Carbon tetrachloride hydrodechlorination with organometallics-based platinum and palladium catalysts on MgO

V. Dal Santo [a], C. Dossi [b], S. Recchia [b], P.E. Colavita [c], G. Vlaic [c], R. Psaro [a,*]

[a] CNR Research Centre "CSSCMTBSO" and Dipartimento di Chimica Inorganica, Metallorganica e Analitica,
Università degli Studi di Milano, Via Venezian 21, 20133 Milan, Italy
[b] Dipartimento di Scienze Chimiche, Fisiche e Matematiche, Università dell'Insubria, Via Valleggio 11, 22100 Como, Italy
[c] Dipartimento di Scienze Chimiche, Universita' di Trieste, Via L. Giorgieri 1, 34100 Trieste, Italy

Abstract

Hydrodechlorination of carbon tetrachloride was performed at atmospheric pressure over Pd and Pt catalysts supported on various inorganic oxides (Al_2O_3, MgO, CeO_2) and obtained from different organometallic precursors ($Pd(acac)_2$, $[Pd(C_3H_5)Cl]_2$, $Pt(acac)_2$ and $Pt(CH_3CN)_2Cl_2$). Generally, Pd-based catalysts show low conversion levels and high selectivity to C_1–C_{7+} hydrocarbons with a distribution that fits a typical Schulz–Flory mechanism for alkyl polymerization.

On the other hand, Pt catalysts show high and stable activity, the major products are $CHCl_3$ and in lesser extent methane. Catalytic performances depend on the stability, under reaction conditions, of the metal phase, that could be related to the nature of chlorine species pre-adsorbed on catalysts. Owning to their superior catalytic performances, the structural modifications of Pt catalysts under reaction conditions were characterized by EXAFS spectroscopy. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrodechlorination; Carbon tetrachloride; Palladium; Platinum; Heterogeneous catalysis

1. Introduction

Carbon tetrachloride, together with other chlorinated compounds like PCBs and CFCs, possesses noxious effects on environment, particularly a high ozone potential depletion. It was, in fact, classified in the IV group among CFCs and so its use was banned, in developed countries, from 1996.

Among the more diffuse CFCs disposal methods, like thermal combustion [1] and catalytic combustion [2], catalytic hydrogenation is one of the more promising, owning to the low reaction temperature and the production of useful compounds, without pollutants by-products like dioxins, CO, Cl_2 and $COCl_2$.

Pt-based catalysts were widely used in CCl_4 hydrodechlorination reactions, in the pioneer work of Weiss et al. [3] over peripherally deposited Pt on η-Al_2O_3 catalysts $CHCl_3$ and CH_4 at constant molar ratio were produced. However, such processes have been marked with poor selectivity, rapidly declining catalytic activity and short reactor operating cycles. Various treatments have been explored to improve activity and selectivity, Holbrook and Horley [4] reported a new process in which by-product production is decreased and duration of catalyst activity is improved.

* Corresponding author. Tel.: +39-02-58354401;
fax: +39-02-58354405.
E-mail address: rpsaro@csmtbo.mi.cnr.it (R. Psaro).

The mechanism of C–Cl bond hydrogenolysis in heterogeneous systems is still far from understood and a number of catalytic models has been proposed to account for the observed catalytic trends [5]. Many aspects such as the nature of the reactive adsorbed species, the catalytically active sites and the source of catalysts deactivation are still not established.

Choi et al. [6] reported the effect of different Pt precursors on the oxidation states of metallic particles and, in turn, on the catalytic properties.

The influence of particle size and support effect on activity, selectivity and durability was studied by several authors, and is not very clear: Coq et al. [7] suggest that small particles would be more resistant to Cl poisoning, but the major effect is due to the support Pt/AlF_3 was the most active selective and durable catalyst since the metallic particles are electron deficient. Zhang and Beard [8] showed that Pt/Al_2O_3 catalysts containing large, aggregated particles show remarkable durability.

It has been reported that catalysts obtained from H_2PtCl_6 on MgO [9,10] showed good conversion and selectivities for the hydrodechlorination of CCl_4 to $CHCl_3$, being less prone to deactivation than Pt/Al_2O_3 at lower H_2/CCl_4 ratio. This behavior was ascribed to the basicity of MgO that retards the coking.

On the other hand, Pd catalysts were used, with good results, for the partial, gas phase, dehalogenation of chloro-fluorocarbons to hydrofluorocarbons [11–17], of polychloroalkenes [18], and of chlorobenzenes and other alogenated aromatics (i.e. PCB), both in gas and liquid phase [5,19–22].

Pd-based catalysts were tested using a large variety of supports like Al_2O_3, AlF_3, SiO_2, Carbon, etc. and with various substrates but at present there are few studies on palladium supported on basic oxides (i.e. MgO) in the hydrodechlorination of chlorinated aliphatic substrates like CCl_4.

