



Coke analysis by temperature-programmed oxidation: Morphology characterization

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ABSTRACT

Temperature-programmed oxidation (TPO) profiles obtained using high final temperature are usually very similar in shape and it is not possible to easily distinguish among different kinetic models. Typically, statistical criteria are used to select the one that best fits the experimental TPO profile. In this work, we show that using final temperatures selected in such a way that the coke is still reacting with oxygen, relevant information can be obtained from the experimental profile. Coked naphtha reforming catalysts, obtained from an industrial reactor, are characterized by running TPO analyses using intermediate temperatures. Results clearly show that the coke reaction order changes as the coke conversion increases. When the initial coke content is approximately 5 wt% or higher, coke has a tridimensional structure that leads to a low reaction order, close to 0.2. At high conversion levels, approximately 80%, the coke reaction order starts increasing until reaching a value of 1 at conversion close to 1. This information is easily obtained by plotting the experimental coke reaction order using the data at constant temperature. In this way, it is possible to easily distinguish among different models, and to replicate the experimental results.

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1. Introduction

Catalyst deactivation due to coke deposition is one of the most common causes leading to the need for catalyst regeneration in the refining industry. In order to optimize and properly design the regeneration of deactivated catalysts, knowledge of the coke burning kinetics is highly desirable. However, this information is often unknown, due to the complexities of such systems. The kinetics of coke combustion depends on many factors, such as H/C ratio, amount of coke, coke particle size and its distribution, location of coke particles on the catalytic surface, and coke morphology.

One of the most widely used techniques for coke characterization is temperature-programmed oxidation (TPO) [1]. Using this or similar techniques such as differential thermal analysis (DTA) [2], thermo-gravimetric analysis (TGA) [2], or differential scanning calorimetry (DSC), coke has been studied on a large variety of catalytic systems. However, in most publications the kinetics of coke combustion is considered to be first order with respect to coke and oxygen [1,3]. In this type of kinetics, either one or several types of coke have been considered. For example, on acid catalysts typically one type of coke with order 1 was considered in order to

obtain the kinetics for coke combustion [4–6], while many peaks were used to fit the TPO profiles for reforming catalysts [7,8], typically using a linear combination of power-law expressions [9–11]. In recent publications, the first order for coke oxidation was also used to study coke combustion on FCC catalysts [12–14] and on ferrierite [15]. However, in the work of Brown and co-worker [13] a more complex mechanism was introduced to account for the production of CO and CO₂, as well as in the contributions by Keskitalo et al. [15] and Kanervo et al. [14], who proposed different reaction mechanisms to fit the experimental TPO. In some cases, the TPO was deconvoluted by fitting the profile with several Gaussian curves [16].

Few publications have analyzed the different relationships between the exposed coke surface and conversion [17,18]. The reaction between coke and oxygen involves the exposed carbon; therefore, in the reaction rate expression, coke is represented by its exposed surface area and the reaction order related to this area is one. However, the relationship between the exposed surface area and the coke conversion during combustion is not linear and involves the surface/volume ratio. This ratio depends on the geometric parameters of the coke particles, such as size and shape. The ratio between the coke surface and its volume is directly related to the coke reaction order.

If the TPO technique is carried out up to high temperatures, in such a way that all the soot is burned, it is difficult to get useful information regarding coke morphology. In two previous

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Nomenclature

r_i	rate of CO ₂ production from coke i (mol (s g _{catal}) ⁻¹)
A_i	pre-exponential factor (mol(s (cm ² /100 g _{catal}) g _{catal} atm ^m) ⁻¹)
E_i	activation energy for i th type of coke (kcal/mol)
T	temperature (°C)
S_i	coke i exposed area (cm ² /100 g _{catal})
S_{i0}	coke i initial exposed area (cm ² /100 g _{catal})
P_{O_2}	oxygen partial pressure (atm)
X_i	coke conversion
m, n	oxygen and coke reaction order, respectively
C_{i0}	initial coke concentration of the i th type of coke (g _{coke} /100 g _{catal})
R_{i0}	initial coke particle radius (cm)
d_c	coke density (g/cm ³)
A_{is}	pre-exponential factor as defined in Eq. (5) (mol(s (g _{coke} /100 g _{catal}) g _{catal} atm ^m) ⁻¹)
F_n	total flow-rate (mol/s)
y_{CO_2}	CO ₂ molar fraction
w	catalyst loaded into the cell (g)
X_A	coke conversion at which reaction order starts changing
X_B	coke conversion at which reaction order reaches the value 1

publications of our group, we reported having taken advantage of using TPO up to intermediate temperatures [3,19], and very useful information was obtained in both cases.

In this work, the usefulness of running the TPO analysis up to intermediate temperatures is presented. A power-law kinetic model, corresponding to the shrinking core model, is used for the phenomenological interpretation of the experimental results obtained with a naphtha reforming catalyst, coked in an industrial reactor.

