

TAP studies of Pt–Sn–K/ γ -Al₂O₃ catalyst for propane dehydrogenation

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A Pt–Sn–K/ γ -Al₂O₃ catalyst was prepared by incipient wet impregnation and studied with a temporal analysis of products (TAP) reactor for propane dehydrogenation. Previously to TAP analyses, the catalyst samples were used for propane dehydrogenation in two different reactors: a conventional fluidized bed reactor (FBR) where the catalyst was deactivated in time; and a two zone fluidized bed reactor (TZFBR) where propane and oxygen are fed at different levels, providing separated zones for the reaction and catalyst regeneration thus allowing a continuous mode operation. Several operating conditions were also investigated: different times on stream in the FBR, and in TZFBR at steady state the temperature, the oxygen flow rate and the location of the propane feeding point. Samples of catalyst were obtained at several axial positions in the bed. The amount of coke deposited on the catalyst surface has been determined by thermogravimetric analysis. TAP results show that activation energies for propane conversion are markedly different for catalysts used in FBR and TZFBR; these differences have been related to the different nature of coke present on the catalyst surface.

1. Introduction

The initial activity and presence of different active sites on the catalyst surface are critical factors determining the yields of heterogeneous catalytic reactions. But it is necessary to take into account that other process could modify the catalyst activity and thus the process yields. The loss of activity of the catalyst can be caused by many different processes such as coking, surface restructuring, sintering, loss of active phase and poisoning. So, to know how the reaction takes place, the study of the active sites of partially deactivated catalyst is essential.

In this context, the temporal-analysis-of-products or TAP reactor has been recognized as an important transient experimental set-up for the study of heterogeneous catalytic reactions. A TAP pulse response experiment involves injecting a very small amount of gas per pulse. As a result, the pressure rise in the micro-reactor is small, and gas molecules move through the reactor by Knudsen diffusion. The time-dependent exit flow rate of each gas is detected by a mass spectrometer and the intensity of the transient response is proportional to the exit flow rate of the corresponding gas. TAP-2 is a version of this equipment designed to operate in the transient mode in the milliseconds time range and a sample can be tested without exposing it to ambient conditions [1].

Quantitative information of the phenomena in the reactor can be extracted from the size and shape of the responses by the use of appropriate mathematical models [1–8]. Kinetic evaluation of TAP experiments is typically based on analytical or numerical solution of partial differential equations describing chemical and diffusion process in the micro-reactor. Different methods have been proposed in the literature, including moment analysis [2–4], thin-zone model [5,6] and a numerical solution [7]. In a previous study, the first order rate constant for the propane conversion over stable samples (no coke) has been evaluated by moment analysis, the thin-zone model and regression analysis of the full pulse response for different catalyst bed lengths and temperatures. This has shown that the three methods yield comparable results for both the values of the rate constant and the corresponding activation energies. However, the expression derived from the thin-zone model is the easiest to use and give reasonable order of magnitude estimates of the first order rate constant [8].

In several previous studies, the dehydrogenation process was studied in a two-zone fluidized bed reactor (TZFBR) and in a conventional fluidized bed reactor (FBR). The experimental evidence shows an important advantage of the two-zone fluidized bed reactor in dehydrogenation processes, where the catalyst becomes deactivated by coking in the reaction zone and is regenerated at the oxidizing zone; this reactor allows working in a continuous mode, with “in situ” catalyst regeneration. Moreover in the TZFBR the heat quantity necessary for the endothermic reaction can be supplied in part by the sensible heat stored in the catalyst in the exothermic regeneration zone [9–13]. Although, the use of a suitable catalyst

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Nomenclature

$D_{e,cat}$	effective Knudsen diffusivity in the catalyst zone, $cm^2 s$
$D_{e,II}$	effective Knudsen diffusivity in the second inert zone, $cm^2 s$
d_p	diameter of particle, μm
E_a	activation energy, kJ/mol
ε_b	fractional voidage of the package bed in the reactor
F	exit flow rate, mol/s
FBR	fluidized bed reactor
h_a	propane feed point in the TZFBR, cm
H	total bed height in the TZFBR, cm
h_s	sampling point height, cm
k'_a	apparent kinetic constant, s^{-1}
k'_{a0}	pre-exponential factor, s^{-1}
L	height of the reactor, cm
L_{II}	height of the second inert zone, cm
L_{cat}	height of the catalyst zone, cm
M_0	zeroth moment of the exit flow rate in the TAP reactor
PI	integral of normalized flow curves
t	time, s
T	reaction temperature, $^{\circ}C$
TAP	temporal analysis of products
TZFBR	two zone fluidized bed reactor
u_0	gas velocity, $cm^3 (STP)/cm^2 s$
u_{mf}	minimum fluidization velocity, $cm^3 (STP)/cm^2 s$
u_r	relative gas velocity, $u_r = u_0/u_{mf}$
u_{r1}	relative gas velocity in reaction zone, $u_{r1} = u_{0, reaction\ zone}/u_{mf}$
W_{cat}	mass of catalyst, mg
WHSV	weight hourly space velocity, s^{-1}
$X_{C_3H_8}$	conversion of propane