The aim of this work is to study different Pt and Pd catalysts supported on various inorganic oxides, in particular MgO, in the hydrodechlorination of CCl_4. Particular attention was devoted to the choice of the organometallic precursor, in order to maintain the properties of supports, allowing to pointing out their role in catalytic properties.

2. Experimental

2.1. Catalyst preparation

$Pd(acac)_2$ was synthesized in our laboratory according to the literature procedure [23].

$[Pd(C_3H_5)Cl]_2$ was obtained from Strem Chemicals; $Pt(acac)_2$, and $Pt(CH_3CN)_2Cl_2$ from Aldrich and used as received without further purification.

Pumice powder is waste from the building material manufactured by Pumex S.p.A. at Lipari (Italy), and prior use was treated according to Ref. [24], and was kindly supplied by Prof. G. Deganello. CeO_2 was kindly supplied by Prof. A. Trovarelli. Al_2O_3 support (AKZO 000-1.5E), was used as received.

Magnesium oxide (Merck 97% batch No. 308 TA 390565) was refluxed in deionized water for 3 h, and then dried in air overnight at 110 °C as reported in literature [25–27]. Following this treatment, MgO surface area was increased to $300 m^2 g^{-1}$.

All the oxide supports were pretreated overnight in high vacuum at 500 °C for MgO (MgO^{500}) and Al_2O_3 ($Al_2O_3^{500}$), and at 300 °C for CeO_2 (CeO_2^{300}). In order to get information on the effects of thermal treatments on MgO, a sample of this oxide was simply evacuated in mechanical vacuo overnight at ambient temperature. This sample is referred to as MgO^{AIR}.

Toluene and CH_2Cl_2 (Aldrich) were dried over activated molecular sieves in inert atmosphere. The oxide supports were impregnated at room temperature under Argon atmosphere with a diluted solution of metal precursor in anhydrous solvent, obtaining a 2 wt.% metal loading for each sample. The solvent was removed in vacuo, and the sample dried overnight in vacuo.

Samples with different MgO surface properties and different chlorine/platinum molar ratio were synthesized by the above procedure, namely AIR-Cl/Pt = 0.0, was obtained from MgO^{AIR} and a toluenic solution of $Pt(acac)_2$; Cl/Pt = 0.0 from MgO^{500} and a toluenic solution of $Pt(acac)_2$; Cl/Pt = 0.9 from MgO^{500} and a dichloromethane solution of $Pt(acac)_2$ and Cl/Pt = 2.6 from MgO^{500} and a dichloromethane solution of $Pt(CH_3CN)_2Cl_2$.

The Cl content was determined by argentimetric titration as already reported [28], and Cl/Pt ratios were calculated from experimental values of Cl and Pt contents. The chloride contents are significantly higher

than the expected Cl/Pt ratios, when dichloromethane is used for sample preparation.

Metal loadings were determined by ICP-AES (Pt) and AAS (Pd) after dissolution of the catalyst in a HCl/HNO$_3$ mixture.

Metal dispersion was measured by H$_2$ pulse chemisorption technique at 100 °C on samples reduced at 500 °C and Ar purged at 350 °C using a Micromeritics Pulse Chemisorb 2700 instrument.

2.2. Catalytic tests

Prior to the catalytic runs, the impregnated catalysts were reduced in flowing hydrogen from 25 to 500 °C at 10 °C/min and kept at 500 °C for 1 h. Oxidative regeneration of used catalysts was done by heating in O$_2$ flow (50 ml/min) from 25 to 500 °C at 10 °C/min; the sample was then left at 500 °C for 1 h in O$_2$, cooled down in flowing Ar, and reduced by standard treatment.

The hydrodechlorination of CCl$_4$ (Merck GR batch No. K22643522605) was performed in a continuos flow, fixed bed glass microreactor, working at atmospheric pressure, with H$_2$/CCl$_4$ ratios varying from 5 to 20. Gases were all reagent grade (99.999% obtained from SIAD).

The reaction mixture was obtained by bubbling H$_2$ or H$_2$/Ar in CCl$_4$ thermostated at various temperatures in order to obtain the desired H$_2$/CCl$_4$ ratio. Flow rates of the gas mixture vary from 22.0 to 33.0 ml/min depending on the desired contact time; namely, for 100 mg of 2% Pd catalyst, for $\tau = 9$ s the total flow rate is 33.0 ml/min.

Quantitative analyses of reactants and products were carried out on an on-line gas-chromatograph (Carlo Erba Instruments HRGC 5160) fitted with a thermostated sampling valve and FID, using a 50 m, 0.2 mm cross-linked methylsilicone (Hewlett-Packard PONA) capillary column.

The HCl evolution vs. time-on-stream (t.o.s.) was monitored by an on-line potentiometric cell, as described previously [28].