2. Experimental

2.1. Coked catalysts

A commercial bimetallic Pt(0.3%)-Re(0.3%)/Al₂O₃ catalyst coked during an operation cycle in a petrochemical company was used. The catalyst samples were taken during the course of the eighth cycle of operation from the third reactor. Before the cycle, the catalyst had 0.85% chlorine, 0.3% sulphur and a specific surface area of 160 m² g⁻¹. The length of the cycle was 208 days, the pressure 15 kg cm⁻² and 27.5 barrels of feed were passed over each pound of catalyst.

2.2. Temperature-programmed oxidation (TPO)

TPO analyses were carried out using a modified technique [20] which consists in circulating the gases from the reactor outlet to a methanation reactor, where CO and CO₂ were converted into CH₄. Then, CH₄ was continuously measured by an FID detector. The methanation reactor contains a Ni catalyst and operates at 400 °C. Under these conditions (400 °C, 6% O₂, 40 ml/min) 100% of conversion of CO_x to CH₄ was measured. Typically, 10 mg of coked catalysts were loaded into the analysis cell. The equipment was calibrated by sending pulses of CO₂ diluted in He.

3. Model formulation

The power-law kinetic model, which physically corresponds to the shrinking core model, has been thoroughly analyzed in a previous publication [3]. In summary, the equations to be considered to model the kinetics of coke combustion in a fixed bed reactor, for a single type of coke i , are the following:

$$r_i = A_i \cdot \exp\left(-\frac{E_i}{RT}\right) \cdot S_i \cdot P_{O_2}^m \quad (1)$$

$$S_i = S_{i0} \cdot (1 - X_i)^n \quad (2)$$

$$S_{i0} = \frac{3C_{i0}}{R_{i0} \cdot d_c} \quad (3)$$

$$r_i = A_{is} \cdot \exp\left(-\frac{E_i}{RT}\right) \cdot C_{i0} \cdot (1 - X_i)^n \cdot P_{O_2}^m \quad (4)$$

$$A_{is} = \frac{A_i \cdot 3}{R_{i0} \cdot d_c} \quad (5)$$

$$F_n^0 \cdot \frac{\partial y_{CO_2}}{\partial w} = A_{is} \cdot \exp\left(-\frac{E_i}{RT}\right) \cdot C_{i0} \cdot (1 - X_i)^n \cdot P_{O_2}^m \quad (6)$$

If there is more than one type of coke, such as in reforming catalysts, there will be as many of this set of Eqs. (1)–(5), as types of coke. In this case, Eq. (6) becomes:

$$F_n^0 \cdot \frac{\partial y_{CO_2}}{\partial w} = \sum_i r_i \quad (7)$$

Being the total rate of CO₂ generation:

$$r = \sum_i r_i \quad (8)$$

Eq. (3) corresponds to spherical particles. For any other particle shape, in Eq (3) the coefficient 3/R_{i0} should be replaced.

In this work, the main modification to this model is to include the possibility for the coke reaction order to change as a function of the conversion. The most general case is represented by:

$$n = N^0, \quad X_i \leq X_A \quad (9)$$

$$n = f(X_i), \quad X_A \leq X_i \leq X_B \quad (10)$$

$$n = 1, \quad X_i \geq X_B \quad (11)$$

Variable N^0 is the initial coke reaction order, i.e. before the oxidation begins. If the coke particles are three-dimensional, the coke reaction order may have values between 0 and 1. If the coke particles are very large the order may be 0, if the shape of the particle is spherical or a prism with the three dimensions changing proportionally as coke is converted, the order is 2/3. When the coke content is very low, all the carbon atoms are exposed and, therefore, the coke amount is directly proportional to the exposed surface area. This corresponds to coke reaction order 1.

Taking the logarithm to Eq. (4), and using reaction rate data taken at *constant temperature*, the reaction order may be estimated. From expression (4):

$$n = \frac{\log(r_i^{j+1}/r_i^j)}{\log((1 - X_i^{j+1})/(1 - X_i^j))} \quad (12)$$

where r_i^{j+1} and r_i^j are reaction rate data taken at conversions X_i^{j+1} and X_i^j , respectively.

