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Kinetic study of the thermal decomposition of methane using carbonaceous catalysts

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Abstract

Thermo-catalytic decomposition of methane over different carbonaceous materials has been studied using a thermobalance by monitoring the mass gain (the amount of carbon deposited) with time. A kinetic study has been carried out using one carbon black, BP2000, and an activated carbon, CG Norit, to compare the behaviour of two carbon samples of different origin/nature as catalysts for this process. The reaction order of the carbon growth over CG Norit and BP2000 catalysts may be practically said to be 0.5. The activation energies over these catalysts were 141 and 238 kJ/mol, respectively. Methane decomposition reaction over carbon catalysts seems to be controlled by two simultaneous processes: first, decrease in methane decomposition rate due to the blocking of catalytic active sites by the carbon species deposited, and secondly, an increase in methane decomposition rate due to the formation of catalytically active carbon species produced from methane.

Keywords: Hydrogen production; Methane decarbonization; Carbon catalysts; Kinetic study

1. Introduction

Nowadays, among the different technologies used for large scale hydrogen production, steam reforming of natural gas, SMR, is the most widely used. However, SMR produces large amount of CO_2 emissions. One alternative to this process is single-step thermo-catalytic decomposition (TCD) of natural gas (NG) into hydrogen and carbon [1–4]. Due to the absence of oxidants (e.g., H_2O and/or O_2), no carbon oxides are formed during the reaction, thus obviating the need for water gas shift and CO_2 removal stages, which significantly simplifies the process. In addition, pure carbon that could have an added value, instead of carbon dioxide, is produced [5].

The TCD reaction can be written as follows:

$$CH_4 \rightarrow 2H_2 + C(s), \Delta H = 75.6\,\text{kJ/mol}$$

Methane decomposition is a moderately endothermic reaction: the thermal energy requirement per mol of hydrogen produced is only 37.8 kJ/mol H_2 compared to 69 kJ/mol H_2 for SMR [6].

Thermal decomposition of methane (as main component of NG) occurs at elevated temperatures, above 1200 °C, thus the use of catalysts allows reducing the temperature of the process and increasing the process kinetics. Many references can be found in the literature related to the methane decomposition using metal catalysts [7–13]. More recently, carbon catalysts have been proposed as an alternative to metallic ones [14–17] for this process 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-sustained.

Thermo-catalytic decomposition of methane using carbonaceous catalysts has been extensively studied by our research group using a bench scale fixed bed reactor. In a first approach [17], activated carbons with different textural properties and surface chemistry were used to study the influence of these properties on the efficiency of methane decomposition. The results obtained indicated that the activated carbons tested show an acceptable initial reaction rate but they become rapidly deactivated. The surface chemistry and the pore size distribution played an important role on the initial conversion rate of methane and the long-term sustainability of the catalyst, respectively. Microporous carbons with high content of oxygenated surface groups exhibited high initial conversion rates but they become rapidly deactivated. Mesoporous carbons with high surface area

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provided more stable and sustainable hydrogen production. In a second stage [18], different carbonaceous samples, carbon blacks, showing an external surface area, open and easily accessible to methane molecules were studied as a possible way of delaying the rapid deactivation observed for the activated carbons. In fact, catalyst deactivation is one of the main drawbacks for the use of carbonaceous materials as catalysts for hydrogen production by TCD of methane and so that, in a previous work [19] the evolution of a selected carbon catalyst during successive cycles of TCD of methane and regeneration of the deactivated carbon particles, using CO_2 as activating agent was also studied. The optimum operation conditions for catalysts regeneration were 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.

The kinetics of the carbon catalysts used in the TCD of methane have been commonly measured by monitoring the outlet hydrogen concentration as function of reaction temperature using different space velocities in a fixed bed reactor [20–23] or in a fluidized bed reactor [24]. One of the main problems associated to the kinetic parameters determination is the fact that the carbon catalysts studied presented a high initial reaction rate, which decreased rapidly with reaction time. The determination of the kinetic data available in the literature used the method proposed by Kim et al. [20] in which the initial activity was calculated by plotting the Neperian logarithm of the reaction rate versus time through extrapolating to zero time. In this case, the first analysis was done 5 min after methane was flowed. Other authors [22] calculated the reaction rate from the average concentration between 20 and 30 min time on-stream.