2.3. EXAFS characterization

X-ray absorption spectra were collected at the D42 beamline of LURE (Orsay-France) operating at 2 GeV of positron energy and at a storage ring current of 200 mA. The experimental station was equipped with a Si(3 3 1) channel-cut crystal monochromator. Second harmonics are absent due to the extinction rule of the Si(3 3 1); third harmonic is negligible due to the low photon flux at that energy. Pt metal foil has been used for the angle/energy calibration. All spectra were recorded at 25 °C in transmission mode at the Pt L$_{III}$-edge (11.56 keV) over the range 11.35–12.50 keV.

The powder samples were loaded under inert atmosphere in the catalysis-EXAFS cell (Lytle type). Sample homogeneity was checked by taking low-exposition photographs of the samples. The spectra of Pt(acac)$_2$/MgO^{500} impregnated from toluene and CH$_2$Cl$_2$ solutions were recorded after in situ reduction at 500 °C and after the catalytic tests at 150 °C in H$_2$/CCl$_4$ = 10.

The single scattering data analysis was performed with the "EXAFS pour le Mac" [29] software. Experimental $\chi(k)$ data were extracted from the absorption data by a conventional procedure (linear pre-edge background subtraction; 5th polynomial fit for the atomic-like contribution, subtracted following the procedure proposed by Lengeler and Eisenberger [30] normalization to edge height). The k^3-weighted $\chi(k)$ data were Fourier transformed (Kaiser window, $\tau = 2.5$) in a typical k range of 3–14 Å^{-1}, and the main contributions to the Fourier transform modulus were filtered in order to obtain metal nearest-neighbor shells. The so-obtained filtered contributions were analyzed using the non-linear least-squares fitting programs developed by Michalowicz [31]. Experimental phase shift and amplitude functions of the scattering oxygen and platinum atoms used in the fit of the supported samples were extracted from pure Pt(acac)$_2$ and Pt foil, respectively.

3. Results and discussion

Pd and Pt catalysts supported on various inorganic oxides were synthesized in order to evidence the effects of their different acid–base character on catalytic properties. They were synthesized by impregnation of the pretreated support from anhydrous solutions (in toluene or CH$_2$Cl$_2$) of the appropriated organometallic precursors.

This method allows obtaining a high degree of interaction between the metal precursor and the

Table 1
Catalytic performances of Pd-supported catalysts[a]

Catalyst	Conversion (mol%)	Selectivity (mol%)				
		CH_4	C_2H_6	C_{3+}	$CHCl_3$	$(C_xCl_y)_2$
Pd/CeO_2	1.8	41.8	23.9	12.2	2.7	19.3
Pd/Pumice	2.5	53.7	30.8	13.5	0.0	4.9
Pd/MgO^{500}	4.1	17.6	30.6	19.1	6.8	3.5

[a] Values taken after 150 min at $R = 5$, $\tau = 9$ s, $T = 150\,°C$.

support, as already reported for Pd/MgO catalysts [32,33].

Stable metal phases could be obtained by simply reduction, without altering the acid–base properties of activated supports, as it would otherwise occur using aqueous solutions of the inorganic salts conventionally used for impregnation. It is remarkably that the chloride contents are higher than the expected Cl/M value (M = Pd, Pt), when a dichloromethane solution is used for sample preparation. The same effect has been previously observed in magnesia-supported Pd samples prepared from CH_2Cl_2 solutions of $Pd(acac)_2$ [28,33]. It was shown the chlorinated solvent released some chlorine via a metal-catalyzed base assisted rupture of C–Cl bonds with formation of surface Mg–Cl sites.

3.1. Pd-based catalysts

Pd-based catalysts generally promote the formation of hydrocarbons (from C_1 to C_7), mainly methane and ethane whereas hydrochlorocarbons ($CHCl_3$ and CH_2Cl_2) and chlorinated dimers as C_2Cl_6, C_2Cl_4 are produced in a lower amount (see Table 1). By comparing the performance listed in Table 1 is evident that a basic support is required in order to maintain a quite high conversion level, and depress the production of chlorinated dimers like hexachloroethane that represent a very noxious by-product.

This peculiar hydrogenolytic activity of Pd/MgO catalysts leading to the complete cleavage of C–Cl bonds could be ascribed to the strong hydridic character of hydrogen atoms chemisorbed on the electron-rich Pd particles in strong contact with O^{2-} sites of MgO [32,33]. We cannot exclude the presence of some form of chlorine–palladium interaction, but this effect may be indirect, occurring via the support, and the metal-support interface may well play a dominant role in the overall process. In fact it is also known that large, electron poor Pd particles on γ-alumina are less active in complete hydrogenation of CCl_2F_2 to CH_4 [15].

