Microwave-assisted CO_2 reforming of coke oven gas: An exception to the general rule?

J. M. Bermúdez, A. Arenillas, J. A. Menéndez*

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

Reformado de gas de horno de coque con CO_2 asistido con microondas: Una excepción a la regla general?

Reformat de gas de forn de coc amb CO_2 assistit amb microones: Una excepció a la regla general?

RESUMEN

En publicaciones anteriores se ha demostrado que los resultados del reformado seco de metano mejoran cuando éste se lleva a cabo utilizando calentamiento con microondas. En este artículo, el calentamiento con microondas se aplica al reformado con CO_2 de gas de batería. Los resultados obtenidos difieren mucho de los que previamente se han publicado para el reformado con CO_2 de CH_4, ya que en el caso del gas de batería el calentamiento con microondas tan solo mejora las conversiones ligeramente cuando se utiliza un carbón activo como catalizador, mientras que los resultados obtenidos con mezclas de carbón activo y un catalizador de Ni/Al_2O_3 fueron incluso peores que los obtenidos con el calentamiento convencional. Se consideraron diversas hipótesis para tratar de hallar una explicación a estos pobres resultados, siendo probablemente la naturaleza de los microplasmas formados durante el proceso de calentamiento en microondas el factor más influyente. Cuando el reformado seco de gas de batería se lleva a cabo, en el interior del reactor hay una elevada proporción de H_2, lo que parece provocar microplasmas de temperaturas superiores a los que se producen en el reformado seco de metano. Esto da lugar a la sinterización de las partículas de Ni, provocando una caída de las conversiones.

Palabras clave: reformado con CO_2, gas de horno de coque, Microondas, carbón activo, catalizador de Ni/Al_2O_3

SUMMARY

It has been previously reported that the dry reforming of methane can be enhanced by means of microwave heating. In this article, this technology is applied to the CO_2 reforming of coke oven gas (COG). The results obtained were opposite to those reported in the CO_2 reforming of CH_4, since in the case of the COG, microwave heating only slightly enhanced the conversions when an activated carbon was used as catalyst, whereas the results achieved when mixtures of activated carbon and Ni/Al_2O_3 were employed as catalyst were even worse than those obtained in a conventional oven. Several hypotheses were considered in order to find an explanation for these poor results, the nature of the microplasmas formed during the process being the most likely factor. The high proportions of H_2 present in the reactor when the dry reforming of coke oven gas is carried out may give rise to microplasmas of higher temperature than in the dry reforming of CH_4. This will cause the Ni particles to sinter significantly, leading to a decrease in the conversions.

Keywords: CO_2 reforming, Coke oven gas, Microwave, Activated carbon, Ni/Al_2O_3 catalyst

RESUM

S'ha publicat que el reformat sec de metà pot ser millorat mitjançant calefacció amb microones. En aquest article, s'ha aplicat aquesta tecnologia al reformat amb CO_2 de gas de forn de coc (GFC). Els resultats obtinguts són oposats als publicats en el reformat de CH_4 amb CO2, ja que en el cas del GFC, la sola calefacció amb microones va millorar lleugerament les conversions quan es va utilitzar carboni activat com a catalitzador, mentre que els resultats aconseguits quan es van utilitzar com a catalitzador barreges de carboni activat i Ni/Al_2O_3 van ser fins i tot pitjors que els obtinguts en un forn convencional. Es van considerar diverses hipòtesis per explicar aquests pobres resultats, essent el factor més probable la naturalesa del microplasma format durant el procés. L'alta proporció d'H_2 present en el reactor quan es duu a terme el reformat sec de gas de forn de coc pot donar lloc a la formació de microplasma de temperatura més alta que en el reformat sec de CH_4. Això causarà una significativa sinterització de partícules de Ni, ocasionant una disminució en les conversions.

Paraules clau: reformat amb CO_2, gas de forn de coc, microones, carbó actiu, catalitzador de Ni/Al_2O_3.

