



# Influence on hydrogen production of the minor components of natural gas during its decomposition using carbonaceous catalysts

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## ABSTRACT

In this work, the catalytic decomposition of the minor hydrocarbons present in natural gas, such as ethane and propane, over a commercial carbon black (BP2000) is studied. The influence of the reaction temperature on the product gas distribution was investigated. Increasing reaction temperatures were found to increase both hydrocarbon conversion and hydrogen selectivity. Carbon produced by ethane and propane was predominantly deposited as long filaments formed by spherical aggregates with diameters on the order of nanometres. Furthermore, the influence of ethane and propane on methane decomposition over BP2000 was also investigated, showing enrichment in hydrogen concentration with the addition of small amounts of these hydrocarbons in the feed. Additionally, the positive catalytic effect of H<sub>2</sub>S on methane decomposition over BP2000 is addressed.

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## 1. Introduction

Catalytic decomposition of natural gas (CDNG), with carbon captured as a product of added value, is an interesting alternative to steam reforming for hydrogen production [1–5]. In previous works, it has been established that carbonaceous catalysts are suitable for the catalytic decomposition of methane (CDM) [6–25]. Particularly, active carbons show high initial reaction rate, but are rapidly deactivated. However, carbon blacks, displayed lower reaction rates, providing a sustainable behaviour in CDM during several hours on stream, predominantly due to the high textural development [16,17,24]. The activation energy of the BP2000 carbon black in methane decomposition was found to be 236 kJ mol<sup>-1</sup>, significantly lower than the methane C–H bond energy of 440 kJ mol<sup>-1</sup>, pointing out the catalytic effect of such carbonaceous material [16].

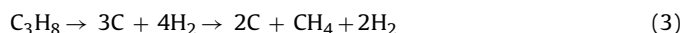
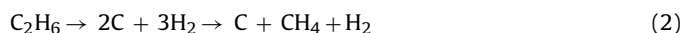
Methane, as the major component of natural gas, has been the hydrocarbon feedstock most commonly studied for catalytic decomposition over carbonaceous materials. However, for future process scale-up, natural gas should be the preferred feed, given its availability. Natural gas is defined as a mixture of hydrocarbons, with methane as the major component. Depending on the origin of the natural gas, it can also be composed of other minor hydrocarbons, such as ethane, propane and ethylene, as well as nitrogen, CO<sub>2</sub> and H<sub>2</sub>S. Accordingly, in order to gain knowledge about the CDNG, the role of the minor components of the natural gas must be elucidated.

Increasing attention has been devoted to the study of the production of hydrogen and added value carbon by means of the decomposition of light alkanes and alkenes using metal catalysts [26–33]. For example, ethane decomposition for carbon nanofiber and rich H<sub>2</sub> stream co-production has been accomplished over metal catalysts, obtaining 100% conversion with temperatures lower than 600 °C [31]. The use of carbonaceous catalysts for the decomposition of non-methane hydrocarbons, to the best of our knowledge, has only been carried out by Muradov et al. In these studies, the decomposition of propane and methane–propane mixtures was examined [5,34], showing that the addition of hydrocarbons higher than methane increased the hydrogen concentration without catalyst deactivation. Additionally, for carbonaceous catalysts, higher temperatures are needed to reach complete conversion (around 800 °C). According to the same author, one of the major advantages of the use a feed composed of higher hydrocarbons, such as propane, ethylene, acetylene and benzene, is that carbon deposits seem to be more active toward methane decomposition than the carbon produced by the methane decomposition itself [5].

The general equation for alkane decomposition is



In the case of ethane and propane, thermal decomposition leads to carbon and hydrogen production, but some methane is also formed by hydrogenation of the produced carbon [30], according to the following reactions:



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**Table 1**  
Composition of the ashes of BP2000 sample.

Al <sub>2</sub> O <sub>3</sub>	0.59
CaO	40.85
Fe <sub>2</sub> O <sub>3</sub>	0.13
K <sub>2</sub> O	1.1
MgO	0.13
Na <sub>2</sub> O	0.51
SiO <sub>2</sub>	0.41
Cr <sub>2</sub> O <sub>3</sub>	0.18
Ni <sub>2</sub> O <sub>3</sub>	0.12
SO <sub>3</sub>	56

Regarding the effect of the presence of H<sub>2</sub>S in the feed, it is well-known that sulphur compounds provoke rapid deactivation of metal catalysts [30]. According to the literature [20], one of the main advantages of using carbonaceous materials in the CDNG, is that the carbon materials are capable of withstanding sulphur compounds in the feed without suffering from deactivation.

In an effort to expand our previous work on the decomposition of methane over carbonaceous catalysts, we examined the catalytic decomposition of undiluted ethane and propane over a commercial carbon black, BP2000, widely studied for methane decomposition in previous works [14,16,17,24]. Furthermore, after the reaction tests the catalysts were characterized via SEM and TEM measurements in order to determine the appearance of the carbon deposited during the course of the reaction. Additionally, the catalytic decomposition of binary and ternary mixtures of methane–ethane, methane–propane, and methane–ethane–propane was studied, in order to investigate the effect of the minor hydrocarbons present in natural gas on the catalytic decomposition of methane (CDM). The influence of the presence of H<sub>2</sub>S in the feed was also studied.

