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Thermogravimetric determination of coke deposits on alumina-supported noble metal catalysts used as hydrodechlorination catalysts

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Abstract

The deactivation of 0.5 wt.% Pd on alumina, 0.5 wt.% Rh on alumina and 0.5 wt.% Pt on alumina catalysts for the hydrodechlorination of tetrachloroethylene (TTCE) in organic matrix has been studied. Experiments were carried out in a continuous fixed-bed reactor at 250°C, 5 bar, 1.3 g catalyst min/mmol TTCE and 0.8 nl/min of hydrogen. The Pd catalyst is the most stable at the studied conditions, followed by Rh and Pt.

In order to study the causes of deactivation, fresh and used catalysts were characterised by nitrogen porosimetry, X-ray diffraction (XRD), thermogravimetry (TG), X-ray photoelectron spectroscopy (XPS), temperature-programmed oxidation (TPO) and pulse hydrogen chemisorption. Characterisation results indicate that the deactivation is caused mainly by the formation of carbonaceous deposits, being negligible the effects of poisoning by HCl. It was observed that in addition to the amount of coke, its combustion temperature is an important parameter, showing a higher capacity to deactivate the catalysts the cokes with lower combustion temperatures (obtained from differential thermogravimetry (DTG) profiles). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Tetrachloroethylene; Hydrodechlorination; Pd catalyst; Pt catalyst; Rh catalysts; Catalyst deactivation; Coke determination

1. Introduction

Chlorinated organic solvents, specially tetrachloroethylene (TTCE), are widely used in many industries, being the main applications dry-cleaning and preparation of textile fibres, degreasing of metals, extraction of organic compounds and cleaning of electronic devices. So in these uses, organic wastes with high content in TTCE are produced, being the disposal of these wastes a major environmental and social problem because of the TTCE toxicity and its capability for accumulating in the environment for long time.

The incineration of these wastes is feasible, but it can lead to the release of even more toxic compounds, such as dioxins and furans [1]. Hence, catalytic hydrodechlorination (treatment with hydrogen, yielding hydrocarbons and hydrogen chloride) might be an interesting alternative [2].

Although, the catalysts most extensively studied for the hydrodechlorination of organochlorinated compounds in organic matrix are the hydrotreatment ones [3], in previous works of our research group it was observed that precious metal catalysts are more active [4]. In addition, these catalysts are active at moderate pressures and temperatures (1–5 bar, 250°C), while

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the hydrotreatment catalysts operate at more severe conditions (100 bar, $T > 350°C$). The most active metals for these reactions were found to be Pd, Rh and Pt [4].

The most important issue in the development of hydrodechlorination processes is the catalyst selection. Some authors report the deactivation of noble metal catalysts used in hydrodechlorination reactions [5–7]. However, there is not unanimity about the causes that lead to the deactivation of the catalysts. Some authors state that the most important deactivation cause is the poisoning by the HCl formed in the reaction [5,6], whereas other authors state that the deactivation is caused mainly by coking [7,8]. Regarding the effect of the support, some studies assert that the inorganic supports are unstable, and propose the use of organic supports, such as activated carbons. In this way, two important considerations should be made. On one hand, most of these studies have been carried out for the hydrodechlorination of CFCs, reaction in which HF (more reactive than HCl) is formed. On the other hand, a poor performance of carbon-supported catalysts was observed in previous works of our group [9], in which a progressive collapse of the microporous structure caused by coke deposition was observed, resulting in a pronounced decay in the activity of the catalysts.

Regarding the determination of carbonaceous deposits, thermal methods, such as thermogravimetry (TG), are preferred to methods based on leaching of the catalysts with different solvents, because of the low solubility of these deposits in most solvents [10]. In addition, the solubility could vary in a great extension with the properties of the carbonaceous deposits, such as chlorine concentration or density.

The aims of this work are to compare the activity for TTCE hydrodechlorination of Pd, Pt and Rh supported on alumina, studying the causes that lead to the catalyst deactivation, and to characterise the nature of the carbonaceous deposits formed, trying to correlate the deactivation with the coke characteristics.

2. Experimental

2.1. Materials

Three commercially available catalysts supplied by Engelhard, Italy, 0.5 wt.% Pd, 0.5 wt.% Rh and 0.5 wt.% Pt, all of them supported on γ-alumina, were used (Table 1). The catalysts, available in extrusions, were milled and crushed, and the fraction between 100 and 200 μm was selected. Inert corundum (Janssen, Belgium, maximum particle size 100 μm) was used to dilute the catalyst. The same inert corundum was used to fill the reactor.