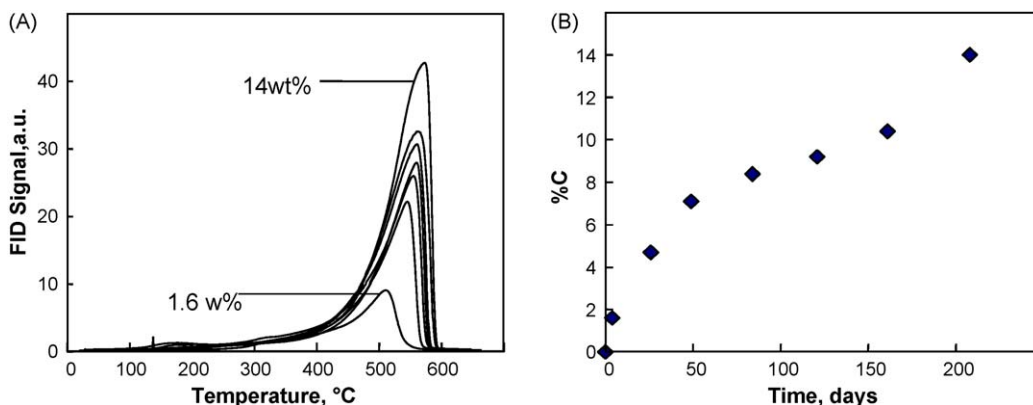


Fig. 1. Results obtained with Pt-Re-S/Al₂O₃ catalysts coked in a commercial reforming unit. (A) TPO profiles and (B) coke content as a function of time-on-oil.

4. Results and discussion

4.1. Catalysts coked in a commercial reactor

Fig. 1 shows results obtained with the Pt-Re-S/Al₂O₃ catalysts coked in a commercial reforming unit. Fig. 1A shows the TPO profiles, and Fig. 1B shows the coke content, as a function of time-on-oil. The maximum in the TPO profiles shifts to higher temperatures as the time-on-oil increases. Fig. 1B shows that the coke deposition is faster at the beginning of the cycle, then it increases at a lower rate and finally it accelerates again. Note that the last point taken at the end of the cycle has 14 wt% coke, and the sample taken at day 161 has 10.4 wt%. This fast increase at the end of the run is due to an increase in the reactor temperature, which typically is applied to compensate for catalyst deactivation, in order to keep the octane number of the product.

Fig. 2 shows results obtained by TPO experiments, but instead of heating up to high temperatures where all the coke is burnt, an intermediate final temperature was selected, based on the TPO shown in Fig. 1A. These TPO profiles were obtained by heating from room temperature up to 450 °C, and holding this temperature until the FID signal returns to the baseline. We will refer to this type of TPO analysis, as *partial burning experiments*. The sample with the lowest amount of coke (1.6%) displays a profile different from the one corresponding to all the other samples. These other samples have a coke content between 5 and 14%, approximately. The profile that corresponds to the first sample displays a continuous and fast decrease after the final temperature is reached. This corresponds to a typical behavior observed in samples with a low initial coke

content and, therefore, with a coke reaction order of 1 or close to 1 [3]. However, the other samples display a significantly different profile. In the case of the samples with higher coke content, there are three distinct zones in the TPO profile once the final temperature (450 °C) is reached. In the first zone, a fast decrease in the burning rate occurs, followed by a second zone where the reaction rate is almost constant, in fact showing a steady and slow decrease. The third zone corresponds to a sigmoid curve with a fast burning rate decrease.

It has to be taken into account, as mentioned above, that in the extreme situation in which the coke reaction order is zero, the reaction rate at constant temperature must also be constant. These results shown in Fig. 2 cannot be reproduced with the model most extensively used in the literature, in which a given coke reaction order is assumed to be constant during the reaction.

Fig. 3 shows another set of experiments, carried out with the sample with the highest amount of coke. These TPO profiles were obtained using the following final temperatures: 450, 470, 510, 530, and 545 °C. The higher the final temperature, the shorter the time during which the reaction rate is almost constant. At 530 and 545 °C, the rate decay is fast; nevertheless, the change in the slope that occurs in these profiles is noticeable.

Fig. 4 shows the reaction order, obtained from the experimental reaction rate data shown in Fig. 2, corresponding to the sample with 9.2% coke (sample taken at 121 days on oil). This plot was obtained applying Eq. (12) to the experimental data. Fig. 4A also shows the fraction of unconverted coke and the temperature profile. It is interesting to observe the reaction order values obtained after the constant temperature was reached, since only

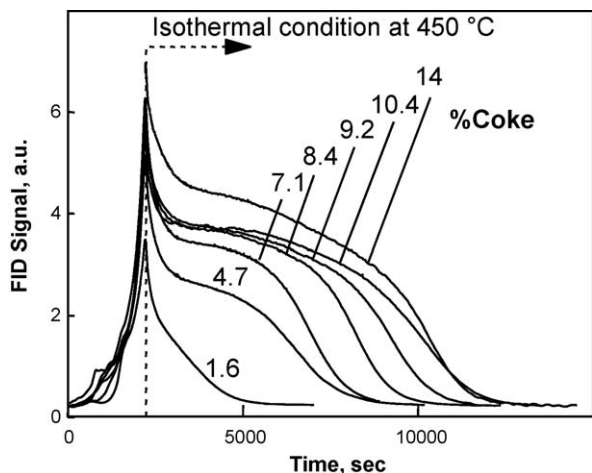


Fig. 2. Partial burning experiments, heating up to 450 °C for catalysts with different coke contents.

