,39]. Figure 4(b) shows that the oxygenated surface groups determined by XPS were not directly related to the initial catalytic activity of different carbon catalysts, which was represented by the threshold temperature defined as the temperature at which hydrogen production reached 0.1 mmol/g.

Regarding the loss of catalytic activity of carbon catalysts, most authors related catalyst deactivation to pore blockage and a decrease in surface area caused by carbonaceous deposits from methane. Presumably, the total rate of CH₄ decomposition is the sum of the rate of carbon nucleation and rate of carbon crystalline growth. Disordered carbon catalysts with large surface areas tend to have a higher initial activity since the rate of carbon nucleation is proportional to the specific surface area and the number of high energy sites. However, the low initial reaction rate obtained over ordered carbon catalysts may be due to the high activation energy of the nucleation stage and the high rate of crystalline growth [15].

In the case of activated carbon catalysts, the loss of catalytic activity was related to the blockage of the pore mouths by carbonaceous deposits, which led to a dramatic drop in micropore volume and BET surface area [8,16–18,20,24,28,32,33,37]. Some authors even stated that the decomposition of methane occurred inside the micropores [24,27,31,34]. During CH₄ decomposition over amorphous carbon catalysts, the rate of growth of deposited carbon seemed to be higher than the rate of nucleation. Therefore, an activated carbon becomes deactivated by carbon growth next to the mouths of the micropores that makes the diffusion of CH₄ molecules inside the pores much slower [15]. Dufour et al.

[26] proposed two possible reasons for the reaction of CH₄ at the pore mouths: (i) the H₂ produced impeded the diffusion of methane into the pores, and (ii) the reactivity of CH₄ with porous solids is so high that diffusion through the pores does not occur.

In the case of carbon black catalysts, unlike that of activated carbon catalysts, most of the surface is open and easily accessible to CH₄ during the decomposition reaction. Initially, carbonaceous deposits do not accumulate inside the pores but on the external surface, and so, methane molecules continue to gain access to the inside of the pores, at least until most of the surface is covered by carbonaceous deposits. For this reason, carbon black catalysts with large surface areas exhibit steadier long-term catalytic activity compared to activated carbon catalysts [15,21,29–32].

As is shown in Fig. 5, independently of the carbon and deactivation mechanism, the loss of catalytic activity is related to the quantity of carbon deposited [17,28]. The stability of a carbon material as a long term catalyst is therefore correlated with the BET areas and especially with the microporosity. Thus, a higher volume of micropores can tolerate a greater accumulation of carbonaceous deposits before deactivation takes place [21,27,28,33,34,37].

There are different opinions about the nature and catalytic activity of the carbonaceous deposits from CH₄ decomposition. Some authors consider the catalytic activity of deposited carbon lower than the activity of the original carbon since methane decomposition does not become autocatalytic and methane conversion diminished with time [15,28,32,40]. However, other authors emphasized the heterogeneity of the deposits formed and the heterogeneity of their catalytic activity that depend on the initial carbon used and the operating conditions [15,28,32,35,37]. The SEM images of two different activated carbon catalysts before and after CH₄

Fig. 5. Influence of textural properties on the catalytic activity of carbon in methane decomposition. (a) Correlation between CH₄ conversion and evolution of the surface area (Reprinted from Ref. [8] with permission from Elsevier); (b) Surface area and total volume of pores vs. deposited carbon with respect to the initial mass of catalyst (Reprinted from Ref. [33] with permission from Elsevier).

decomposition carried out under identical operating conditions are shown in Fig. 6. Carbon nanofilaments were observed on the first activated carbon catalyst, probably grown from metal particles, whereas only amorphous deposits were seen on the second one. In the case of carbon black catalysts, their characteristic steady long-term catalytic activity may be due to that some of the deposits from methane were catalytically active and act as new active centres for the decomposition reaction [21,22,27]. The deactivation of the catalyst with time may be due to the increase in the proportion of more ordered or graphitic carbon, as is illustrated in Fig. 7.