Tetrachloroethylene, supplied by Panreac (99.9% purity), was dissolved in toluene (99.5% purity, Panreac). Hydrogen (>99.9995% purity) was supplied by Air Liquide.

2.2. Reaction studies

Reaction studies were carried out in a continuous fixed-bed reactor, consisting of a 45 mm long, 9 mm i.d. stainless steel cylinder placed inside a tubular electric furnace, and equipped with five thermocouples at different reactor lengths. The catalysts (0.5 g with particle size 100–250 μm), previously dried at 110°C and diluted with inert corundum (75–100 μm), were placed in the mid-section of the reactor, occupying a height of approximately 2 cm, being filled the lower and upper sections with low area inert corundum (100–200 μm) in order to heat the reactants and ensure plug flow conditions. Hydrogen flow rate (0.8 Nl/min) was controlled by a Brooks 5850TR/X-5879E mass flow controller. The liquid feed (10 wt.% TTCE dissolved in toluene) was impelled by a Kontron LC T-414

Table 1
Characteristics of the catalysts used in this work

Catalyst	Metal	BET surface area (m^2/g)	BJH mesopore volume (cm^3/g)	Average pore diameter (nm)	Dispersion (H_2 chemisorption, %)
ESCAT 26	0.5% Pd	103.35	0.45	16.5	30.8
ESCAT 36	0.5% Rh	114.88	0.45	13.2	54.9
ESCAT 16	0.5% Pt	88.20	0.42	16.9	96.7

metering pump with a flow rate of 0.7 ml/min. Pressure inside the reactor was controlled by a Tescom back-pressure regulator. The reactor effluent was collected into a 100 ml stainless steel teflon-coated cylinder, acting as gas–liquid separator and reservoir for liquid reaction products. A two-valve system allowed periodical withdrawn of liquid samples. Catalysts were reduced in situ before use by passing 0.8 Nl/min of hydrogen at 350°C during 6 h.

Hydrodechlorination reactions were carried out at 250°C and 5 bar total pressure. Although, in previous experiments a negligible effect of pressure in the range 1–20 bar on the conversion was observed, pressure was set at 5 bar, in order to minimise the losses of TTCE or solvent in the vapour phase. The temperature was chosen in order to ensure that the reaction mixture was a gas, leading higher temperatures to more severe catalyst deactivation.

Reactions were started maintaining the catalyst at reaction temperature in hydrogen flow for 3 h. The liquid feed was then started. The hydrogen flow rate used in the reaction ensures a great excess of hydrogen (90:10), so that hydrogen will not be a limiting reactant.

2.3. Analysis and catalysts characterisation

Reaction feed and liquid products were analysed by gas chromatography in a Hewlett-Packard apparatus equipped with a 60 m semipolar VOCOL column. Light alkanes formed in the reaction were analysed by injecting samples of the gas reaction product in the same chromatograph using a carbowax-packed column. Hydrogen chloride concentration was measured by absorption in distilled water and titration with NaOH.

When the reaction was stopped, the catalyst was cooled "in situ" by flowing nitrogen and then separated form the corundum by sieving and collected for subsequent characterisation. Fresh and used catalysts were characterised by different techniques. Nitrogen porosimetry measurements were performed in a Micromeritics ASAP 2000 apparatus. Exposed metal was measured by pulse chemisorption of hydrogen at 70°C in a Micromeritics TPD-2900. The operation temperature was chosen in order to avoid the absorption of hydrogen in the bulk phase, that occurs at lower temperature. Before the pulse measurements, catalysts were reduced during 1 h in hydrogen (1 ml/min) at 500°C and then cooled to the operation temperature in argon.

Crystallographic changes in the catalysts were studied by X-ray diffraction (XRD) in a Philips PW1710 diffractometer, working with the Kα line of copper. X-ray photoelectron spectroscopy (XPS) spectra were recorded using SSX-100 ESCA spectrometer with Mg Kα source ($h\nu = 1253.6$ eV). The binding energy of C 1s at 284.6 eV for carbon was used as the reference for the binding energy calibration.