* Corresponding author: angelmd@incar.csic.es ; Tel.: +34 985 18972; Fax: +34 985297672

1. INTRODUCTION

The CO_2 reforming, or dry reforming, of methane (reaction 1) has been proposed as a promising alternative to steam reforming during recent years, since it has considerable advantages over the conventional method, especially the consumption of two important greenhouse gases, CO_2 and CH_4 [1-3].

$$CH_4 + CO_2 \leftrightarrow 2\,H_2 + 2\,CO \qquad \Delta H = 247\ kJ/mol$$
(reaction 1)
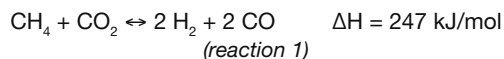
This process can be carried out with different CH_4 feedstocks, such as natural gas [4], biogas [5], landfill gas [6] or coke oven gas [7-9]. The upgrading of coke oven gas is currently the focus of much attention, since it is an important source of GHG emissions, resource wastage and energy inefficiency in the steel industry [10, 11]. In addition, the CO_2 reforming of COG yields a synthesis gas suitable for methanol production in a process which can be regarded as a partial recycling of CO_2 [7, 8, 12, 13]. Several papers have reported the use of microwave heating to favor heterogeneous catalytic reactions [14, 15]. Moreover, the CO_2 reforming of CH_4 under microwave heating has been studied with a series of different catalysts in previous tests, the results of which were consistently better than those obtained under conventional heating [16, 17]. The main reason for this improvement of heterogeneous catalytic processes seems to be the hot spots that appear when microwave heating is used [18, 19]. These hot spots are microplasmas [18], where the temperature is considerably higher than the average temperature of the catalyst bed. They are therefore able to increase the reaction rate, giving rise to higher conversions.

Although some studies have dealt with the microwave-assisted dry reforming of methane, there are no references to the topic of coke oven gases. The main objective of the present article is to study the dry reforming of coke oven gases under microwave heating, paying special attention to the effect of the presence in the feed of hydrogen, that has been demonstrated to be of critical importance when the process is carried out with conventional heating [7-9].

2. MATERIAL AND METHODS

2.1. Preparation and characterization of the Catalyst

A series of physical mixtures consisting of grains of a commercial activated carbon FY5 and cylindrical pellets of an in-lab prepared Ni/Al_2O_3 were used as catalyst. A detailed preparation of the catalyst and its characterization has been described elsewhere [8]. Samples of the FY5 and the Ni/Al_2O_3 before and after the reaction were examined using a scanning electron microscope (SEM) from Carl Zeiss SMT. The reason for choosing these mixtures was their dielectric properties. Activated carbons are easily heated by microwaves, but alumina is not a good absorber of microwave energy, so it is not possible to achieve the reaction temperatures. Whereas when the mixtures are employed, the activated carbon absorbs the microwaves and is heated up to the reaction temperature and the Ni/Al_2O_3 is heated by conduction through the heat provided by the activated carbon. Moreover, mixtures of this kind have shown a very interesting synergetic effect in the dry reforming of CH_4 [20] and COG [8]. The catalyst composed

exclusively of FY5 was labeled 100AC, whereas the mixtures were labeled XXAC/YYNi, where XX and YY are the weight percentages of FY5 and Ni/Al_2O_3 respectively.

2.2. CO_2 reforming experiments

The CO_2 reforming experiments were performed in a fixed-bed quartz tube reactor heated by two different devices: a conventional oven (CH), i.e. an electric furnace, and a microwave oven (MW).

A gaseous stream composed of 54% H_2, 23% CH_4 and 23% CO_2 was used. This mixture will be referred to as gas ternary mixture (GTM). With this composition, it is possible to maintain the H_2/CH_4 ratio of the COG and to ensure the stoichiometric conditions of CH_4 and CO_2 necessary for the dry reforming of methane.

The tests were performed at atmospheric pressure, at a temperature of 800 ºC (which was monitored and controlled in the middle of the catalyst bed using a thermocouple) and at a volumetric hourly space velocity of $1.00\ L\ g^{-1}\ h^{-1}$. Before the reaction, the system was purged with N_2 for 15 min. Then it was heated up to the reaction temperature. Once the reactor reached 800 ºC, the N_2 flow was stopped and the reactant gases were introduced to start the reaction. One of the products of the reaction was water (due to the reverse water gas shift reaction, RWGS, see reaction 4 of section 3. Results and discussion). To collect the water, a condenser was placed at the outlet of reactor. The gaseous products were collected in Tedlar® sample bags and analyzed in a Varian CP-3800 gas.

