Hydrodechlorination of tetrachloroethylene over vanadium-modified Pt/Al_2O_3 catalysts

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The influence of the addition of different amounts of vanadium on the activity and resistance to poisoning of a 0.5% Pt/Al_2O_3 catalyst used in the hydrodechlorination of tetrachloroethylene was studied. Experiments carried out at 350 °C were devoted to compare the effect of different vanadium loads on the deactivation of the catalyst. A catalyst with 0.12% V and reduced at 500 °C presents the best performance. The performances of this catalyst and the non-doped Pt/Al_2O_3 were compared at 250 °C in a longer experiment (85 h), resulting better the bimetallic catalyst.

KEY WORDS: hydrodechlorination; tetrachloroethylene; bimetallic catalysts; platinum–vanadium catalysts

1. Introduction

Catalytic hydrodechlorination has been shown to be an environmentally and economically interesting alternative for the abatement of organochlorinated pollutants in organic media. In this technique, only hydrogen chloride and hydrocarbons are produced, no harmful products, such as phosgene or dioxins being formed [1]. However, in thermal incineration, the most extended treatment of these wastes, these compounds can be produced [2].

The most active hydrodechlorination catalysts are supported precious metals. Most studies of hydrodechlorination of chloro-aliphatic compounds have been carried out using precious metal catalysts: Rh/SiO_2 was used by Bozelli et al. [3] for 1,2-dichloroethane and trichloroethylene, the catalyst being quickly deactivated; Pt on alumina was used by Kim et al. for carbon tetrachloride [4], by Noelke and Rase for chloroform [5] and by Weiss and Krieger [6] for vinyl chloride and dichloroethylenes. However, these catalysts are not stable under the conditions of this reaction. Some authors ascribe this instability to the poisoning effect of the HCl produced in the reaction [7]. Other authors associate this effect to the trend of these catalysts to bear carbonaceous deposits in a reductive environment in presence of organic molecules [8].

The catalytic properties of supported metal catalysts can be modified by several means: size of metallic particles, interaction between the metal and the support, and doping or alloying procedures. The first method is not feasible for the catalysts used in these reactions, since the particle size changes in high extension during the reaction due to the formation and decomposition of unstable metallic halides [9]. Modification of conventional supports of noble metal catalysts was reported [10,11]. So, Owens and Kung [10] state that the addition of La, Ce or alkaline-earth metals increases the dispersion of the supported metals, decreases the acidity of the support (alumina) and increases the thermal stability of the catalysts. Considering the hydrodechlorination reactions, Srinivas et al. [11] determine a positive effect of TiO_2 addition to the performance of alumina-supported Pt catalysts.

Concerning the alloying, this phenomenon has been widely studied on the hydrogenolysis of C–C (reforming processes), developing very active Pt–Ir, Pt–Sn and Pt–Re reforming catalysts [12,13]. However, the use of bimetallic catalysts for hydrodechlorination reactions has not been very studied yet.

So, in the case of palladium catalysts, hydrodechlorination of chlorobenzene [14], difluorodichloromethane [15,16], 1,1,2-trichlorotrifluoroethane [17] and 1,2-dichloroethane [18] was studied. In these studies, Pd was alloyed with different metals, such as Rh or Sn [14], Fe, Co or Ag [15,18], Re [16], Bi and Tl [17]. The main conclusion of these studies is that the alloying decreases the selectivity for total dehalogenation (except in the case of Fe and Co) and does not improve the stability of the catalyst, except in the case of Ag [18].

Better results have been obtained with platinum-based bimetallic catalysts. So, Srinivas and co-workers studied the hydrodechlorination of chlorobenzene over Pt, suggesting that the addition of other metal, such as vanadium, molybdenum or tungsten, improves the stability of the catalyst, although the added metal can also act as a poison [19]. The same authors found that the best metal, considering both effects, was the vanadium. Bimetallic Pt–Sn catalysts were studied by Early et al. [20] for the hydrodechlorination of 1,2,3-trichloropropane. In this case, although SnPt catalysts achieve higher selectivities for total hydrodechlorination, they present poorer resistance to deactivation than the monometallic catalysts. Coq et al. studied the performance of Pt/Al_2O_3 alloyed with Sn, Pb, Ge, Al or Zn in the hydrogenation of *p*-nitrochlorobenzene [21]. In all the cases, se-

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lectivities for hydrodechlorination reaction were lower than in the case of the monometallic catalyst.

