



Deactivation and regeneration of Pt/Al₂O₃ catalysts during the hydrodechlorination of carbon tetrachloride

T.F. Garetto^{a,*}, C.I. Vignatti^a, A. Borgna^b, A. Monzón^c

^a GICIC, Instituto de Investigaciones en Catálisis y Petroquímica INCAPE (FIQ-UNL-CONICET), Santiago del Estero 2654, (3000) Santa Fe, Argentina

^b Institute of Chemical and Engineering Sciences (ICES – A*Star), 1 Pesek Road, Jurong Island 627833, Singapore

^c Department of Chemical and Environmental Engineering, Faculty of Science, University of Zaragoza, 50009 Zaragoza, Spain

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ABSTRACT

Deactivation and regeneration of Pt/Al₂O₃ catalysts during the hydrodechlorination of carbon tetrachloride were studied. The effect of reactant partial pressures and temperature on the catalyst deactivation was investigated. A deactivation model with residual activity was developed to quantify the kinetic deactivation parameters. The effect of the regeneration atmosphere was also investigated. Regeneration under air allowed for the full recovery of the catalytic performance of fresh catalysts while treatments under flowing hydrogen resulted in a superior catalytic performance, increasing both the initial and residual activities. This was ascribed to a combined effect, redispersion of the metallic phase and formation of surface defects.

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1. Introduction

Volatile chlorinated organic compounds (VOC-Cl), especially carbon tetrachloride (CTC), are pollutants widely disseminated in the atmosphere, residual waters and contaminated soils. These compounds are harmful for the environment, responsible for the destruction of the ozone layer, and dangerous for human health but, since the Montreal Protocol signed in 1996, their consumption has been strongly reduced. High-temperature thermal incineration (ca. 900 °C), catalytic combustion (ca. 500 °C), and catalytic hydrodechlorination (HDCl) at low temperatures (200 °C) are the most common methods for the abatement of chlorinated organic compounds. While combustion processes are highly energy intensive processes since they require high temperatures to reach full combustion, and can lead to the formation of highly toxic partial oxidation products such as CO, dioxines and phosgene (COCl₂), catalytic HDCl requires significantly lower temperatures (100–200 °C) and rules out any possibility of generating partial oxidation products. Besides, it has the additional advantage of allowing the recovery and eventual recycling of the non-chlorinated hydrocarbon, and the

obtention of by-products such as CHCl₃ and HCl. In order to carry out the HDCl of VOC-Cl's reactions, noble metal (Pt, Pd and Rh) supported catalysts are usually employed. However, severe catalyst deactivation is the main drawback of the hydrodechlorination catalytic process.

Catalysts based on noble metals Pt, Pd and Rh [1–3], transition metals such as Ni [4], and bimetallic catalysts are active in hydrodechlorination reactions.

Some authors [1] have studied the effect of particle size and metallic dispersion on activity in the hydrodechlorination reaction. In general, small particles rapidly deactivate due to strongly adsorbed chlorine [5,6] and to an increase in coke formation. On the contrary, larger particles having surface metallic atoms with high coordination numbers would adsorb CTC slightly weaker and, therefore selectivity to CHCl₃ and the catalyst stability might be increased [7].

Ohnishi et al. [8] reported that Pt, Pd, Rh and Ru catalysts are active and selective for the abatement of chlorine atoms but have a high metallic load. Depending on the reaction conditions and the type of reactant, Pt/Al₂O₃ catalysts are efficient for the removal of chlorine atoms. Several papers have been published using platinum-based catalysts [9–12] in dehalogenation of volatile organic compounds.

Process variables such as temperature, pressure and reactant concentration also have an influence on deactivation. In Pd catalysts,

* Corresponding author. Tel.: +54 342 4533858; fax: +54 342 4531068.

E-mail address: tgaretto@fiq.unl.edu.ar (T.F. Garetto).

Nomenclature

a	activity
a_s	residual activity
D	metallic dispersion (%)
h	number of active sites involved in the controlling step of the side reaction responsible for the deactivation
k	kinetic constant rate
k_d	intrinsic kinetic constants of deactivation
k_r	intrinsic kinetic constants of regeneration
m	number of active sites involved in the controlling step of the main reaction, hydrodechlorination of CTC
m_0	kinetic order respect to H_2
n_0	kinetic order respect to CTC
n_d, m_d	kinetic orders with respect to CTC and H_2 , for ψ_d
n_r, m_r	kinetic orders with respect to H_2 , for ψ_r
p_{CTC}	partial pressure of CTC
p_{H_2}	partial pressure of H_2
$(-r_{CTC})_0$	initial reaction rate
$(X_{CTC})_0$	initial conversion
$(X_{CTC})_s$	residual conversion
<i>Greek symbols</i>	
ψ_G	global kinetic function
ψ_d	deactivation kinetic function
ψ_r	regeneration kinetic function

it has been found that when the reaction is carried out at high temperature, the initial activity is high but the deactivation is fast. It has also been reported that high H_2 concentration increases both the catalyst activity and stability [3,13,14]. In order to optimize the process, not only the catalyst composition should be taken into account but also the most appropriate operation conditions to obtain high catalyst activity, stability and selectivity.

In order to analyze the causes and consequences of deactivation during the HDCl reaction of Pt/ Al_2O_3 catalysts with low metallic load, we studied the influence of the partial pressure of reactants and temperature on the catalytic activity and deactivation rate. In addition, we analyzed the effect of different regeneration treatments on the kinetic behaviour in the HDCl reactions of CTC. In order to study the effect of the deactivation and regeneration treatments, we developed a deactivation model with residual activity (DMRA) whose parameters depended on the operating conditions.

2. Experimental

2.1. Catalysts

Platinum supported on commercial γ - Al_2O_3 (Cynamid, CK-300) was employed. The CK-300 alumina has as a BET area of $180 \text{ m}^2/\text{g}$ and a pore volume of $0.49 \text{ cm}^3/\text{g}$. The catalysts were prepared by incipient wetness impregnation, employing H_2Cl_6Pt (Aldrich) or $Pt(NH_4)_4(NO_3)_2$ (Alfa) as metallic precursors. Two catalysts were prepared: one with chlorine on the support, PC, the other without chlorine on the support, PNC. Impregnations were performed at room temperature for 6 h, and the drying at $120 \text{ }^\circ\text{C}$ for 12 h [15]. Calcinations were performed at $500 \text{ }^\circ\text{C}$ in air for 6 h. The catalysts

Table 1

Main characteristics of the catalysts used in this work.