The CH_4 and CO_2 conversions were calculated on the basis of the amount of water collected in the condenser and the product gaseous stream compositions using an iterative method, based on the Newton method for non-lineal equations and Solver Microsoft Excel® tool. The mass balances were closed to within a margin of error of ± 5%. These parameters were calculated as follows:

$$CH_4\ conversion,\ \% = 100 \times (CH_{4\,in} - CH_{4\,out}) / CH_{4\,in}$$
(Eq. 1)

$$CO_2\ conversion,\ \% = 100 \times (CO_{2\,in} - CO_{2\,out}) / CO_{2\,in}$$
*(Eq. 2)*

where $CH_{4\,in}$ and $CO_{2\,in}$ are moles of each gas at the inlet of the reactor and $CH_{4\,out}$ and $CO_{2\,out}$ are moles of each gas at the outlet.

3. RESULTS AND DISCUSSION

The results of the conversions of CH_4 and CO_2 are shown in Figure 1.

As can be seen, there are clear differences between the results of conventional heating and those of microwave heating. When the catalyst is composed exclusively of activated carbon (100AC), the conversions achieved under microwave heating are better than those of conventional heating (methane and carbon dioxide increased approximately 10% when microwave heating is used), although this improvement is considerably lower than that obtained in the dry reforming of methane (where methane conversion increases 25% and CO_2 conversions increases a 35%, approximately) [16]. When the mixtures are used, the conversions are better under conventional heating. As the Ni/Al_2O_3 content in the mixture is increased, the gap

between the results of conventional heating and those of microwave heating increases. This suggests that whatever the cause of the difference in the results is, it has a greater effect on Ni/Al$_2$O$_3$ than on the activated carbon. This is the opposite to what happens in the case of the dry reforming of methane, where both, the activated carbon and the mixtures, lead to better results under microwave heating than under conventional heating [17]. Besides, the difference in the results when Ni/Al$_2$O$_3$ fraction increases is larger in the case of CH$_4$ conversion, may be due because the methane decomposition takes places preferably over the Ni/Al$_2$O$_3$ than over the AC [17].
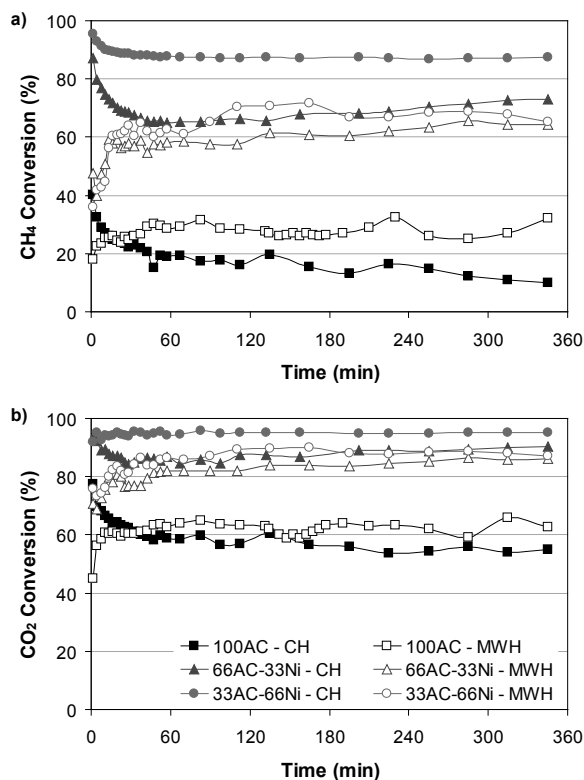
Fig. 1. *CH$_2$ and CO$_2$ conversions in the CO$_2$ reforming of GTM (800 °C, 1 atm, CH$_4$/CO$_2$ = 1, VHSV = 1.00 L g^{-1} h^{-1}, 1 atm) under different kinds of heating (microwave or conventional)*

Moreover these results were confirmed by repeating each test 3 times. The findings contradict all previous research, not only for the microwave-assisted dry reforming of methane [5, 16, 17] but also for other heterogeneous catalytic reactions [15, 18], like NO$_x$ reduction studied by Kong and Cha [21, 22] or SO$_2$ reduction studied by Cha and Kim [23]. The only difference between the dry reforming of methane and the dry reforming of coke oven gases is the presence of hydrogen in the feed, which leads to a higher hydrogen content inside the reactor. This higher content in hydrogen may be the factor responsible for the poorer results obtained with the mixtures of activated carbon and Ni/Al$_2$O$_3$ used as catalyst.