Considering the monometallic catalysts, in previous studies of our group has been observed that the platinum catalysts are more active than the palladium catalysts [22]. However, the platinum catalysts have two important drawbacks: they suffer deactivation in higher extension and they have a high activity for the hydrogenation of aromatic structures [23]. This latter aspect is very important since organic unsaturated or aromatic compounds are usually present in wastes containing chlorinated compounds.

Taking into account the drawbacks of the monometallic Pt catalysts and the good performance of PtV bimetallic systems reported by Srinivas et al. [19] for the hydrodechlorination of chlorobenzene, the present work is devoted to study the effect of the addition of different amounts of V to a Pt/Al_2O_3 catalyst. Reducing the catalyst at different temperatures, the effect of the oxidation state of the vanadium can also be studied. The reactive system studied, tetrachloroethylene (TTCE) solved in an organic solvent (toluene), is of great practical importance. Typical dry cleaning wastes (per slurry) consist of a mixture of TTCE, greases and dust and they present a viscous or solid aspect. So, it is necessary to solve it in an organic solvent for subsequent treatments, such as hydrodechlorination [24].

2. Experimental

2.1. Materials

The platinum on alumina catalyst (ESCAT-26) was supplied by Engelhardt, Italy, the content of active metal being 0.5% (w/w). The catalyst, available in extrusions, was milled and crushed and a fraction between 100 and 200 μm was selected for the reaction and the doping with vanadium. The vanadium was introduced into the catalyst by incipient wetness of aqueous solutions of ammonium metavanadate (Fluka), different concentrations being used according to the desired final concentration of vanadium in the solid. The catalysts were dried overnight in air at 100 °C and calcined in an oven at 500 °C. Catalyst samples containing 0.05, 0.12, 0.25 and 0.5% (w/w) vanadium were produced. A 0.5% V/Al_2O_3 catalyst was made from pure γ-alumina (BASF) by the above mentioned systematic.

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

2.2. Reaction studies

Catalysts were tested in a continuous fixed-bed reactor. The reactor was a stainless-steel tube of 9 mm i.d. and 450 mm long placed inside an electrically heated furnace. Five thermocouples measured the temperature at different reactor positions. The temperature of the reaction zone, located in the centre of the bed, was kept constant at the desired value using a PID controller. Catalysts (0.25 g in the experiments carried out at 350 °C and 0.5 g in the experiments carried out at 250 °C) were diluted in inert corundum (Janssen, Belgium) with size minor than 100 μm and placed in the middle section of the reactor.

Hydrogen gas flow rate (0.8 Nl/min) was controlled by a Brooks 5850TR/X-5879E mass flowmeter and controller. The liquid feed, which consisted of 10% of TTCE (w/w) dissolved in toluene, was impelled by a Kontron LC T-414 pump with a constant flow of 0.7 ml/min. Pressure inside the reactor was maintained by a Tescom back-pressure regulator.

The reactor effluent was collected into a 100 ml stainless-steel Teflon-coated cylinder acting as a gas–liquid separator and a reservoir for liquid reaction products. A two-valve system allowed periodical withdrawal of liquid samples. Catalysts were reduced *in situ* before use by passing 0.8 Nl/min H_2 at 350 or 500 °C for 6 h.

Hydrodechlorination reactions were carried out at 250 °C and total pressure of 0.5 MPa. Although in previous works a negligible effect of the pressure on the conversion was observed, pressure was set at this value in order to avoid losses of TTCE or toluene in the vapour phase. The catalyst was heated up to the reaction temperature in hydrogen, this temperature being kept constant for 3 h. After this, the liquid feed was fed to the reactor. In these reaction conditions, the reaction mixture is a gas. The hydrogen flow used in the reaction ensures a great excess of hydrogen (90 : 1) so that hydrogen will not be a limiting reactant. The previous set of experiments was carried out at 350 °C, in order to study the catalyst deactivation at a temperature at which the deactivation phenomena are faster. A second set of experiments with the selected catalyst was carried at a lower temperature (250 °C) in which the deactivation of the hydrodechlorination catalysts is not so fast [25].