allows achieving high reaction rates and selectivity, it is necessary to define the optimal synergy between catalyst design and reactor engineering. From this perspective it is interesting to study the influence of the changes in the catalyst nature in the behaviour of the TZFBR.

In this work, propane dehydrogenation over samples of Pt-Sn-K/ γ -Al₂O₃ catalyst has been studied in a TAP-2 reactor system. The aim of this work is to study the effect of the coke deposits in the catalyst when different reactors systems were used.

2. Experimental

The dehydrogenation catalyst Pt-Sn-K/ γ -Al₂O₃ was prepared by an incipient wet impregnation procedure already published [14]. Details of the catalyst preparation have been given elsewhere [15]. Before TAP experiments, samples of Pt-Sn-K/ γ -Al₂O₃ catalyst were used in propane dehydrogenation. There are two types of catalysts samples obtained after propane dehydrogenation:

- Samples obtained at different reaction times in a conventional fluidized bed reactor (FBR). The operating conditions were as follows: temperature: 500 °C, relative gas velocity ($u_r = u/u_{mf}$): 1.7, flow rate ratio of Ar:C₃H₈ = 1:1, $W_{cat} = 10$ g.
- Samples taken in a two zone fluidized bed reactor (TZFBR) [12,13,15] at different operating conditions: flow of oxygen fed to the reactor, reaction temperature and location of propane feed point in the bed (Table 1). Once steady state was reached under reaction conditions, the flow of gas was suddenly cut

Table 1

Operating conditions in a TZFBR. Balance with argon as inert gas.

Studied variable	% O ₂	T (°C)	(H - h _a)/h _a	u _{r1}	W _{cat} (g)	% C ₃ H ₈
O ₂ flow rate	5	500	1.0	2.8	60*	50
	15					
Reaction temperature	10	500	1.0	4.0	35**	50
		520				
		540				
(H - h _a)/h _a	5	500	2.0	2.8	60*	50
			1.0			
			0.3			

* H = 14 cm.

** H = 8 cm.

off and then a small flow of argon was fed (insufficient to fluidize the catalyst) and the reactor temperature was down to room temperature. Samples of the catalyst at several axial positions (h_s) were taken with a movable quartz vacuum probe. The sampling point, h_s , indicates the distance from this point to the bottom of the TZFBR; for example, the sample taken at $h_s = 1$ cm ($0 < h_s < h_a$), was in the regeneration zone and the sample taken at $h_s = 14$ cm ($h_a < h_s < H$) was in the reaction zone. Then, besides the operating conditions, the influence of the axial position was studied.

Fig. 1 shows a schematic drawing of both the FBR and the TZFBR reactors.

In order to obtain the coke content in the catalyst samples, these samples were analyzed by thermogravimetric procedure in a Mettler-Toledo TGA/SDTA 851^e micro-thermobalance by combustion tests at non-isothermal conditions under air flow (50 cm³ (STP)/min). In these temperature-programmed oxidation (TPO) experiments, the temperature was programmed from 30 to 800 °C with a heating rate of 5 °C/min [15].

Vacuum transient experiments were carried out in the TAP-2 reactor in single pulse mode to know the influence of coke content of catalyst, on propane dehydrogenation. A detailed description of the equipment is given elsewhere [1]. Therefore, only the specific conditions used in the present work are outlined below. In each experiment, the Pt-Sn-K/ γ -Al₂O₃ catalyst sample ($d_p = 160$ – 250 μm) was placed in the micro-reactor made of steel between two inert zones. The inert material is used to thermally

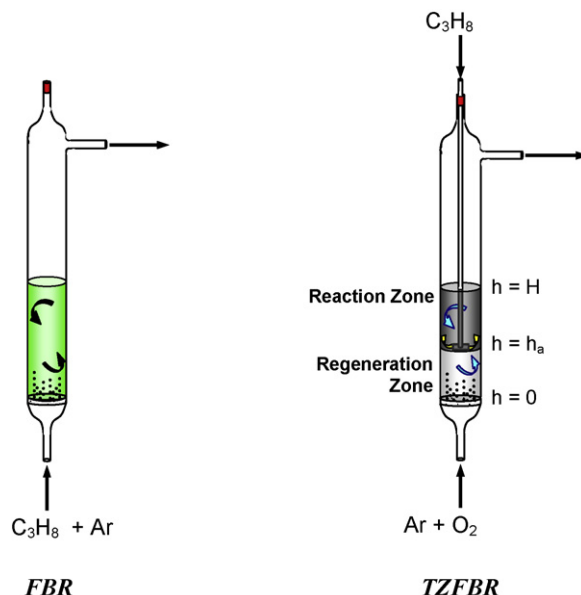


Fig. 1. Schematic drawing of FBR and TZFBR.