Thermogravimetric studies, devoted to evaluate the carbonaceous deposits in the catalysts, were carried out in a Mettler TA4000-TG50 thermobalance in a synthetic air oxidant atmosphere from room temperature to 1100°C. In order to improve the quantification of the coke deposits, the following alternative methodology was also used: the catalyst sample (15 mg) was heated up to 200°C in nitrogen flow (10 ml/min), keeping the sample at this temperature during 2 h in nitrogen atmosphere, in order to desorb the moisture and volatile organic compounds. Then, nitrogen was substituted by air, applying a temperature ramp of 10°C/min. Typical combustion temperatures for the combustion of carbonaceous deposits found in the literature are in the range 200–750°C, depending on the noble metal, catalyst support or coke precursors [11]. In this work, the weight losses detected between 200 and 800°C will be ascribed to coke deposits ($\Delta\omega_c$), whereas the temperature of combustion of these deposits (T_c) was taken as the temperature of the minimum of the main peak of the DTG profiles.

Temperature-programmed oxidation (TPO) studies were carried out in a Micromeritics TPD-2900 apparatus connected to a mass spectra analyser Gaslab 300. For this purpose, the sample was heated at 10°C/s in a 10 ml/min flow of a mixture 10 vol.% O_2/90 vol.% He.

3. Results and discussion

3.1. Catalyst performance

The only organic reaction products detected for the three catalysts tested were ethane and trichloroethylene, formed according to the reactions:

$$C_2Cl_4 + H_2 \rightarrow C_2HCl_3 + HCl$$

$$C_2Cl_4 + 5H_2 \rightarrow C_2H_6 + 4HCl$$

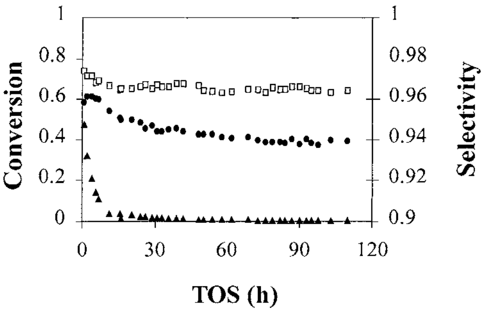

Fig. 1. Evolution of TTCE conversion (□), selectivity for ethane formation (●), and solvent conversion (▲), with time-on-stream for the Pd/Al_2O_3 catalyst at 5 bar and 250°C.

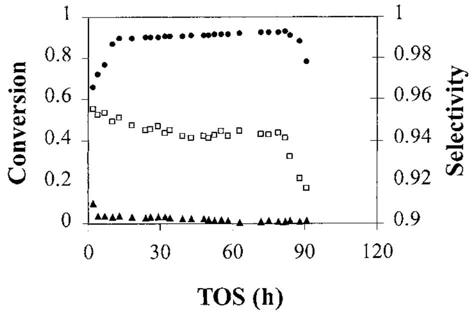

Fig. 3. Evolution of TTCE conversion (□), selectivity for ethane formation (●), and solvent conversion (▲), with time-on-stream for the Rh/Al_2O_3 catalyst at 5 bar and 250°C.

The chlorine mass-balance was checked at selected reaction times, being the fitting in all cases higher than 95%. The solvent (toluene) was also partially hydrogenated, yielding methyl-cyclohexane (MCH). TTCE total conversions (defined as moles of TTCE reacted per mole of TTCE fed to the reactor), selectivities for ethane formation (defined as moles of ethane produced per mole of TTCE reacted) and toluene conversions are depicted in Figs. 1–3 (Pd, Pt and Rh catalysts, respectively). The yields for total dechlorination of the feed (i.e. moles of ethane formed per mole of TTCE in the feed) for the studied catalysts are depicted in Fig. 4.

Pd is the catalyst that shows a better performance, since it yields the highest conversion and is not severely deactivated during the time-on-stream (TOS) studies. During this time, the Pt and Rh catalysts suffer fatal deactivation (at 50 and 80 h on stream, respectively), i.e. the conversion produced is too low, and then they are not useful for industrial hydrodechlorination processes. Regarding the selectivity for the ethane formation, which is a very important aspect since the final aim of the process is the conversion of organic chlorine into inorganic chlorine, the three catalysts produce high selectivities in the period of constant activity.