Catalyst	Support	Sg (m^2/g)	Cl (%)	Pt (%)	D (%)
PC	Al_2O_3	180	0.92	0.40	70
PNC	Al_2O_3	175	–	0.41	60

were finally reduced in H_2 at $500 \text{ }^\circ\text{C}$ for 4 h. Table 1 shows the characteristics of the catalysts used in the present work.

2.2. Catalysts characterisation

Pt dispersion was determined by H_2 chemisorption. Volumetric adsorption experiments were performed at $25 \text{ }^\circ\text{C}$ in a vacuum equipment with an MKS Baratron pressure gauge. The catalysts were previously reduced in H_2 flow at $400 \text{ }^\circ\text{C}$ and then evacuated at $500 \text{ }^\circ\text{C}$ prior to the chemisorption experiments. The hydrogen consumption was determined by the double isotherm method. After cooling at room temperature, the first isotherm corresponding to total hydrogen consumption was obtained (HC)_t. After 1 h evacuation at room temperature, the second isotherm was obtained to determine the amount of weakly adsorbed hydrogen (HC)_r. The amount of irreversible H_2 , (HC)_i was calculated as the difference between (HC)_t and (HC)_r. The isotherm pressure range was 1–100 Torr. A stoichiometric ratio (HC)_i/Pt = 1 was used to calculate Pt dispersion.

The Pt content was determined by atomic absorption spectroscopy. The specific surface (Sg) was determined by N_2 physisorption at $-196 \text{ }^\circ\text{C}$ using a Quantachrome Nova-1000 sorptometer and BET analysis. The TEM studies were carried out using JEOL 100X-CX equipment operated at 100 kV.

Coke formed on the catalysts during reaction was measured by temperature-programmed oxidation (TPO). Samples (20–50 mg) were heated in a 3% O_2/N_2 stream at $10 \text{ }^\circ\text{C}/\text{min}$ from room temperature to $600 \text{ }^\circ\text{C}$. The evolved CO_2 was converted to methane by means of a methanation catalyst (Ni/kieselghur) operating at 673 K and monitored using a flame ionization detector.

2.3. Reaction studies

The hydrodechlorination reaction of CTC (Merck 99.5%) was carried out at 1 bar in a fixed-bed tubular reactor (9 mm o.d.). The temperature was measured with a J-type thermocouple placed into the catalytic bed. In all cases a H_2/CTC ratio of 28 and a catalyst weight (W) of 0.1 g were used. The existence of internal and external diffusional limitations was studied varying particle size between 0.15 and 0.5 mm; and contact times between 100 and 700 g catalyst h mol^{-1} CTC, respectively. In order to avoid internal diffusional effects, the fraction with particle diameter ranged from 0.35 to 0.42 mm, and varying contact times between 300 and 600 g catalyst h mol^{-1} was selected for the kinetic experiments. The CTC was fed by means of a syringe pump and vaporized in H_2 flow before entering the reaction zone. The gaseous stream was analyzed on-line using a Varian 3380 GC equipped with an FID detector and a packed Chromosorb 102 column 1/8 in. \times 3 m. The reactor outlet, containing the reaction products and non-converted reactants was bubbled in a NaOH solution employing methyl orange as indicator in order to adsorb the generated HCl. In every case, and prior to the hydrodechlorination reaction, the catalysts were reduced in situ in H_2 flow at 300 for 1 h. The reaction products detected were CH_4 and $CHCl_3$. In addition, to minimize experimental errors, all catalytic experiments have been performed at least twice. In all cases, low dispersion of the values has been obtained and average values have been used.

3. Results and discussion

3.1. Catalyst characterisation

Table 1 shows the specific surface, metal loading, chlorine level and Pt dispersion (D) values of two different catalysts. As it can be observed, both catalysts present practically the same specific surface and dispersion values. These values are not affected by the precursor employed in the impregnation step, i.e. these values are independent of the nature of platinum precursors.

3.2. Influence of the operating conditions

This section analyzes the influence of both the operation temperature and the partial pressure of the reactants on catalyst activity, selectivity and stability during the hydrodechlorination of CTC.

3.2.1. Influence of H_2 partial pressure

In order to study the influence of the partial pressure of H_2 , catalytic tests were carried out at 100 °C and the partial pressure of CTC was kept constant at 0.044 atm. The partial pressure of H_2 was varied between 0.3 and 1 atm. Fig. 1a shows the time-evolution of the conversion at different partial pressures of H_2 . This figure reveals that CTC conversion decreases as a function of time for different partial pressures of H_2 . The same behaviour was observed in the PNC catalyst (Fig. 1b). It can be observed that when the H_2 /CTC ratio increased, both the initial (X_{CTC}^0) and steady-state conversions (X_{CTC}^s) increased. Therefore, the partial pressure of H_2 has a beneficial effect on the catalytic activity.

3.2.2. Influence of CTC partial pressure

In order to determine the influence of the CTC partial pressure, several experiments were carried out at 100 °C and a constant H_2 partial pressure equal to 0.956 atm. The CTC partial pressure varied between 0.025 and 0.08 atm. Under these conditions, the H_2 /CTC ratio varied between 12 and 38. Fig. 2 shows the time-evolution of the conversion as a function of the CTC partial pressure. The results obtained show that when the CTC partial pressure increases it produces a slight increase in the initial conversion. However, the residual conversion decreases dramatically when the CTC partial pressure increases. This fact shows that the catalyst deactivation is strongly affected by the concentration of CTC in the reaction atmosphere. Besides, in all cases the residual activity of the catalyst decreases as the H_2 /CTC ratio decreases.

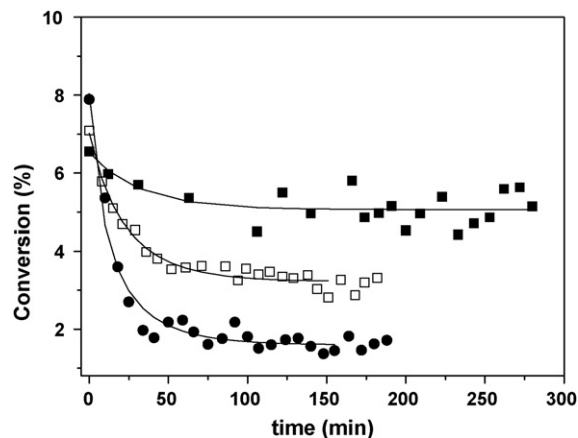


Fig. 2. Influence of the CTC partial pressure. (■) $p_{CTC} = 0.032$ atm; (□) $p_{CTC} = 0.044$ atm; (●) $p_{CTC} = 0.051$ atm. Catalyst PC. Solid lines: model data.