During the catalytic test, even working at low conversion, there is a progressive deactivation (see Fig. 1) that could be due to chlorine poisoning, as reported in literature for the hydrodechlorination of CCl_2F_2 [13] and/or formation of high molecular weight hydro(chloro)carbons that cover active sites [14,34]. The formation of such hydro(chloro)carbons could account for the fact that, generally, the sum of % selectivity values for Pd-supported catalysts is not equal to 100%.

A similar behavior was already reported for Pd supported on carbon reduced with molecular hydrogen [34], in this case the fast deactivation was ascribed to a formation of a polymer film on the surface that poisons active sites.

The same mechanism could operate also in our systems, were a distribution of hydrocarbons fitting a Schulz–Flory model [35,36] for alkyl polymerization mechanism was found.

Increasing the H_2/CCl_4 ratio results in a net increase in the hydrocarbons selectivity against the chlorinated products. Selectivity to methane is strongly depressed at low H_2/CCl_4 ratios (R); this evidence indirectly confirms the formation of methane by hydrogenolysis of heavier hydrocarbons (see Table 2). In fact, the hydrodechlorination of CCl_4 with Pd-based catalysts requires an excess of hydrogen to convert all CCl_4 into hydrocarbons. The similarity of $R = 10$ and 20 is to be attributed to the fact that no effects of partial pressure of H_2 are occurring once the stoichiometric ratio is exceeded.

The effect of varying the reaction temperature is not so enhanced on total hydrocarbons selectivity (see Table 3), but their distribution is strongly influenced. At low temperature the production of higher
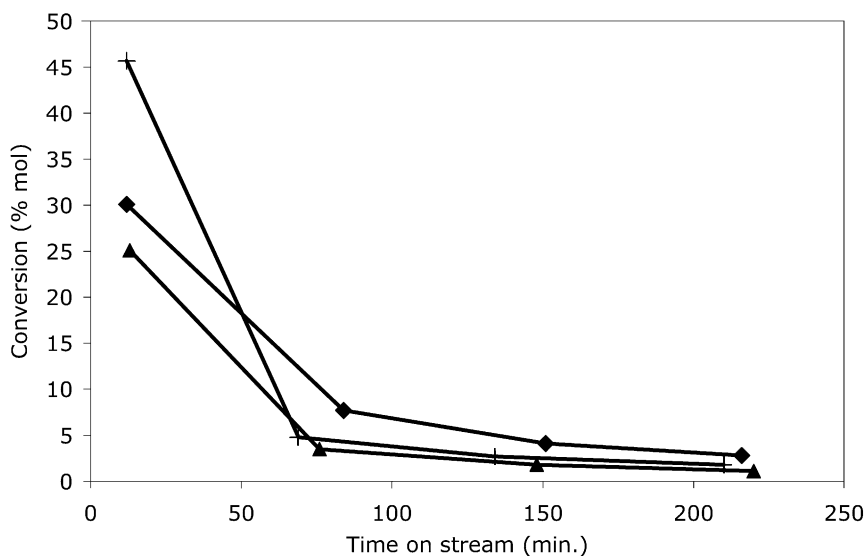
Fig. 1. Activity of Pd-based catalysts at $T_R = 150\,^\circ$C, $\tau = 9$ s; $R = 5$. (▲) CeO_2; (◆) MgO; (+) Pumice.

Table 2
Effect of H_2/CCl_4 (R) ratio on hydrocarbon selectivities for $Pd(acac)_2/MgO^{500a}$

$Pd(acac)_2/MgO^{500}$	Selectivity (mol%)		
	$R = 5$	$R = 10$	$R = 20$
CH_4	13.6	38.4	36.5
C_2H_6	29.2	35.5	35.7
C_3H_8	14.0	10.0	10.2

[a] $T = 150\,^\circ$C, $\tau = 9$ s, selectivities values are taken at 8% conversion.

hydrocarbons is enhanced and hydrogenolysis to methane is depressed. As could be expected the conversion decreases at low reaction temperature.

Major drawbacks of Pd-based catalysts are their low activity and catalytic lifetime, moreover any attempt of reactivate them by reduction was ineffective.

It is also not advisable to regenerate them by conventional oxidative treatment, since this results in a massive loss of active phase by volatilization of $PdCl_2$ originated from the reaction between metallic Pd and Cl_2 evolved from combustion of hydrochlorocarbons film adsorbed on Pd particles.