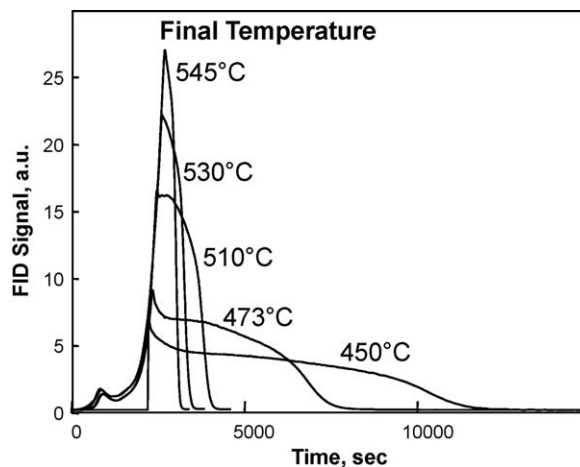


Fig. 3. Partial burning experiments, heating up to different final temperatures for the catalyst with the highest coke content (14%).

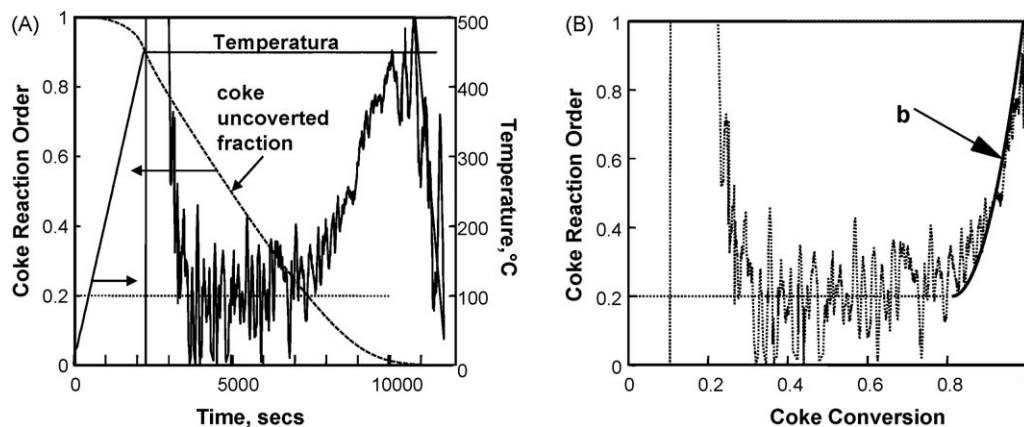


Fig. 4. Coke reaction order for sample with 9.2 wt% coke, from experimental data applying Eq. (10); (A) as function of time, coke conversion, temperature profile; (B) as function of coke conversion, and (b) quadratic dependence of coke reaction order with coke conversion.

under this condition this plot represents the coke reaction order. It can be observed that the average value is 0.2 from 3500 to 7000 s. At this time, the order starts increasing up to almost 1. In the same figure, the fraction of unburned soot ($1 - X$) is represented. It can be seen that the order is 0.2 between conversion values of 0.3–0.7 or 0.8, approximately. This plot clearly indicates that if the TPO profile is fitted with a constant coke reaction order, it will not be capable of predicting the behavior observed at constant temperature shown in Figs. 2 and 3. Fig. 4B also shows curve (b), which corresponds to a quadratic dependence of the reaction order with conversion, after 7000 s, time at which a coke conversion of 80% was reached. This curve follows very closely the value of the experimental coke reaction order. This plot and these experimental results obtained at constant temperature indicate that the coke reaction order is constant in a given conversion range (in this case up to 80% conversion), and then increases up to 1, following a quadratic function with the coke conversion.

4.2. Kinetics models for solid–gas reactions

There are several models that have been used in the literature to analyze the coke combustion, both to be able to model the catalyst regeneration, and to gather basic information regarding the deactivation process. For example, several kinetic models have been tested in the coke combustion on wet oxidation catalysts [17]. Table 1 shows such models, as well as an empirical equation recently applied for soot reaction with oxygen and nitrogen oxide [21]. The general relationship between the exposed surface area

and the coke conversion is as follows:

$$S_i = S_{i0} \cdot \varphi(X) \quad (13)$$

Table 1 shows the most common functions $\varphi(X)$ that have been developed.

Fig. 5 shows simulation carried out using these models. The TPO analyses carried out up to high temperatures look very similar in these simulations. Comparing the experimental profiles shown in Fig. 1 with those shown in Fig. 5A, it can be seen that even though the models are different from each other, the complete TPO profile does not show differences that could provide information regarding which of them might be the right one. In other words, all of them look similar. Fig. 5B shows the simulation of partial burning experiments using the models listed in Table 1. In some cases, an increase in the reaction rate is observed due to an increase in the coke-exposed surface during the initial stages of the reaction. Using any of these well known models, it was not possible to obtain profiles similar to those found experimentally, shown in Figs. 2 and 3.