3.2.3. Influence of temperature

In order to study the influence of temperature, experiments were performed in 100–130 °C temperature range, at fixed H_2 and CTC pressures (0.956 and 0.032 atm, respectively). Fig. 3 shows the results obtained. Note that when the temperature increases, both the initial and residual conversions also increase.

From the values of the initial slope of the conversion–time curves, it can be observed that as the temperature increases, the deactivation rate also increases. Similar results were obtained by other authors [16] employing Pd catalysts.

3.3. Deactivation–regeneration cycles

In order to study deactivation processes, reaction–regeneration cycles were carried out analyzing both the regeneration atmosphere and temperature. Those deactivation–regeneration cycles had five consecutive steps and were designed in order to elucidate the effect of the reaction atmosphere during regeneration. The five steps corresponded to three reaction steps interspersed with two regeneration steps: (i) reaction at 100 °C; (ii) regeneration with H_2 or O_2 , at different temperatures (200, 350 and 500 °C); (iii) reaction as in step (i); (iv) regeneration as in step (ii); (v) reaction as in step (i).

3.3.1. Reaction–regeneration cycles in oxidant atmosphere

Fig. 4 shows the conversion vs. time plots obtained on the catalyst PC. Note that conversion decreases in all the reaction steps.

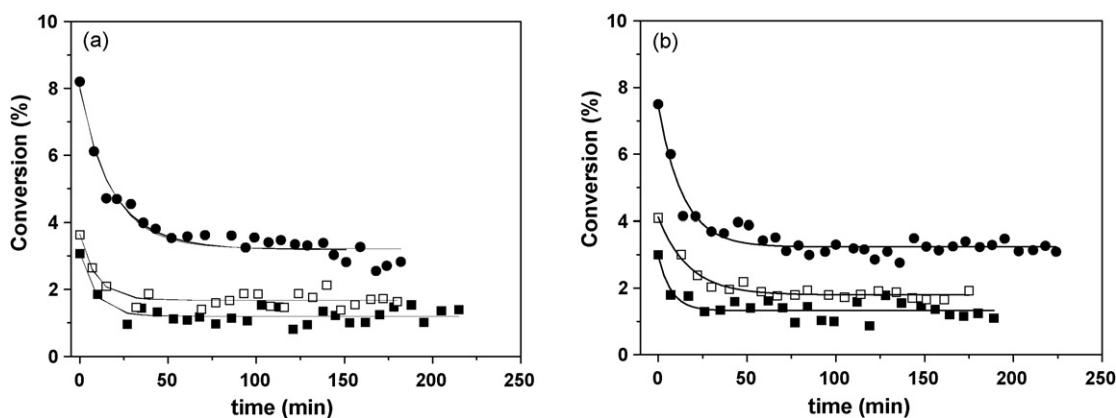


Fig. 1. (a) Influence of the H_2 partial pressure: (■) $p_{H_2} = 0.431$ atm; (□) $p_{H_2} = 0.755$ atm; (●) $p_{H_2} = 0.956$ atm. Catalyst PC experimental points. Solid lines: model data. (b) Influence of the H_2 partial pressure: (■) $p_{H_2} = 0.431$ atm; (□) $p_{H_2} = 0.755$ atm; (●) $p_{H_2} = 0.956$ atm. Catalyst PNC experimental points. Solid lines: model data.

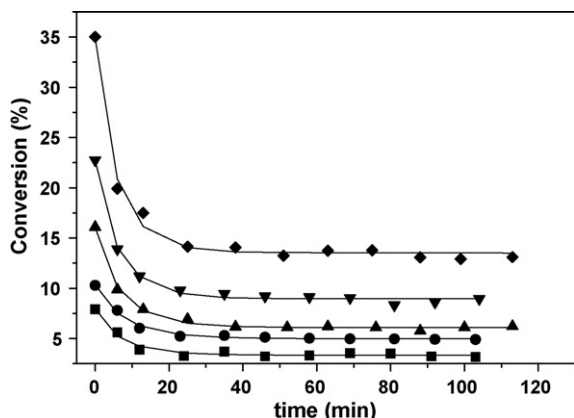


Fig. 3. Influence of the temperature. Catalyst PC. (■) $T = 100\text{ }^{\circ}\text{C}$; (●) $T = 110\text{ }^{\circ}\text{C}$; (▲) $T = 115\text{ }^{\circ}\text{C}$; (▼) $T = 120\text{ }^{\circ}\text{C}$; (◆) $T = 130\text{ }^{\circ}\text{C}$.

As the catalyst was subjected to a regeneration step for 1 h at $350\text{ }^{\circ}\text{C}$ in a mixture O_2 (3%)/ N_2 and subsequently to a second reaction step at $100\text{ }^{\circ}\text{C}$ (second run), the behaviour was similar to the one observed during the first reaction step (first run). The mixture O_2 (3%)/ N_2 employed in both experiments, TPO and regeneration steps, was the same. O_2 level employed in TPO experiments and temperatures reached not produced a modification of the accessible metal fraction according to the results obtained in sintering–redispersion studies [15]. After regeneration, a slight decrease in the initial conversion was also observed but after deactivation the residual conversion was similar to that of the first run. When the catalyst is again subjected to a regeneration step under the same conditions as in step (ii) and then a reaction is carried out at $100\text{ }^{\circ}\text{C}$ (third run), the deactivation produces a residual conversion similar to that of the first run but the initial conversion is slightly higher than that in the second run. The same behaviour was observed as the regeneration steps were carried out at 200 and $500\text{ }^{\circ}\text{C}$ (results not shown). The coke content at the end of each reaction step was determined by TPO measurements. The values obtained ranging between 0.23 and 0.29% C in all cases. Therefore, these results indicate that oxygen regeneration does not modify the subsequent coke formation and it allows recovering the catalyst initial activity but not an increase of the catalyst stability. Since these experiments were carried out without a reduction treatment after the regeneration step, it could be argued that the drop in the initial catalytic activity is due to the fact that the catalyst is not totally reduced. In order to explain this, we carried out O_2 regeneration experiments in which a subsequent reduction

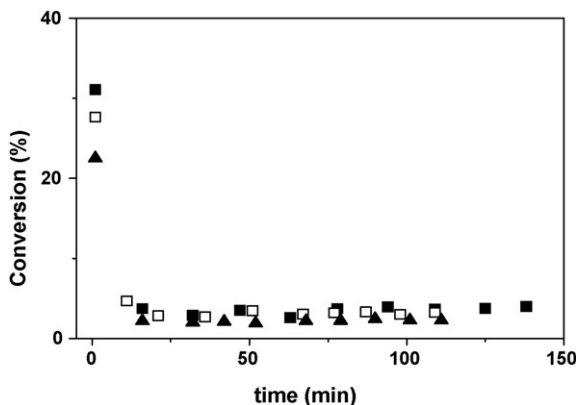


Fig. 4. Regeneration in oxidizing atmosphere. $T = 350\text{ }^{\circ}\text{C}$; (■) first run; (□) second run; (▲) third run.

of the catalyst was performed prior to the reaction. In this case, the results obtained are the same as those shown in Fig. 4, which allows us to rule out the possibility that catalyst is not active for not being totally reduced.