3.2. Pt-based catalysts

As a general consideration Pt-based catalysts reach high conversion values and show a remarkable durability (see Fig. 2) producing $CHCl_3$, with some methane and, in lower amount, ethane. The highest conversion levels are obtained with alumina and magnesia as supports (see Table 4). Pt/Al_2O_3 catalyst promotes a remarkable high production of CH_2Cl_2 and methane at the expenses of $CHCl_3$.
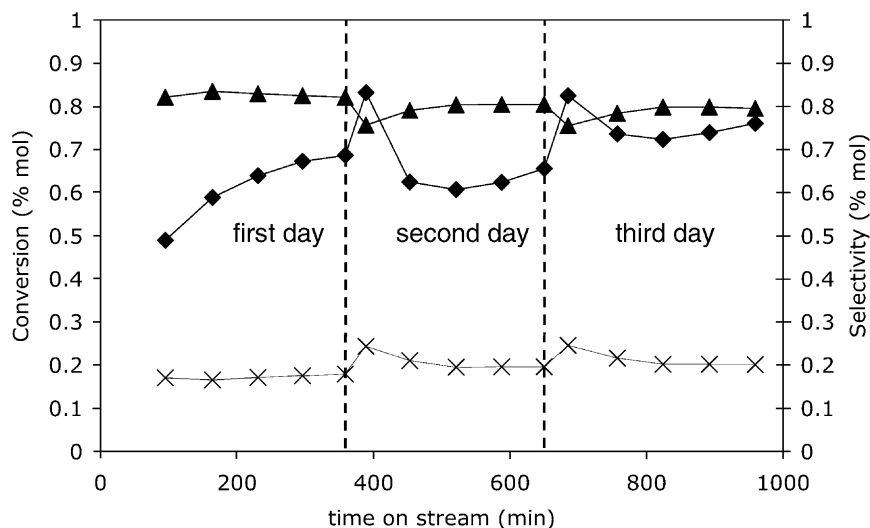
Table 3
Catalytic performances of Pd-based catalysts[a]

Catalyst	T ($^\circ$C)	Conversion (mol%)	Selectivity (mol%)				
			C_1	C_2	C_{3+}	$CHCl_3$	$(C_xCl_y)_2$
Pd/MgO^{500}	150	12.1	32.1	35.0	17.3	1.3	0.9
	125	10.8	23.8	35.4	19.8	2.7	1.2
	100	5.8	15.2	26.1	22.3	0.1	2.3

[a] Values taken after 150 min t.o.s. at $R = 20$; $\tau = 9$ s.

Fig. 2. Activity of Pt/MgO^{500} (Cl/Pt = 0.9) catalysts at $T_R = 150\,^\circ$C, $\tau = 6$ s; $R = 10$. (▲) Conversion; selectivity to (◆) CHCl$_3$, to (×) hydrocarbons.
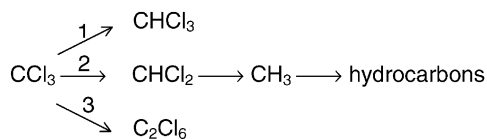
Table 4
Catalytic performances of Pt-supported catalysts[a]

Catalyst	Conversion (mol%)	Selectivity (mol%)				
		CHCl$_3$	CH$_2$Cl$_2$	CH$_4$	Others C$_x$H$_y$	(C$_x$H$_y$Cl$_z$)$_2$
Pt/CeO$_2$	43.3	72.6	1.0	23.8	2.4	0.1
Pt/Pumice	81.1	66.4	1.1	28.7	3.8	0.0
Pt/MgO^{500}	95.0	80.7	1.3	12.6	8.4	0.0
Pt/Al$_2$O$_3$	100	36.9	22.9	38.2	1.6	0.2

[a] Pt/MgO^{500} has a ratio Cl/Pt = 0.9 (see text). Reaction conditions: $T = 150\,^\circ$C; H$_2$/CCl$_4$ = 10; pH$_2$ = 691 mm Hg; $\tau = 6$ s.

This behavior has never been reported in literature, both kinetic studies performed by Weiss et al. [3] and catalytic ones by other authors [6,7,9,10,37] report only CHCl$_3$ and CH$_4$ as major products. Only in TPSR experiments of adsorbed CCl$_4$ at high H$_2$ pressure, or using CHCl$_3$ as reactant in standard hydrodechlorination reaction at low conversion, high selectivity to CH$_2$Cl$_2$ were achieved by Bae et al. [37].

In the case of our Pt/Al$_2$O$_3$ catalyst the high selectivity to CH$_2$Cl$_2$ and methane could be ascribed both to the high time of contact, compared to those used by previously cited authors, both to the presence of acidic Al^{3+} sites, that lead to a decrease in the electronic density on Pt particles increasing the bonding energy of adsorbed CCl$_3$ fragments [6]. The reaction pathway 2 in Scheme 1 [3,10] becomes favored due to

$$CCl_3 \begin{array}{c} \nearrow^{1} \ CHCl_3 \\ \xrightarrow{2} \ CHCl_2 \longrightarrow CH_3 \longrightarrow hydrocarbons \\ \searrow_{3} \ C_2Cl_6 \end{array}$$

Scheme 1.

an increase of the residence time of CH$_{3-n}$Cl$_n$ fragments on metallic surface.

By increasing the contact time of from 1.5 to 6 s results in an increase in CH$_2$Cl$_2$ and CH$_4$ production against CHCl$_3$ (pathway 1) and dimers (pathway 3) (Table 5).