4.3. Variable coke reaction order model

Fig. 6 shows additional simulations carried out using the power-law model. These TPO profiles were obtained with a given pre-exponential factor and activation energy, changing only geometrical parameters, such as particle size, coke reaction order (particle shape), particle size distribution, or the parameter associated with the orders transition regime (X_A and X_B). It is interesting to emphasize that these profiles, obtained with only one value of E and A , could be fitted using two or more peaks with first order and different pairs of values of E and A .

Therefore, it is important to establish an experimental methodology to identify if there are morphological parameters associated with a given type of coke, or if several types of coke with different activation energies and pre-exponential factors are present on the catalyst.

Fig. 6A shows that the right side of the TPO profile is different depending upon the coke reaction order. If it is 1, the peak is more symmetrical than when the order is less than one. In this latter case, the right side of the profile displays a faster decrease in reaction rate falling to 0 in a shorter time after the TPO maxima.

At high coke content, the shape of the experimental TPO profiles shown in Fig. 1A resembles those obtained with a coke reaction order less than 1, such as the profile obtained with order 0.66

Table 1
Pore models tested for coke combustion.

Pore model	$\varphi(X)$	Reference
Power-law (grain) model	$(1 - X)^n$	[22]
Pore tree model	$(1 - X)\sqrt{\frac{X}{\varepsilon_0} + (1 - X)}$	[23]
Random pore model	$(1 - X)\sqrt{1 - \varphi \ln(1 - X)}$	[24]
Random capillary model	$(1 - X)\sqrt{1 - \frac{B_0}{2\pi B_1^2} \ln(1 - X)}$	[25]
Bifurcated pore model	$(1 - X)\sqrt{1 - \frac{1}{\ln(1/1 - \varepsilon_{\text{micropore},0})} \ln(1 - X)}$	[26]
Empirical	$(1 - X)(1 + fX)^{1/q}$	[21]

n : coke reaction order, related to coke morphology (shape/size).

ε_0 : initial porosity.

φ : structure parameter.

B_0 : total pore length.

B_1 : total pore surface.

$\varepsilon_{\text{micropore},0}$: initial micropore porosity.

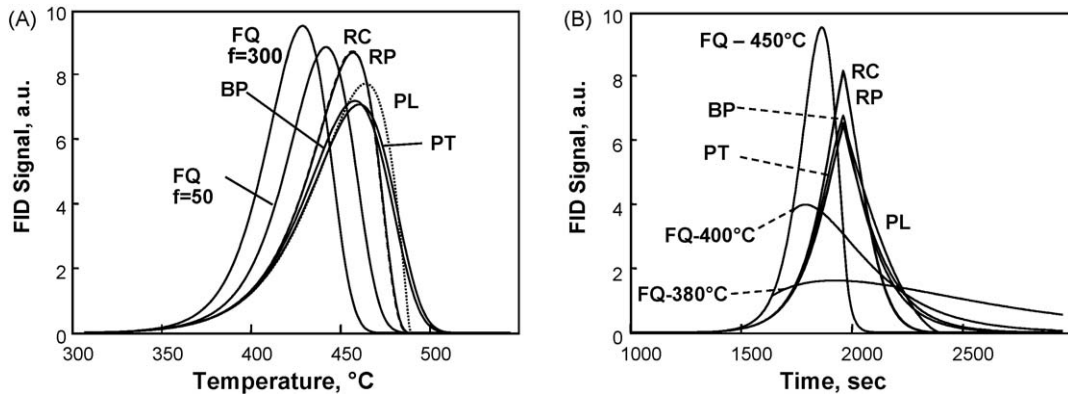


Fig. 5. Simulated TPO profiles, according to models listed in Table 1. (A) conventional TPO, (B) partial burning experiments. PL: power-law ($n = 0.66$), PT: pore tree ($\epsilon_0 = 0.5$), RP: random pore ($\varphi = 2.9$), RC: random capillary ($B_0 = 1.37$, $B_1 = 0.27$), BP: bifurcated pore ($\epsilon_{\text{micropore},0} = 0.33$), FQ: empirical ($f = 300$, $q = 3$); $E = 40$ kcal/mol, $A = 6.6 \times 10^7$.