Finally, it should be added that none of the authors who

studied the influence of the metal content of carbon catalysts on the catalytic activity in methane decomposition observed any effect [8,26,31,34].

3 Carbon materials as catalysts for CO₂ reforming of methane

The bibliography on CO₂ reforming of CH₄ over carbon catalysts is not as extensive as the publications on the methane decomposition reaction. Fidalgo et al. [41] investigated microwave-assisted CO₂ reforming of CH₄ using a commercial activated carbon as catalyst. Their study focused on the influence of the heating device and different

Fig. 6. SEM images that illustrate the heterogeneous nature of the carbon deposits from methane decomposition on different activated carbon catalysts. (a) Nanofilaments on the surface of the activated carbon CCN-SCR; (b) Amorphous deposits on the surface of the activated carbon CCN-UN. Reprinted from Ref. [23] with permission from Elsevier.

Fig. 7. Decomposition of methane over a carbon black (BP2000, 950 °C, 360 h⁻¹). (a) Evolution of H₂ production with time; (b) Change in the d_{002} with time. Reprinted from Ref. [21] with permission from IJHE.

operating conditions. They found that CO₂ reforming of methane was enhanced when microwave heating was used instead of conventional heating. A temperature range of 700–800 °C was selected and the importance of the quantity of CO₂ introduced was noted. A higher percentage of CO₂ introduced gave higher and steadier CO₂ and CH₄ conversions. The authors suggested a simple reaction mechanism in which dry reforming occurred as a combination of CH₄ decomposition and gasification of the carbonaceous deposits by CO₂. Thus, at least the more reactive carbonaceous deposits from methane (amorphous carbon) were gasified by CO₂, and the active centres were therefore continuously regenerated. Part of the original carbon catalyst was also gasified. Similar results were found when the authors studied microwave-assisted dry reforming reaction using a K-rich char from coffee hulls as catalyst [35]. In a later work by this research group [39], various carbon materials were compared to evaluate the influence of porosity and oxygen surface groups on catalytic activity in microwave-assisted dry reforming of CH₄. They found that, as in the case of methane decomposition, CO₂ reforming of CH₄

occurred mainly in the micropores and that, in addition to a large micropore volume, the carbon material used as catalyst needs good reactivity to CO₂. It was also demonstrated that oxygen surface groups dramatically reduced the catalytic activity of activated carbon catalysts for the dry reforming reaction, especially under microwave heating. The low conversions obtained over the oxidized carbon catalysts were believed to be due to the decrease in the reactivity of the carbon catalysts after oxidation. Figure 8 illustrates the different conversions with microwave heating achieved over an activated carbon catalyst as received and after it was oxidized.

Song et al. [42] also investigated CO₂ reforming of CH₄ over activated carbon. Their work was not so much focused on evaluating the catalytic activity of the activated carbon as on the influence of the operating conditions on the CH₄ and CO₂ conversions. The effects of changing temperature, space velocity, and partial pressures of carbon dioxide and methane were studied. Like Fidalgo et al. [41], they suggested a reaction mechanism based on the adsorption and cracking of CH₄ on the activated carbon surface followed by

Fig. 8. CO₂ and CH₄ conversion in the microwave-assisted dry reforming of methane over two activated carbon catalysts. (a) As received, FY5; (b) Oxidized, FY5ox. Reaction conditions: 800 °C, 55%CH₄-45%CO₂, 0.29 L/(h·g), 150 min. Reprinted from Ref. [39] with permission from Elsevier.

the adsorption of CO_2 and gasification of surface carbon to produce CO. Without going into details, Song et al. pointed out that the catalytic activity of activated carbon may be related to the large surface area and the existence of surface groups, as in the case of CH_4 decomposition. In addition, these authors explored the causes for the loss of carbon catalytic activity and concluded that deactivation was due to the blockage of the surface area and microporosity by carbonaceous deposits from methane. They also suggested that

the use of suitable operating conditions can minimize catalyst deactivation, and that regeneration of the porosity and surface groups can be carried out by using oxidizing agents. Table 2 summarizes the changes in the textural parameters of the activated carbon when it was used as catalyst due to carbon deposits from CH_4 . As can be seen, the loss of surface area and micropore volume at 950 °C was lower than at 900 °C because, according to the authors, the deposition of carbon was slowed down at the higher temperature.