Other important aspect is the reaction of the solvent (toluene), since solvent reaction causes an undesired additional consumption of H_2. In this aspect, the behaviour of the catalysts tested was very different. Almost 70% of toluene was hydrogenated by the Pt catalyst at initial time, decreasing this value progressively as TTCE conversion decreases. However, in the case of Rh and Pd, although a significant MCH formation at initial time was observed, the catalysts are quickly deactivated for this reaction, showing different

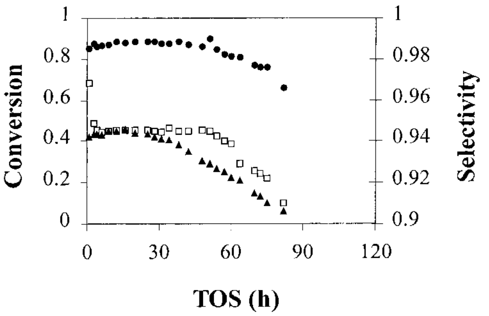

Fig. 2. Evolution of TTCE conversion (□), selectivity for ethane formation (●), and solvent conversion (▲), with time-on-stream for the Pt/Al_2O_3 catalyst at 5 bar and 250°C.

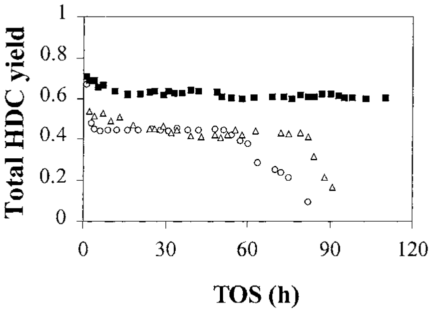

Fig. 4. Evolution of the total hydrodechlorination yield (moles of ethane formed per mole of TTCE fed to the reactor) with time-on-stream for Pd/Al_2O_3 (■), Pt/Al_2O_3 (○), and Rh/Al_2O_3 (△) catalysts.

behaviour with the variations with time-on-stream of the activities for hydrodechlorination and hydrogenation. This could indicate that the active sites for both reactions are the same in the case of Pt, whereas in the case of Rh and Pd are different.

3.2. Catalyst characterisation

Samples of catalysts, fresh and used after 110 h time-on-stream, were characterised in order to investigate the causes of the catalysts deactivation. The techniques used were: N_2 physisorption, XRD, TG, XPS, hydrogen pulse chemisorption, and temperature-programmed oxidation coupled with mass spectrometry. Due to the low height of the catalytic bed (2 cm), no difference was observed between catalyst particles placed at different bed heights, showing all the used catalyst particles uniform aspect.

3.3. XPS and XRD studies

XPS analysis of the fresh and used catalysts are shown in Table 2 (surface concentrations) and Fig. 5 (XPS spectra of the active metal for the fresh and used catalysts). These results reveal no important changes in the active phase, as there are no differences in the oxidation state and chemical environment between the fresh and used catalysts in the three cases.

XPS analysis allows discerning between different chemical states of the elements. In our samples, chlorine appears at two different binding energies: 199 eV, corresponding to inorganic chlorides, and 200–201 eV, corresponding to chlorine in organic and polymeric structures, probably associated to coke deposits which have a polymeric structure. The presence of chlorine in the coke deposits could indicate that TTCE, or products from TTCE partial dechlorination, play an important role in the formation of these carbonaceous deposits.

In the same way, no aluminium halides were detected by XRD in both fresh and used catalysts, being γ-alumina the only crystallographic phase detected, although some authors claim that the formation of aluminium halides is an important deactivation cause in hydrodechlorination reactions over alumina-supported catalysts [8].

Another cause for catalyst deactivation is the possible volatilisation of the active phase, considering that some metallic chlorides are volatile. XPS analyses are not reliable to evaluate this phenomenon, since XPS is a surface-sensitive technique. So, in order to determine accurately the noble metal content in the samples, fresh and used catalysts were digested in an HF solution, and the metal content in the resulting solution was analysed by ICP-MS. It was found that metal concentration was the same in the fresh and used catalysts, being then the volatilisation of active phase negligible.

3.4. Coke analysis (TG)

Typical TG–DTG profiles for used Rh/Al_2O_3, using the two procedures described in Section 2 (heating in air, and heating in air after treatment in nitrogen) are depicted in Fig. 6A and B, respectively. Although, the second procedure is considered as more accurate for the quantification of carbonaceous deposits [12], values of weight losses between 200 and 800°C and temperatures of the minimum of DTG curves are very similar for both procedures (discrepancies lower than 5%). TG and DTG profiles for Pd/Al_2O_3 and Pt/Al_2O_3 are shown in Fig. 7.