## 2. Experimental

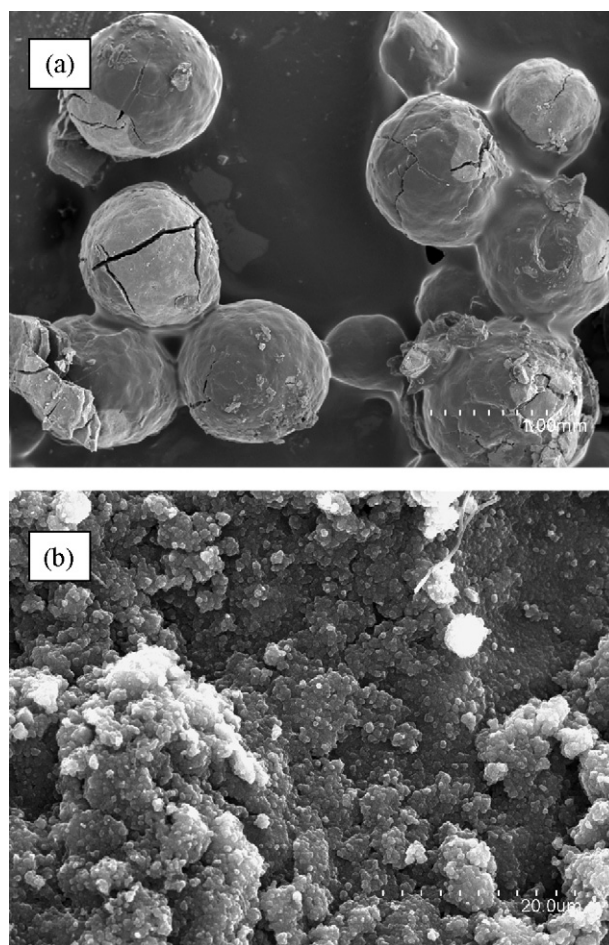
### 2.1. Samples

A commercial carbon black BP2000, supplied by Cabot, was used as a catalyst for natural gas decomposition. This carbonaceous material, widely studied in previous works [14,16,17,24] presents an open macro/meso-porosity, with high surface area (1400 m<sup>2</sup> g<sup>-1</sup>) and pore volume (3.06 cm<sup>3</sup> g<sup>-1</sup>). Moreover, the proximate and ultimate analysis revealed that the BP2000 sample presented a small amount of sulphur in its composition, a high carbon content (around 97%) and an ash content lower than 1%. The ash analysis by means of ICP, shown in Table 1, reveals that the content in the ashes of metal active catalyst for CDNG is lower than 0.12% for Fe and 0.13% for Ni, which implies in fact that the amount of Fe and Ni taking as a reference the BP2000 sample weight is 12 and 13 ppm, respectively. This assures no interference by metal-catalyzed hydrocarbon decomposition, as was previously concluded regarding the same material in [15].

Fig. 1 shows SEM images of the BP2000 sample used as catalyst in the present work. Fig. 1a shows BP2000 treated under nitrogen atmosphere at 850 °C. The carbon black particles form spherical aggregates ranging from 0.5 to 1 mm. Magnification of Fig. 1a, Fig. 1b, shows that the spherical particles are formed by carbon agglomeration of ca. 200 nm.

### 2.2. Experimental setup

Hydrocarbon catalytic decomposition experiments were run in a laboratory-scale fixed-bed quartz reactor, 60 cm height, 18 mm i.d., heated by and electric furnace. In order to stabilize the catalyst, it was pre-treated under nitrogen at the reaction temperature for 3 h before the reaction tests, and then cooled and weighted. All experiments were conducted at atmospheric pressure.



**Fig. 1.** SEM images of the fresh BP2000 samples used in CDNG.

All experiments were carried out using 1.2 g of fresh catalyst. In the case of the decomposition of undiluted ethane and propane, the study was performed by varying the operating temperature over 600–950 °C, using a flow rate of 20 ml min<sup>-1</sup>, which corresponds to a weight hour space velocity (WHSV) of 11 g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, defined as the volume of methane fed per hour per gram of fresh catalyst. The influence of ethane and propane in the CDM was studied at 900 °C using a total flow rate of 50 ml min<sup>-1</sup> of simulated natural gas (SGN), composed of methane (85 vol.%), ethane (10 vol.%) and propane (5 vol.%). Binary mixtures were also used and nitrogen was used to close the balance: (i) methane (85 vol.%), ethane (10 vol.%) and nitrogen (5 vol.%) and (ii) methane (85 vol.%), propane (5 vol.%) and nitrogen (10%).

The influence of H<sub>2</sub>S in the CDM was investigated at 900 °C by means of adding a methane stream containing 1 vol.% of H<sub>2</sub>S. The total flow rate used was 60 ml min<sup>-1</sup>, with a methane partial pressure of 0.67 atm (N<sub>2</sub> balanced).

The analysis of the gas flowing from the reactor was carried out by sampling the gas stream with gas sampling bags. The first bag was typically taken some minutes after the gas was introduced, when the nitrogen initially present in the reaction system was flushed out. The gas samples were analysed by means of gas chromatography. Hydrogen and methane analysis were performed in a micro GC Varian CP4900, equipped with two packed columns and a TCD detector. The analysis of ethane, propane and ethylene were performed in a Varian 3400 equipped with an alumina packed column and a TCD detector.