Table 2 Changes in the surface properties of an activated carbon after experiments of CO_2 reforming of CH_4 at 900 and 950 °C (adapted from Ref. [42])

Sample	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_t/(\text{cm}^3/\text{g})$	$V_{\text{mic}}/(\text{cm}^3/\text{g})$	Average pore width (nm)	Average pore diameter (nm)
Fresh activated carbon	760	0.44	0.15	2.33	3.56
Activated carbon used at 900 °C	364	0.22	0.07	2.52	4.12
Activated carbon used at 950 °C	591	0.38	0.09	2.58	3.84

Haghighi et al. [43] studied dry reforming of methane using a char from bituminous coal as catalyst. The work did not focus on the correlation between the properties of the char and its catalytic activity, but on the thermodynamic and mechanistic aspects of the process. They found that the main products were CO, H_2 , and carbon deposits, and that the reaction mechanism is a combination of methane decomposition and gasification of carbon deposits by CO_2 . They agreed with Fidalgo et al. [39] and Song et al. [42] in that the loss of catalytic activity in char was due to the blockage of the active centres by inactive carbonaceous deposits. Thus, the decrease in the catalytic activity of char during the dry reforming reaction occurred when the reaction of methane decomposition was faster than the gasification of the carbon deposits. Figure 9 shows the differences observed on the char surface before and after the reforming reaction that were due to the presence of carbonaceous deposits.

Since CO_2 reforming of CH_4 over carbon catalysts can be considered a combination of CH_4 decomposition and gasification of the carbon deposits by CO_2 , the physical and

chemical properties that influence the catalytic activity of carbon materials and the causes of deactivation are presumably the same as those involved in methane decomposition (Section 2). Some authors have studied the process as a succession of decomposition/ CO_2 regeneration cycles [40,44,45]. Since the characteristics that carbon materials must have in order to act as catalyst in CH_4 decomposition are well known, these authors focused on the optimum operating conditions, mainly temperature, time, and flow rate of CO_2 , for regenerating the catalyst and restoring the initial surface area and concentration of oxygen surface groups. After regeneration with CO_2 , high methane conversions were again obtained. However, after several decomposition/regeneration cycles, a progressive loss of catalytic activity was observed. The authors believed that this loss was because the initial carbon, which was more amorphous and reactive to CO_2 , was more susceptible to gasification than the carbon deposited, which was more ordered and less reactive to CO_2 . They suggested that in addition to optimizing the regeneration stage, it was necessary to adjust the operating conditions during the CH_4 decomposition stage to

Fig. 9. SEM images of a char surface used as catalyst for the CO_2 reforming of CH_4 . (a) Before reaction; (b) After reaction. Reprinted from Ref. [43] with permission from Elsevier.

Fig. 10. Long-term stability of a carbon catalyst represented by the mass gain with time over six decomposition/regeneration cycles. (a) 850 °C/950 °C; (b) 950 °C/1000 °C. Reprinted from Ref. [40] with permission from IJHE.

favour the deposition of non-ordered carbon that is more reactive to CO₂. As an example, Figure 10 represents the results obtained by Abbas et al. [40] during the investigation of the catalytic activity of an activated carbon after several decomposition/regeneration cycles under different operating conditions. It was observed that the long-term stability was improved when the decomposition and regeneration temperatures increased since more reactive carbon was deposited.