Table 2
Atomic concentration (%) of active metal, C, Cl and O by XPS for Pt/Al_2O_3, Rh/Al_2O_3 and Pd/Al_2O_3 before and after reaction

	Pt/Al_2O_3		Rh/Al_2O_3		Pd/Al_2O_3	
	Fresh	Used	Fresh	Used	Fresh	Used
Pt $4d_5$	0.08	0.06				
Rh $3d_5$			0.19	0.13		
Pd $3d_5$					0.15	0.16
C 1s	10.02	12.43	10.4	15.64	11.18	16.79
Cl (inorganic, binding energy ~ 200–202 eV)	0.05	0.016	0.04	0.11	0.06	0.08
Cl (organic, binding energy ~ 198–199 eV)	0.23	0.57	0.3	0.52	0.24	0.63

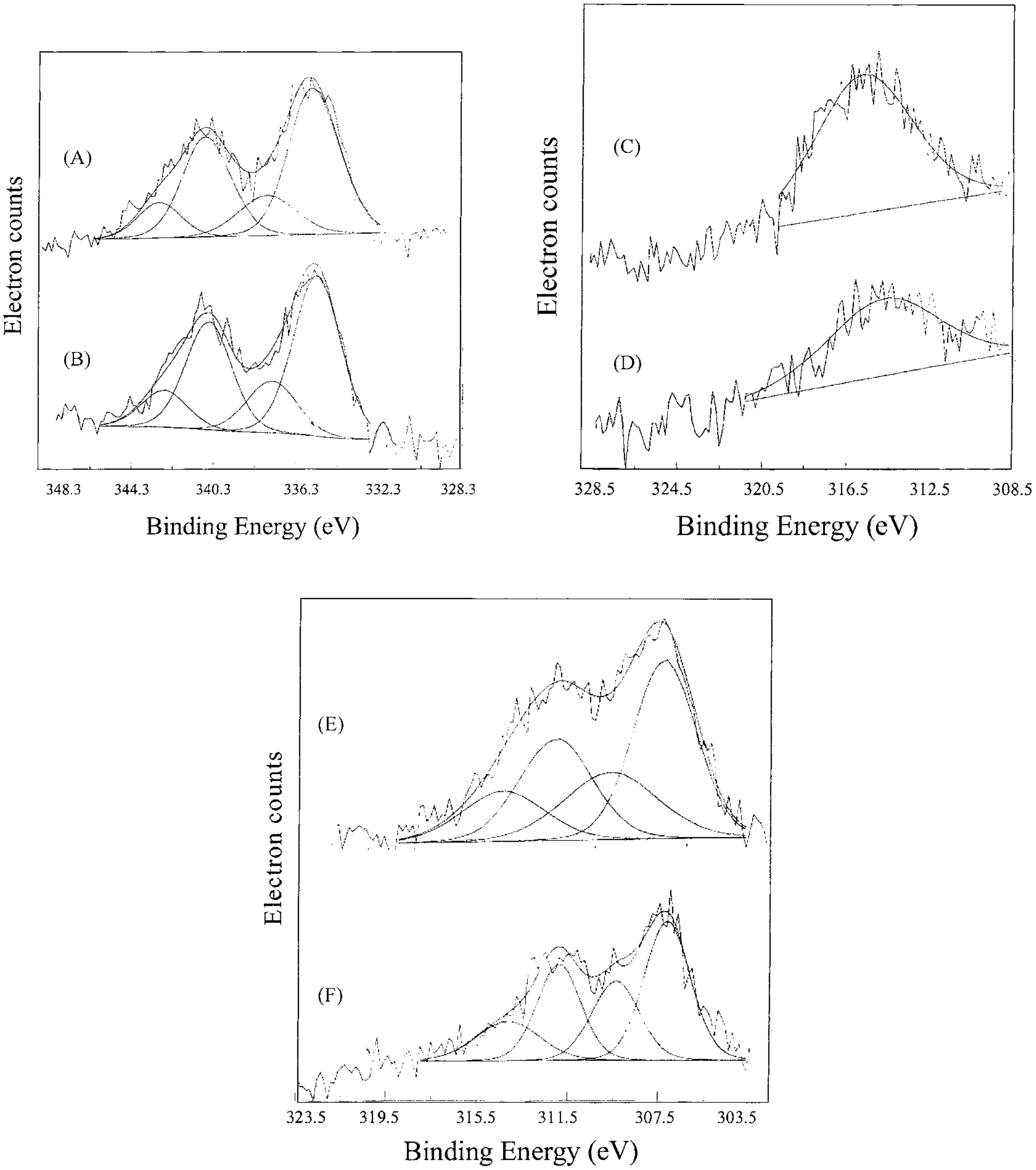

Fig. 5. Deconvoluted XPS spectra of Pd in: Pd/Al_2O_3 fresh catalysts (A), and used catalysts (B); Pt in: Pt/Al_2O_3 fresh catalysts (C), and used catalysts (D); Rh in: Rh/Al_2O_3 fresh catalysts (E), and used catalysts (F).

TG and DTG profiles for the fresh catalysts show that the weight losses were noticeably lower than in the case of used catalysts ($\Delta\omega_c < 1\%$). DTG profiles showed a linear trend without marked maximums (Fig. 8).

Values of the weight losses and main combustion temperatures for the used catalysts are shown in Table 3. Considering the values of the weight losses, which are mainly caused by the combustion of carbonaceous deposits, and the results of the deactivation

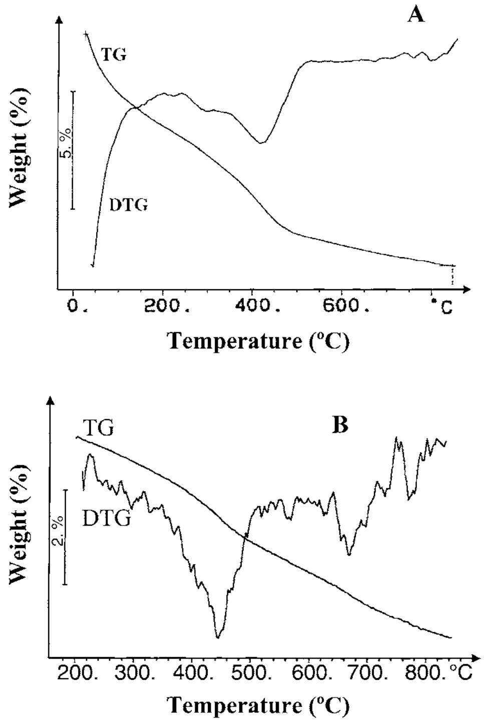