2.3. Analysis and characterisation

Gas and liquid reaction products were analysed by gas chromatography in a Hewlett–Packard 5890A apparatus equipped with a FID detector. A DB-1 30 m fused silica capillary column and tetrahydronaphthalene as internal standard were used for the liquid samples, while the gas samples were analyzed with a 60/80 Carboxen-1000 $1/8''$ packed column. Peak assignment was performed by GC-mass spectrometry (Hewlett–Packard 5987A), and response factors were determined using standard calibration mixtures (Supelco).

The concentration of vanadium and platinum in the impregnated catalysts was determined by ICP-MS (Finnigan MAT-*Element*), after dissolving in a mixture of hydrochloric and nitric acids in a microwave oven. Nitrogen porosimetry measurements were performed in a Micromeritics ASAP 2000 apparatus. Crystallographic structures of the catalysts were studied by X-ray diffraction in a Philips PW1710 diffractometer, working with the K_α line of copper. Thermogravimetric studies of the catalysts were carried out in a Mettler TA4000-TG50 thermobalance in an oxidant atmosphere (synthetic air), in order to evaluate the carbonaceous deposits on the used catalysts. Temperature-programmed reduction (TPR) of the fresh catalysts was carried out in a Micromeritics TPD-2900 apparatus, equipped with TCD detector. For this purpose, samples were heated at 10 °C/min in a 10 ml/min flow of a reductive mixture (10% H_2 in Ar). Energy dispersive X-ray analysis (EDX) was carried out in a Jeol-JSM-6100 to study the dispersion of the vanadium in the bimetallic catalysts, and microprobe analysis (EPMA, Jeol JXA333) was used to measure the chlorine content in used catalysts.

3. Results and discussion

3.1. Catalyst characterisation

Results of ICP-MS analysis and BET surface area are depicted in table 1. Only very slight differences in the surface area were observed in the catalysts, the surface area of the platinum catalyst decreasing slightly as the content of vanadium increases.

XRD analyses of the fresh reduced (at both temperatures) catalysts do not reveal any crystallographic difference, γ-alumina being the only crystalline phase found in the catalyst. Pt and V phases were not observed in any case, probably because of their low concentration in the catalysts. EDX distribution maps of the elements reveal a good dispersion of both metals in the bimetallic catalysts.

TPR profiles showed, as is depicted in figure 1 for the Pt, V and 0.5%V–Pt, the presence of two different reduction peaks, one near 500 °C (in the V/Al_2O_3 catalyst) corresponding to the reduction of vanadium species, and another one near 200 °C, corresponding to the reduction of platinum. The peak of Pt appears at the same temperature in the monometallic and doped catalyst, whereas the peak of V is shifted to lower temperatures in the case of bimetallic catalysts.

3.2. Deactivation studies at 350 °C

The first set of experiments was carried out at 350 °C, conditions at which the deactivation of the platinum catalysts is relatively fast. Two reduction temperatures were tested: 350 °C, corresponding to the vanadium essentially in an oxidised state and the platinum in reduced state, and 500 °C, corresponding to both metals in reduced state.

When the catalysts were reduced at 350 °C, the presence of vanadium causes a decrease in the activity. Thus, higher amounts of vanadium lead to a less active catalyst. Even, the presence of vanadium accelerates the deactivation of the catalyst. So, after 28 h reaction time, the undoped platinum catalyst exhibits the higher conversion, closely followed by the catalyst doped with the lower amount of vanadium.

Considering the results of the TPR profiles (figure 1), the vanadium will be in a partially oxidised form. This phase could have two different effects: a physical coating of the active metal and a modification of the properties of the support and its interaction with the active metal. These aspects could cause this behaviour, especially the first one, considering that higher amounts of vanadium lead to a worst performance of the catalysts.

Table 1
Composition and surface area of the catalysts used in this work (fresh calcined catalysts).