4 Conclusions

This review has shown that the catalytic activity of carbon catalysts in methane decomposition depends on the physical and chemical properties of the material. In general, active sites for the decomposition are high energy surface defects, which may be correlated with the specific surface area although not linearly. Initial catalytic activity seems to be related to the BET area and oxygen surface groups, specifically those desorbed as CO in TPD experiments. The long term stability of a carbon catalyst correlates with the BET surface area and micropore volume since the loss of catalytic activity depends on the quantity of carbonaceous deposits that it can tolerate before it gets deactivated. A higher carbon crystallinity results in a lower catalytic activity. For this reason, activated carbon and carbon black catalysts are the carbon materials with the best activity. Activated carbon catalysts have a high initial activity but they are rapidly deactivated as carbonaceous deposits block their pore mouths. In contrast, carbon black catalysts show a lower initial catalytic activity but are steadier with time since carbon is deposited on the external surface and the pores remain accessible to methane for a longer time. The carbonaceous deposits from methane and their catalytic activities are heterogeneous. Some deposits may act as new active sites for the decomposition reaction. The less active

deposits tend to accumulate, and as a result the initial carbon catalyst gradually becomes deactivated.

The catalytic activity of carbon catalysts for CO₂ reforming of methane was also reviewed. Publications on this subject were less extensive than CH₄ decomposition. In general, dry reforming reaction can be considered as a combination of methane decomposition and gasification of the carbon deposits by CO₂. Consequently, the physical and chemical properties that influence the catalytic activity of carbon materials and their deactivation are the same as those involved in methane decomposition. In addition, since gasification of the carbon deposits by CO₂ is a key reaction in the process, the initial carbon catalyst and the carbonaceous deposits from methane need to be highly reactive to carbon dioxide in order to give high and steady conversions. When dry reforming is studied as a succession of decomposition/regeneration cycles, the operating conditions of both stages must be optimized in order to retain the porosity and surface groups of the initial carbon catalyst and prevent the progressive loss of activity.

Acknowledgments

The authors acknowledge the financial support received from the Carburos Metálicos-Air Products Group (Project CEN-2008-1027, Program Ingenio 2010, CDTI). Beatriz FIDALGO is grateful for the support received from the CSIC I3P Programme co-financed by the European Social Fund (ESF).

References

- 1 Rostrup-Nielsen J R, Sehested J, Norskov J K. *Adv Catal*, 2002, **47**: 65
- 2 International Energy Agency, IEA. "Hydrogen production and storage. R&D priorities and gaps". www.iea.org, 2005
- 3 Ross J R H. *Catal Today*, 2005, **100**: 151