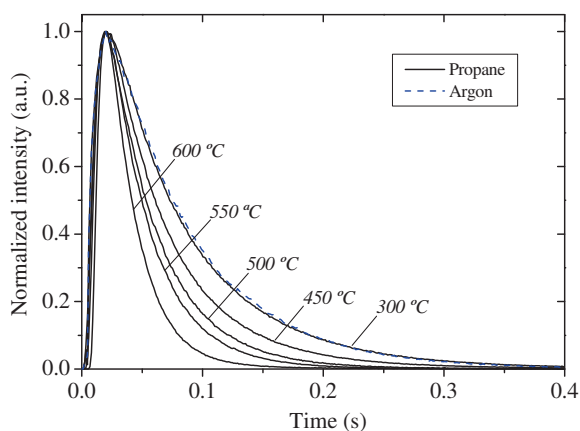


Fig. 2. Height-normalized flow of transient responses for argon and propane at different temperatures. 20 mg of Pt-Sn-K/ γ -Al₂O₃ catalyst.

insulate the catalyst, and reduce axial temperature gradients in the catalyst bed [1]. The TAP experiments were performed through the admission of a single pulse onto the catalyst (10 experiments were averaged in order to increase the signal-to-noise ratio). The range of operating conditions was as follows: temperature, 300–600 °C; molar fraction of propane, 0.5; molar fraction of argon, 0.5; catalyst weight, 20 mg. The catalyst was heated to the desired reaction temperature under vacuum at a rate of 10 °C/min. The response signals to the gas pulses at the reactor outlet were recorded by a quadrupole mass spectrometer and smoothed. Mass peak at $m/e = 40$, and $m/e = 29$ were used to monitor the responses of argon and propane, respectively. Pulse intensities of $<10^{15}$ molecules per pulse were used to insure Knudsen flow conditions. Quantification of the results, i.e. calculation of propane conversion, was performed using argon as internal standard. Knudsen diffusivities for all species were determined by experiments over a quartz bed.

$$M_0 = \frac{1}{\cosh \sqrt{k'_a \varepsilon_b L_{cat}^2 / D_{e,cat}} + (D_{e,cat} L_{II} / D_{e,II} L_{cat}) \sqrt{k'_a \varepsilon_b L_{cat}^2 / D_{e,cat}} \sinh \sqrt{k'_a \varepsilon_b L_{cat}^2 / D_{e,cat}}} \quad (3)$$

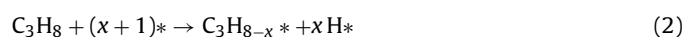
In TAP experiments, the observable quantity or experimental response is an ion current produced in the ionizer of the mass spectrometer. The intensity of the current is proportional to the flow of the corresponding component, so the measured variable is the exit flow rate [2]. TAP response data can be expressed in a normalized form by dividing the flow that exits the reactor by the number of moles in the input pulse. This quantity is called the normalized flow and is used in the analysis of pulse response experiments. So, the normalized flow of component i is given by F_i / N_{pA} where F_i is the exit flow of gas i and N_{pA} is the number of moles of limiting reactant gas A in the inlet pulse [3]. Taking this into account, the propane conversion at a temperature T was obtained from the following mass balance, assuming no propane conversion at 300 °C:

$$X_{C_3H_8} = \frac{PI(300^\circ C) - PI(T)}{PI(300^\circ C)} \quad (1)$$

where PI is the integral of normalized flows over the total time interval.