Catalyst	% V (w/w)	% Pt (w/w)	Surface area BET (m^2/g)
Pt/Al_2O_3	0.008	0.53	102
0.06% V–Pt/Al_2O_3	0.06	0.52	101
0.12% V–Pt/Al_2O_3	0.12	0.51	95
0.26% V–Pt/Al_2O_3	0.26	0.52	91
0.51% V–Pt/Al_2O_3	0.51	0.51	90
V/Al_2O_3	0.58	0	110

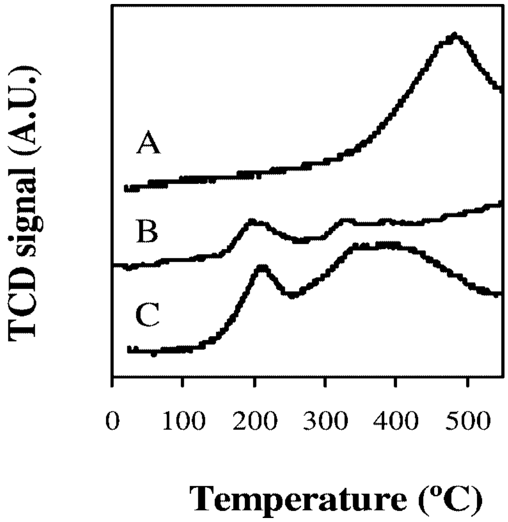

Figure 1. TPR profiles for the fresh calcined catalysts: (A) V/Al_2O_3, (B) Pt/Al_2O_3 and (C) Pt–V/Al_2O_3 (0.51% of V).

The activity of the catalyst with the reaction time was also studied for the same catalyst reduced at 500 °C (figure 2). The reduction temperature had not any effect on the conversion for the non-doped platinum catalyst. However, in the case of doped catalysts the reduction temperature had important effects.

Experiments with 0.5% V over alumina (without platinum) reduced both at 350 and 500 °C were also carried out, yielding negligible conversion at 350 °C. So a catalytical effect of the vanadium is discarded, the only profitable effect of this metal being promotional effects.

In order to get a numerical study of the deactivation of the catalyst, especially in the case of catalysts reduced at 500 °C, a first-order deactivation model was used to fit the deactivation data:

$$x = x_0 \exp(-k_{\mathrm{d}} t). \qquad (1)$$

So, the conversion is correlated with the reaction time through an initial conversion (conversion at 0 h reaction time, x_0), and a deactivation constant (k_{d}, h^{-1}). The evo-

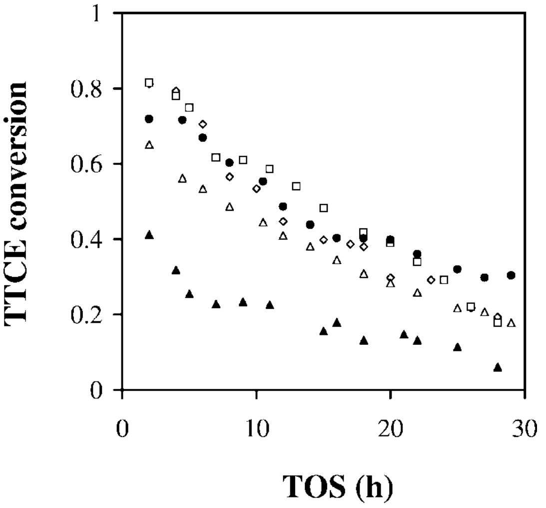

Figure 2. Effect of time-on-stream (TOS, h) on overall conversion for the following catalysts reduced at 500 °C: Pt/Al_2O_3 (□), 0.06% V–Pt/Al_2O_3 (◇), 0.12% V–Pt/Al_2O_3 (•), 0.26% V–Pt/Al_2O_3 (△) and 0.5% V–Pt/Al_2O_3 (▲).