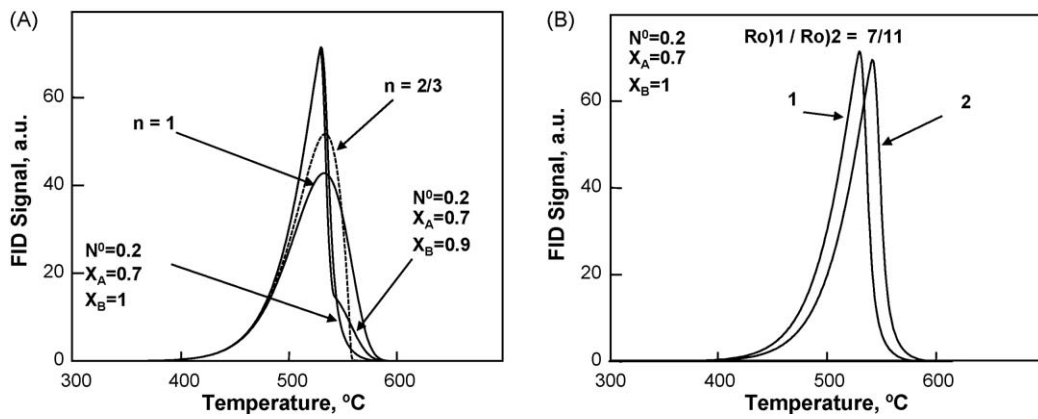


Fig. 6. Simulated TPO profiles, using the power-law model. (A) Different coke reaction orders; (B) TPO obtained with different particle sizes, $(R_0)_1/(R_0)_2 = 7/11$. $E = 47$ kcal/mol, $(A_{is})_1 = 4.85 \times 10^8$, $(A_{is})_2 = 3.06 \times 10^8$.

(Fig. 6A) or the profile obtained with coke reaction order 0.5 (see ref. [3], Fig. 3). Only the TPO profile obtained with the first sample taken from the reactor is different (Fig. 1A), with a shape more similar to a 1st order reaction. All these profiles could be fitted with several peaks as it has often been reported in the literature. However, to predict the burning rates obtained under different conditions, e.g. at constant temperature as shown in Figs. 2 and 3, this model fails in the same way as the models previously reported (see Table 1) and used in the literature in many systems. Fig. 6B shows two simulated TPO profiles, only changing the particle size

(R_{i0}). As the particle size increases, the TPO profile shifts to higher temperature.

Fig. 7 shows several TPO profiles simulated using an intermediate final temperature. Fig. 7A shows few examples in which the coke reaction order is constant during the reaction. It can be seen that in all cases after the final temperature is reached, the reaction rate decreases steadily. Fig. 7B shows the same type of simulation, but considering that the reaction order changes as a function of the coke conversion. Simulations presented in Fig. 7B include two types of coke. One of them, with a small quantity

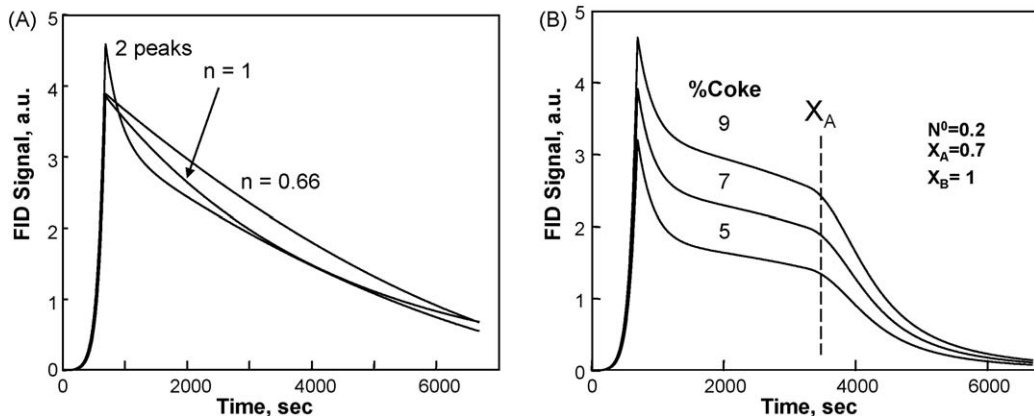
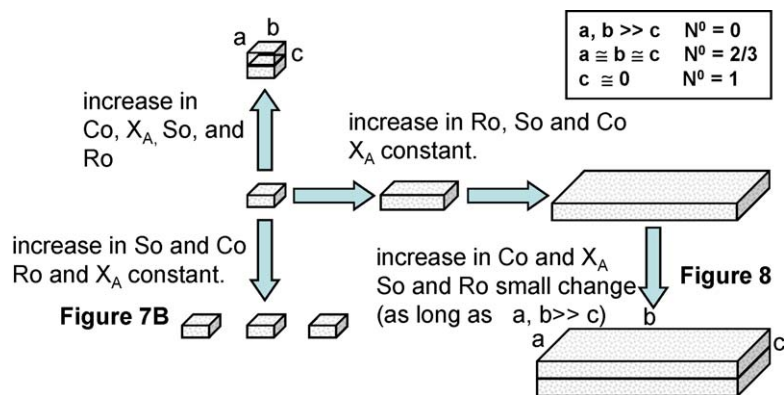


Fig. 7. Simulated TPO profiles, partial burning experiments. (A) Different coke reaction order, (B) different coke content, coke reaction order changes with conversion—two peaks: $E_1 = 46$, $(A_{is})_1 = 3.58 \times 10^9$, $n_1 = 1$, $C_{01} = 0.4\%$; $E_2 = 47$ kcal/mol, $(A_{is})_2 = 4.85 \times 10^8$, $C_{02} = 11$, $(X_A)_2 = 0.7$, $(X_B)_2 = 1$, $(N^0)_2 = 0.2$.