Ethane conversion and selectivity to hydrogen were calculated as follows, taking into account the hydrogen mass balance and the

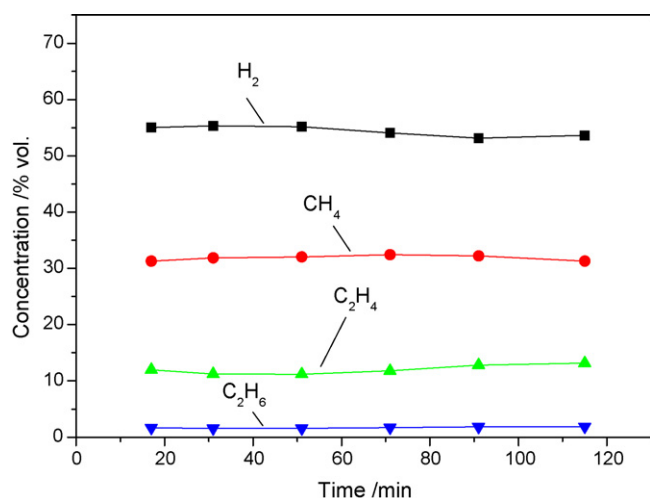


Fig. 2. Product gas composition vs. time for the ethane decomposition test carried out over BP2000 at 850 °C.

stoichiometries of H<sub>2</sub> formation from C<sub>2</sub>H<sub>6</sub>:

$$\text{C}_2\text{H}_6 \text{ conversion} = \frac{\text{moles of C}_2\text{H}_6 \text{ reacted}}{\text{moles of C}_2\text{H}_6 \text{ fed}} \times 100 \quad (4)$$

$$\text{H}_2 \text{ selectivity} = \frac{(1/3)\text{moles of H}_2 \text{ formed}}{\text{moles of C}_2\text{H}_6 \text{ reacted}} \times 100 \quad (5)$$

Similarly, propane conversion and selectivity to hydrogen were calculated as follows:

$$\text{C}_3\text{H}_8 \text{ conversion} = \frac{\text{moles of C}_3\text{H}_8 \text{ reacted}}{\text{moles of C}_3\text{H}_8 \text{ fed}} \times 100 \quad (6)$$

$$\text{H}_2 \text{ selectivity} = \frac{(1/4)\text{moles of H}_2 \text{ formed}}{\text{moles of C}_3\text{H}_8 \text{ reacted}} \times 100 \quad (7)$$

Carbon deposition in the quartz tube was only observed for the case of the tests carried out at higher temperatures, that is, 900 and 950 °C. In these cases, the quantity of the carbon deposition in the inner wall was negligible with respect to the mass gained by the catalyst. In the experiments carried out at lower temperatures, no carbon deposits on the tube walls were observed.

### 2.3. Characterization

The morphology of the deposited carbon was studied in an electron microscope (SEM) (Hitachi S-3400) coupled with a Si/Li detector for energy dispersive X-ray (EDX) analysis. TEM images for determination of sample morphology were obtained using a 300 kV Philips CM-30. For these measurements, the samples were suspended in ethanol or *n*-hexane with ultrasonic dispersion for 3 min. Then a drop of this suspension was deposited on a carbon grid and observed after drying.

## 3. Results and discussion

### 3.1. Ethane catalytic decomposition

Fig. 2 shows the evolution of the gas product distribution along with reaction time for a typical decomposition run carried out at 850 °C using ethane as feedstock and BP2000 as catalysts. The WHSV was fixed at 1 l g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. The product distribution shows that the outlet gases are composed of a mixture of hydrogen (55%), methane (32%) and ethylene (11%). A small amount of ethane (lower than 2%) was also detected in the outlet gases, implying that ethane conversion is almost complete at this temperature. The concentra-

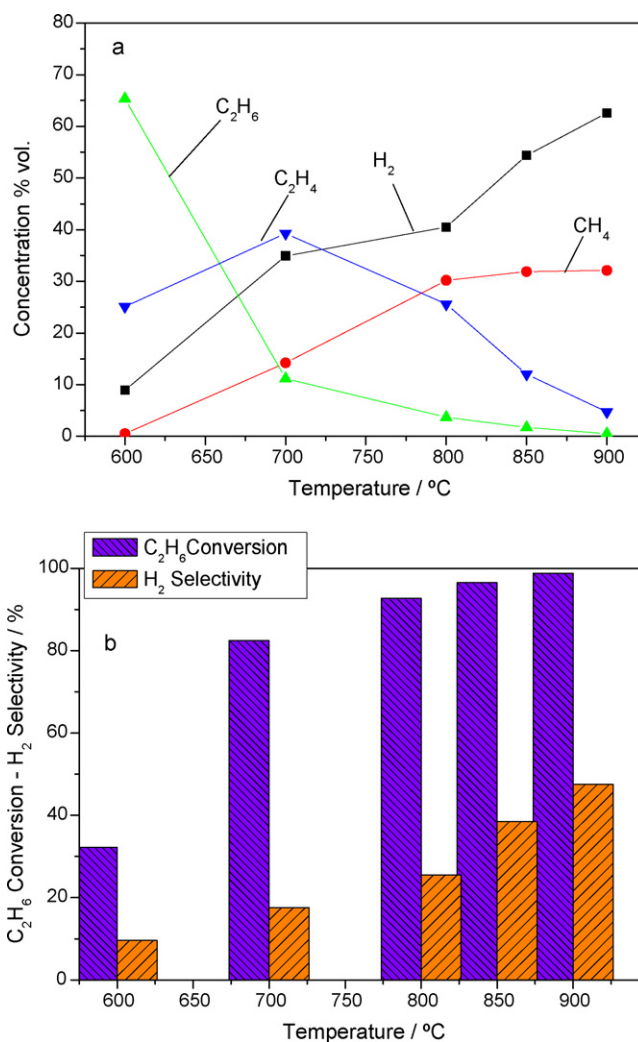


Fig. 3. (a) Product gas composition vs. reactor temperature for ethane decomposition over BP2000. (b) Ethane conversion and H<sub>2</sub> selectivity as a function of reactor temperature.

tion of the gases did not decay with time, suggesting that catalytic activity remains constant during the entire run.

Fig. 3a shows the variation of the gas distribution products with an increase in operating temperature. It can be observed that the ethane concentration curve drops to a value lower than 5% at a temperature higher than 800 °C. The ethylene concentration curve shows a maximum at 700 °C. Hydrogen and methane concentration curves increase with the increase in the reaction temperature. At temperatures higher than 800 °C, the hydrogen concentration increases and ethylene concentration decreases. Meanwhile, the methane curves do not change significantly with the increase in operating temperature.

Fig. 3b shows the ethane conversion and the selectivity for H<sub>2</sub> production for the ethane decomposition runs carried out at various operating temperatures. Both parameters increase with the reaction temperature. At a temperature higher than 800 °C, ethane conversion reaches values higher than 90%. H<sub>2</sub> selectivity reaches maximum values of 47% at 900 °C, the highest temperature tested.

### 3.2. Propane catalytic decomposition

The study of propane decomposition over BP2000 was performed analogously to that of ethane. The results are shown in Fig. 4 for the evolution of the product gas distribution along with



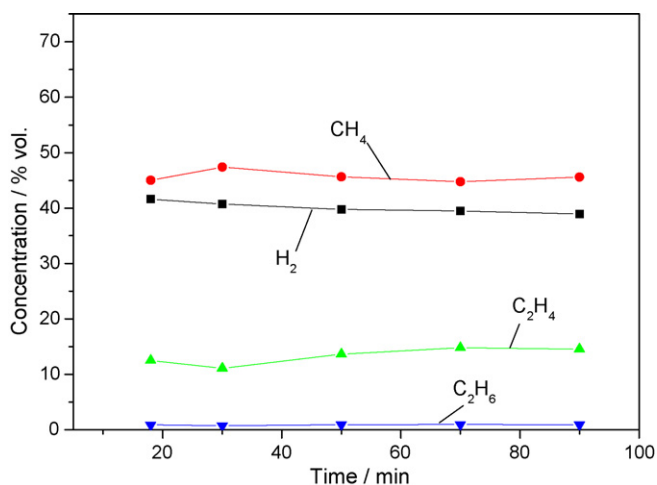


Fig. 4. Product gas composition vs. time for the propane decomposition test carried out over BP2000 at 850 °C.

the reaction time for the run carried out at 850 °C, using propane as feedstock and BP2000 as catalysts. The outlet gases are composed of mainly hydrogen (39%), methane (45%) and ethylene (ca. 15%). Traces of ethane (lower than 1%) were also detected. It is worth mentioning that at 800 °C no propane was detected in the outlet gases, indicating that complete conversion of propane was achieved. Again, the concentration of the species detected remained constant throughout the run.

The changes in the concentration of the different species detected in the outlet gases as the reaction temperature is increased are shown in Fig. 5a. Propane concentration drops to values lower than 2% at 700 °C. Ethylene again shows a maximum at 700 °C, as observed in the case of ethane decomposition. This can be attributed to the fact that ethylene is an intermediate of the reaction. A small amount of ethane was also detected. Hydrogen and methane concentration both increase, first with the reaction temperature, but from 800 °C and onwards, the concentration curves for these gases diverge. This fact can be explained by the catalytic effect of the BP2000, which converts the produced methane into hydrogen and carbon products, increasing the hydrogen concentration in the outlet gases.

The changes in the conversion of propane and the selectivity to H<sub>2</sub> with the increase in temperature, shown in Fig. 5b, revealed that propane conversion reached 100% at temperatures higher than 800 °C. The selectivity to hydrogen increases with the reaction temperature, and reaches a value of 40% at 950 °C. The production of a relatively steady flow of hydrogen-rich gas was also reported by Muradov [34] using carbonaceous samples in propane decomposition. The author explained this fact by the catalytic action of the carbon particulates, produced during thermal decomposition of hydrocarbons at elevated temperatures.

### 3.3. Characterization of the carbon product

The BP2000 samples after ethane decomposition were observed with SEM. Fig. 6 shows typical forms of carbon deposited from ethane during a two hour test, carried out at 850 °C over the BP2000. The carbon appears in the form of nanofilaments that cover the original surface of the BP2000. This form is comparable to those reported for hydrocarbon decomposition when metal catalysts are used. In that case, the carbon nanofiber growth has been very well observed, occurring in the presence of metal particles that promote methane decomposition, allowing carbon to diffuse and precipitate on the opposite side of the particle. However, the presence of such structures in hydrocarbon decomposition using carbonaceous

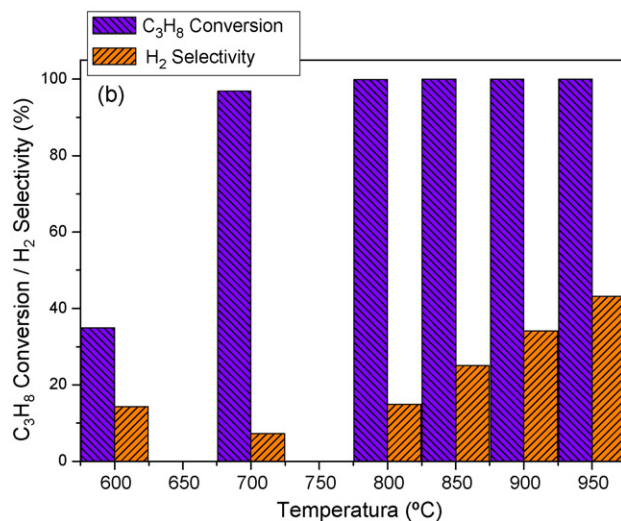
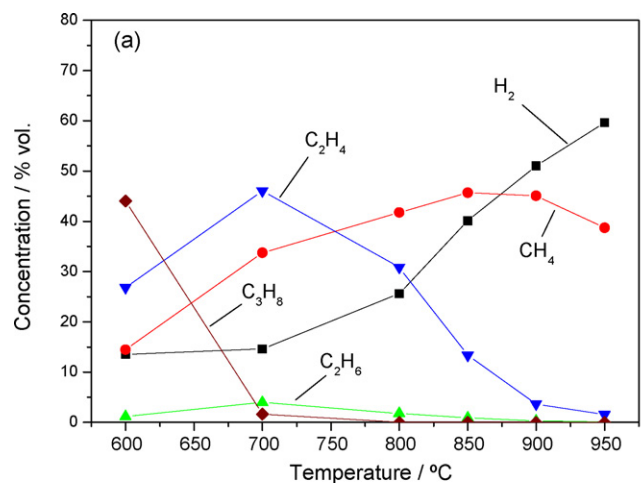


Fig. 5. (a) Product gas composition vs. reactor temperature for propane decomposition over BP2000. (b) Propane conversion and H<sub>2</sub> selectivity as a function of reactor temperature.

materials has not been reported as frequently. For example, the formation of multi-walled carbon nanotubes by means of chemical vapour deposition of ethylene over a carbon black has been reported [35]. Other authors [36] have observed the presence of filament-like structures in the carbonaceous samples used in methane decomposition via microwave heating. The growth of such filaments has been attributed to the presence of metal traces in the composition of the carbonaceous samples used [37]. However, in the case of the present study, the carbon deposition in form of nanofilaments cannot be attributed to the presence of metal active particles, given the low concentration of such metals (few ppm of Fe and Ni with respect to the total carbon black mass), as the ICP analysis of the ashes revealed (Table 1).

In order to elucidate the morphology of the filamentous structures observed for the deposited carbon from ethane over the BP2000, the samples were observed with TEM, as shown in Fig. 7. The images show that filaments are formed by spherical aggregates of 20–50 nm diameters, showing a preferential growth direction. These spherical particles may be correlated to the crystallites from ethane decomposition. As a consequence, it is clear that these structures differ considerably from the carbon nanofibers produced in the presence of active metal particles. Additionally, high resolution TEM micrographs show that the graphene dispositions on the inner parts of these filaments are completely disordered.

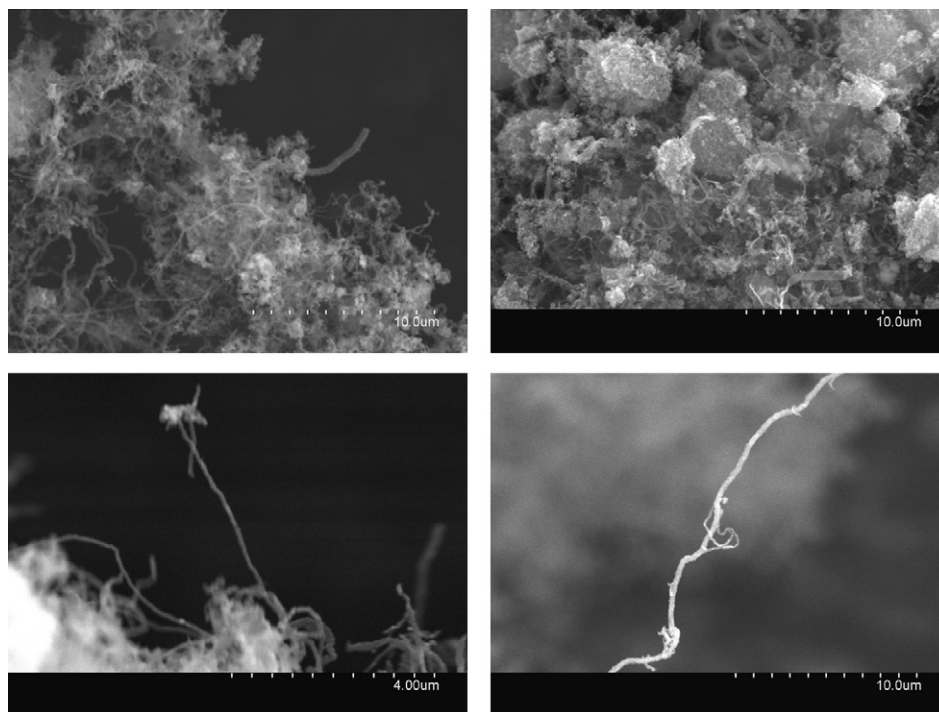


Fig. 6. SEM micrographs of used catalyst BP2000 tested in the ethane decomposition tests at 850 °C.

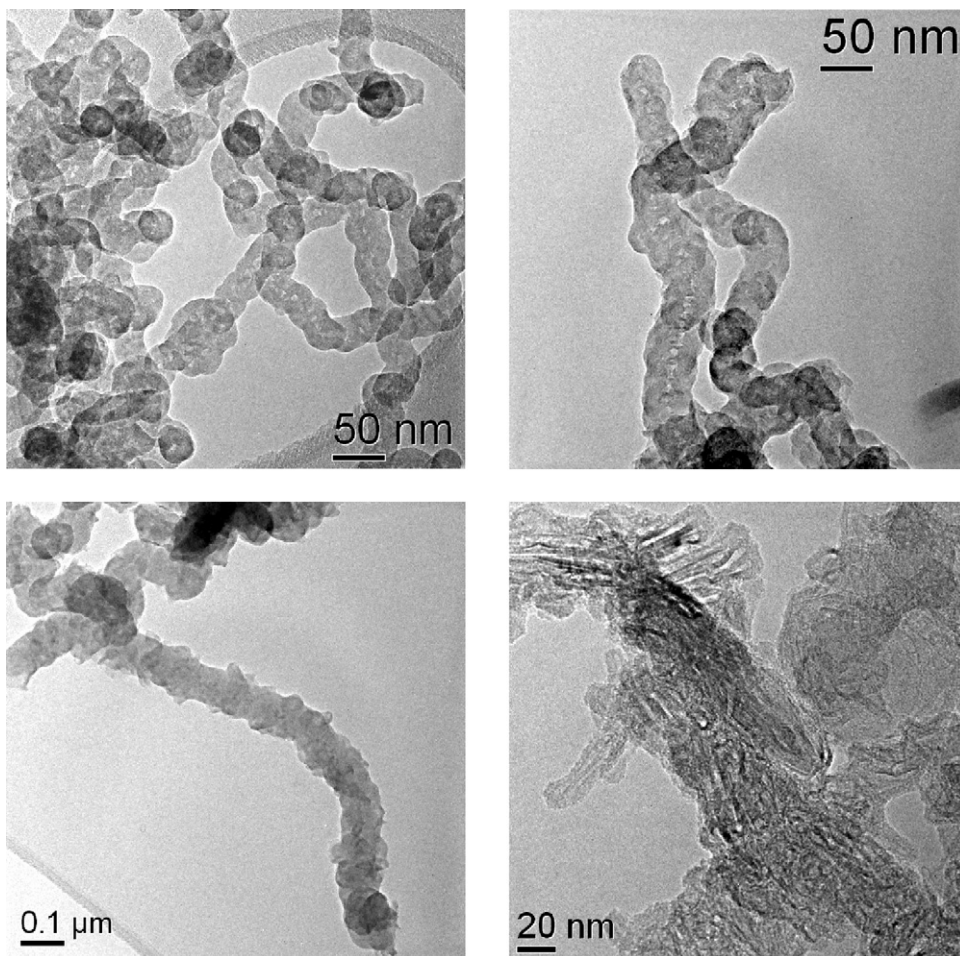


Fig. 7. TEM micrographs of used catalyst BP2000 tested in the ethane decomposition tests at 850 °C.

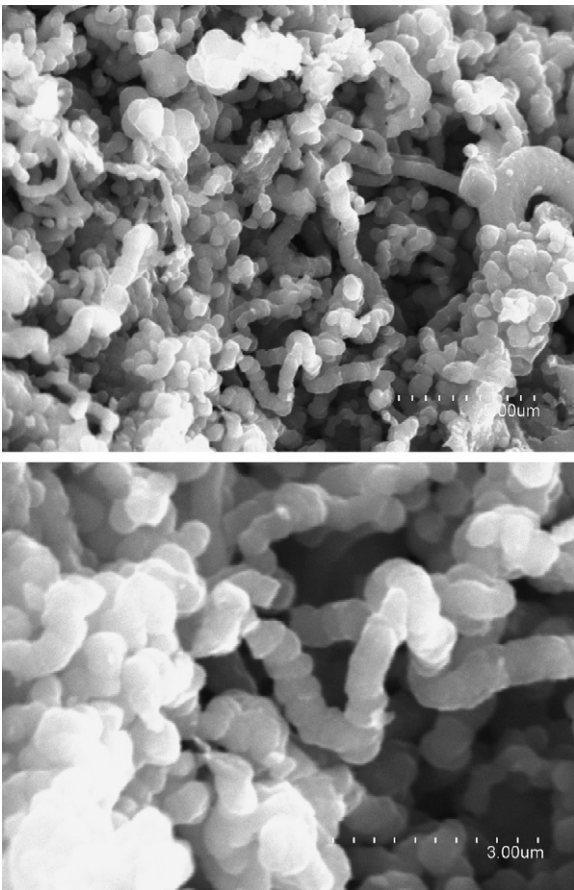


Fig. 8. SEM micrographs of used catalyst BP2000 tested in the propane decomposition tests at 850 °C.

Samples obtained after propane decomposition at 850 °C for 2 h also present filamentous structures covering the BP2000 surface (Fig. 8). However, in this case the filaments are thicker (100–200 nm), which allow the resolution of these structures by means of SEM. Again, the filaments appear to be composed of spherical aggregates that are joined together to form long filaments.

### 3.4. Simulated natural gas decomposition

The presence of ethane and propane on the catalytic decomposition of methane was investigated at 900 °C. The composition of the components of the simulated natural gas (SNG) was fixed at 85% methane, 10% ethane and 5% propane. Tests were performed using binary mixtures of methane–ethane and methane–propane ( $N_2$  balanced) and ternary mixtures of methane–ethane–propane (SNG). A stream composed only of methane (85%,  $N_2$  balanced) was also studied in order to compare the effect of the presence of ethane and propane.

Fig. 9 shows the changes in the hydrogen concentration in the test carried out at 900 °C using different hydrocarbon mixtures. It is worth noting that in all cases, the only reaction products detected were hydrogen and methane. From this observation it is clear that ethane and propane are completely decomposed at 900 °C when they are fed with methane in the typical natural gas concentrations.

The hydrogen concentration curves fell slightly after 30 min at which point a quasi-steady state was reached. When the feed stream was only methane, BP2000 catalyst provides a constant  $H_2$  concentration around 25%. The decomposition of methane–propane mixtures slightly increases the hydrogen concentration at the quasi-steady state, reaching 32%. When binary

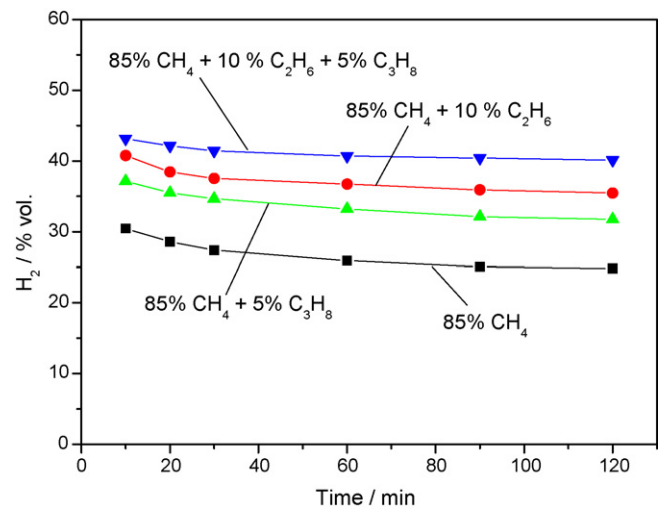


Fig. 9. Effect of ethane and propane on hydrogen yield from methane decomposition over BP2000 at 900 °C.

mixtures of ethane and methane are fed to the reactor, a  $H_2$  concentration of 35% was achieved. The best results were accomplished when the feed gas consists of SNG, given that the hydrogen concentration reached a value of 40%.

Thus, it can be concluded that the presence of ethane and/or propane in the CDM using the BP2000 catalyst has a promoting effect, given that hydrogen concentration in the outlet gases increased, mainly due to the higher  $H_2$  content in those hydrocarbons. Additionally, it is important to note that BP2000 promotes a relative steady state hydrogen concentration for all hydrocarbon mixtures studied, implying that the carbon deposited from ethane and propane decomposition do not provoke catalyst deactivation.

### 3.5. Effect of the $H_2S$ in the CDM

Fig. 10 shows the effect of  $H_2S$  in a methane decomposition test carried out at 900 °C over the BP2000 catalyst. In a first stage, methane decomposition was carried out until the hydrogen concentration reached approximately 36% and the rate of decline in  $H_2$  production had slowed to less than  $5\% h^{-1}$ . Then, a methane stream with 1%  $H_2S$  was introduced to the reactor, showing an increase in the hydrogen concentration, from 36 to 45%. Theoretical calcula-

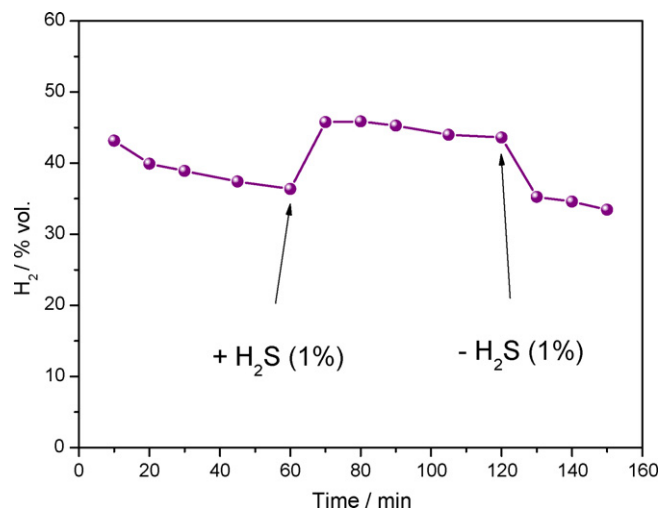


Fig. 10. Effect of  $H_2S$  on hydrogen yield from methane decomposition over BP2000 at 900 °C [ $H_2S$ ]: 1%.

tion revealed that, even supposing that the H<sub>2</sub>S fed was completely decomposed into its elements, H<sub>2</sub> and S, the increase in H<sub>2</sub> concentration would only be about 1%. Thus, it is clear that the presence of H<sub>2</sub>S has a catalytic effect on the methane decomposition rate. This effect has been previously reported by Muradov [38] who explained this effect by the formation of HS• radicals, which are capable of attacking methane molecules, resulting in the formation of hydrogen and carbon as a final state. Additionally, this effect is reversible, provided that after the removal of H<sub>2</sub>S from the gas feed, H<sub>2</sub> concentration reaches the quasi-steady state value measured prior to the H<sub>2</sub>S addition.

This behaviour of carbonaceous catalyst in the presence of H<sub>2</sub>S could be advantageously used given that metal catalysts suffer from severe deactivation in the presence of sulphur compounds [39]. Thus, in the case of carbonaceous catalysts, an exhaustive desulphurization of the natural gas fed to the CDNG reactor would not be needed.

#### 4. Conclusions

The decomposition of undiluted ethane and propane, at temperature higher than 850 °C using a commercial carbon black as catalyst, BP2000, produced an enriched hydrogen stream of at least 40 vol.%. Hydrocarbon conversion and hydrogen selectivity increased with increasing operating temperature. Carbon was deposited as filaments formed by spherical aggregates with diameters on the order of nanometres.

The presence of ethane and propane in the methane decomposition increased the hydrogen concentration in the outlet gases. It was concluded that the BP2000 catalyst is capable of decomposing simulated natural gas without suffering from deactivation. Additionally, the presence of H<sub>2</sub>S in the stream has a positive catalytic effect on methane decomposition over BP2000, which is reversible when H<sub>2</sub>S is eliminated from the stream.

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#### References

- [1] D. Hart, P. Freud, A. Smith, *Hydrogen Today and Tomorrow*, IEA GHG Programme, April 1999, ISBN: 1 898373248.

- [2] CO<sub>2</sub> Abatement by the Use of Carbon-rejection Processes, IEA GHG Report PH3/36, February 2001.
- [3] M. Steinberg, *Int. J. Hydrogen Energy* 23 (1998) 419–425.
- [4] N.Z. Muradov, T.N. Veziroglu, *J. Hydrogen Energy* 30 (2005) 225–237.
- [5] N.Z. Muradov, *Int. J. Hydrogen Energy* 26 (2001) 1165–1175.
- [6] N. Muradov, *Catal. Commun.* 2 (2001) 89–94.
- [7] M.H. Kim, E.K. Lee, J.H. Jun, G.Y. Han, S.J. Kong, B.K. Lee, T.-J. Lee, K.J. Yoon, *Korean J. Chem. Eng.* 20 (2003) 835–839.
- [8] M.H. Kim, E.K. Lee, J.H. Jun, S.J. Kong, G.Y. Han, T.J. Lee, K.J. Yoon, *Int. J. Hydrogen Energy* 29 (2004) 89–93.
- [9] R. Moliner, I. Suelves, M.J. Lázaro, O. Moreno, *Int. J. Hydrogen Energy* 30 (2005) 293–300.
- [10] Z. Bai, H. Chen, B. Li, W.J. Li, *Anal. Pyrol.* 73 (2005) 332–341.
- [11] J. Ashok, S. Naveen Kumar, A. Venugopal, V. Durga Kumari, S. Tripathi, M. Subrahmanyam, *Catal. Commun.* 9 (2007) 164–169.
- [12] E.K. Lee, S.Y. Lee, G.Y. Han, B.K. Lee, T.J. Lee, J.H. Jun, K.J. Yoon, *Carbon* 42 (2004) 2641–2648.
- [13] B.H. Ryu, S.Y. Lee, D.H. Lee, G.Y. Han, T.-J. Lee, K.J. Yoon, *Catal. Today* 123 (2007) 303–309.
- [14] I. Suelves, M.J. Lázaro, R. Moliner, J.L. Pinilla, H. Cubero, *Int. J. Hydrogen Energy* 32 (2007) 3320–3326.
- [15] N. Muradov, F. Smith, A. T-Raissi, *Catal. Today* 102–103 (2005) 225–233.
- [16] J.L. Pinilla, I. Suelves, M.J. Lázaro, R. Moliner, *Chem. Eng. J.* 138 (2008) 301–306.
- [17] I. Suelves, J.L. Pinilla, M.J. Lázaro, R. Moliner, *Chem. Eng. J.* 140 (2008) 432–438.
- [18] Z. Bai, H. Chen, W. Li, B. Li, *Int. J. Hydrogen Energy* 31 (2006) 899–905.
- [20] N. Muradov, Z. Chen, F. Smith, *Int. J. Hydrogen Energy* 30 (2005) 1149–1158.
- [21] J.L. Pinilla, I. Suelves, R. Utrilla, M.E. Gálvez, M.J. Lázaro, R. Moliner, *J. Power Sources* 169 (2007) 103–109.
- [22] K.K. Lee, G.Y. Han, K.J. Yoon, B.K. Lee, *Catal. Today* 93–95 (2004) 81–86.
- [23] A.M. Dunker, S. Kumar, P. Mulawa, *Int. J. Hydrogen Energy* 31 (2006) 473–484.
- [24] M.J. Lázaro, J.L. Pinilla, I. Suelves, R. Moliner, *Int. J. Hydrogen Energy* 33 (2008) 4104–4111.
- [25] S.Y. Lee, J.H. Kwak, G.Y. Han, T.J. Lee, K.J. Yoon, *Carbon* 46 (2008) 342–348.
- [26] N. Shah, Y. Wang, D. Panjala, G.P. Huffman, *Energy Fuels* 18 (2004) 727–735.
- [27] Y. Wang, N. Shah, G.P. Huffman, *Catal. Today* 99 (2005) 359–364.
- [28] N.M. Rodríguez, M.S. Kim, F. Fortin, I. Mochida, R.T.K. Baker, *Appl. Catal. A: Gen.* 148 (1997) 265–282.
- [29] C. Park, M.A. Keane, *J. Catal.* 221 (2004) 386–399.
- [30] K. Otsuka, Y. Shigeta, S. Takenaka, *Int. J. Hydrogen Energy* 27 (2002) 11–18.
- [31] S.Y. Chin, Y.-H. Chin, M.D. Amiridis, *Appl. Catal. A: Gen.* 300 (2006) 8–12.
- [32] W. Shen, Y. Wang, X. Shi, N. Shah, F. Huggins, S. Bollineni, M. Seehra, G.P. Huffman, *Energy Fuels* 21 (2007) 3520–3529.
- [33] K. Otsuka, S. Kobayashi, S. Takenaka, *Appl. Catal. A: Gen.* 210 (2001) 371–379.
- [34] N. Muradov, *J. Power Sources* 118 (2003) 320–324.
- [35] J.-H. Lin, C.-S. Chen, H.-L. Ma, C.-W. Chang, C.-Y. Hsua, H.-W. Chen, *Carbon* 46 (2008) 1619–1623.
- [36] B. Fidalgo, Y. Fernandez, L. Zubizarreta, A. Arenillas, A. Domínguez, J.J. Pis, J.A. Menéndez, *Appl. Surf. Sci.* 254 (2008) 3553–3557.
- [37] Y. Fernández, B. Fidalgo, A. Domínguez, A. Arenillas, J.A. Menéndez, *Carbon* 45 (2007) 1706–1709.
- [38] N. Muradov, *Proceedings of the 2002 U.S. DOE Hydrogen Program Review NREL/CP-610-32405*, 2002.
- [39] J. Sehested, *Catal. Today* 111 (2006) 103–110.