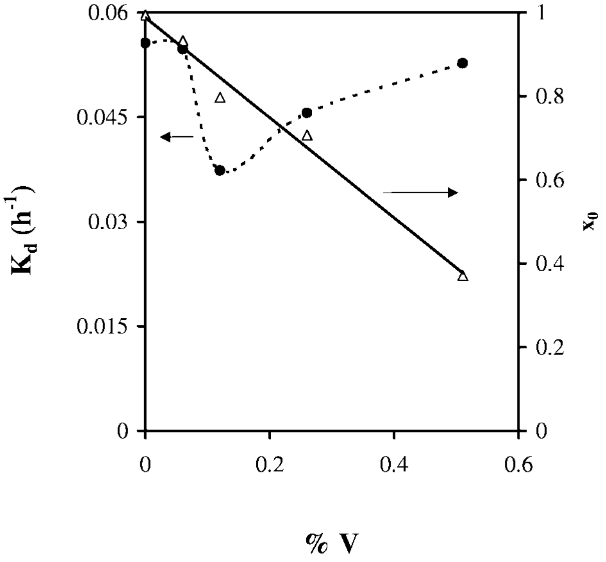

Figure 3. Evolution of the initial conversion (△) and the deactivation constant (•) with the vanadium content of the catalysts (definition of parameters in equation (1)).

lution of the values of these parameters with the vanadium content of the catalyst is represented in figure 3. Similar deactivation models are proposed in the literature for the deactivation of metallic catalysts used in hydrodechlorination reactions [26].

In equation (1), the value of x_0 is related with the inhibitory effect of the vanadium over the platinum catalyst. A decrease of the initial conversion as the content of vanadium increases is observed in figure 3. This behaviour could be caused by a partial covering of a part of the platinum surface with another non-catalytically active metal.

However, the evolution of the deactivation constant (k_d) with the vanadium content presents a minimum (catalyst more resistant to the poisoning) at 0.12%. In figure 2 is also observed that after 24 h on stream, the conversion of the 0.12% V catalyst is clearly higher than the conversion attained with the other catalysts.

Table 2
Toluene conversion for the different catalysts used in this work in the deactivation experiments carried out at 350 °C.

Catalyst	Reduction temperature (°C)	Toluene conversion	
		TOS = 2 h	TOS = 28 h
Pt	500	0.29	0.02
0.06% V–Pt	350	0.31	0.02
	500	0.09	0.01
0.12% V–Pt	350	0.01	0.00
	500	0.14	0.01
0.26% V–Pt	350	0.03	0.01
	500	0.06	0.01
0.52% V–Pt	350	0.01	0.00
	500	0.04	0.01

Regarding the reaction products, the main one was ethane, while also little amounts of trichloroethylene were produced, with selectivities higher than 97% in all the cases. As general trend the selectivities for trichloroethylene were higher in the case of catalysts reduced at 350 °C than for the same catalysts reduced at 500 °C. In the case of the non-doped platinum catalyst, the reduction temperature has no effect on the selectivity for TCE.

The solvent (toluene) was also partially hydrogenated (especially at the first reaction hours) yielding methylcyclohexane. The results of toluene conversion at 2 and 28 h reaction time for the catalysts tested in this work are shown in table 2. The most active catalyst for this reaction was the non-doped platinum catalyst (the influence of the reduction temperature being negligible). Concerning the catalysts reduced at 350 °C, only the catalyst with minor vanadium content yielded high toluene conversions (close to the non-doped catalyst). In all the other cases, toluene conversions were very low, even at the first hours on stream. Bimetallic catalysts reduced at 500 °C yield methylcyclohexane in lower extension than the non-doped catalyst; this conversion decreases as the amount of vanadium increases.

3.3. Deactivation studies at 250 °C

In the experiments carried out at 350 °C, it was observed that the bimetallic catalyst with 0.12% V and reduced at 500 °C presented the best performance. The deactivation of this catalyst was studied at 250 °C. As was shown in previous works [23], the precious metal catalysts are more stable at lower temperatures, being the chosen temperature the lowest one at which the reaction turns out in gaseous phase.

The performance of the selected bimetallic catalyst was compared with the performance of the non-doped Pt/Al_2O_3 catalyst. In figure 4 (TTCE conversion vs. time on stream for both catalysts), is observed that the selected Pt–V catalysts is more resistant to the deactivation in the reaction time observed (80 h).