Several studies show that properties of pulse response curves give information about the processes that occur during the reaction. Fig. 2 shows the transient responses for argon and propane when a 1:1 mixture of propane/argon was pulsed over a Pt-Sn-K/ γ -Al₂O₃ catalyst, at different temperatures under vacuum. The height-normalized flows of transient responses of propane were used to facilitate time comparison. At 300 °C, the pulse response curves

of argon and propane are equal, i.e., the zeroth moment (M_0) of the exit flow rate in the TAP reactor are 1, so there is no conversion of propane at this temperature; and the transient responses curves present typical diffusion curves shapes. When these height-normalized flow were compared at higher temperatures, it may be seen that the width of the peak decrease with the temperature, and the peak area also decreases, i.e. lower amount of propane moles leaves the reactor. Furthermore, the height-normalized flow for the diffusion-only case (experiment at 300 °C) is higher than the curves obtained at higher temperatures and they do not cross the curve for the only-diffusion case. This result has also been observed by several authors [1,2] and constitutes a fingerprint for irreversible first-order reactions. So, from the propane pulse response shape as a function of the temperature (Fig. 2) it was deduced that the reaction of propane runs irreversible over the catalyst and the following reaction is assumed that agree with the fact that the limiting step of light paraffins dehydrogenation on platinum catalysts is the dissociative adsorption of paraffins with elimination of at least the first hydrogen atom [15]:



where * represent an active site of the catalyst.

Furthermore it was assumed that this reaction is first order in propane and the number of active sites does not change by admitting a lower series of single propane pulses. This last condition is usually fulfilled as typically the quantity of gas molecules pulsed (1–5 nmol) amounts to 1–10% of the number of active sites [1]. The apparent constant rate, k'_a , corresponding to a given conversion can be calculated by modeling the full pulse response curve or by a moment analysis. In the case of moment analysis, for first order irreversible reaction, the analytical expression for zeroth moment of the exit flow rate can be determined following the method described by Phanawadee [2] in which the set of equations were transformed into Laplace domain. So, the apparent constant rate, k'_a , could be calculated from the experimental data with the following expression for the zeroth moment:

where k'_a has a temperature dependence described by the Arrhenius equation in a re-parameterised form. When an irreversible reaction occurs, the conversion is related with the zeroth moment [1] by

$$X_{C_3H_8} = 1 - M_0 \quad (4)$$

3. Results and discussion

In a previous study [15], coke formation during propane dehydrogenation over a Pt-Sn-K/ γ -Al₂O₃ catalyst was studied as a function of time with thermogravimetric experiments. The coke content increases rapidly with time-on-stream during approximately the first ten minutes followed by a more moderate linear increase during the rest of the reaction stage. A monolayer-multilayer coke deposition model successfully describes the coking behaviour of catalyst during propane dehydrogenation. Several samples of Pt-Sn-K/ γ -Al₂O₃ catalyst with different coke content, i.e., diverse time-on-stream, were obtained after propane dehydrogenation in a conventional fluidized bed reactor. These samples of catalysts were studied in the TAP-2 reactor system by pulse a 1:1 C₃H₈/argon mixture at different temperatures. Fig. 3 shows propane conversion obtained by mass balance (Eq. (1)) as a function of temperature for these samples. As the time-on-stream increases, propane conversion decreases, due to the increase of coke concentration in the surface of catalyst, which reduces the activity of catalyst. Moreover, after the first min-

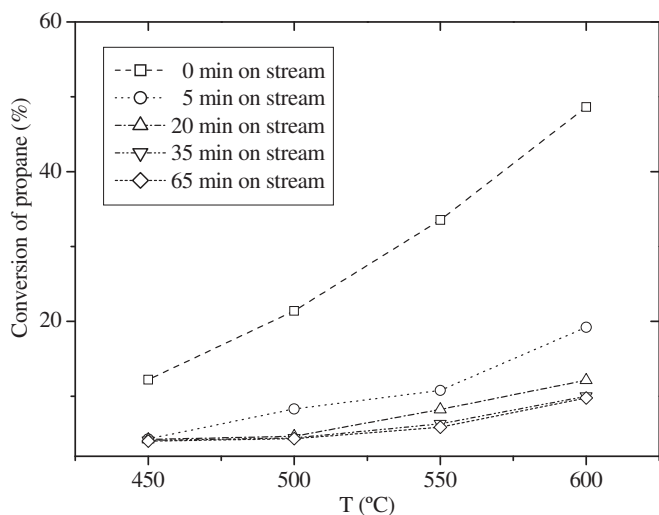


Fig. 3. Propane conversion versus temperature. Samples are gotten in a conventional FBR at different times-on-stream. Transient experiments of pulses of a 1:1 C₃H₈/argon mixture over Pt–Sn–K/γ–Al₂O₃ catalyst, W_{cat} = 20 mg (symbols are experimental data and the lines are a visual help).

utes on-stream, when the monolayer of coke was formed over the catalyst surface, the decrease of propane conversion slows down.