In the present paper, the thermo-catalytic decomposition of methane over different carbonaceous materials has been studied using a thermobalance by monitoring the mass gain (the amount of carbon deposited) with time. This method overcomes the plugging problems that occur when fixed bed reactors are used [25,26] and allowed us to measure the initial decomposition rate as well the long-term behaviour of the catalysts, that is, the carbon mass that the catalyst can accumulate before deactivation occurs. The direct measure of the initial reaction rate allowed us to determine, the intrinsical kinetic parameters of the carbon catalysts in the TCD of methane more accurately. This method has been widely used in the TCD of methane using metal catalysts [27–30], but not many references can be found in the literature related to the use of carbon catalysts.

2. Experimental

2.1. Samples

The kinetic study has been carried out for one carbon black, BP2000and an activated carbon, CG Norit, to compare the behaviour of two carbon samples of different origin/nature as catalysts for this process. These samples have been selected among the carbon catalysts samples tested in our previous works [17,31]. The CG Norit is a granular activated carbon, used in special applications in food, chemical, and pharmaceutical industries. The carbon has a very open (macro/meso) pore structure, and a special surface chemistry. CG Norit is produced by chemical activation using the phosphoric acid process. The Black Pearls 2000 (Cabot) is produced by the oil furnace process using heavy petroleum fractions as feedstock. Table 1 shows the ultimate and proximate analysis of the samples and the surface area and pore volume of them both before and after the reaction. The BP2000 sample shows high carbon content (around 97%), and the CG Norit sample presents high oxygen content and high volatile matter.

2.2. Experimental set-up

Methane decomposition experiments were conducted in a Cahn TG 151 Thermogravimetric Analyzer. This experimental set-up allows continuous recording of the sample weight changes and temperature during reaction. At atmospheric pressure, the thermobalance can operate at up to 1000 °C. The thermobalance consists of three main sections: the hardware (pressure balance, furnace, stand), the software (electronic components and display) and the external flow, pressure and temperature controllers. An internal quartz tube sealed at both ends with O-rings separates the reactor chamber from the furnace. The loading and unloading of the sample is accomplished by opening the joint and lowering the furnace with the help of an automatic elevator. The temperature inside the reactor chamber is measured and controlled by a 1/8-in. Chromel-Alumel thermocouple located just below the sample holder. The sample holder was a quartz basket (14 mm diameter and 8 mm height) to reduce mass transfer resistance around the solid sample. Operating conditions were: carbon weight 30 mg, methane flow rate: 3 l/min. A flow rate of methane of 3 l/min was used in order to avoid mass transfer phenomena and assure the kinetic regime. In order to determine the intrinsic kinetic parameters, the temperature (800–950 °C) and CH_4 percentage (15–100 vol.%) balanced with N_2, were varied. The desired temperature was reached using a heating rate of 20 °C/min.

Table 1
Main properties of the samples

	C	H	N	S	O*	Moisture	Ash	Volatile matter	S_{BET}* (m^2/g)		Vp* (cm^3/g)	
									Fresh	Final	Fresh	Final
CG Norit	70.24	2.87	0.13	0	26.76	9.78	2.77	11.74	1300	52.3	1.11	0.07
BP2000	97.08	0.2	0.16	0.73	2.56	0.5	1.02	1.65	1337	51.9	3.06	0.14

* Calculated by difference.