This is so, not only with the short-time deactivation (as could be inferred from the deactivation experiments carried

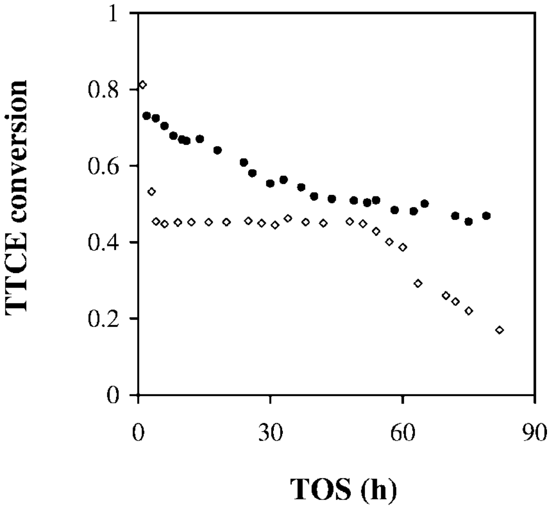

Figure 4. Evolution of TTCE conversion with time-on-stream for the hydrodechlorination of TTCE at 250 °C and 0.5 MPa over Pt/Al_2O_3 (◇) and 0.12% $V–Pt/Al_2O_3$ (●).

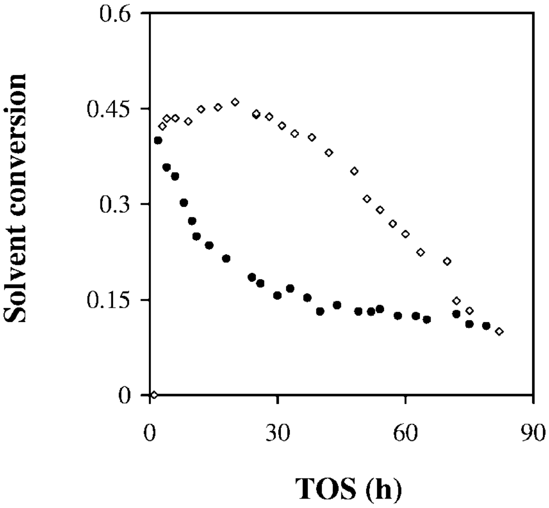

Figure 5. Evolution of solvent conversion with time-on-stream for the reactions carried out at 250 °C and 0.5 MPa over Pt/Al_2O_3 (◇) and 0.12% $V–Pt/Al_2O_3$ (●).

out at 350 °C), but also the Pt–V catalyst is more resistant to the long-term deactivation. This is an important point, since the causes of the deactivation are different in these cases. So the short-term deactivation would be related with poisoning effects of the chloride ions in the structure of the active phase, especially electronic effects [3,27].

On the other hand, the long-term deactivation is mainly caused by coke deposition, with the subsequent blockage of the active phase [28,29]. The profitable effect of the vanadium in order to avoid the chlorine poisoning was already cited in the bibliography [19], but there are no references about the ability of this element to minimise the formation of coke. Although the cause of this is not clear, in previous works of our group with alumina and activated carbon-supported catalysts was observed that platinum catalysts have a more marked trend to bear carbonaceous deposits than other noble metals, such as palladium [23,25]. This result implies that the platinum could catalyse some reactions involved in the formation of coke. The vanadium may inhibit the capacity of the Pt to catalyse these reactions.

Regarding the selectivity, with both catalysts the only reaction products were ethane and trichloroethylene, the selectivity for ethane being higher than 95% in both cases, even when the catalysts are very deactivated. In the references it is stated that, as general trend, the doping of a noble metal lead to less selective catalysts for total hydrogenation. However, in the studied system the selectivity attained with the bimetallic is only slightly lower than in the case of the non-doped platinum catalyst (99 ± 1% in the case of the monometallic catalyst and 98 ± 1% in the case of the bimetallic one).