Four different possible explanations for these poor results are presented and discussed below:
• Blockage of the porosity of the activated carbon, which is the main factor responsible for the catalytic activity of this material [24], and inability of the reactant gases to gain access to the active centers of the

Ni/Al$_2$O$_3$ catalyst, due to the formation of carbon deposits [1].
• An increase in the rate of side reactions
• The different natures of the carbon deposits, which may be less reactive in the case of microwave heating
• The different nature of the microplasmas formed during the heating.

Hypothesis 1: blockage due to carbon deposits
In order to study this hypothesis, N$_2$ adsorption isotherms of the materials used as catalysts, before and after the reaction, were performed. The results of this textural characterization are presented in Table 1.

Table 1. *Porous textural properties of the activated carbon FY5 and the Ni/Al$_2$O$_3$ catalyst before and after the experiments.*

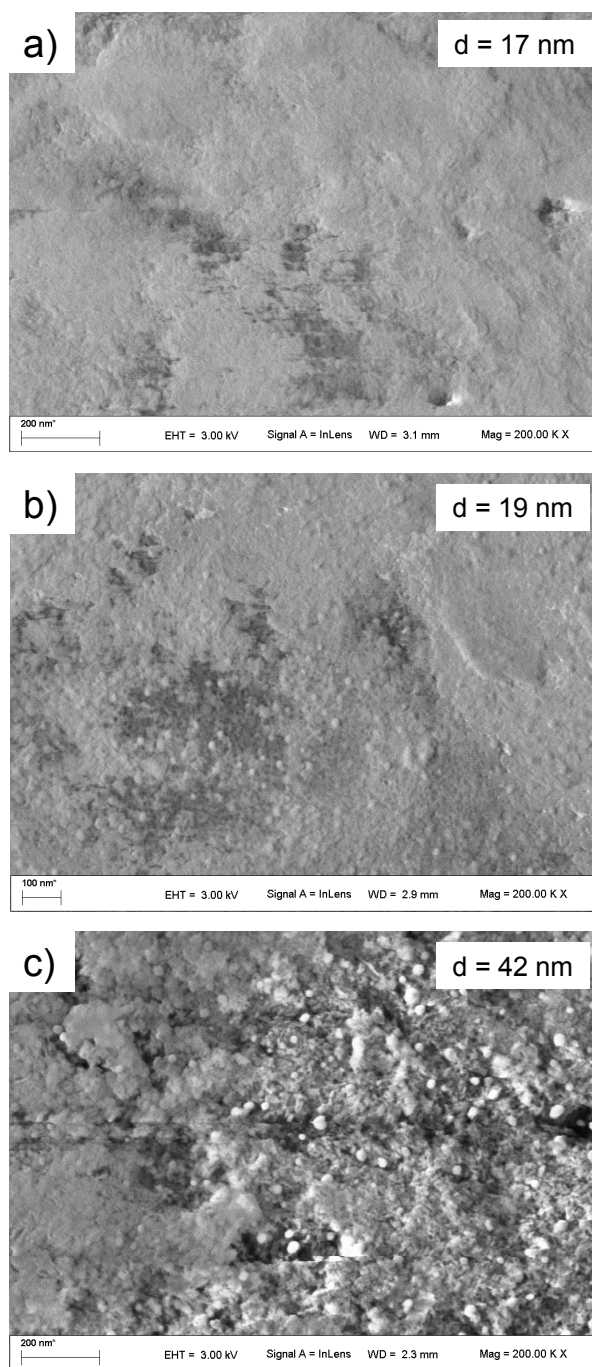|	FY5			Ni/Al$_2$O$_3$		
	S_{BET} [a] (m^2/g)	V_t [b] (cm^3/g)	V_{mic} [c] (cm^3/g)	S_{BET} [a] (m^2/g)	V_t [b] (cm^3/g)	V_{mic} [c] (cm^3/g)
Before	1153	0.51	0.44	166	0.53	0.06
100AC-CH	953	0.42	0.35	n.a	n.a	n.a
100AC-MW	938	0.41	0.35	n.a	n.a	n.a
66AC/33Ni-CH	1013	0.44	0.37	163	0.52	0.06
66AC/33Ni-MW	1106	0.52	0.42	166	0.55	0.06
33AC/66Ni-CH	1060	0.47	0.40	163	0.52	0.06
33AC/66Ni-MW	1074	0.51	0.39	156	0.55	0.06