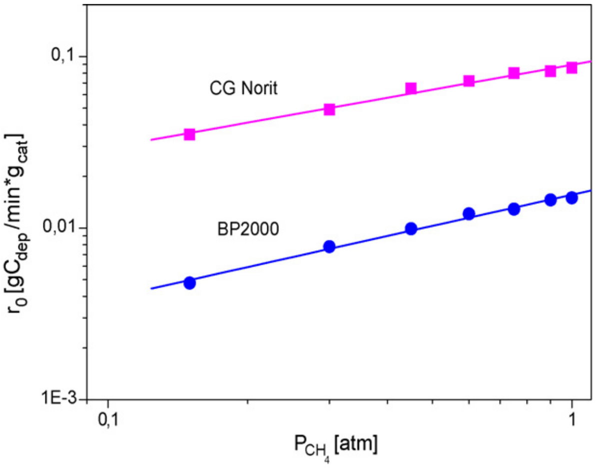

Fig. 1. Initial rate of methane decomposition over carbonaceous catalyst vs. methane partial pressure. $T = 900\,^{\circ}\mathrm{C}$.

3. Results and discussion

3.1. The reaction order

The experiments were carried out at 900 °C by changing the partial pressure using N_2 as diluent. The mass gained with time was measured, and the initial reaction rates (r_0) were determined from the derivatives of the curves of the mass gained versus time. As previously mentioned, the use of a thermobalance allows us to measure directly the initial reaction rate. Plotting reaction rate (r_0) against methane partial pressure in a log–log graph form derives a line and the slope is just the reaction order. The results obtained are shown in Fig. 1. The reaction order or the slopes, over CG Norit and BP 2000 were 0.48 and 0.6, respectively, with correlation coefficients higher than 0.99 for both carbonaceous samples. Therefore, the reaction order of the carbon growth over these catalysts may be practically said to be 0.5, whatever the nature of the carbon, activated carbon or carbon black. The rate equation is

$$r_0 = k_{\mathrm{p}} P_{\mathrm{CH_4}}^{0.5}$$

where k_{p} is the reaction rate constant and $P_{\mathrm{CH_4}}$ the partial pressure of methane.

This data could be the first report of the reaction order for TCD of methane over carbonaceous catalyst that has been obtained in a thermobalance and confirms the results previously published in the literature [20,21,23] using a fixed bed reactor. A half-order reaction is often observed for a heterogeneous catalytic reaction where a reactant adsorbs with dissociation requiring two surface-active sites and the rate determining step is the subsequent elementary reaction involving an adsorbed intermediate. However, when metal catalysts are used, a first order reaction was reported [20].

3.2. Effect of temperature

The effect of the reaction temperature on the ratio of deposited carbon to initial carbon catalysts weight (relative carbon gain) and the carbon formation rate for CG Norit catalyst is shown in Fig. 2a and b, respectively. Carbon formation rate curves have been calculated from the numerical derivative of the experimental carbon content versus time curves. Note that the reaction at 800 °C was not run until complete deactivation has occurred.

The ultimate ratio of deposited carbon to initial carbon catalysts weight (C_{dep}/C_0) for the CG Norit sample is not dependent on the temperature, reaching values of 0.7 g C_{dep}/C_0. It is worth to mention that when metal catalyst is used in the TCD of methane, the maximum amount of carbon that the catalyst can accumulate before deactivation depends strongly on the reaction temperature [12,29,30]. The different trend observed for the carbonaceous sample evidences the different reaction mechanism for both types of catalyst.

From the analysis of these data, it can be also concluded that the higher the temperature used, the faster the catalyst reaches the maximum amount of catalyst that it can accumulate.