Scheme 1.

(0.4 wt%) that generates a low temperature peak with order 1, and a main component (9 wt%) which displays a more complex behavior regarding the reaction order. The initial reaction order was assumed to be 0.2 according to the experimental result shown in Fig. 4. Taking into account this result it was assumed that the order was constant until the conversion reached a value of 0.7. Afterwards, the coke reaction order was supposed to increase, reaching a value of 1 when the conversion is 1. The shape of the simulated profile is pretty much in agreement with the experimental results shown in Fig. 2. This is a very interesting result since a complex behavior can be simulated with simple geometric considerations. Fig. 7B displays the simulations for different samples, containing 5, 7, and 9 wt% C, with the same initial reaction order, same activation energy and pre-exponential factor. It was also assumed that this order was constant until the coke conversion reached 70% (X_A), for the three catalysts. This situation corresponds to an increase in the number of the same type of coke particles, with the same shape and size, as depicted in Scheme 1. In this case, the coke-exposed surface increases proportionally to the total amount of coke. Because of this, the signal increases proportionally to the amount of coke once the constant temperature is reached. In this condition, the contribution of the first peak to the whole envelope is negligible, and only the reaction rate due to the main peak contributes to the signal. Comparing these results with those shown in Fig. 2, it can be seen that the second (4.7 wt% C), and the third (7.1 wt% C) samples follow this trend, i.e. an increase in the reaction rate without changing the conversion required for the reaction order to start increasing, which is indicated in Fig. 7B as X_A . However, with a further increase in the coke content, it can be seen that at constant temperature the reaction rate is practically constant. Compare samples 4 (8.4 wt%

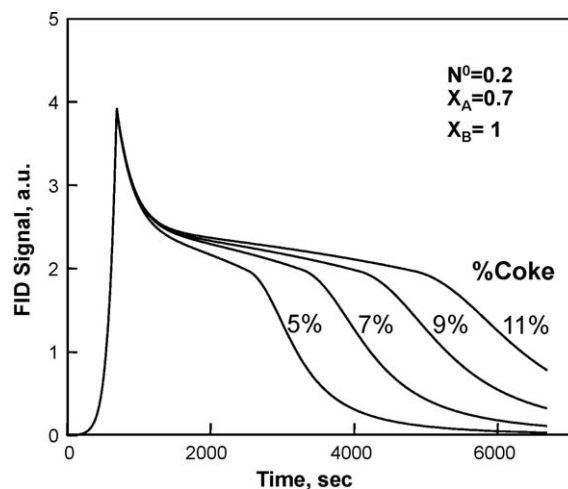


Fig. 8. Simulated TPO profiles, partial burning experiments. $E = 47$ kcal/mol, 5% C: $A_{is} = 6.75 \times 10^8$, 7% C: $A_{is} = 4.85 \times 10^8$, 9% C: $A_{is} = 3.74 \times 10^8$, 11% C: $A_{is} = 3.06 \times 10^8$.

C), 5 (9.2 wt% C), and 6 (10.4 wt% C) at, e.g. 4000 s. This indicates that after certain level of coke has accumulated, no new particles are generated and only a growth in particle size occurs without significantly changing the exposed surface. The simulation that corresponds to this behavior is shown in Fig. 8. These results were obtained by considering that the coke content increases (C_{i0}) due to an increase in particle size (R_{i0}) and consequently, a decrease of A_{is} , in such a way that the exposed surface practically does not increase as a function of the coke content (see Scheme 1).

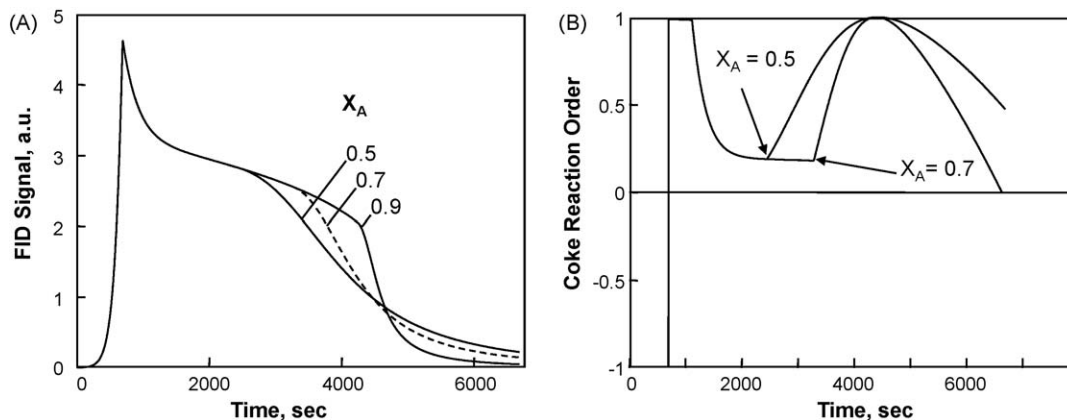


Fig. 9. (A) Simulated TPO profiles, partial burning experiments. $E = 47$ kcal/mol, $A_{is} = 4.85 \times 10^8$, $N^0 = 0.2$, $X_B = 1$. (B) Coke reaction order, Eq. (10), applied to simulated data.

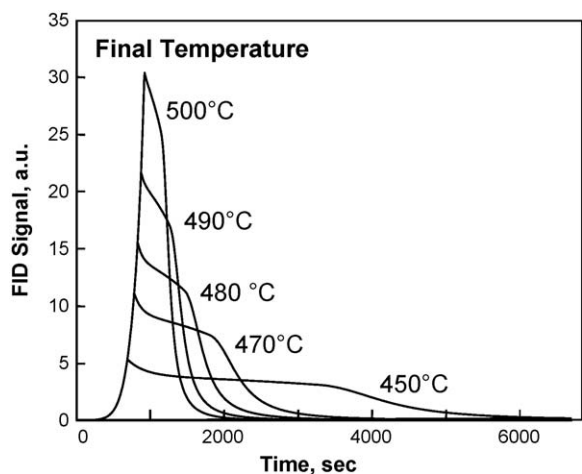


Fig. 10. Simulated TPO profiles, partial burning experiments. Different final temperatures. Two peaks: $E_1 = 46$, $(A_{is})_1 = 3.58 \times 10^9$, $n_1 = 1$, $C_{O_1} = 0.4$; $E_2 = 47$ kcal/mol, $(A_{is})_2 = 4.85 \times 10^8$, $C_{O_2} = 11$, $(X_A)_2 = 0.7$, $(X_B)_2 = 1$, $(N^0)_2 = 0.2$.

Fig. 9A shows the simulated profile obtained using different values of the fraction of coke at which the initial reaction order starts increasing (X_A). It can be seen that this parameter not only affects the time needed to reach the third zone of the TPO profile at constant temperature, but also changes the slope of the fast-decreasing part of the profile. Fig. 9B shows the plot corresponding to the apparent reaction order, and it can be seen that the shape of these curves agrees with that experimentally found and shown in Fig. 4. This type of plot can be used to determine the initial coke reaction order, the conversion at which this order starts to increase, the relationship between the coke reaction order and the conversion during this stage of fast increase of coke reaction order, and the conversion at which the order becomes one. This very important information regarding the modeling of the coke combustion kinetics is not possible to be obtained with the straight TPO.

Fig. 10 shows the simulated profiles, obtained by changing the final temperature of the experiment. By comparison with the experimental results shown in Fig. 2, it can be concluded that the model correctly predicts the general behavior of the system. This cannot be achieved with models listed in Table 1, previously used in many publications.

5. Conclusions

The characterization of coke deposits is often a difficult task. In this work, a simple modification of the classic Temperature-Programmed Oxidation analysis is used to obtain information regarding the coke reaction order, its dependence with coke conversion, and coke morphology.

Data obtained at constant temperature make it possible to be processed in order to obtain the dependence of coke reaction order with coke conversion. Straight TPO carried out up to high temperatures does not allow discriminating among the many available models. The TPO performed using an intermediate

temperature, at which coke is still reacting at an appreciable rate, allows the obtention of valuable information. Using the data obtained at constant temperature it is possible to determine:

- if the particles are large enough in order to have a combustion rate almost constant;
- the average coke reaction order, by plotting the coke reaction order as a function of coke conversion;
- the conversion at which the coke reaction order rapidly increases, reaching the value of 1.

TPO profiles are usually fitted using several peaks, each of them representing a different type of coke, with a given activation energy and pre-exponential factor. In this work, it is shown that this complex behavior may be explained by just considering that coke particles grow both by increasing the number of particles, and by increasing the size of each of them. Using only one activation energy but taking into account that the coke reaction order changes as a function of coke conversion due to changes in the surface/volume ratio, experimental observations can be explained.

It has to be emphasized that in order to discriminate among coke combustion kinetic models, TPO experiments carried out up to intermediate temperatures are a very useful tool.

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