[a]BET surface area obtained from the N$_2$ adsorption isotherms at -196 ºC.
[b]Total specific pore volume, defined as the liquid volume adsorbed at p/p^0 = 0.95 from the isotherm of nitrogen at -196 ºC.
[c]Specific volume of micropores (pores of internal width <2 nm), calculated from the isotherm of nitrogen at -196 ºC.

In view of the results, the first hypothesis can be discarded, at least in so far as the blockage of the porosity of the activated carbon is concerned. It can be seen that, only when the 100AC is used, is the porosity of the activated carbon after the reaction lower under microwave heating. In any case, the differences between the final porous textures in the experiments carried out under microwave heating and under conventional heating are so small that they should not be taken into consideration.

In the case of Ni/Al$_2$O$_3$, the porosity was not affected during the reaction, so it would appear that there were no carbon deposits blocking access of the reactant gases to the active centers of the catalysts. To confirm this, several SEM images were taken, some of which are shown in Figure 2.

a) d = 17 nm

200 nm | EHT = 3.00 kV | Signal A = InLens | WD = 3.1 mm | Mag = 200.00 K X

b) d = 19 nm

100 nm | EHT = 3.00 kV | Signal A = InLens | WD = 2.9 mm | Mag = 200.00 K X

c) d = 42 nm

200 nm | EHT = 3.00 kV | Signal A = InLens | WD = 2.3 mm | Mag = 200.00 K X

Fig. 2. *SEM images of the Ni/Al$_2$O$_3$ catalyst: (a) before the reaction; (b) after the reaction under conventional heating; and (c) after the reaction under microwave heating. The mean size of the Ni particles of each sample (determined by XRD diffraction) is indicated inside the white boxes in the right upper corner of each SEM image.*
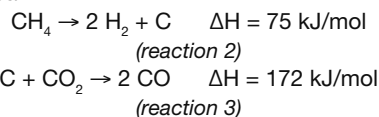
In these photographs, there is no evidence of carbon deposits. Although there are differences in appearance between each sample, these are due to other causes, which will be discussed below.
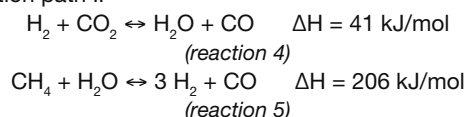
Hypothesis 2: side reactions

To justify this hypothesis, it is necessary to consider the possible reaction mechanisms involved in the process. It has previously been reported [9] that the CO$_2$ reforming of coke oven gas can take place through two different reaction pathways: direct dry reforming, which is normally considered as the sum of methane decomposition (reaction 2) followed by the gasification of carbon (reaction 3), or the reverse water gas shift (reaction 4) followed by the steam reforming of methane (reaction 5) [8, 9].

Reaction path I
$$CH_4 \rightarrow 2\ H_2 + C \qquad \Delta H = 75\ kJ/mol$$
(reaction 2)
$$C + CO_2 \rightarrow 2\ CO \qquad \Delta H = 172\ kJ/mol$$
(reaction 3)

Reaction path II
$$H_2 + CO_2 \leftrightarrow H_2O + CO \qquad \Delta H = 41\ kJ/mol$$
(reaction 4)
$$CH_4 + H_2O \leftrightarrow 3\ H_2 + CO \qquad \Delta H = 206\ kJ/mol$$
(reaction 5)

The problem with reaction path II (RWGS followed by steam reforming) is that the RWGS reaction can act as a side reaction. If all the water produced through RWGS does not react with the methane it will give rise to large amounts of water [25, 26].