The propane transient response obtained was fitted at different temperatures. To do this, using the above model and appropriate boundary conditions, the series of propane transient responses, at different temperatures, were modeled. The optimal values of k'_{a0} and E_a were obtained (Table 2) in the fitting of experimental responses by minimizing the sum of squared residuals of the normalized MS-signal, using a Laplace and Fast Fourier transformations. The values of activation energy, E_a , obtained, were close and they slightly increase with time-on-stream, i.e., with the coke content of the catalyst. In order to compare the k'_{a0} obtained for the different samples, E_a was fixed at an average value of 71 kJ/mol and the curves were fitted again. Results obtained are plotted in Fig. 4. It may be seen that the ratio $k'_{a0}/k'_a(0 \text{ min})$, that is equal to $k'_a/k'_a(0 \text{ min})$ taking into account that E_a has been set at a constant value, markedly decreases when the coke content in the catalyst increases, i.e. during the first minutes on-stream, and then this decrease is less steep. This change in the slope is because of the coke multilayer content in the catalyst increase with time-on-stream, as is expected from the kinetic model on coke formation previously developed [15].

Propane dehydrogenation over Pt–Sn–K/γ–Al₂O₃ catalyst in a two-zone fluidized bed reactor (TZFBR) has been studied under a variety of operating conditions [11]. The main reactor-related variables studied were: the amount of oxygen fed to the reactor as percentage of the total feed flow in the bottom of the reactor, the bed temperature (T), and the relative height of the regeneration and reacting zones, $((H - h_a)/h_a)$. The most significant conclusions were:

Table 2

Values of activation energies and pre-exponential factor for the apparent reaction rate constants obtained by numerical solution. TAP conditions in Fig. 3.

Sample (TOS in FBR)	E_a (kJ/mol)		k'_{a0} (s ⁻¹)	
	Value	S.D. 95% C.I.	Value	S.D. 95% C.I.
0 min	69.65	± 3.44	8.03E – 2	± 0.56E – 2
5 min	70.58	± 2.14	2.28E – 2	± 0.69E – 2
20 min	70.82	± 1.39	1.01E – 2	± 0.38E – 2
35 min	72.04	± 1.45	9.69E – 3	± 0.13E – 2
65 min	72.80	± 2.08	1.11E – 3	± 0.64E – 3

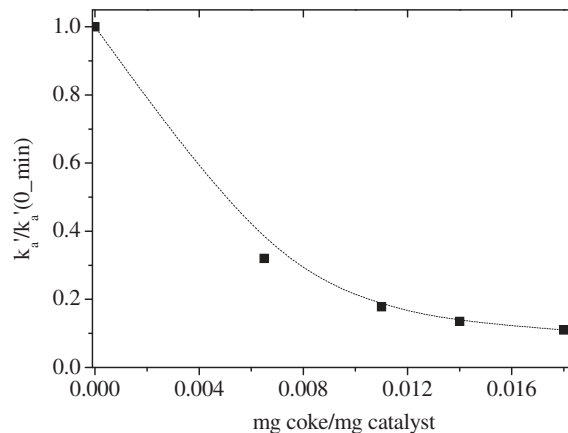


Fig. 4. $k'_a/k'_a(0 \text{ min})$ versus coke concentration. Samples are gotten in a conventional FBR at different times-on-stream (symbols are experimental data and the line is a visual help).

- The coke content in the catalyst is influenced by the point of the reactor in which the sample was taken. The samples taken in the reaction zone have coke content higher than the samples taken in the regeneration zone.
- Coke formation during the propane dehydrogenation in a TZFBR increases with low amounts of oxygen fed in the reactor, high temperatures and relatively small regeneration zones $((H - h_a)/h_a) > 1$.

In order to study the behaviour of TZFBR, the experiments collected in Table 1 were performed and diverse samples of catalyst were taken at different axial positions in the reactor. These samples were studied in the TAP-2 reactor system with pulses of a 1:1 C₃H₈/Ar mixture at different temperatures. In each case, the conversion of propane is obtained by mass balance with Eq. (1). As stated above, applying the moment analysis to the TAP response data, Eq. (3) can be used to determine the apparent reaction rate constant, k'_a , from experimental data. In an Arrhenius plot (not shown) $\ln k'_a$ is plotted versus $1000/T$ and the value of activation energy was obtained from the slope.

The results obtained with TAP studies, confirm the trends observed in the performance of propane dehydrogenation in a TZFBR [12], where the coke content on the catalyst was a key factor for the yields reached. To illustrate this, Fig. 5 shows propane conversion along the catalyst bed for 10 samples that were taken at different bed length in experiments performed with two different O₂ flow fed in a TZFBR [12]. In the TAP experiments performed with the samples taken after propane dehydrogenation with 15% O₂, higher conversion of propane was obtained. This could be explained because with more oxygen fed, more coke is burned and the activity of the catalyst is higher in propane dehydrogenation. These results are consistent with those obtained in a previous works [10–13].