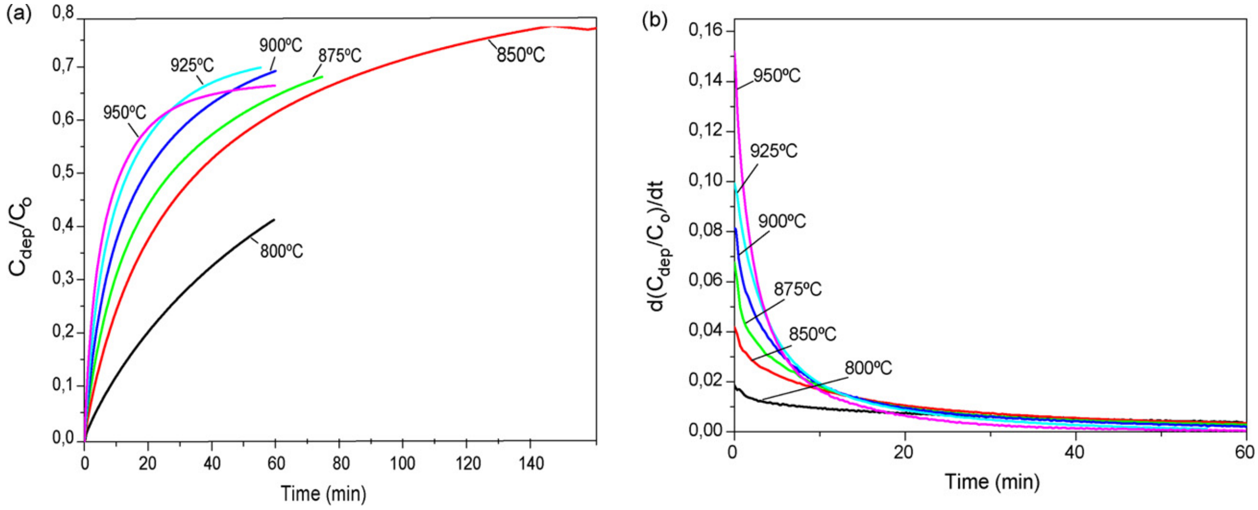

Fig. 2. (a) Evolution of the relative carbon gain with time for CG Norit at different reaction temperatures. (b) Evolution of the carbon formation rate along time rc (g carbon/g cat. min) vs. time (min) for CG Norit at different reaction temperatures.

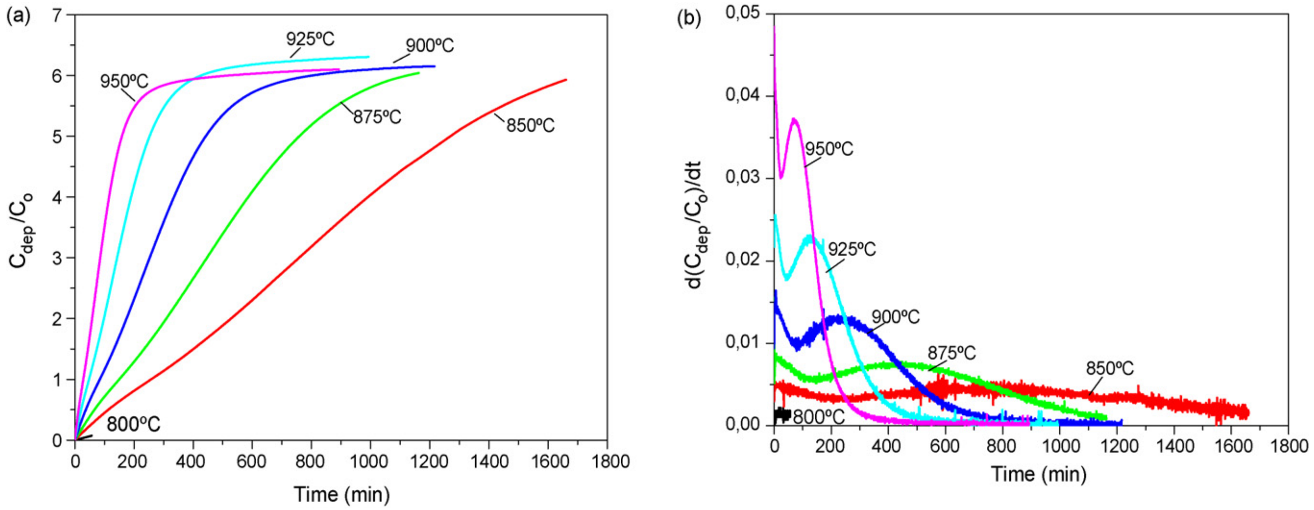

Fig. 3. (a) Evolution of the relative carbon gain with time for BP2000 different reaction temperatures. (b) Evolution of the carbon formation rate along time rc (g carbon/g cat. min) vs. time (min) for BP2000 at different reaction temperatures.