Fig. 6. TG and DTG profiles for the Rh/Al_2O_3 after 100 h time-on-stream. TG profiles in an oxidant atmosphere recorded: without previous purge with N_2 (A); with N_2 purge (B).

tests, it can be seen that the weight losses are higher in the case of the Pt catalyst that presents the fastest deactivation, whereas the catalyst more resistant to deactivation, Pd, shows the lower values of $\Delta\omega_c$. So, it appears that there is a relation between the amount of coke and the deactivation of the catalyst, as can be seen in Fig. 9.

It is important to remark that the differences in the coking behaviour of the catalysts should be mainly caused by the different active phase, since all the catalysts have the same support and are treated (preparation and reduction) and reacted at the same conditions.

The other thermogravimetric parameter, the temperature of the minimum of the DTG curve, is also correlated with the catalyst performance. The Pt catalyst has the lowest value of this parameter, increasing in the order Pt < Rh < Pd. Lower values of T_c are correlated with coke which burns more easily. Typically, these cokes have low molecular weight and low density, hence occupying more volume and blocking

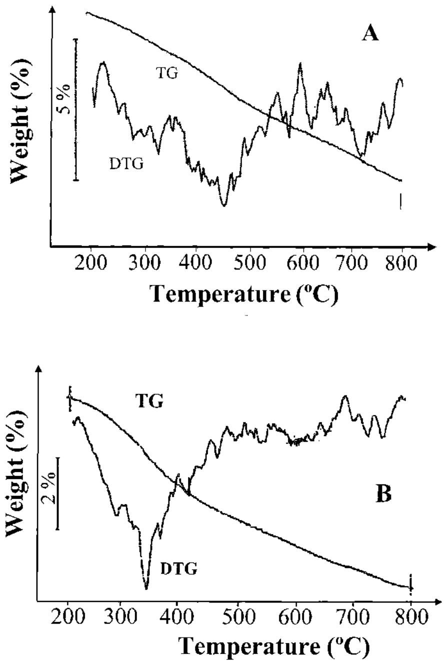

Fig. 7. TG and DTG profiles for Pd/Al_2O_3 (A) and Pt/Al_2O_3 (B) after 110 h on stream.