The activation energy obtained from the moment analysis is plotted versus the coke content (Fig. 6) for the different variables studied. It may be seen that for all the operating conditions, the samples with higher amount of coke show higher activation energy than the others. Moreover, Fig. 6a shows two groups of samples: samples taken in the regeneration ($0 < h_s < h_a$) zone and samples taken in reaction zone ($h_a < h_s < H$), with higher coke content, and clearly, the latter have higher activation energy.

As said above, the coke content in the catalyst decreases with the amount of oxygen used in the TZFBR test; therefore the samples taken after the test performed with 15% O₂, have lower coke content and show higher values of propane conversion and lower values of E_a (Fig. 6a). The coke content in the catalyst surface increases with reaction temperature (Fig. 6b), and it causes the decrease of the cat-

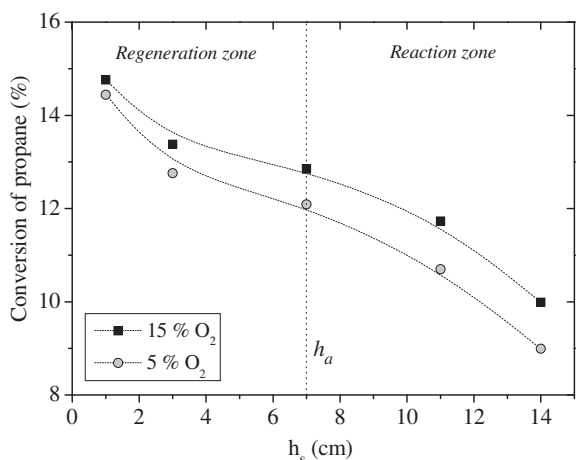


Fig. 5. Propane conversion along the catalyst bed for samples obtained in experiments performed with different O_2 flow fed in the TZFBR (operating conditions are collected in Table 1). Transient experiments of pulses of a 1:1 C_3H_8 /argon mixture, $W_{cat} = 20$ mg, $T = 600^\circ C$ (symbols are experimental data and the lines are a visual help).

alyst activity, that has been observed by several authors [15–21]. For example samples from experiments in TZFBR at $540^\circ C$ show higher activation energy (Fig. 6b) and a lower propane conversion in the TAP experiment. The ratio between the heights of the reaction and regeneration zones, $((H - h_a)/h_a)$, has two effects on the operation of the TZFBR. An increase in this ratio involves a lower

WHSV in the reaction zone and a smaller size of the regeneration zone. With a larger regeneration zone, the equilibrium between coke formation and coke combustion in the TZFBR will be reached at lower coke content and so the activity of the catalyst will be higher (Fig. 6c). The samples that are obtained in experiments performed in TZFBR with higher regenerating zone (lower values of $((H - h_a)/h_a)$) have a lower coke content and show a lower values of activation energy (Fig. 6c) and a higher conversion of propane.

Unlike a FBR, the TZFBR allows working continuously, with “in situ” catalyst regeneration. Therefore, when both constant exit flow rates and constant effluent compositions are achieved in a TZFBR, equilibrium has been reached between coke formation in the reacting zone and coke burning in the regeneration zone. This implies that coke deposits in the catalyst surface are burned at the same rate as they are formed [12].

Fig. 7 shows the derivative of the weight curve for samples of Pt-Sn-K/ γ - Al_2O_3 catalyst taken in a FBR, at different time-on-stream (Table 2). It may be seen that for all samples the coke combustion rate reaches a peak at $370^\circ C$ and this peak becomes more marked as the time-on-stream increases, probably due to the increase of coke content in the catalyst. And other smaller peak at $445^\circ C$ was observed.

Samples taken at different heights of catalyst bed (h_s) in TZFBR, after propane dehydrogenation test ($T = 500^\circ C$; Ar: $C_3H_8 = 1:1$; $((H - h_a)/h_a) = 2$; $H = 14$ cm; $h_a = 5$ cm; $5\% O_2$; $u_{r1} = 2.8$) were analyzed by TPO. The results obtained were collected in Fig. 8. For all samples, the coke combustion rate reaches a peak at $445^\circ C$; moreover, as said above, the coke content increases along the bed length (Fig. 6c). So, for the sample taken in the regeneration zone ($h_s = 1$ cm) the