The derivatives of these curves (Fig. 2b) also show the influence of the temperature on the initial reaction rate. As expected, the higher carbon growth rate was found for the maximum temperature used, that is, 950 °C, due to the endothermicity of the reaction. As the reaction temperature decreases, the initial carbon formation rate also decreases. An exponential decay in the carbon formation rate is followed, and 30 min after the beginning of the TCD tests, all curves converge to negligible value.

The effect of the reaction temperature on the relative carbon gain and carbon formation rate for BP 2000 is shown in Fig. 3a and b, respectively. In this case, reactions at 800 and 850 °C were not run until complete deactivation has occurred. BP 2000 reaches higher values of C_{dep}/C_0 ratio compared to CG Norit, 6 g C_{dep}/C_0 (one order of magnitude higher). However, the initial carbon formation rate (Fig. 3b) is one order of magnitude lower, reaching the maximum value when 950 °C is used.

A different pattern can be observed for BP2000 from the study of Fig. 3b. A high initial carbon formation rate is followed by a rapid decline. The reaction rate for the BP 2000 presents an inflexion point from which it increases until a maximum is reached and then decreases progressively. The same trend is observed for all temperatures tested, but it is necessary to run the experiments several hours until the pattern is evident.

The activation energies for both catalysts were calculated from the Arrhenius plot shown in Fig. 4. The activation energies over CG Norit and BP2000 were 141 and 238 kJ/mol, respectively, with correlation coefficients higher than 0.99 for both carbonaceous samples. These activation energies were calculated using the initial reaction rate measured directly in the thermobalance, from the derivative of the initial weight change of the carbonaceous catalysts. These activation energies are much lower than the methane C–H bond energy of 440 kJ/mol.

The activation energy reported in the literature in a fixed-bed reactor using an initial average reaction rate for these kinds of materials ranged from 160 to 200 kJ/mol for activated carbon and 200–230 kJ/mol for carbon blacks [21].

According to Muradov [15], the total rate of the methane decomposition reaction is the sum of the rates of carbon nuclei formation, which has an activation energy of 316.8 kJ/mol, and carbon crystallites growth, which has an activation energy of 227 kJ/mol.

From these values obtained in a thermobalance, we can observe that the activated carbon sample account lower activation energy than for both processes that take place in the decomposition of methane. This fact means that the activated carbon has a catalytic effect on the methane decomposition reaction. The CG Norit sample has a high amount of oxygen surface groups, which are known to play an important role in the initial stage of the methane decomposition reaction [17–19]. However, this catalytic effect is rapidly inhibited by the deposition of crystallites from methane, which apparently did not show activity towards methane decomposition.

On the other hand, the activation energy value obtained for the carbon black sample is close to the carbon crystallite growth activation energy.

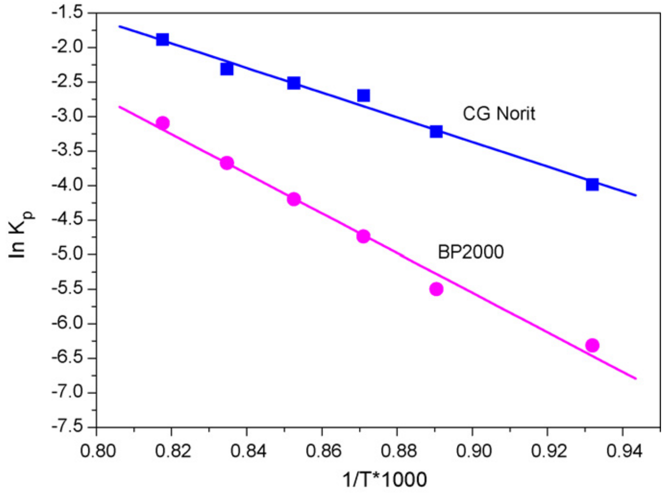

Fig. 4. Arrhenius plot of ln *k* as a function of 1/*T* for CG Norit and BP2000. Initial reaction rate.