3.3.2. Reaction–regeneration cycles in reducing atmosphere

The catalysts were evaluated in reaction–regeneration cycles in H_2 at 200 , 350 and $500\text{ }^{\circ}\text{C}$. Fig. 5 shows CTC conversion results as a function of time on stream for the fresh and after regeneration in H_2 at $350\text{ }^{\circ}\text{C}$. It can be observed that after the first regeneration, and in second run, both the initial and the residual conversions are significantly higher than in the first run step. After the second regeneration, in the third reaction step, an increase in the residual activity is again observed (third run). When the regeneration steps were carried out at 200 or $500\text{ }^{\circ}\text{C}$, a similar behaviour was observed (results not shown).

On the other hand, the coke content of the samples was determined after the third reaction step (third run), obtaining a value of 0.03% , which is almost an order of magnitude lower than the one obtained with O_2 regeneration.

Different catalytic performances depending on either regeneration is performed under O_2 or H_2 . When the regeneration is carried out in oxidizing atmosphere, the catalyst surface is clean, i.e. free from the compounds which might act as coke precursors and the catalyst, after each regeneration step, practically behaves as the fresh catalyst. In addition, when the regeneration is carried out in reducing atmosphere, a different mechanism occurs which leads to a surface reorganization of Pt particles generating surface defects (see Fig. 10). These defects would be responsible of higher activity. The treatment of the catalyst deactivated in H_2 atmosphere was employed by other authors [14,17] in order to recover the catalyst activity.

3.4. Kinetic modelling of catalyst deactivation

In many deactivation process as the one being dealt within this paper, it can be noted that the catalyst deactivation is not complete, even at high operation times, reaching a certain level of residual activity. The presence of residual activity in a catalyst may be ascribed to various causes, such as the nature of the active surface or the mechanism through which the deactivation takes place. Depending on whether different types of sites exist on the catalysts surface, as mentioned above, the catalyst behaves either homogeneously or heterogeneously. Also depending on whether the coke deposition is produced reversibly or irreversibly, it may occur that the catalyst becomes totally deactivated after a certain time or, on the contrary, it maintains a level of residual activity during time on stream. In this latter case, it is necessary to use more complex kinetic models which would allow the adequate prediction of the catalyst behaviour during operation time. Kinetic deactivation models that take into account these aspects have been developed [15] which, based on reaction–deactivation mechanisms can theoretically predict the presence of residual activity.

In the present case, and since there is significant excess of hydrogen in the reaction atmosphere, this hydrogen reacts with the coke formed on the catalyst surface, partially regenerating it. This process accounts for the presence of some residual activity of the catalyst and how this residual activity is a function of the operation conditions [14,17,20–24]. Starting from the definition of activity [19,20], and given that the experiments are performed under differential conditions, it yields:

$$a(t) = \frac{(-r_{\text{CTC}})_t}{(-r_{\text{CTC}})_0} \Big|_{p_i, T} \Leftrightarrow (-r_{\text{CTC}})_t = (-r_{\text{CTC}})_0 a(t) \quad (1)$$

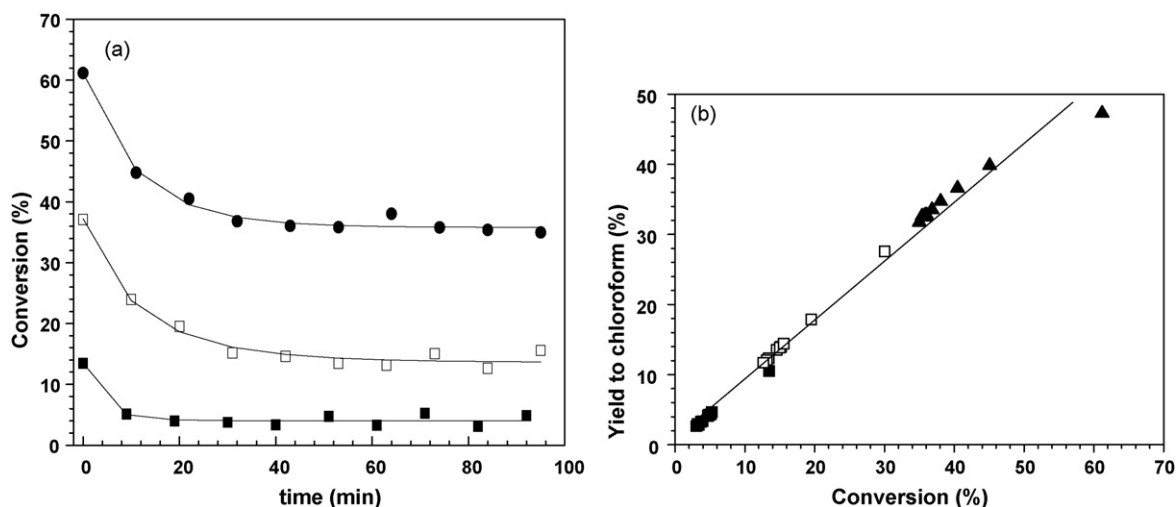


Fig. 5. (a) Regeneration with hydrogen. $T = 350$ °C; (■) first run; (□) second run; (●) third run. (b) Yield to chloroform during H_2 regeneration cycles: (■) first run; (□) second run; (▲) third run.