Table 2. *Water production obtained in the different experiments expressed as volume percentage of the products.*
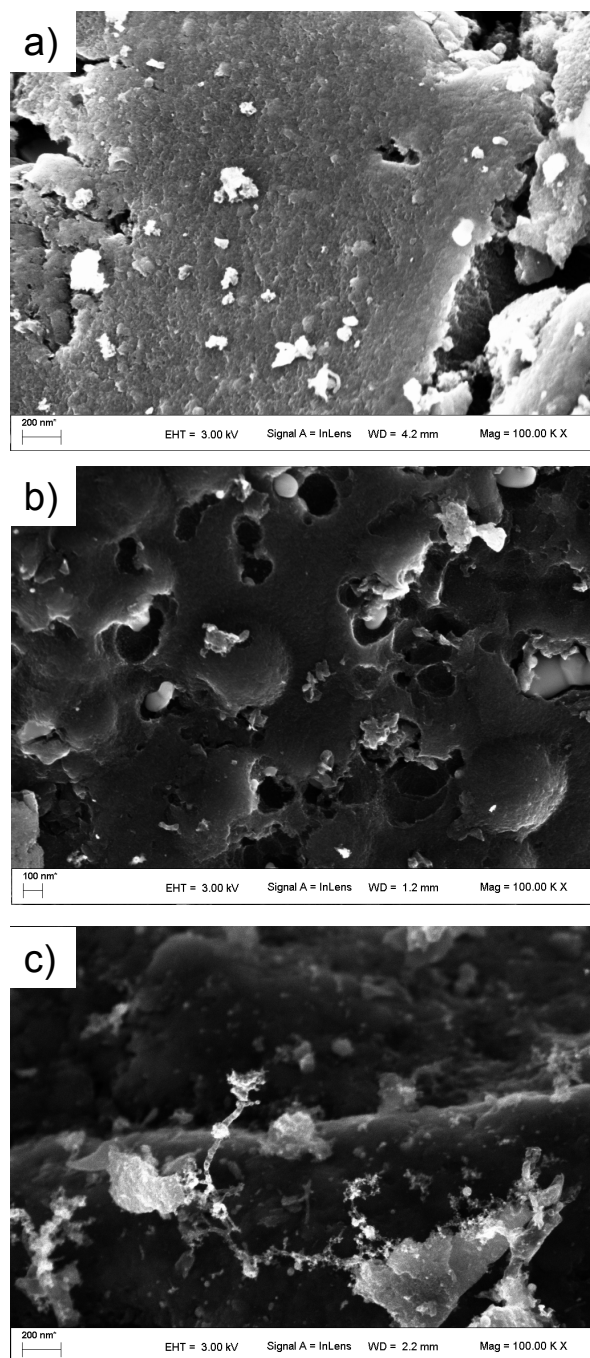
	Conventional Heating	Microwave Heating
100AC	10.5 %	8.0 %
66AC/33Ni	4.3 %	5.1 %
33AC/66Ni	2.1 %	5.0 %

The water produced in the experiments is reported in Table 2. As can be seen, in the case of 100AC, water production is higher when conventional heating is used, whereas when the catalysts are the mixtures, water production is higher under microwave heating. Again the differences between the results of both heating mechanisms are only slight and the conversion of CO$_2$ follows the same pattern as that of CH$_4$, i.e. in both cases conversions are higher in the microwave oven when the 100 AC is used as catalyst but lower in the microwave oven when the mixtures are used as catalyst. Consequently, the different behaviors observed in the dry reforming of COG and in the dry reforming of methane cannot be fully explained by this hypothesis alone.

Hypothesis 3: carbon deposits nature

When methane decomposition takes place, it gives rise to different kinds of carbon deposits. Not only is the amount of these carbon deposits important for the catalytic activity of the materials used as catalyst, but also their reactivity. In the case of Ni/Al$_2$O$_3$ (see SEM images in Figure 2) the formation of carbon deposits can be discarded. In the case of the activated carbon, its BET surface is reduced during the process, suggesting that its pores must have been blocked. The amount of carbon deposits is probably similar irrespective of the heating device used, since no significant differences in the BET surface area of the activated carbon at the end of the experiment in the two heating devices can be seen. However, this does not rule out the possibility that the nature of the deposits may be different. Figure 3 shows SEM images of the activated car-

bon before and after the reaction in the different heating mechanisms.