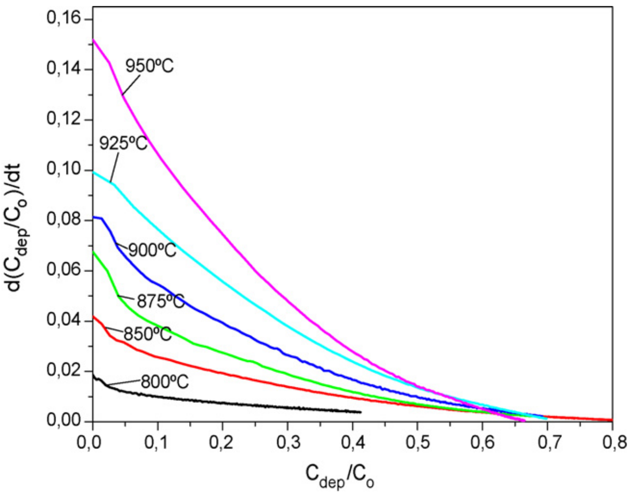

Fig. 5. Carbon deposition rate as a function of the amount of carbon deposited at different temperatures for CG Norit.

3.3. Relationship between the relative carbon gain and reaction rate

Fig. 5 shows the evolution of the reaction rate as the relative carbon gain increases for the CG Norit sample. It can be observed that the reaction rate decreases as the relative carbon gain increases. The kinetic curves follow an exponential decay.

Fig. 6 shows the evolution of the reaction rate as the relative carbon gain increases for the BP 2000. It can be observed the relationship that exists between the amount of carbon deposited and the form of the kinetic curves. For example, the inflexion point for all the curves obtained at different temperatures is found to take place for a value of C_{dep}/C_0 of 0.9.

The curves can be divided into three main zones: (1) that corresponds to the exponential decay in the reaction rate: this decay may be due to the decrease in the surface oxygenated groups. It has been previously reported [17–19] that the surface oxygen groups play a key role in the initial reaction rate. Methane thermal decomposition is a free radical process where methane molecules become attached to the active sites present on the carbon surface, the operation of such mechanism is confirmed by the existence of enough stable free radicals on the pyrolitic carbon surface [32]; (2) a pseudo steady state, which is governed by the activity of the crystallites produced from methane; Muradov [5] reported that at certain conditions carbon produced by thermal decomposition of methane would be able to catalyze the process. Other authors [23] observed the slight activity of the carbon produced from methane decomposition, when the reaction was carried out over an inert contact solid, alumina. Besides, the relative maximum point for all the curves obtained at different temperatures is found to take place for a value of C_{dep}/C_0 of 2.3. This would correspond to the time in which the original surface area is covered by the carbon crystallites produced from methane, and thus the maximum of the reaction rate due to the crystallites growth is obtained; and (3) an exponential decay due to the lack of surface area/pore volume where the carbon crystallite could be decomposed.

In the pseudo steady state, the increase in the rate of methane decomposition due to the increase in the amount of crystallites from methane decomposition is balanced by the decrease in the rate of methane decomposition of the original carbon black sample. That would explain the form of the kinetic curve.

The fact that the increase in the reaction rate, or the pseudo steady state, is not observed when using CG Norit sample can be explained paying attention to the deactivation time, that is, the time in which the mass gained with time is negligible. For the CG Norit sample, the deactivation time occurs between 30 and 60 min, whereas it takes between 15 and 65 h (850 and 950 °C) to the BP 2000 to be deactivated. This long time until deactivation occurs allowed us to distinguish between both reaction contributions.