Pt particles on MgO are supposed to be more electron rich, owning to the interaction with basic O^{2-} sites. This fact would, in turns, favor pathway 1.

Table 5
Effect of (τ) on Pt/Al$_2$O$_3$ and Pt/MgO catalysts performances

Catalyst	Contact time (s)			
	1.5	2	3	6
Pt/Al$_2$O$_3$				
Conversion (mol%)	78.4	79.6	99.9	100.0
Selectivity (mol%)				
CHCl$_3$	58.4	59.4	49.6	36.8
CH$_2$Cl$_2$	9.6	10.1	14.9	23.0
C$_x$H$_y$	31.2	29.8	34.8	39.7
C$_2$Cl$_6$	0.6	0.4	0.1	0.0
Pt/MgO (Cl/Pt = 0.9)				
Conversion (mol.%)	74.1	78.2	84.0	95.0
Selectivity (mol%)				
CHCl$_3$	79.1	80.3	80.1	79.3
CH$_2$Cl$_2$	1.0	0.8	1.1	1.3
C$_x$H$_y$	19.8	18.6	18.7	19.0
C$_2$Cl$_6$	0.0	0.2	0.0	0.3

The contact time has effect only on conversion, since selectivity remains practically unchanged, according to data reported in literature [10]. This constancy in the range of contact times explored, and the very low percentages CH$_2$Cl$_2$ and C$_2$Cl$_6$ suggest that the ratios of reactions 2 and 3 are negligible compared to 1.

The principal effect of low H$_2$/CCl$_4$ ratios, apart a net conversion decrease, is represented by an increased production of chlorinated dimers, mainly hexachloroethane and tetrachloroethene (Table 6). At values of H$_2$/CCl$_4$ ratio close to the stoichiometric value of 4, and operating at integral conditions, the dimerization of adsorbed CCl$_3$ fragments became not negligible (see Scheme 1).

Table 6
Effect of varying the H$_2$/CCl$_4$ ratio on Pt/MgO Cl/Pt = 0.9 catalysts[a]

	H$_2$/CCl$_4$ ratio	
	5	10
Conversion (mol%)	67.8	95.0
Selectivity (mol%)		
CHCl$_3$	73.0	79.3
C$_x$H$_y$	14.5	19.0
Cl-dimers	5.6	0.3

[a] $T = 150\,^\circ$C, $\tau = 6$ s, pH$_2$ = 691 mm Hg.

In Table 7 are shown the catalytic performances of platinum catalysts supported on various MgO supports, whose surface properties were modified both by decreasing their highly basic character, sample AIR-Cl/Pt = 0.0, both by introducing appropriate amounts of chlorine, but keeping its basic properties, samples Cl/Pt = 0.0, Cl/Pt = 0.9, Cl/Pt = 2.6. The higher activity is observed with the Cl/Pt = 0.9 catalyst, having an intermediate Cl/Pt ratio. The selectivity to CHCl$_3$ is also higher at a Cl/Pt ratio of 0.9.

Increasing Cl/Pt ratio, catalytic activity tends to decrease again, with a parallel increase in the hydrocarbon selectivity. The presence of chlorine deriving from the impregnation solvent (Cl/Pt = 0.9) induces a beneficial effect on the catalytic properties when a chlorine-free Pt precursor was used. On the contrary, the use of a chlorine-containing Pt precursor decreases the catalytic performances.

Owning to the basic character of MgO support its reactivity toward HCl, a major product of the hydrodechlorination reaction, plays an important role

Table 7
Effect of MgO surface properties on Pt/MgO catalysts[a]

	Pt/MgO sample			
	AIR-Cl/Pt = 0.0	Cl/Pt = 0.0	Cl/Pt = 0.9	Cl/Pt = 2.6
Conversion (mol%)	65.2	88.0	95.0	87.3
Selectivity (mol%)				
CHCl$_3$	80.9	79.5	80.7	75.7
CH$_2$Cl$_2$	1.5	0.7	1.3	1.3
CH$_4$	14.9	15.8	12.6	21.0
C$_2$H$_6$	2.0	3.8	0.4	1.4
C$_{3+}$	0.4	0.2	3.8	0.8
C$_2$Cl$_6$	0.2	0.0	0.2	0.0

[a] $T = 150\,^\circ$C, H$_2$/CCl$_4$ = 10, $\tau = 6$ s.

in catalytic behavior of our samples. Choi et al. [10] also reports the formation of a phase of $MgCl_2 \cdot xH_2O$ in Pt/MgO catalysts after hydrodechlorination experiments.