Fig. 3. *SEM images of FY5: (a) before the reaction; (b) after the reaction under conventional heating; and (c) after the reaction under microwave heating.*

The most important difference is that, in the case of microwave heating, nanofibers were formed on the carbon surface in all cases, but not under conventional heating. However this also occurred in the case of the dry reforming of methane, so the presence of such deposits does not explain the differences in conversion [5]. Also worth noting is that these fibers did not appear on Ni/Al$_2$O$_3$, even though Ni is a typical catalyst used for the production of this kind of fibers [27, 28]. However, they appeared on the surface of the activated carbon (which only has a small percent-

age of inorganic ashes) in every mixture (i.e., 66A/33Ni and 33AC/66Ni). However this issue will not be discussed further since it lies outside the scope of this paper.

Hypothesis 4: nature of the microplasmas

During the microwave heating of carbon materials microplasmas are produced [19]. The improvement in catalytic activity produced by microwave heating in the heterogeneous process has been attributed to these microplasmas, since at these points the temperature is able to reach values considerably higher than the mean temperature of the catalyst bed [15, 29]. Moreover, Zhang *et al.* [15] have suggested that these microplasmas may result in apparent shifts of the equilibrium constant. It is therefore possible to talk about a "pseudo-catalytic" effect produced by these microplasmas in microwave heating.

In this work, the microplasmas were observed during the process as in the case of the dry reforming of methane. However, as mentioned before, the gases present in the reactor exhibit one very important difference: a much higher proportion of H$_2$ in the case of coke oven gas. It is therefore possible to state that the nature of the microplasmas is different. A possible consequence of this difference in the microplasmas can be seen in the SEM images of Ni/Al$_2$O$_3$ (Figure 2). The appearance of the surface of the Ni/Al$_2$O$_3$ catalyst under conventional heating is completely different to that of the Ni/Al$_2$O$_3$ catalyst after reaction under microwave heating. In the catalyst used in the microwave oven, tiny granules can be seen on the surface of the material. At first sight, it seems that the Ni particles have experienced sintering during the reaction. Indeed, this was confirmed by DRX analysis performed in order to determine the Ni particle size employing Scherrer's equation. The results of the Ni particle size (d) are included in Figure 2. As can be seen, the Ni particle size of the catalyst after reaction in the microwave oven is considerably greater than that of the catalyst after reaction in the conventional oven (it is even higher than when the reaction was carried out in a conventional oven over a 50-hour period [9]). Considering that the mean temperature in the microwave is the same as in the conventional oven, a possible explanation or the difference may be that the microplasmas have created hot spots with temperatures high enough to promote the sintering of the Ni particles. Since microplasmas were also formed in the microwave-assisted dry reforming of methane, it seems that the presence of such high proportions of hydrogen gives rise to microplasmas with higher temperatures. The sintering of the Ni particles alone will lead to deactivation, but sintering will also ultimately promote the formation of carbon deposits, thereby increasing the deactivation rate of the catalysts even further [30, 31]. To sum up, the nature of the microplasmas is the main cause of the bad behavior of the microwave assisted dry reforming of coke oven gas, although the other three hypotheses will also have contributed to the final results.

4. CONCLUSIONS

The use of microwave energy in the dry reforming of coke oven gas yields better results than those obtained under conventional electric heating if the process is carried out with an activated carbon as catalyst. However, when the process is carried out with mixtures of activated carbon and Ni/Al$_2$O$_3$ as catalyst, the results obtained in the micro-

wave oven are worse than those obtained in a conventional oven. These results differ significantly from those achieved in the dry reforming of CH_4, which are considerably higher in the case of the microwave oven, independently of the kind of catalyst, with conversions of 100 % being achieved for both gases.

Several hypotheses have been proposed in order to explain the differences, which must be due to the presence of H_2 in the reactant gases, since this is the only difference between the two processes. These hypotheses were: (i) blockage of the carbon porosity by carbon deposits; (ii) increase in the gases reacting through side reactions; (iii) the nature of the carbon deposits; (iv) the nature of the microplasmas formed during the heating. All of these causes contribute to the poor results achieved in the microwave-assisted dry reforming of coke oven gas, although the last hypothesis, the nature of microplasmas, is the most influential, since it causes a very important sintering of the Ni particles. Furthermore the microplasmas formed in the presence of such high proportions of H_2 can reach higher temperatures than in the case of the microwave-assisted dry reforming of methane. This promotes the sintering process which in turn leads to a decrease in the conversions.