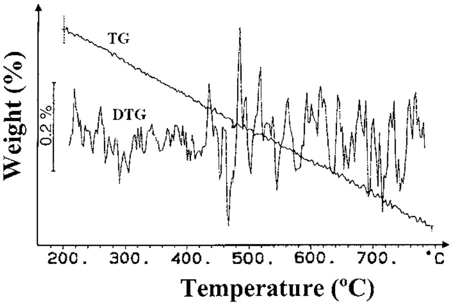

Fig. 8. TG and DTG profiles for fresh Rh/Al_2O_3 catalysts.

Table 3
Weight loss between 200 and 800°C and combustion temperature (T_c) for the catalysts after 110 h on stream

	Pt/Al_2O_3	Rh/Al_2O_3	Pd/Al_2O_3
T_c (°C)	350	440	470
$\Delta\omega_c$	5.61	4.42	4.21

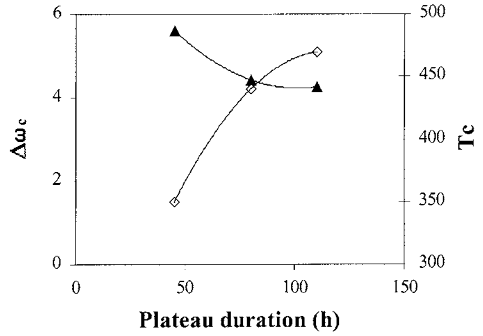

Fig. 9. Relationship between the constant activity period of the catalysts and their thermogravimetric parameters T_c (◇) and $\Delta\omega_c$ (▲).

active sites in higher extension. This could also contribute, in addition to its high content of coke, to the fast deactivation observed for the Pt catalyst.

It is interesting to correlate the properties of the coke with its chemical composition. So, the thermogravimetric parameters ($\Delta\omega_c$ and T_c) are represented in Fig. 10 as a function of the chlorine and carbon content of the coke deposits, expressed as the ratio between the XPS chlorine concentration (corrected with the values of the fresh catalysts), and the coke amount determined by TG, respectively. For this purpose, the carbon content of the coke deposits of the used catalysts was calculated as the difference between the carbon content of the fresh and used catalysts, whereas for the calculation of chlorine content in the carbonaceous deposits, only chlorine atoms with binding energies corresponding to organic environments (198–199 eV) were considered. A sharp increase of combustion temperature with carbon content and, in minor extension, with chlorine content is observed. It is important to remark that only qualitative conclusions can be drawn, because XPS analysis were carried out at vacuum conditions, at which a portion of the carbonaceous deposits could be volatilised.

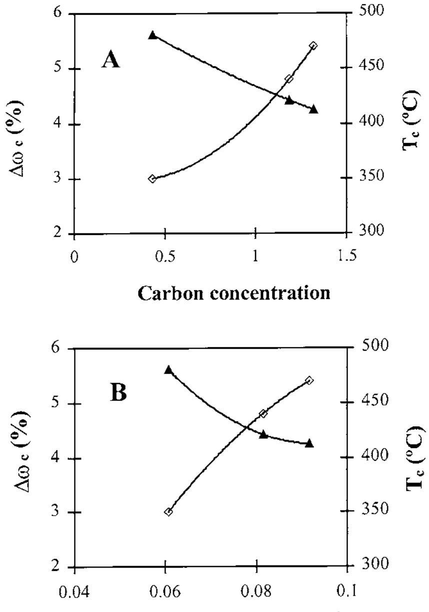

Fig. 10. Evolution of the thermogravimetric parameters of the used catalysts with their content in carbon (A) and organic chlorine (B). Symbols same as in Fig. 9.