- 4 de Lima S, Assaf J M. *Catal Lett*, 2006, **108**: 63
- 5 Muradov N Z. *Energy Fuels*, 1998, **12**: 41
- 6 Fidalgo B, Domínguez A, Pis J J, Menéndez J A. *Int J Hydrogen Energy*, 2008, **33**: 4337
- 7 Bradford M C J, Vannice M A. *Appl Catal A*, 1996, **142**: 73
- 8 Muradov N, Smith F, T-Raissi A. *Catal Today*, 2005, **102-103**: 225
- 9 Radovic L R, Rodríguez-Reinoso F. In: Thrower P A Ed. *Carbon Materials in Catalysis*. Vol. 25. New York: Marcel Dekker, 1997. 312
- 10 Rodríguez-Reinoso F. *Carbon*, 1998, **36**: 159
- 11 Stüber F, Font J, Fortuny A, Bengoa C, Eftaxias A, Fabregat A. *Top Catal*, 2005, **33**: 3
- 12 Auer E, Freund A, Pietsch J, Tacke T. *Appl Catal A*, 1998, **173**: 259
- 13 Bansal R C, Donnet J P, Stoeckli F. *Active carbon*. New York: Academic Press, 1998. 413
- 14 Coughlin R W. *Ind Eng Chem Prod Res Dev*, 1969, **8**: 12
- 15 Muradov N. *Catal Commun*, 2001, **2**: 89
- 16 Muradov N, Chen Z, Smith F. *Int J Hydrogen Energy*, 2005, **30**: 1149
- 17 Abbas H F, Wan Daud W M A. *Fuel Process Technol*, 2009, **90**: 1167
- 18 Domínguez A, Fidalgo B, Fernández Y, Pis J J, Menéndez J A. *Int J Hydrogen Energy*, 2007, **32**: 4792
- 19 Dufour A, Celzard A, Ouattassi B, Broust F, Fierro V, Zoulalian A. *Appl Catal A*, 2009, **360**: 120
- 20 Kim M H, Lee E K, Jun J H, Kong S J, Han G Y, Lee B K, Lee T J, Yoon K J. *Int J Hydrogen Energy*, 2004, **29**: 187
- 21 Lázaro M J, Pinilla J L, Suelves I, Moliner R. *Int J Hydrogen Energy*, 2008, **33**: 4104
- 22 Lee E K, Lee S Y, Han G Y, Lee B K, Lee T J, Jun J H, Yoon K J. *Carbon*, 2004, **42**: 2641
- 23 Lee K K, Han G Y, Yoo K J, Lee B K. *Catal Today*, 2004, **93-95**: 81
- 24 Bai Z, Chen H, Li B, Li W. *J Anal Appl Pyroly*, 2005, **73**: 335
- 25 Chen J, He M, Wang G, Li Y, Zhu Z J. *Int J Hydrogen Energy*, 2009, **34**: 9730
- 26 Dufour A, Celzard A, Fierro V, Martin E, Broust F, Zoulalian A. *Appl Catal A*, 2008, **346**: 164
- 27 Krzyzynski S, Kozlowski M. *Int J Hydrogen Energy*, 2008, **33**: 6172
- 28 Moliner R, Suelves I, Lázaro M J, Moreno O. *Int J Hydrogen Energy*, 2005, **30**: 293
- 29 Pinilla J L, Suelves I, Lázaro M J, Moliner R. *Chem Eng J*, 2008, **138**: 301
- 30 Serrano D P, Botas J A, Pizarro P, Guil-López R, Gómez G. *Chem Commun*, 2008: 6585
- 31 Serrano D P, Botas J A, Fierro J L G, Guil-López R, Pizarro P, Gómez G. *Fuel*, 2010, **89**: 1241
- 32 Suelves I, Lázaro M J, Moliner R, Pinilla J L, Cubero H. *Int J Hydrogen Energy*, 2007, **32**: 3320
- 33 Suelves I, Pinilla J L, Lázaro M J, Moliner R. *Chem Eng J*, 2008, **140**: 432
- 34 Bai Z, Chen H, Li W, Li B. *Int J Hydrogen Energy*, 2006, **31**: 899
- 35 Domínguez A, Fernández Y, Fidalgo B, Pis J J, Menéndez J A. *Energy Fuels*, 2007, **21**: 2066
- 36 Muradov N Z. *Energy Fuels*, 1998, **12**: 41
- 37 Ashok J, Kumar S N, Venugopla A, Kumari V D, Tripathi S, Subrahmanyam M. *Catal Commun*, 2008, **9**: 164
- 38 Fidalgo B, Fernández Y, Domínguez A, Pis J J, Menéndez J A. *J Anal Appl Pyroly*, 2008, **82**: 158
- 39 Fidalgo B, Arenillas A, Menéndez J A. *Fuel*, 2010, **89**: 4002
- 40 Abbas H F, Wan Daud W M A. *Int J Hydrogen Energy*, 2009, **34**: 8034
- 41 Fidalgo B, Domínguez A, Pis J J, Menéndez J A. *Int J Hydrogen Energy*, 2008, **33**: 4337
- 42 Song Q, Xiao R, Li Y, Shen L. *Ind Eng Chem Res*, 2008, **47**: 4349
- 43 Haghighi M, Sun Z, Wu J, Bromly J, Wee H L, Ng E, Wang Y, Zhang D. *Proc Combust Inst*, 2007, **31**: 1983
- 44 Abbas H F, Wan Daud W M A. *Int J Hydrogen Energy*, 2010, **35**: 141
- 45 Pinilla J L, Suelves I, Utrilla R, Gálvez M E, Lázaro M J, Moliner R. *J Power Sources*, 2007, **169**: 103