This expression allows us to obtain the evolution of conversion with time starting from the variability of catalyst activity with time. On the other hand, the initial reaction rate may be expressed as a function of the operation conditions using a power-law equation:

$$(-r_{CTC})_0 = k p_{CTC}^{n_0} p_{H_2}^{m_0} \quad (2)$$

In order to advance in the knowledge referring to catalyst deactivation, and in the analysis data of deactivation, kinetic models based on reversible deactivation mechanisms, DMRA [18,20–26] instead of empiric expressions we employed. Thus, assuming that the controlling step of the deactivation mechanism is reversible, the net deactivation rate is given by the following expression [22,23]:

$$-\frac{da}{dt} = \psi_d a^d - \psi_r (a - a^{d_m}) \quad (3)$$

where ψ_d and ψ_r are the deactivation and regeneration kinetic functions, respectively. These kinetic functions include the influence of the operation conditions on the catalyst deactivation kinetics. Thus, if a power-law dependence is assumed for both kinetic functions, the following expressions can be written:

$$\psi_d = k_d p_{CTC}^{n_d} p_{H_2}^{m_d} \quad (4)$$

$$\psi_r = k_r p_{CTC}^{n_r} p_{H_2}^{m_r} \quad (5)$$

The parameters k_d and k_r are the intrinsic kinetic constants of deactivation and regeneration, respectively and depends on the temperature according to the Arrhenius law. The parameters n_d , m_d , n_r , and m_r are the kinetic orders with respect to CTC and H_2 , for ψ_d and ψ_r , respectively. k_d and k_r also depend on the temperature according to the Arrhenius law.

According to DMRA mechanism, the kinetic orders d and d_m appearing in Eq. (3) are simple fitting parameters but are directly depending on the number of active sites involved in the deactivation mechanism, and are calculated by the following expression [18–21]:

$$d = \frac{m + h - 1}{m}; \quad d_m = \frac{m - 1}{m} \quad (6)$$

In this equation, m is the number of active sites involved in the controlling step of the main reaction, hydrodechlorination of CTC,

and h represents the number of active sites involved in the controlling step of the side reaction responsible for the deactivation.

The value of the residual activity of the catalyst, a_s , is calculated from the following condition for the deactivation rate: $da/dt = 0$. Therefore, the value of a_s will be the solution of the following expression:

$$\psi_d a_s^d - \psi_r a_s^{d_m} = 0 \quad (7)$$

Eq. (3) may be analytically solved assuming different values for m and h , i.e. different values for d and d_m according to Eq. (6). However, we have considered only the cases more probable physically for m and h , i.e. values minor equal to 2. This is not probable that three or more active sites are involved in any elementary step of the chemical mechanism of the reaction. This assumption gives four different cases, as illustrated in Table 2. Once the values of m and h have been fixed, the only kinetic parameters that must be estimated from the experimental data are ψ_d and ψ_r together with the catalyst initial conversion, which is given by the kinetics of the CTC hydrodechlorination reaction. The results of the application of the deactivation kinetic model to the different experimental condition studied are presented below.

3.4.1. Influence of the hydrogen partial pressure upon the deactivation kinetics

The conversion vs. time data presented in Figs. 1–5 was fitted using the integrated forms of Eq. (3), considering the four different cases shown in Table 2.

As an example, in Table 2 are presented the values of the statistical parameters χ^2/DoF and R^2 corresponding to the study of the influence of H_2 concentration. These statistical parameters are

Table 2
Statistical parameters of the fittings obtained with the cases derived from the kinetic model. Data corresponding to the study of the influence of p_{H_2} .

Case	h	m	d	d_m	χ^2/DoF^a	R^2
1a	1	1	1	0	0.0651	0.9693
1b	1	2	1	0.5	0.0629	0.9703
2a	2	1	2	0	0.0603	0.9715
2b	2	2	1.5	0.5	0.0614	0.9710

^a Degrees of freedom = number of experimental points – number of parameters.

direct indicators of the quality of the fittings since, in all cases, we used the same number of kinetic parameters: $(X_{CTC})_0$, ψ_d and ψ_r , allowing us to discriminate directly between each case, considering that the best case is the one giving a higher value of R^2 and a lower value of χ^2/DoF . The values in Table 2 indicate that the best case corresponds to the following values: $m = 1$, $h = 2$. With these values of m and h , the deactivation rate can be expressed as:

$$-\frac{da}{dt} = \psi_d a^2 - \psi_r (1 - a) = \psi_d (a - a_S)(a - a_S^*) \quad (8)$$

After integration of this equation the analytical relationship between catalyst activity and time on stream is:

$$a = \frac{a_S - a_S^* J \exp(-\psi_G t)}{1 - J \exp(-\psi_G t)} \quad (9)$$

In Eq. (8) and (9) the parameters ψ_G , a_S , a_S^* and J are given by the following expressions:

$$\begin{aligned} \psi_G &= \sqrt{\psi_r^2 + 4\psi_d\psi_r}; & a_S &= \frac{-\psi_r + \psi_G}{2\psi_d}; \\ a_S^* &= \frac{-\psi_r - \psi_G}{2\psi_d}; & J &= \frac{1 - a_S}{1 - a_S^*} \end{aligned} \quad (10)$$

The term a_S is the residual activity predicted for the kinetic model and, as is shown in Eq. (10), is a function of ψ_d , and ψ_r , and therefore, of the operating conditions used during the experiment.

From Eq. (1), now the evolution of the CTC variation of the reaction rate along time can be calculated as:

$$(-r_{CTC})_t = (-r_{CTC})_0 \left(\frac{a_S - a_S^* J \exp(-\psi_G t)}{1 - J \exp(-\psi_G t)} \right) \quad (11)$$

and the residual CTC conversion as:

$$(X_{CTC})_S = (X_{CTC})_0 a_S \quad (12)$$

Fig. 1 shows that the model fits very satisfactorily the experimental data. The values of the kinetic parameters corresponding to the catalyst PC are shown in Table 3 and Fig. 6, as a function of the hydrogen partial pressure. Fig. 6 shows the kinetic parameters in, indicating that the increase of the H_2 partial pressure results in an increase of the initial conversion of the CTC hydrodechlorination and a decrease of the deactivation function, ψ_d . The regeneration function, ψ_r , decreases slightly with the H_2 concentration. Therefore, the hydrogen effect, due to an effect of competence for the surface active sites, is actually rather a deactivation inhibition than an effective increase of the regeneration of the coke deposited on the catalyst [26]. In addition, as a consequence of the values of ψ_d and ψ_r , the residual activity, a_S , suffers a slight increase because the inhibition effect of p_{H_2} over ψ_d is higher than on the parameter ψ_r . On the other hand, the value of the parameter ψ_G decreases with p_{H_2} , given that both ψ_d and ψ_r decrease with p_{H_2} . Similar results with respect to the evolution of ψ_r were found by Monzón et al. [15] in a kinetic study of deactivation–redispersion of a Pt/Al₂O₃ catalyst. Finally, the increase of both initial conversion and residual activity explains the increase in the catalyst residual conversion.