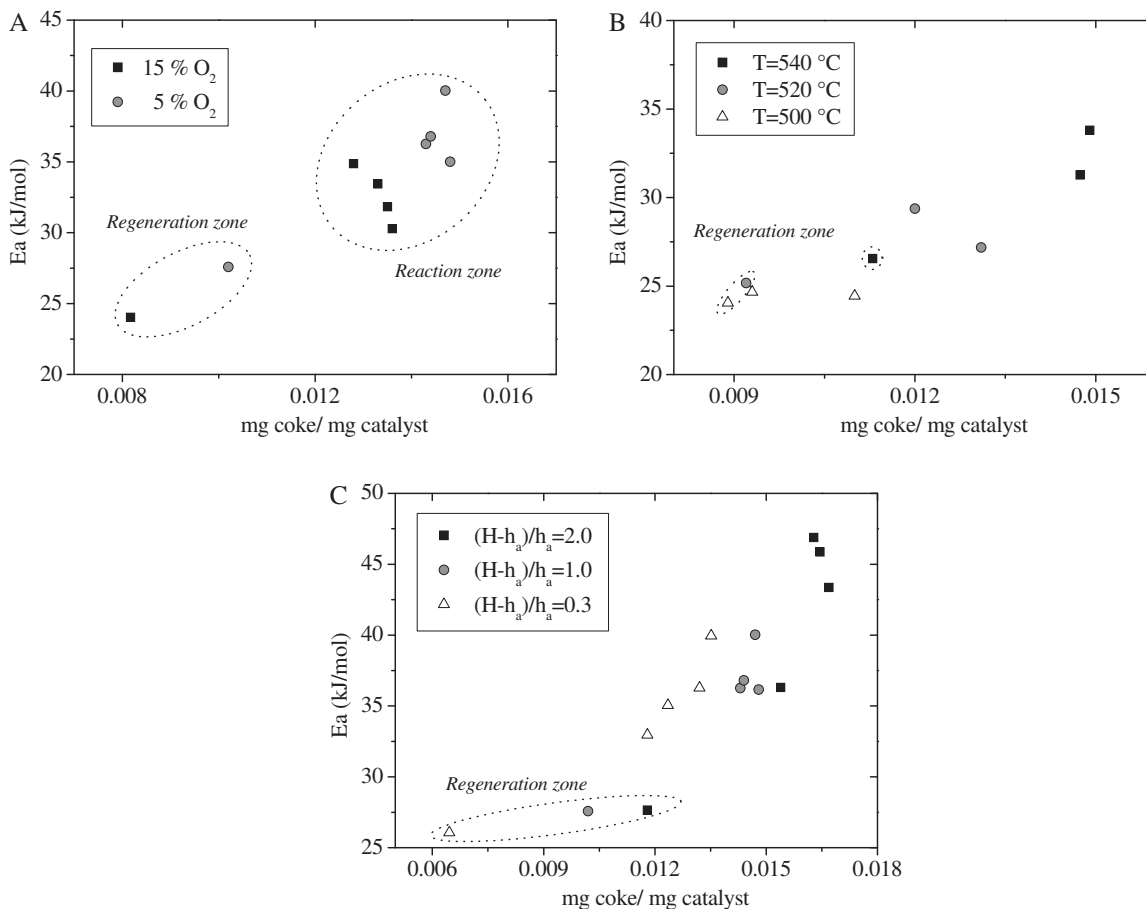


Fig. 6. Activation energy versus coke concentration: (a) for two different O_2 flow fed in the TZFBR; (b) for different reaction temperatures in the TZFBR and (c) for samples obtain in experiments performed with different $(H - h_a)/h_a$ ratios in a TZFBR.

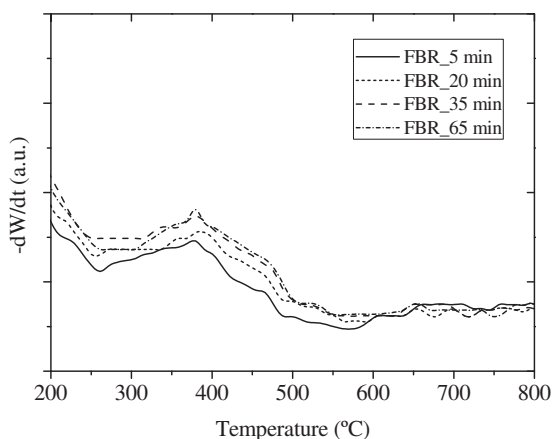


Fig. 7. Temperature-programmed oxidation of the coke deposits on the catalyst after propane dehydrogenation in a FBR (different time-on-stream).

amount of the coke is so low that TPO results indicate an insignificant weight loss. For the rest of samples, the peak at 445 °C is higher. Furthermore, as the coke content of the samples increases (larger sampling point height, h_s) this peak increases.