At the beginning of catalytic runs we observe a sharp increase in the temperature of the catalytic bed (up to $40\,^{\circ}C$ for chlorine-free materials), after this induction period the temperature of the catalytic bed reaches steady-state conditions. During this induction period no HCl evolution could be detected, during steady-state conditions evolution of HCl takes place with a rate predictable on the basis of the distribution of reaction products. After catalytic runs, the catalysts were analyzed for their chlorine content and they show a chlorine/magnesium ratio equal to 0.33.

According to literature data [38,39] for mixed magnesium oxo-chloride phases the formula of our support phase during steady-state catalytic reaction could be ascribed to a Sorel-type $MgO–Mg(OH)_2–5MgO$ $MgCl_2 \cdot xH_2O$.

The profound influence on the catalytic activity of the initial chlorine content of the Pt/MgO material could be related to the prevention of overheating phenomena at the beginning of the catalytic run. However, a too high initial chlorine doping results in a similar effect, and lower steady-state conversions are obtained.

In order to rationalize the catalytic behavior we tried to correlate catalytic data with the metal dispersion, of freshly reduced catalysts, measured by hydrogen chemisorption in a pulse mode at $100\,^{\circ}C$. The H/M values on AIR-Cl/Pt = 0, Cl/Pt = 0 and Cl/Pt = 0.9 are 0.053, 0.956 and 0.177, respectively.

The low value for AIR-Cl/Pt = 0.0 sample could explain the low reaction rate, but the markedly lower value observed for Cl/Pt = 0.9 sample, the most active catalyst, is consistent with Pt particles partially covered by Cl adsorbate.

Chemisorption measurements are not allowed on used catalyst, because the presence of chlorine and organic residues on metal particles. To overcome these coverage problems we performed an ex situ EXAFS investigation on the more significant catalysts, freshly reduced and after catalytic runs (see Figs. 3 and 4) (fit results reported in Table 8).

Sample Cl/Pt = 0.9 after reduction exhibits small Pt clusters (CN(Pt) = 4.6), in close contact with the oxygen atoms of support (CN(O) = 2.3), and no presence of chlorine in contact with the metal phase (see Table 8). The mean particle diameter of metal particles could be estimated, in the hypothesis of f.c.c. packing and cubocthaedral geometry, around 11 Å, consisting of 30 atoms clusters [40]. Chlorine is adsorbed on
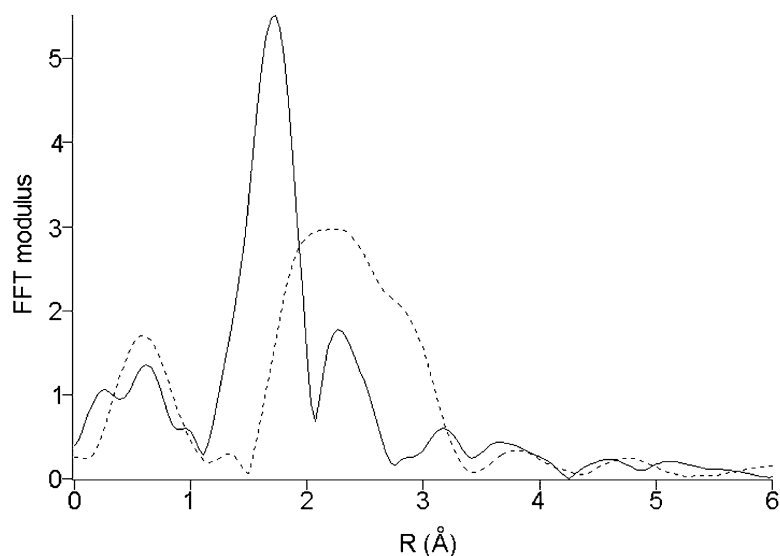

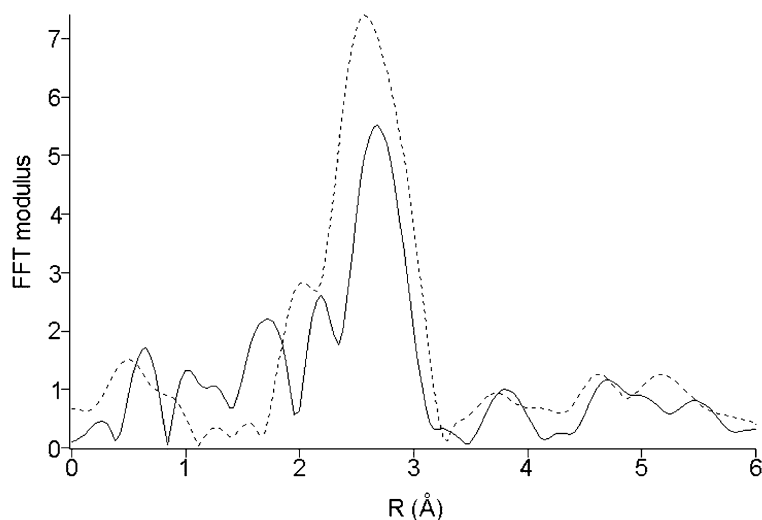Fig. 3. RSF of Pt/MgO^{500} (Cl/Pt = 0.0) reduced (solid line) and after catalytic run (dotted line).