Table 3
Influence of p_{H_2} over the deactivation kinetic parameters (Case 2a).

p_{H_2} (atm)	$(X_{CTC})_0 \pm e.e.$	$10^2 (\psi_d \pm e.e.)$ min^{-1}	$10^2 (\psi_r \pm e.e.)$ min^{-1}	$(X_{CTC})_S$	a_S
0.481	3.1 ± 0.2	8.93 ± 3.67	2.19 ± 0.90	1.20	0.387
0.755	3.7 ± 0.2	6.71 ± 2.25	2.58 ± 0.79	1.67	0.392
0.956	8.0 ± 0.2	3.92 ± 0.42	1.01 ± 0.11	3.18	0.395

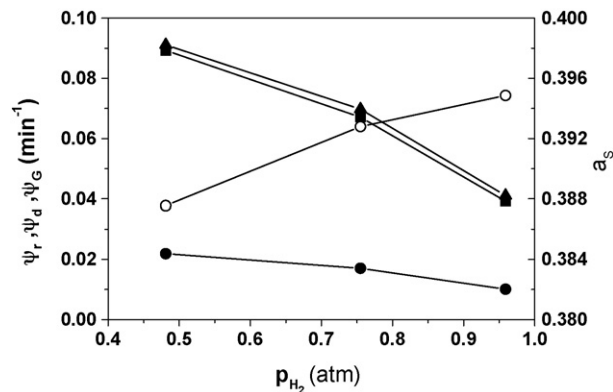


Fig. 6. Influence of the H_2 partial pressure on kinetic parameters. (●) ψ_r ; (■) ψ_d ; (▲) ψ_G ; (○) a_S .

3.4.2. Influence of the CTC partial pressure

The study of the effect of the CTC partial pressure was carried out similarly to that of the H_2 partial pressure. In Fig. 2 can be seen again the good quality of the fitting attained with the model. The results of the kinetic parameters are presented in Table 4 and Fig. 7, as a function of the CTC partial pressure. In these figures can be seen that that an increase of p_{CTC} results in an augment of the rate of CTC hydrodechlorination as well as an strong increase of the deactivation function, ψ_d , and a decrease of the regeneration function ψ_r . These results indicate that, as was expected, an increase of CTC concentration enhances the deactivation reaction and, at the same time, inhibits the catalyst regeneration stage. Therefore, the increase of the p_{CTC} leads to a severe deactivation of the catalyst and therefore, the residual activity strongly decreases as p_{CTC} increases. This severe deactivation causes the decrease of the residual conversion of CTC observed in Fig. 2.

3.4.3. Influence of the reaction temperature

In the case of the study of the effect of the reaction temperature, the results of the fitting are presented in Figs. 3 and 8. As was expected, the increase of the reaction temperature increases the values of $(-r_{CTC})_0$, ψ_d and ψ_r , but the operation temperature affects more the hydrodechlorination reaction than the deactivation reaction. From these values, the apparent activation energies of each parameter can be calculated as depicted in the Arrhenius plot in Fig. 8. The values of apparent activation energies are: 65.2 ± 7.5 kJ/mol for the main reaction, $(-r_{CTC})_0$, 16.3 ± 11.2 kJ/mol for the deactivation step, ψ_d , and 1.7 ± 5.4 kJ/mol for the regeneration step, ψ_r . The low values of apparent activation energies associated with the deactivation and regeneration processes (16.3 and 1.7 kJ/mol, respectively) indicate that these processes are strongly affected by the adsorption of the different reactants involved in both the deactivation and regeneration, which results in a weak net effect of temperature.

Lopez et al. [27] studied the hydrodechlorination of dichloromethane, tetrachloroethylene (TTCE), chlorobenzene, and 1,2-dichlorobenzene, using Pd/Al₂O₃ catalysts. The authors postulate that the results obtained in the hydrodechlorination of the pure compounds (not mixtures) can be fitted with a pseudo-first-order

Table 4
Influence of p_{CTC} over the deactivation kinetic parameters (Case 2a).

p_{CTC} (atm)	$(X_{CTC})_0 \pm e.e.$	$10^2 (\psi_d \pm e.e.)$ min^{-1}	$10^2 (\psi_r \pm e.e.)$ min^{-1}	$(X_{CTC})_S$	a_S
0.032	6.5 ± 0.3	0.73 ± 0.40	1.949 ± 0.885	5.06	0.77
0.044	7.1 ± 0.3	2.63 ± 0.43	1.023 ± 0.161	3.23	0.46
0.051	8.1 ± 0.3	7.45 ± 0.79	0.366 ± 0.063	1.60	0.20

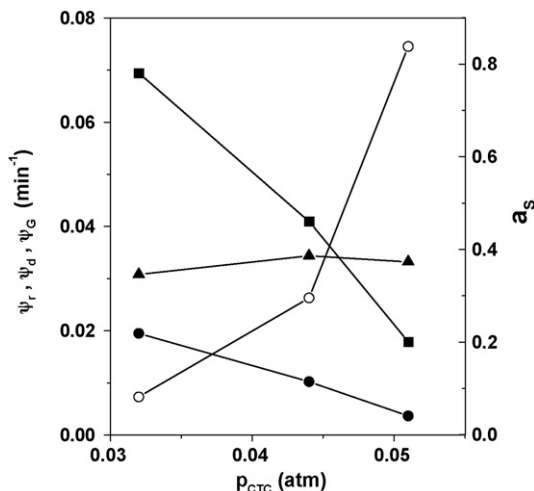


Fig. 7. Influence of the CTC partial pressure on kinetic parameters. (●) ψ_r ; (■) ψ_d ; (▲) ψ_G ; (○) a_s .

kinetics and activation energies between 40 and 90 kJ/mol, depending on the compounds were determined. However, the experimental data were taken after under pseudo-steady-state conditions. Therefore, the results consider only the period during which conversion is constant, i.e. after the initial deactivation that the catalyst may suffer.

In our case, the values obtained for the activation energies are 65 kJ/mol, for the main reaction $(-r_{CTC})_0$ and ca. 60 kJ/mol taking the constant conversion data. The values of the activation energies values obtained in this work are in good agreement with the values reported in the literature [29,30,33]. Values in the range 50–80 kJ/mol also have been reported for other chlorinated compounds.

Ordoñez et al. [28] have studied the hydrodechlorination of TTCE in Pd/Al₂O₃ catalysts. They analyzed the effect of temperature and space-time upon conversion, during the period of constant catalytic activity. They found that the results obtained could be adjusted by a kinetic model that assumes order one in TTCE and order zero in H₂. The activation energy determined by these authors was 26 kJ/mol.