TPO experiments were carried out in order to confirm the presence of chlorine atoms in the carbonaceous deposits. Profiles of HCl and CO_2 evolution for the Pt catalyst are depicted in Fig. 11. The CO_2 profile presents a maximum at a temperature (330°C) very close to the temperature of combustion recorded in the thermogravimetric experiment (350°C). In the case of the HCl profile, two maximums were recorded, the first at the same temperature than the maximum of the CO_2 release, and the second (with an HCl release lower than in the first maximum) at higher temperature (800°C). The first peak can be associated to the combustion of chlorine-containing carbonaceous deposits, whereas the second one could correspond to the inorganic chlorine present in the catalyst surface detected by XPS. These results are in a good agreement with the high ability of chlorinated alkenes to

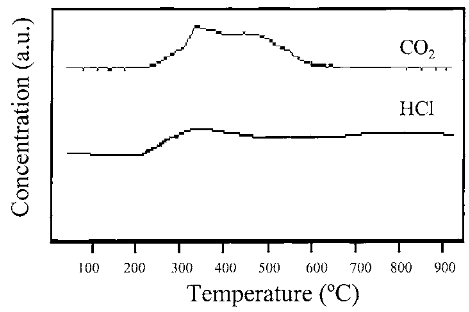

Fig. 11. Evolution of CO_2 and HCl signal with temperature in the TPO experiment for Pt/Al_2O_3.

Table 4
Surface parameters and exposed metal of the catalysts fresh and after 110 h on stream

	Pt/Al_2O_3		Rh/Al_2O_3		Pd/Al_2O_3	
	Fresh	Used	Fresh	Used	Fresh	Used
BET surface area (m^2/g)	88.20	75.6	114.88	85.5	103.35	90.6
BJH mesopore volume (cm^3/g)	0.42	0.440	0.45	0.38	0.45	0.41
Average pore diameter (nm)	16.9	22.3	13.2	16.5	16.5	17.4
Exposed metal (H_2 chemisorption, %)	96.7	5.15	54.9	5.26	30.8	6.9

induce polymerisation reactions that lead to coke formation [13].

3.5. Surface area and active area

Surface parameters, calculated from the models of Brunauer–Emmet–Teller (surface area and average pore diameter) and Barret–Joyner–Hallenda (pore volume), for the fresh and used catalysts are shown in Table 4. Although, the three catalysts suffer a decrease in the surface area, this decrease does not correlate with the deactivation of the catalysts, i.e. Pt and Pd catalysts, respectively, the most and less severely deactivated, suffer a similar relative decrease in surface area. Similarly, changes in mesopore volume and average pore diameter do not correlate with changes in catalytic activity. In the same way, no morphological changes in the used catalysts were observed by SEM.

The values of exposed metal percentage, calculated from H_2 chemisorption data considering a hydrogen/metal stoichiometry 1:1, are disclosed in Table 4. It can be seen that the exposed metal percentage decreases for the three catalysts, following this parameter the same trend as the catalyst deactivation. So, the Pt catalyst suffers the most important decrease, followed by Rh and Pd.

Two different causes can lead to the decrease in the exposed metal: blocking of active sites by carbonaceous deposits, and sintering of the crystallites of the active phase. It is very difficult to study the effect of the last phenomenon because of the nature of the support (secondary peaks of γ-alumina overlap the 111 peaks of the metals in XRD, being not possible to apply the Warren–Scherrer equation to evaluate the metal dispersion), and the low concentration of the active phase (it is very difficult to obtain reproducible data by transmission electron microscopy). On the other hand, the reactive environment (hydrogen, organochlorinated compounds and HCl) is considered as a system that increases the dispersion of noble metal catalysts [14]. Even, the treatment with organohalogenated compounds and hydrogen has been proposed for increasing the catalysts dispersion [15]. Hence, blocking of the active metal by carbonaceous deposits can be assumed as the main cause of the decrease of the exposed metal percentage, and by this reason, this parameter correlates well with the weight losses determined in the thermogravimetric studies.

4. Conclusions

Among the catalysts tested in this work, Pd/Al_2O_3 is the most effective for TTCE total hydrodechlorination, as it provides the highest yields for ethane and hydrogen chloride (the environmentally desired products), besides that it is the most resistant to deactivation.

Concerning to the deactivation causes, XPS studies of the fresh and deactivated catalysts discard important poisoning effects at these reaction conditions, whereas TGA analysis reveals a great importance of the fouling by carbonaceous deposits in the deactivation of the catalysts. The behaviour of the catalysts can be explained taking into account both the total amount and the combustion temperature of the coke. TPO-MS and XPS studies indicate that the presence of chlorine is important in the formation of the carbonaceous deposits.

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