In TPO profiles, derived from Pt-based catalyst for dehydrogenation of alkanes, the peak obtained at low temperature (280–370 °C) was attributed to coke deposited on or in contact with metal sites. The intermediate temperature peak at 445 °C is associated with coke on acid sites close to the metal; and depending of reaction temperature, other peak could appear at higher temperature (>570 °C), which is produced by coke on acid sites far away from any metal sites [20,22–25].

These results may suggest that, for samples taken in FBR, the peak at 370 °C corresponds to coke deposited on or in contact with metal sites and the smaller peak at 445 °C could be associated with the coke on acid sites close to the metal. However, the first peak did not appear in the samples of TZFBR and the intermediate temperature peak at 445 °C increases respect FBR. Therefore, in the TZFBR, the regeneration of coke deposited on or in contact with metal sites take place, in such way that the metal sites may be free of coke and it would be on acid sites close to the metal. This is consistent with experimental evidences found in TAP test regarding the differences between the activation energy obtained with the samples taken in a FBR (71 kJ/mol) and with the samples taken in a TZFBR (24–47 kJ/mol). Then the metal particles and the acid sites may act during propane dehydrogenation as two active sites of Pt–Sn–K/ γ -Al₂O₃ catalyst with different activation ener-

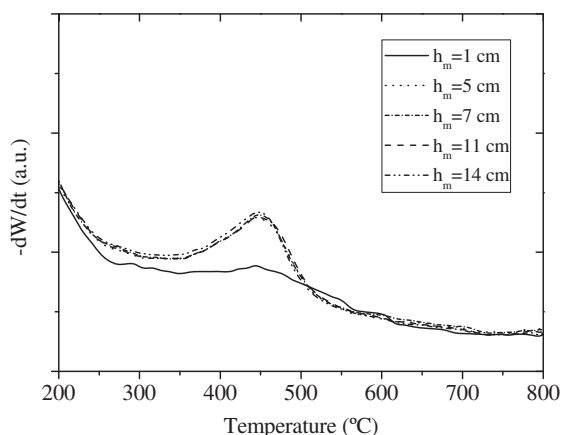


Fig. 8. Temperature-programmed oxidation of the coke deposits on the catalyst after propane dehydrogenation in a TZFBR (different height of catalyst bed, h_s).

gies, indicating that the samples of catalyst taken in a TZFBR are more actives for propane dehydrogenation, probably due to there is no coke on metal sites of the catalyst. It must be also taken in account that propane is converted to propene and also to cracking products and this last reaction occurs mainly in acid sites [14]. In a previous kinetic study with the same catalysts, we have found an activation energy 34.6 kJ/mol for propane dehydrogenation and 137.3 kJ/mol for cracking reaction, then TAP studies of propane conversion shows intermediated activation energy for FBR, and in cases of TZFBR, where acid sites are coked, shows more close activation energy to propane dehydrogenation.

The change in activation energy with the coverage by coke may seem surprising at first glance, but may be expected if the catalytic surface is not homogeneous. The usual approach to the deactivation kinetics assumes that all the active sites are equal, and therefore the catalyst deactivation only changes the number of active sites available but not the activation energy. However, some authors have pointed that actual catalytic surfaces are not homogeneous (e.g. Butt et al. [26]), and that active sites with a distribution of strength may exist (i.e. with a distribution of activation energies). Such heterogeneity of the catalytic surface affects the deactivation kinetics and the separability of the activity in the reaction kinetics [27]. In fact, it is quite intuitive that the most active sites will be deactivated faster, and therefore the mean activation energy of the remaining sites will be different from that of the fresh catalyst. In the case of the bifunctional catalyst studied in this work, the heterogeneity of the surface also came from the existence of two kinds of active sites (i.e. metal particles and acid sites).

4. Conclusions

TAP studies have been done in samples taken from a conventional fluidized bed reactor (FBR) and from a two-zone fluidized bed reactor (TZFBR) at different operating conditions. The main conclusion of this work is that in a FBR reactor, the catalyst deactivation by coke deposition does not have influence in the activation energy for propane dehydrogenation; however in a TZFBR this activation energy is markedly influenced by the quantity of coke over the catalyst surface. This fact is related to the nature of the coke. The low temperature coke, identified in TGA analysis, is burning in the oxidizing zone of TZFBR while the intermediated temperature coke remained. This study shows the TAP as an interesting tool to study the influence of amount and nature of coke in dehydrogenation reactions.

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