Weizz and Kreiger [29], determined an activation energy value of 112 kJ/mol using Pt catalysts in the hydrodechlorination of different isomers of dichloroethylene, assuming a kinetics of order zero. Such a high value may be ascribed to the assumption of order zero for the DCE, which is not experimentally justified. van de Sandt et al. [30], obtained values of the activation energy between 56 and 80 kJ/mol assuming first-order kinetics in the hydrodechlorination of dichlorodifluoromethane and carbon tetrachloride.

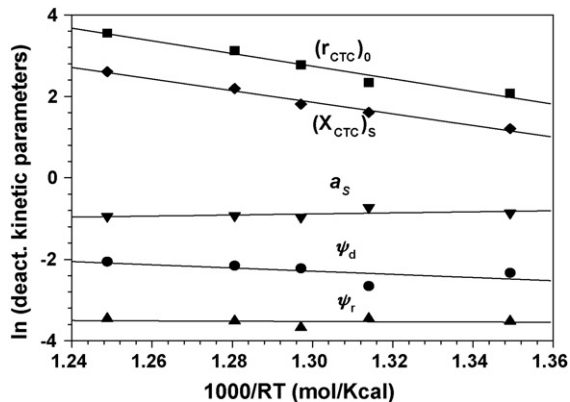


Fig. 8. Influence of the reaction temperature on kinetic parameters.

Park et al. [4] studied the hydrodechlorination of aromatic chlorinated compounds employing Ni catalysts supported on silica (5–15% Ni) in the 200–300 °C temperature range. In these studies, the catalytic activity data correspond to those of the steady-state activity. The authors found that the orders in the aromatic halogenated compound increases from 0.3 to 0.6 in the temperature range between 200 °C up to 250 °C, while the reaction order in hydrogen decreases from 0.7 at a temperature of 220 °C up to 0.3 at $T = 280$ °C.

A wide range of kinetic parameters hydrodechlorination reactions have been reported in the literature [4,27–30]. This discrepancy could be ascribed to the fact that, in some cases, the studies were carried out in liquid-phase reactions whereas in other cases, they have been performed with catalysts or chlorinated compounds very different.

Moreover, it must be taken into account that different kinetic models have been used for the hydrodechlorination reactions, which make that the values of the kinetic parameters not being directly comparable. Besides, the deactivation kinetics for this type of reactions has not been so widely studied, being this work one of the first to approach in depth this aspect of the process. In this work, we have used a more rigorous deactivation kinetic model which takes into account a reversible reactivation–regeneration stage that explains the presence of a catalyst residual activity. On the contrary that in the case of empirical models, the parameters calculated with this model are more related to the real phenomena that occur over the catalyst surface during the deactivation and regeneration.

3.4.4. Influence of regeneration treatment

As is shown in Fig. 5 the PC catalyst deactivates during the first reaction (1st run) and then, after subsequent regeneration in H₂ reaction, both the initial conversion and the steady-state conversion increase (1st and 2nd runs). The PNC catalyst presented the same behaviour. This behaviour during reaction–regeneration stages has been analyzed with the deactivation model to obtain with the kinetic parameters.

Fig. 5 shows the good fitting quality obtained after all the regeneration steps. In this case, the regeneration temperature was 350 °C. In the case of regeneration at 200 and 500 °C very good fittings were also obtained. Table 5 shows the values of the kinetic parameters obtained after each cycle of reaction–regeneration, and for the three regeneration temperatures studied. Figs. 8 and 9 show the evolution of the parameters as a function of the number of regeneration cycles at 350 °C (Fig. 8), and as function of temperature after the third regeneration cycle (Fig. 9).

The values in Table 5 and Figs. 8 and 9 indicate that the regeneration steps produce an activation of the catalyst, i.e. an

Table 5

Influence of regeneration cycles with H₂ over the deactivation kinetic parameters (Case 2a).

Run	$(X_{CTC})_0 \pm e.e.$	$10^2 (\psi_d \pm e.e.) \text{ min}^{-1}$	$10^2 (\psi_r \pm e.e.) \text{ min}^{-1}$	a_s
Temperature of regeneration = 200 °C				
1st	9.50 ± 0.5	20.9 ± 0.079	1.8 ± 0.0082	0.06
2nd	19.1 ± 0.4	18.8 ± 0.035	1.8 ± 0.0039	0.07
3rd	36.8 ± 0.5	12.2 ± 0.008	1.4 ± 0.0013	0.08
Temperature of regeneration = 350 °C				
1st	13.5 ± 1.0	25.6 ± 0.143	3.2 ± 0.021	0.09
2nd	37.2 ± 1.0	6.2 ± 0.007	1.3 ± 0.0022	0.14
3rd	61.1 ± 1.0	4.0 ± 0.004	3.3 ± 0.00384	0.34
Temperature of regeneration = 500 °C				
1st	9.50 ± 0.6	28.3 ± 0.27	4.1 ± 0.042	0.10
2nd	23.7 ± 0.6	7.30 ± 0.03	8.4 ± 0.037	0.40
3rd	57.8 ± 0.6	9.80 ± 0.02	7.9 ± 0.013	0.34

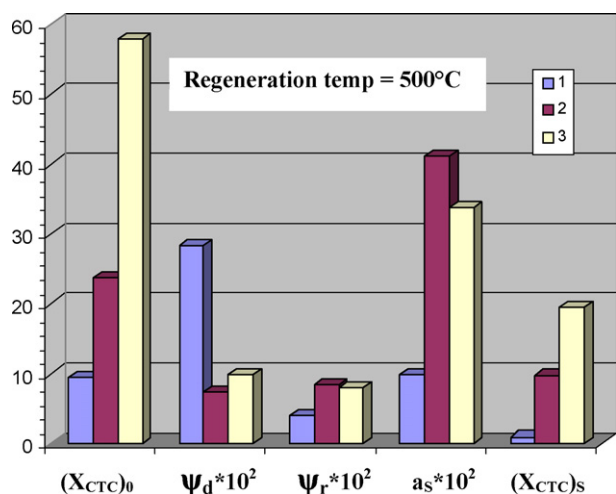


Fig. 9. Parameters evolution during H₂ regeneration at 350 °C.

increase of initial reaction rate, a strong decrease of ψ_d , and a slight increase over ψ_r . In summary, H₂ treatment modifies Pt particle surface and so after each cycle the catalyst are both, more active and resistant to deactivation. These trends are reinforced at increased regeneration temperatures indicating that the surface modification induce by H₂ is greater at higher regeneration temperatures.