Fig. 7 shows the Arrhenius plot for the carbonaceous samples tested, taking the reaction rate for the pseudo steady state, which corresponds to a value of C_{dep}/C_0 of 2.3 The activation energy is about 230 kJ/mol, value close to the value reported in the literature for the crystallite growth.

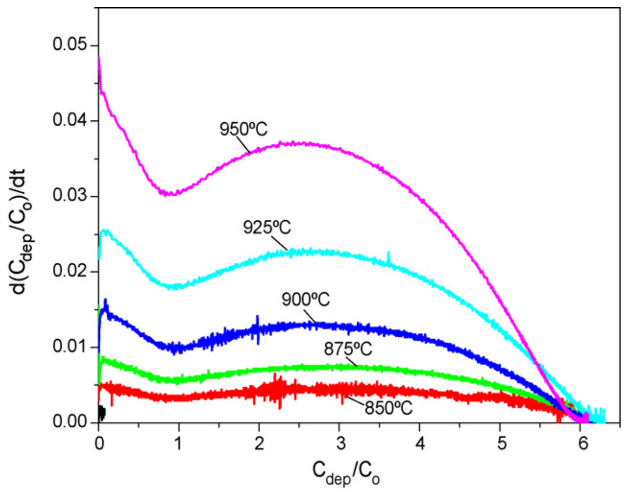

Fig. 6. Carbon deposition rate as a function of the amount of carbon deposited at different temperatures for BP2000.

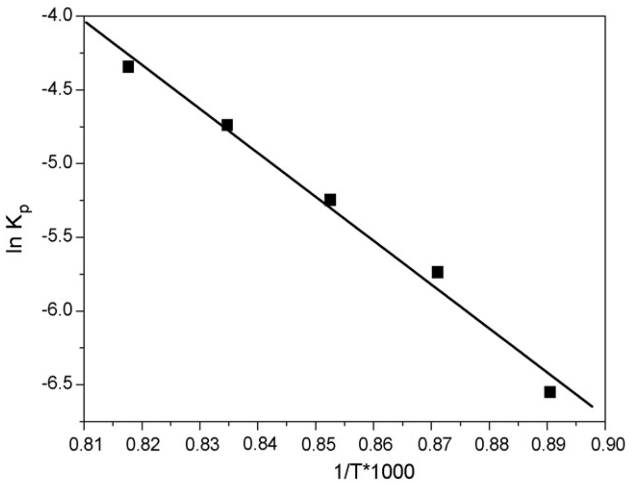

Fig. 7. Arrhenius plot of ln k as a function of $1/T$ for CG Norit and BP2000. Steady state reaction rate.

Thus, if the activation energy over the original carbon sample is lower than the E_a for the methane decomposition over methane crystallites, as occurs for the CG Norit sample, then the methane decomposes preferentially over the carbon surface until all the surface is covered by methane crystallites. On the contrary, for the BP2000 sample, the initial sample activity decreases rapidly, and the activity of the crystallites from methane becomes the rate determining step, which takes place until the surface area/pore volume is occupied by the carbon produced from methane.

4. Conclusions

The kinetics of the thermo-catalytic decomposition of methane over different carbonaceous materials has been studied using a thermobalance by monitoring the mass gain with time. The reaction order of the carbon growth over CG Norit and BP2000 catalysts may be practically said to be 0.5. The activation energies over these catalysts were 141 and 238 kJ/mol, respectively. CG Norit shows high initial activity but becomes rapidly deactivated, whereas the activity of the BP2000 is lower and presents a weight increase of 600%, one order of magnitude higher in comparison with CG Norit.

It can be concluded that the methane decomposition reaction over carbon catalysts is controlled by two simultaneous processes: (1) decrease in methane decomposition rate due to the blocking of catalytic active sites by the carbon species produced via methane decomposition. (2) Increase in methane decomposition rate due to the formation of catalytically active carbon species produced from methane.

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