ACKNOWLEDGMENTS

REFERENCES

1. S. Wang, G.Q. Lu, G.J. Millar, Energy Fuels 10 (1996) 896-904.
2. M.C.J. Bradford, M.A. Vannice, Appl Catal A 142 (1996) 73-96.
3. J.H. Edwards, A.M. Maitra, Fuel Process Technol 42 (1995) 269-289.
4. J.R.H. Ross, Catal Today 100 (2005) 151-158.
5. A. Domínguez, Y. Fernández, B. Fidalgo, J.J. Pis, J.A. Menéndez, Energy Fuels 21 (2007) 2066-2071.
6. F. Barrai, T. Jackson, N. Whitmore, M.J. Castaldi, Catal Today 129 (2007) 391-396.
7. J.M. Bermúdez, B. Fidalgo, A. Arenillas, J.A. Menéndez, Fuel 89 (2010) 2897-2902.
8. J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Int J Hydrogen Energy 36 (2011) 13361-13368.
9. J.M. Bermúdez, B. Fidalgo, A. Arenillas, J.A. Menéndez, Fuel (2011).
10. F. Joseck, M. Wang, Y. Wu, Int J Hydrogen Energy 33 (2008) 1445-1454.
11. B. Yue, X. Wang, X. Ai, J. Yang, L. Li, X. Lu, W. Ding, Fuel Process Technol 91 (2010) 1098-1104.
12. G.J. Tjatjopoulos, I.A. Vasalos, Ind Eng Chem Res 37 (1998) 1410-1421.
13. G.A. Olah, A. Goeppert, G.K.S. Prakash, Beyond oil and gas: the methanol economy, Wiley-VCH, Weinheim, Germany, 2006.
14. A. Zlotorzynski, Crit Rev Anal Chem 25 (1995) 43-76.
15. X. Zhang, D.O. Hayward, D.M.P. Mingos, Catal Lett 88 (2003) 33-38.
16. B. Fidalgo, A. Domínguez, J.J. Pis, J.A. Menéndez, Int J Hydrogen Energy 33 (2008) 4337-4344.
17. B. Fidalgo, A. Arenillas, J.A. Menéndez, Fuel Process Technol 92 (2011) 1531-1536.
18. J.A. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E.G. Calvo, J.M. Bermúdez, Fuel Process Technol 91 (2010) 1-8.
19. J.A. Menéndez, E.J. Juárez-Pérez, E. Ruisánchez, J.M. Bermúdez, A. Arenillas, Carbon 49 (2011) 346-349.
20. B. Fidalgo, A. Arenillas, J.A. Menéndez, Appl Catal A 390 (2010) 78-83.
21. Y. Kong, C.Y. Cha, Carbon 34 (1996) 1035-1040.
22. Y. Kong, C.Y. Cha, Energy Fuels 9 (1995) 971-975.
23. C.Y. Cha, D.S. Kim, Carbon 39 (2001) 1159-1166.
24. B. Fidalgo, A. Arenillas, J.A. Menéndez, Fuel 89 (2010) 4002-4007.
25. G. Zhang, Y. Dong, M. Feng, Y. Zhang, W. Zhao, H. Cao, Chem Eng J 156 (2010) 519-523.
26. J. Xu, G.F. Froment, AIChE J 35 (1989) 88-96.
27. R.T.K. Baker, M.A. Barber, P.S. Harris, F.S. Feates, R.J. Waite, J Catal 26 (1972) 51-62.
28. Z.P. Huang, D.Z. Wang, J.G. Wen, M. Sennett, H. Gibson, Z.F. Ren, Appl Phys A: Mater Sci Process 74 (2002) 387-391.
29. D. Stuerga, P. Gaillard, Tetrahedron 52 (1996) 5505-5510.
30. Z. Xu, Y. Li, J. Zhang, L. Chang, R. Zhou, Z. Duan, Appl Catal A 210 (2001) 45-53.
31. P. Chen, Z. Hou, X. Zheng, T. Yashima, React Kinet Catal Lett 86 (2005) 51-58.