Concerning the influence of the regeneration temperature over the kinetic parameters after the third reaction run presented in Fig. 10, the following observations can be made: (i) as the regeneration temperature increases, $(-r_{CTC})_0$ also increases whereas ψ_d decreases; (ii) if we compare the initial conversion values, $(-r_{CTC})_0$, of the third reaction, i.e. after the catalyst was subjected to two intermediate regenerations in H₂, it can be observed that a regeneration temperature of 350 or 500 °C has little influence; (iii) the values of a_s and $(X_{CTC})_s$ present the same behaviour.

According to the results obtained, it has been found that the Pt catalysts supported on alumina deactivate during the hydrodechlorination reaction of carbon tetrachloride. Various and simultaneous deactivation causes can be invoked: (a) deactivation by the carbon deposition formed during the reaction as previously reported [9]; (b) deactivation by the adsorption of HCl and/or chlorinated compounds, which is a reaction product; (c) deactivation by sintering of the accessible metallic fraction.

Sintering is quite unlikely to occur since the temperature at which the reaction is carried out is relatively low ($T = 100$ °C) and

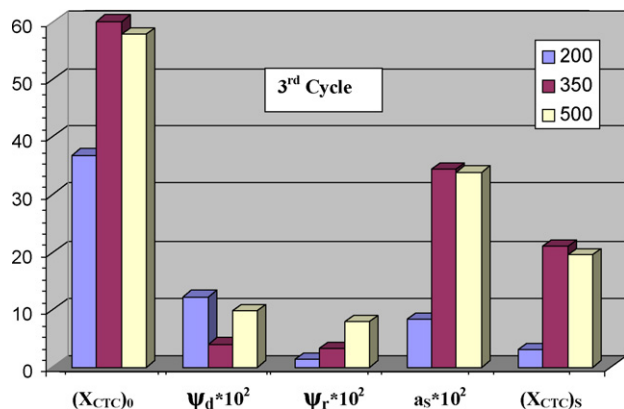


Fig. 10. Influence of the regeneration temperature on kinetic parameters.

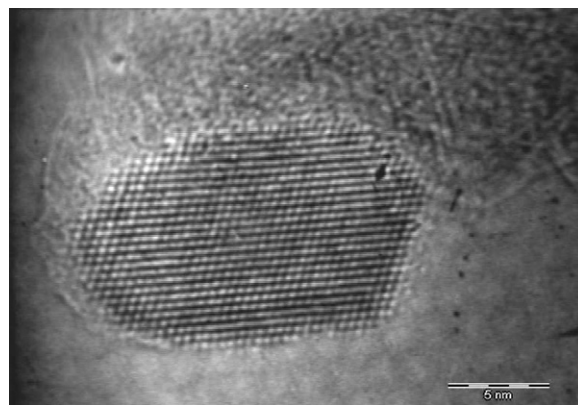


Fig. 11. HRTEM of Pt particle. After reaction–regeneration cycle in H₂ at 350 °C.

in reducing atmosphere. In previous works [15,31,32], we demonstrated that the sintering of Pt/Al₂O₃ catalysts in reducing atmosphere takes place at temperatures higher than 600 °C and during prolonged times. Therefore, regeneration under oxidizing atmosphere, allows us recovering of the catalyst, initial state and, therefore, the catalyst behaves as a fresh one. Hydrogen regeneration treatments result in a more active catalyst exhibiting lower deactivation.

Regeneration under oxidizing atmosphere, allows the complete removal of coke, fully restoring the initial activity. On the contrary, when the regeneration is carried out in H₂, some new metallic active sites are probably formed by partial redispersion of the metallic crystallites. The formation of surface defects could be observed by HRTEM as shown in Fig. 11.

It is of interest to mention that while the formation of coke is not affected by the successive regeneration treatments in oxidizing atmosphere, it is significantly inhibited by regeneration treatments in reducing atmosphere. This fact partially explains the increase of residual activity in the successive H₂ regeneration cycles.

Consequently, during the reaction–regeneration cycles different effects are produced which are opposite on catalyst activity. On the one hand, carbonaceous deposits, and probably adsorption of chlorinated compounds, are produced during the reaction which would lead to a decrease in the catalytic activity. On the other, during the reaction, and along the regeneration step in reducing atmosphere, a certain redispersion of the metallic phase and formation of defects could be produced, provoked by the presence of strongly chemisorbed species. The simultaneous presence of H₂ and chlorinated compounds is an indispensable requisite to lead to the metallic phase redispersion and, probably, to the formation of surface defects of high catalytic activity. This redispersion phenomenon of the metallic phase has been observed in the hydrogenolysis of CCl₂F₂ employing Pt catalysts [33]. This effect is later perceived in an increase of the selectivity and residual activity of the catalyst. This would explain the higher stability of the catalyst observed after regeneration.

4. Conclusions

It has been found that in the CCl₄ hydrodechlorination with Pt/Al₂O₃ catalysts, along the reaction step and afterwards along the regeneration step in reducing atmosphere, two simultaneous phenomena take place of opposed effect upon activity. On the one hand, during the reaction there takes place the formation of carbon deposits and chlorinated compounds that deactivate the catalyst. At the same time, the catalyst activation would occur through a redispersion process of the metal in the presence of HCl, H₂ and

chlorinated compounds. This redispersion process manifests itself after the regeneration step with H₂, where both the carbon deposits and HCl are eliminated, resulting in a modified metallic surface with increased catalytic activity and stability. The formation of coke in a later step is inhibited by the previous regeneration treatments in reducing atmosphere. The regeneration of the catalysts in oxidizing atmosphere neither increases the catalyst activity nor inhibits the ulterior formation of coke.

Deactivation kinetic model employed in this work assumes a reversible deactivation–regeneration process during the reaction which allow us to obtain values of the kinetic parameters related directly to these steps. These results show that an increase in the hydrogen partial pressure produces an inhibition in the deactivation more than in the regeneration of the catalyst. An increase in the CTC partial pressure leads to a strong deactivation of the catalyst and a diminution in the residual activity. The increase in the operating temperature has a low effect on deactivation–regeneration rate. This fact shows that this process is strongly affected by chemisorption terms corresponding to chlorinated species involved in this reaction.

On the other hand, the assumption of a reversible deactivation–regeneration process made possible to apply the model to the H₂ regeneration steps. The results obtained with this model show that the catalyst regeneration produces the redispersion and activation of the active phase. This is increasing the catalyst resistance to deactivation after each regeneration cycle. These results are coincident with the preliminary results obtained at the moment.

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