The other important aspect to consider is the hydrogenation of the solvent. The conversion of the solvent is depicted in figure 5, with methylcyclohexane the only product formed at these reaction conditions. At this point, the activity of the non-doped catalyst is higher for the hydrogenation of the toluene than in the case of doped catalyst. Furthermore, the behaviour is different for the two catalysts: in the case of platinum, deactivation for the hydrogenation of toluene is slower, following a decay trend similar to the deactivation curve of TTCE hydrodechlorination. In the case of vanadium-doped catalyst, the activity for toluene hydrogenation decreases sharply, in a time period in which there is not an important deactivation for the main reaction. This result suggests the formation of a new alloyed catalytic phase. This phase is active for hydrodechlorination reactions, but not very active for toluene hydrogenation. So, the toluene conversion attained with the bimetallic catalyst could be caused by two possible causes. The first one is the remaining of not alloyed platinum atoms. In this case, the faster deactivation would be explained by the minor amount of active phase. The other explanation is that this new phase would be easily deactivated for the toluene hydrogenation. At this point it is important to remark that in the case of hydrodechlorination over palladium catalysts, the initial conversion of the solvent is high and the conversion decreases very quickly with the time on stream [23]. One interpretation for this behaviour is the existence of palladium chlorides that are active for hydrodechlorination reactions, but not for hydrogenation reactions [30]. Similar behaviour could be postulated for the bimetallic system.

This result is very important because it ensures a high selectivity for the hydrodechlorination with respect to the hydrogenation of other unsaturated molecules present in a real waste. So, the consumption of hydrogen in a real process will be lower using these doped catalysts.

The two catalysts, fresh and used after 82 h reaction time, were characterised using nitrogen physisorption (BET), XRD, TGA (in air) and chlorine microprobe analysis (EPMA). In the XRD patterns, only γ-alumina was observed for the four (doped and non-doped, fresh and deactivated) samples. No important differences were observed in the surface area and porous structure of both catalysts (table 3). Regarding to the chlorine concentration, the values

Table 3

Surface area, surface chlorine concentration and thermogravimetric parameters for both Pt/Al_2O_3 and 0.12% $V–Pt/Al_2O_3$ fresh and after 82 h on stream at 250 °C.

	Pt/Al_2O_3		0.12% $V–Pt/Al_2O_3$	
	Fresh	Used	Fresh	Used
BET surface area (m^2/g)	88	75	90	78
Cl surface concentration (%, w/w)	<0.1	2.4	<0.1	1.9
$\Delta\omega_c$ (%, w/w)	–	5.6	–	4.8
T_c (°C)	–	350	–	410

for both deactivated catalysts are shown in table 3, the chlorine content in the fresh catalyst being negligible (<0.1%). The values of the weight loss between 200 and 900 °C ($\Delta\omega_c$, measured by thermogravimetry in an oxidant dynamic atmosphere), and the temperature of the minimum of the derivative of the thermogravimetric profile (T_c) are also shown in table 3. The first parameter indicates the amount of coke borne by the catalyst, whereas the last parameter supplies an idea of the temperature of combustion of the carbonaceous deposits [31]. In the case of fresh catalysts, the weight losses were negligible.

According to these results, the non-doped catalyst bears higher amounts of carbonaceous deposits, which is well correlated with its more pronounced deactivation. The amount of chlorine is also higher in the case of platinum catalyst, the relation between chlorine concentration and weight of coke being identical for both deactivated catalysts (0.4). This aspect indicates that the TTCE plays an important role in the coke formation. More experimental evidence (XPS and TPO-MS of deactivated catalysts) of this behaviour has been found in previous studies of the hydrodechlorination of TTCE over carbon-supported noble metal catalysts (Pd and Pt) [23].

Regarding to the combustion temperatures, the combustion temperature of the coke of non-doped catalyst is lower than that of the doped catalyst. The lower combustion temperature of the deposits in the Pt catalyst would indicate that their H/C or H/Cl ratios in the deposits are higher than in the case of the non-doped catalyst [31]. Therefore, the density of the coke is lower in the case of Pt and the volume higher. This aspect encourages that the fouling effects were more important in the case of non-doped catalyst.

4. Conclusions

The modification of Pt/Al_2O_3 catalyst with vanadium leads to catalysts slightly less active but more resistant to deactivation, especially when the reduction temperature is 500 °C. According to the TPR results, the vanadium is in reduced form at this reduction temperature.

For the catalysts reduced at 500 °C, the optimal amount of vanadium (in the range of concentration tested in this work) is 0.12 %. In experiments carried out at 250 °C (deactivation is slower at this temperature), the selected doped catalyst presents better performance (activity and resistance to deactivation) that the non-doped Pt catalyst. Not only a higher resistance to poisoning caused by chlorine, as cited in the literature, but also a minor trend to bear carbonaceous deposits was observed in the bimetallic catalyst.

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