Fig. 4. RSF of Pt/MgO^{500} (Cl/Pt = 0.9) reduced (solid line) and after catalytic run (dotted line).

MgO support as Cl$^-$ ions deriving from the impregnation solvent, probably close to the metallic particles; a similar behavior is already reported in literature for analogous systems based on Pd [33]. After the catalytic test, a considerable increase in the particle size is observed (CN(Pt) = 9.9). In f.c.c. packing and in the hypothesis of cuboctahedral particles, such a CN value corresponds to a mean particle diameter of about 30 Å, which means a maximum of 30% surface atoms and an even smaller fraction of metal atoms in contact with the support surface. The small oxygen and/or chlorine contribution to the signal is thus covered by the heavy metal scatters.

The non-Cl-containing catalyst (Cl/Pt = 0.0) after reductive activation exhibits a dispersion almost at monoatomic level (CN(Pt) = 1.6) and, after catalytic run, a moderate increase in particle size (CN(Pt) = 4.6) and the presence of chlorine (CN(Cl) = 0.9) on the metallic phase.

These results cannot be rationalized on the basis of the structure insensitivity of the hydrodechlorination reaction, since the catalytic activity increase as the Pt particles size increases.

Catalytic activity seems, therefore, to be related not only to the stability of metal phases under reaction conditions, but primarily to the initial chlorine content.

The good stability of Pt phase, and the absence of appreciable coking, allows performing regeneration by a simple oxidation–reduction treatments of the used catalysts without altering the catalytic properties.

Table 8
Curve fitting results of Pt L$_{III}$-edge EXAFS data of Pt/MgO catalysts before and after a catalytic run

Reduced			After catalysis		
CN	R (Å)	Δσ (Å)	CN	R (Å)	Δσ (Å)
Catalyst Cl/Pt = 0.0					
O: 2.7 ± 0.1	O: 2.030 ± 0.004	O: 0.076 ± 0.004	O: 0.9 ± 0.2	O: 2.31 ± 0.01	O: 0.09 ± 0.02
Pt: 1.6 ± 0.5	Pt: 2.60 ± 0.01	Pt: 0.09 ± 0.01	Pt: 4.6 ± 0.4	Pt: 2.703 ± 0.008	Pt: 0.096 ± 0.05
Catalyst Cl/Pt = 0.9					
O: 2.3 ± 0.4	O: 2.07 ± 0.02	O: 0.12 ± 0.01			
Pt: 4.7 ± 0.5	Pt: 2.757 ± 0.006	Pt: 0.083 ± 0.003	Pt: 9.9 ± 0.9	Pt: 2.753 ± 0.006	Pt: 0.087 ± 0.005

4. Conclusions

Pd- and Pt-supported catalysts show completely different properties, due to different reaction mechanisms. The hydridic character of adsorbed H atoms and the easy cleavage of C–Cl bonds species lead to almost complete hydrogenation of CCl_4 to hydrocarbons on Pd-supported materials. Instead, Pt catalysts show very high activity and selectivity to partial hydrodechlorination to trichloromethane, with methane as major byproduct.

The strong basicity of support is important requirement in order to achieve high and stable conversion levels coupled to a high selectivity to chloroform. Using an acidic support such as alumina results in a increased production of dichloromethane.

The initial chlorine doping of MgO support upon catalyst preparation plays an important role in preventing excessive overheating phenomena at the beginning of the hydrodechlorination reaction, when MgO reacts with HCl to form a Sorel-type magnesium oxo-chloride phase, which is stable under reaction conditions.

Acknowledgements

References

[1] J.V. Michael, K.P. Lim, S.S. Kumaran, J.H. Kiefer, J. Phys. Chem. 97 (1993) 1914.
[2] H. Windaw, M. Wyatt, Platinum Met. Rev. 37 (1993) 186.
[3] A.H. Weiss, B.S. Gambhir, R.B. Leon, J. Catal. 22 (1971) 245.
[4] M.T. Holbrook, A.D. Horley, US Patent 5,105,032 (1992).
[5] B. Coq, G. Ferrat, F. Figuéras, J. Catal. 101 (1986) 434.
[6] H.C. Choi, S.H. Choi, J.S. Lee, K.M. Lee, Y.J. Kim, J. Catal. 166 (1997) 284.
[7] B. Coq, F. Bouchara, D. Tournigant, F. Figuéras, in: G. Centi, et al. (Ed.), Environmental Catalysis, SCI Pub., Rome, 1995, p. 583.
[8] Z.C. Zhang, B.C. Beard, Appl. Catal. A 174 (1998) 33.
[9] S.Y. Kim, H.C. