

# Hydrogen production by thermo-catalytic decomposition of methane: Regeneration of active carbons using CO<sub>2</sub><sup>☆</sup>

J.L. Pinilla, I. Suelves, R. Utrilla, M.E. Gálvez, M.J. Lázaro\*, R. Moliner

*Instituto de Carboquímica CSIC, Miguel Luesma Castán 4, 50015-Zaragoza, Spain*

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## Abstract

Thermo-catalytic decomposition of methane using carbons as catalyst is a very attractive process for free CO<sub>2</sub>–hydrogen production. One of the main drawbacks for the sustainability of the process is catalyst deactivation. In this work, regeneration of a deactivated active-carbon catalyst has been studied using CO<sub>2</sub> as activating agent under different regeneration conditions. It has been stated that during the regeneration stage, a compromise between the regeneration of the initial properties of the catalyst and the burn-off is needed in order to keep the sustainability of the process. Three deactivation–regeneration cycles have been performed for two sets of regeneration conditions. A progressive decreasing in the burn-off, surface area and surface oxygenated groups after each decomposition/regeneration cycle is observed. It can be explained considering that the carbon removed during the regeneration steps is not the carbon deposited from methane but the remaining initial catalyst, which is less resistant to gasification. The implication is that after three cycles of decomposition/regeneration, most of the carbon sample consists of carbon formed during the process since the initial catalyst has been gasified.

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## 1. Introduction

Emissions of carbon dioxide (CO<sub>2</sub>), the main greenhouse gas (GHG) from human activities, are the subject of a worldwide debate about energy sustainability and the stability of global climate [1]. Conventional hydrogen production processes from natural gas (e.g., steam methane reforming) produce large amount of CO<sub>2</sub> emissions. One alternative to conventional processes is single-step thermo-catalytic decomposition (TCD) of natural gas (NG) into hydrogen and carbon [2–5]. Due to the absence of oxidants (e.g., H<sub>2</sub>O and/or O<sub>2</sub>), no carbon oxides are formed during the process, thus obviating the need for water gas shift and CO<sub>2</sub> removal stages, which significantly simplifies the process. In addition, pure carbon, instead of carbon dioxide, is produced [6].

Two different nature catalysts have been used for this process: metallic and carbonaceous catalysts [7–10]. Carbon catalysts

have been proposed as an alternative to metallic ones [11–15] because they offer several advantages: (i) higher fuel flexibility and no sulphur poisoning; (ii) lower price; (iii) the carbon formed can be used as catalyst precursor, so that, the process is self-consistent. However, one of the main drawbacks for the use of these materials is catalyst deactivation mainly as a consequence of: (i) the reduction in catalyst surface area due to carbon deposition and (ii) the lack of catalytic activity of the carbon crystallites formed from methane decomposition.

Muradov et al. [14] have reported that the catalytic activity of deactivated carbon samples can be re-established by treatment with activating agents at elevated temperature. It was demonstrated that the treatment of carbon particles with steam resulted in the increase in surface area and simultaneously in the increase in methane decomposition rate. Authors suggest that at industrial scale, the activation of carbon particles with activating agents could be accomplished in an external reactor where the carbon particles are heated and then recycled into the TCD reactor as energy carrier for the endothermic decomposition reaction.

It is well known that generation of surface area by activation of a carbonaceous material proceeds removing carbon atoms

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\* Corresponding author. Tel.: +34 976733977; fax: +34 976733318.

E-mail address: [mlazaro@icb.csic.es](mailto:mlazaro@icb.csic.es) (M.J. Lázaro).

from the surface. The ratio of mass removed is known as burn-off. Consistently, to assure the sustainability of the process, it should be stated that the burn-off during the regeneration stage (the carbon mass removed from a deactivated carbon particle) is lower than the ratio of carbon deposited during the subsequent methane decomposition stage. In other words, removing of a given quantity of carbon mass from a carbon particle would enable the particle to accommodate a higher quantity of mass carbon in the subsequent decomposition cycle. A mechanism of how that would occur has not been proposed yet.

It has been stated [17] that during activation of carbonaceous materials, a great number of oxygenated surface groups are generated simultaneously to surface area generation. Moliner et al. [15] have shown that the concentration of these groups has a great influence on the methane decomposition rate. The mechanism of actuation of these groups has not been yet elucidated. According to Muradov, it is conceivable that active radicals can be generated from these oxygenated groups. These radicals are capable of attacking methane molecules at high temperatures with the formation of methyl radicals which initiate the chain of consecutive reactions leading to production of carbon via the formation of olefins and aromatics as intermediate reaction products. As formation of active radical can proceed without removing of carbon atoms from the surface, this reaction provides a mechanism to re-establish the catalytic activity of the carbon particles that, in contrast to the mechanism of surface regeneration, does not require removing of the deposited carbon.

The objective of this work is to study the evolution of carbon catalyst during successive cycles of TCD of methane and regeneration of the deactivated carbon particles, using  $\text{CO}_2$  as activating agent. This reactant has been selected to simulate the effect of the flue gas obtained from partial combustion of the recycled carbon particles in the heater of an industrial installation. The results will be used to evaluate the sustainability of the process. In a previous work [18], different kinds of activated carbons (AC) and carbon blacks (CB) were studied as catalyst for TCD of methane. Among them, a commercial activated carbon (CG NORIT) has been selected for the decomposition/regeneration cyclic tests presented here. The optimum operation conditions for catalysts regeneration have been evaluated considering both, the regeneration of surface area and oxygenated surface groups which are essential to reactivate the catalysts and the burn-off of the carbon sample, which is essential for the sustainability of the process.

## 2. Experimental

### 2.1. TCD runs

TCD runs were carried out in a fixed-bed quartz reactor, 20 mm i.d., 600 mm height, using pure  $\text{CH}_4$  as feeding gas. A constant flow of methane of  $20 \text{ ml(STP) min}^{-1}$  was used. A commercial active carbon, CG Norit previously studied [15], was used as catalyst. Samples of 4 g of catalysts were used, corresponding to a space-time for methane of 30 s. The exper-

iments were conducted at  $850^\circ\text{C}$ . The commercial CG Norit releases tar and water during the first stage of the runs. In order to stabilize the catalysts, they were pre-treated under nitrogen at the reaction temperature during 5 h before the reaction tests.

The analysis of the gas stream from the reactor was carried out by sampling with gas sampling bags. The first bag was usually taken some minutes after the  $\text{CH}_4$  was flowed, when the nitrogen initially present in the reaction system was flushed out. The gas samples were analysed by gas chromatography: two packed columns, molecular sieve  $13\times$  and Porapak and a TCD detector were used. Helium was used as carrier for methane analysis while nitrogen was used for hydrogen analysis. In all cases, no methane decomposition products other than hydrogen were detected. The weight of deposited carbon and the volume of gas produced corresponded, within the experimental error ( $\sim 5\%$ ), to that expected from the stoichiometry of the decomposition reaction.

### 2.2. Regeneration runs

Regeneration runs were carried out in a bench scale-fluidized bed reactor. The reactor was made of Kanthal, with 20 mm i.d. and 660 mm height. Kanthal is a steel alloy treated to form an aluminium oxide layer, very stable at high temperatures, that prevents methane from contact with steel components during the reaction. The following conditions were used: (i) activating agent:  $\text{CO}_2$ ; (ii) regeneration temperature: 700, 800, 900, 925 and  $950^\circ\text{C}$ ; (iii) solid residence time: 2 and 4 h.

The minimum fluidization velocity for the CG Norit in the fluidized bed was determined by the method proposed by Wen and You [19] using as constants those proposed by Adánez and Abadanes [20] for carbonaceous materials. The gas velocity used in the regeneration tests was two-fold the minimum fluidization velocity.

### 2.3. Carbon characterization techniques

The textural properties of the fresh and used samples were measured by  $\text{N}_2$  adsorption at 77 K in a Micromeritics ASAP2000 apparatus. The specific surface areas and pore volume were calculated applying the BET method to the  $\text{N}_2$  adsorption isotherms.

The concentration of oxygenated surface groups was evaluated from CO and  $\text{CO}_2$  released during temperature-programmed desorption (TPD) tests. TPD tests were carried out in a fixed bed reactor heated under a constant flow of He at a heating rate of  $10^\circ\text{C min}^{-1}$  up to a temperature of  $1050^\circ\text{C}$ . The eluted gas was collected in separated gas sampling bags corresponding to consecutive temperature ranges of  $100^\circ\text{C}$  and analysed by gas chromatography. The total amount of CO and  $\text{CO}_2$  released was calculated by integrating the area under of the concentration curve versus volume.

Powder X-ray diffraction (XRD) patterns for the study of the crystalline chemical species in the fresh and used catalyst have been also carried out using a Bruker AXS D8 Advance apparatus.

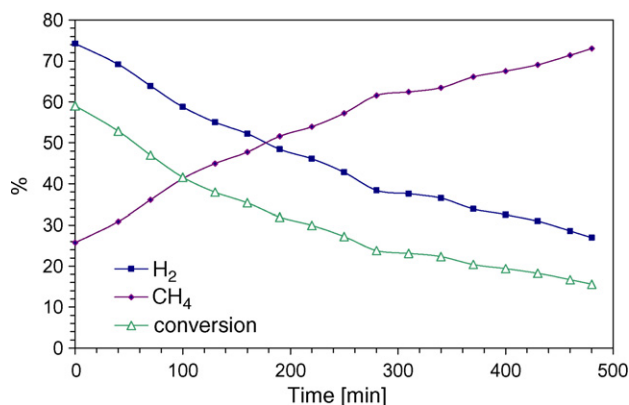


Fig. 1. Gases concentration (vol%) and methane conversion (%) at  $T=850\text{ }^{\circ}\text{C}$ .

Temperature-programmed oxidation (TPO) profiles of the fresh and used carbon catalysts were obtained in a Cahn TG 151 Thermogravimetric Analyzer.

### 3. Results and discussion

#### 3.1. Catalyst deactivation

Fig. 1 shows the evolution of hydrogen and methane concentration at the exit of the reactor and the corresponding methane conversion at  $850\text{ }^{\circ}\text{C}$ . It can be observed a high initial  $\text{H}_2$  production, close to 75%, which corresponds to a methane conversion of 60%, followed by a progressive declining in the  $\text{H}_2$  production until a quasi-steady state. After 8 h on stream,  $\text{H}_2$  concentration is below 30% and methane conversion drops to 15%. A quantity of  $450\text{ mgC g catalyst}^{-1}$  was deposited.

Table 1 shows the specific surface area and the amount of oxygenated surface groups desorbed as CO and  $\text{CO}_2$  during TPD experiments, for both the fresh catalyst and the deactivated catalyst after 8 h on stream at  $850\text{ }^{\circ}\text{C}$ .

CG Norit is a commercial active carbon with high surface area,  $1300\text{ m}^2\text{ g}^{-1}$  in which mesoporosity accounts for about 80%. Comparing the data in Table 1, it is observed that specific areas as well as the amount of oxygenated groups have been drastically reduced during the TCD run. Both parameters play a major role in the behaviour of the carbon catalysts in the TCD of methane. In a previous work [15], we reported that the amount of oxygenated surface groups is related to initial reaction rate and that the specific surface area is related to the capacity of accumulate carbon, which defines the long-term behaviour of the catalyst. Loss in surface area is due to the carbon deposition over catalysts pores, blocking active sites and lowering methane conversion.

Table 1

Textural properties and surface chemistry of the CG Norit catalyst: fresh and deactivated at  $850\text{ }^{\circ}\text{C}$  during 8 h

	$S_{\text{N}_2}$ ( $\text{m}^2\text{ g}^{-1}$ )	$S_{\text{Mesopore}}$ ( $\text{m}^2\text{ g}^{-1}$ )	$S_{\text{Micropore}}$ ( $\text{m}^2\text{ g}^{-1}$ )	CO ( $\text{cm}^3\text{ g}^{-1}$ )	$\text{CO}_2$ ( $\text{cm}^3\text{ g}^{-1}$ )	CO + $\text{CO}_2$ ( $\text{cm}^3\text{ g}^{-1}$ )
CG Norit fresh	1300	1011	289	25.76	3.58	29.34
CG Norit deactivated	52.3	48.5	3.8	7.84	1.34	9.18

Table 2

Burn-off degree (BOD), surface chemistry and textural properties after the regeneration tests

Temperature ( $^{\circ}\text{C}$ )	Time (h)	Burn-off degree (%)	$S_{\text{N}_2}$ ( $\text{m}^2\text{ g}^{-1}$ )	CO + $\text{CO}_2$ ( $\text{cm}^3\text{ g}^{-1}$ )
Fresh catalyst	–	0	1300	29.34
900	2	13.3	303.6	15.45
900	4	41	606.4	25.31
925	2	79.4	1287	21.05
925	4	157.1	1860	36.73
950	2	126.6	1620	28.45
950	4	239.1	2584	–

#### 3.2. Catalyst regeneration tests

The study of regeneration of the catalyst has been carried out using the deactivated catalyst samples described in the previous section. The following parameters have been studied: (i) regeneration of specific surface area, (ii) amount of surface oxygenated groups created, and (iii) weight loss or burn-off degree (BOD) of the catalyst. BOD is here expressed as the ratio between the amount of carbon loss during a regeneration test and the amount of carbon deposited during the previous 8 h TCD test (that is,  $450\text{ mgC g cat}^{-1}$ ). The regeneration conditions must allow regenerating the initial textural parameters (both oxygenated surface groups and surface area recovery) keeping BOD as low as possible. In order to achieve a net increasing of deposited carbon during deactivation–regeneration cycles, which is essential for the sustainability of the process, the initial parameters of the catalyst has to be re-established for a BOD lower than 100%. Otherwise, to regenerate the initial parameters of the catalyst, it would be necessary to eliminate (via gasification) all the carbon deposited during the decomposition stage. This would make the regeneration of the catalyst not feasible since the carbon from methane would be eventually released as  $\text{CO}_2$  which is, of course, not desirable.

Table 2 shows the textural parameters for CG Norit regenerated at temperatures of 900, 925 and  $950\text{ }^{\circ}\text{C}$  and residence time of 2 and 4 h: BOD, specific surface area and amount of oxygenated groups desorbed as CO and  $\text{CO}_2$ . It is noteworthy to say that no weight loss was observed in the regeneration tests carried out at temperatures lower than  $900\text{ }^{\circ}\text{C}$ .

It is observed that the specific surface area and the amount of oxygenated groups increase as the regeneration conditions become more severe. Fig. 2 depicts the BET area of the regenerated samples versus BOD, i.e., the ratio of the carbon mass deposited that has to be released to regenerate a determined sur-

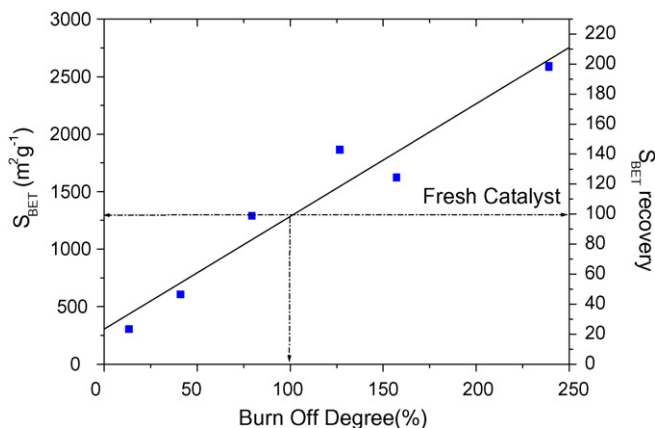


Fig. 2. Regenerated surface area vs. burn-off degree (BOD).

face area. It can be observed that there is a linear relationship between both parameters. The initial surface area of the fresh catalyst can be re-established after  $\text{CO}_2$  activation at  $925^\circ\text{C}$  during 2 h. Surface area values even higher than the initial one can be generated when activation is performed under more severe conditions. However, BOD higher than 100% was measured in all these cases. That means in practice that the new surface area is been generated by additional activation of the initial active carbon sample.

Fig. 3 shows the relationship between the amount of oxygenated superficial groups and BOD. A linear relationship between both parameters is observed. As observed for BET area, regeneration of the initial contents of oxygenated superficial groups in the fresh catalyst requires a BOD close to 100%. Results from Figs. 2 and 3 show that regeneration of the initial surface properties of the deactivated catalyst requires removing almost all the carbon deposited during the decomposition step.

### 3.3. Methane decomposition–catalyst regeneration cycles

In order to study the sustainability of the process, cycles consisting in series of carbon catalyst deactivation by methane decomposition and catalyst regeneration with  $\text{CO}_2$  have been

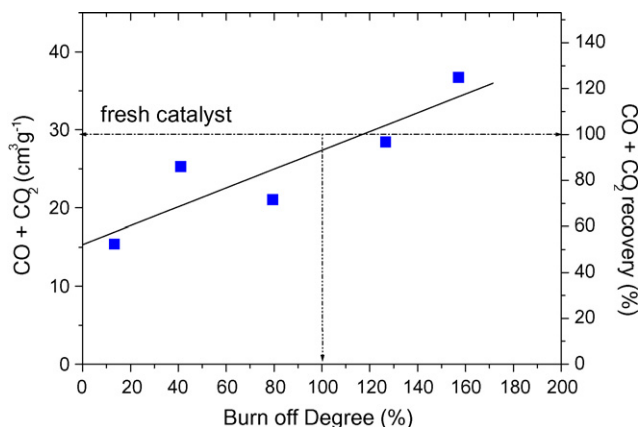


Fig. 3. Regenerated oxygenated groups vs. burn-off degree (BOD).

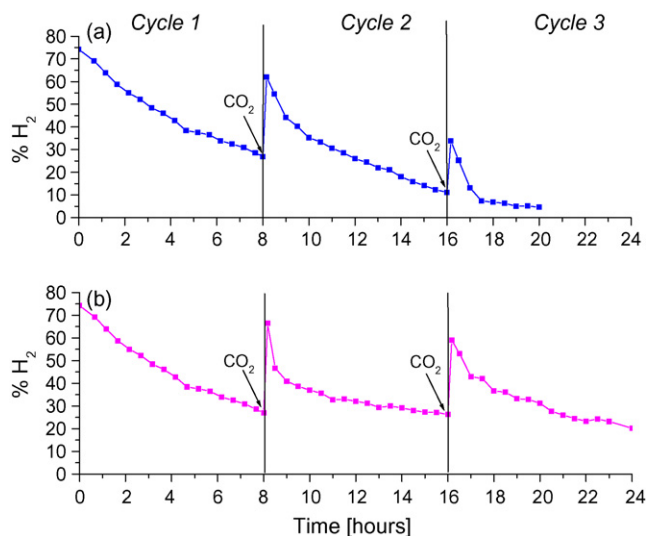


Fig. 4. Hydrogen production after regeneration cycles: (a)  $900^\circ\text{C}$ -4 h and (b)  $925^\circ\text{C}$ -2 h.

performed. As explained before, the regeneration conditions have to be selected among those that proceed with a BOD lower than 100%. The conditions selected were  $900^\circ\text{C}$ -4 h and  $925^\circ\text{C}$ -2 h. In the first case, the recovery of BET area is 50% and the burn-off is about 41% and in the second case, the recovery of BET area is almost complete and the burn-off is about 80% of the carbon. For both conditions, the recovery in the surface oxygenated groups is over 70%.

Fig. 4a shows the hydrogen production with the CG Norit after three successive regeneration cycles at  $900^\circ\text{C}$  and 4 h. It can be observed that the first cycle begins with an initial hydrogen production of 75% which progressively decreases with time on the stream, reaching a 30% hydrogen production after 8 h of reaction. For the second cycle, the initial activity is lower, about 60% and the same pattern is observed, with a progressive decreasing in the  $\text{H}_2$  yield, until a production lower than in the first cycle is reached (about 10%). In the third cycle, a different behaviour pattern is observed. Again the initial activity is significantly lower than in the previous cycles, about 30%, but in this case, the activity dramatically drops after 2 h on stream, reaching values lower than 5%. From these results, it can be concluded that regeneration of the CG Norit with  $\text{CO}_2$  is not sustainable at  $900^\circ\text{C}$  and 4 h.

Fig. 4b shows the TCD–regeneration cycles of CG Norit when the regeneration step is carried out under more severe conditions at  $925^\circ\text{C}$  during 2 h. It is observed that the second and third cycle yield similar results. Both cycles begin with  $\text{H}_2$  values lower than in the first cycle, about 60–65%, followed by a rapid decrease in the  $\text{H}_2$  production until a quasi-steady state is reached, with values of 20–30% after 5 h of reaction, close to those obtain for the first cycle.

It could be concluded from Fig. 4a and b that the activity of the CG Norit is almost completely recovered after three successive  $850^\circ\text{C}$ -8 h deactivation– $925^\circ\text{C}$ -2 h regeneration cycles. However, a more detailed study of the initial conversion rate after each deactivation stage, determined from

Table 3  
Initial activity rate and accumulated carbon after each deactivation tests

Regeneration conditions	Deactivation cycle	$r_o$ (mmol (min g) <sup>-1</sup> )	Accumulated carbon (mg g cat <sup>-1</sup> )-8 h run
900 °C-4 h	D1	0.2	450
	D2	0.15	268
	D3	0.07	53
925 °C-2 h	D1	0.2	450
	D2	0.17	340
	D3	0.14	327

the kinetics curves (not shown) by the method used previously by Moliner et al. [15] and Kim et al. [16] is shown in Table 3. It can be observed that the initial methane decomposition rate decreases after each regeneration step. Furthermore, the carbon accumulated after each decomposition step decreased. The same trend is observed in both set of regeneration conditions but decreasing is slower under the more severe regenerating conditions.

Table 4 shows the evolution in the textural parameters and BOD after each regeneration step. For both set of conditions, it is observed that BOD as well as surface area and surface oxygenated groups decrease progressively after each cycle. For 900 °C-4 h, it is observed that the surface area measured after second and third regeneration stage (179 and 127 m<sup>2</sup> g<sup>-1</sup>, respectively) is very far from the initial surface area value. In the third regeneration step, BOD drops to zero, i.e., the catalyst cannot be reactivated. That explains the behaviour of the catalysts during the third cycle, in which the activity drops dramatically. For 925 °C-2 h, a similar trend is observed but decreasing of surface area and functional groups is slower so that the surface area is 441 m<sup>2</sup> g<sup>-1</sup> after the third regeneration stage.

Fig. 5 shows the initial conversion rate and the carbon accumulated as a function of the BET surface area of the catalyst after each deactivation–regeneration cycle. It is observed that BET area does not correlate with the initial conversion rates since samples with very different surface area exhibits similar initial conversion rate. In contrast, a good correlation exists for BET area and the accumulated carbon, so that, the lower the surface area after the regeneration stage, the lower the amount of carbon accumulated in the subsequent decomposition stage. Fig. 6 shows the initial conversion rate of the catalysts after each deactivation–regeneration cycle as a function of the concentration of oxygenated groups.

Table 4  
Textural properties, surface chemistry and burn-off degree after each regeneration stage

Regeneration conditions	Cycle	Burn-off degree (BOD) (%)	$S_{N_2}$ (m <sup>2</sup> g <sup>-1</sup> )	CO + CO <sub>2</sub> (cm <sup>3</sup> g <sup>-1</sup> )
Fresh catalyst	–	–	1300	29.34
900 °C-4 h	R1	41	606	25.31
	R2	6.6	179	12.09
	R3	0	127	7.61
925 °C-2 h	R1	79	1287	21.05
	R2	46	927	17.92
	R3	20	441	11.2

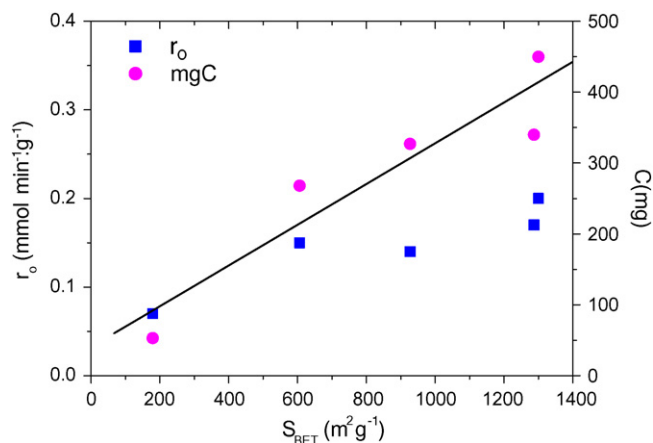


Fig. 5. Initial activity for methane conversion and carbon accumulated as a function of the BET area of the catalysts after deactivation steps.

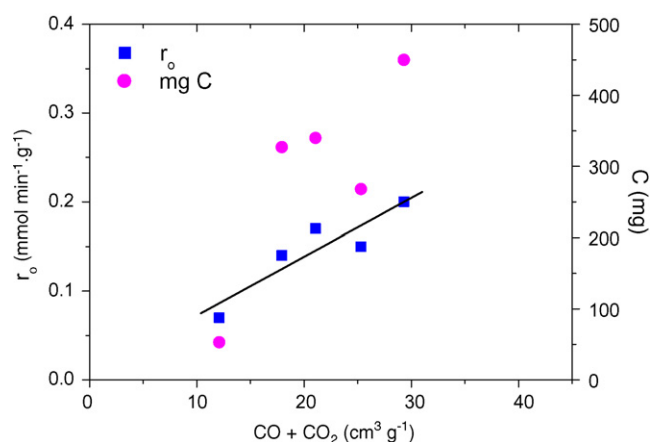


Fig. 6. Initial activity for methane conversion and carbon accumulated as a function of the concentration of oxygenated groups of the catalysts after deactivation steps.

tion of the concentration of oxygenated groups. It can be seen that a good correlation exists between both of them. These results confirm our previous finding, observed for fresh catalyst [15], that the surface area is related to the long-term activity whereas the initial activity is related to the content of oxygenated groups.

The progressive decreasing in BOD, surface area and surface oxygenated groups after each decomposition/regeneration cycle can be explained considering that the carbon removed during the

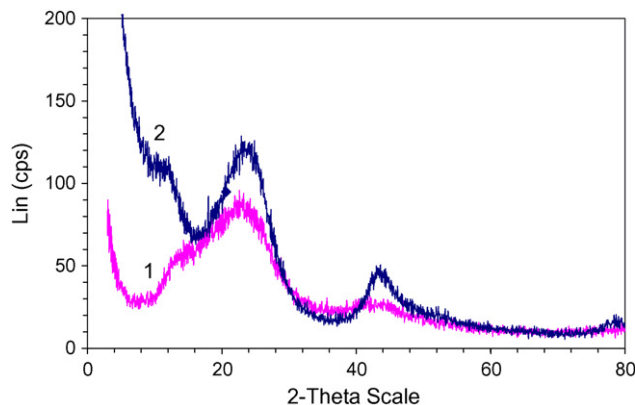


Fig. 7. XRD spectra of CG Norit samples: (1) CG Norit fresh and (2) CG Norit deactivated after exposure to methane at 850 °C for 8 h.

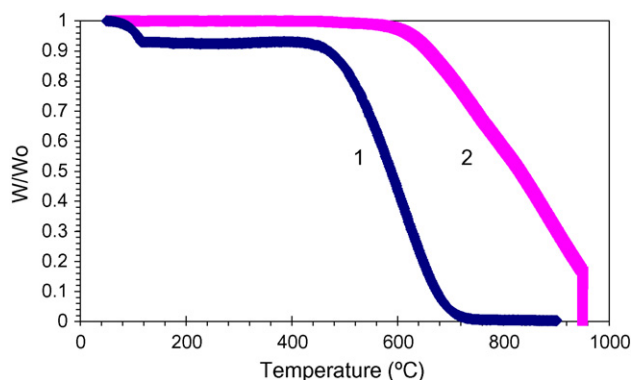


Fig. 8. TPO profiles of CG Norit samples: (1) CG Norit fresh and (2) CG Norit deactivated after exposure to methane at 850 °C for 8 h.

regeneration steps is not the carbon deposited from methane but the remaining initial active carbon, which weight decreases after each regeneration step and becomes less and less accessible. This may be due to the graphite-like structure of the carbon deposited, which is more resistant to gasification. Fig. 7 shows the XRD profiles of the fresh and deactivated catalyst. It can be seen that the carbon catalyst deactivated at 850 °C have more ordered (graphite-like) structure in comparison to fresh catalyst. Fig. 8 shows the temperature-programmed oxidation experiments carried out over fresh and used carbon catalyst. It is observed that carbon deposited from methane is more resistance to oxidation that the fresh catalysts. TPO profiles showed that the oxidation over the fresh catalyst began at 400 °C. For the used catalysts, this temperature is higher, around 600 °C. The slopes of the TPO profiles also revealed that the rate of oxidation is higher for the fresh catalyst.

With this assumption, a mass balance after three-cycle deactivation–regeneration at 925 °C–2 h indicates that carbon deposited represents more than 90% of the carbon sample. The implication in practice is that after three cycles of decomposition/regeneration, most of the carbon sample consists of carbon formed during the process since the initial catalyst has been gasified. Consistently, in the steady state of the process, the regeneration conditions should be chosen according to the prop-

erties of the deposited carbon and not to the ones of the initial catalyst.

#### 4. Conclusions

The specific surface area and the oxygenated surface groups regenerated by CO<sub>2</sub> activation of a deactivated AC catalyst present a positive linear relationship with the burn-off degree. Results obtained show that regeneration of the initial surface properties of the deactivated catalyst requires removing almost of the carbon deposited during the decomposition step. A good compromise between catalyst regeneration and burn-off is obtained by activation at 925 °C and 2 h solid residence time. However, a progressive decrease in textural parameters was observed during successive deactivation–regeneration cycle. This may be explained by the graphite-like structure of the carbon deposited, which is more resistance to gasification, so that, weight loss during regeneration step would come from the remaining CG Norit. After three cycles of decomposition/regeneration, most of the carbon sample consists of carbon formed during the process since the initial catalyst has been gasified. Consistently, in the steady state of the process, the regeneration conditions should be chosen according to the properties of the deposited carbon and not to the ones of the initial catalyst. More efforts should be devoted in order to study if the deposited carbon presents a “historic effect”, i.e., if its properties depend on the initial carbon catalyst used and the regeneration method used.

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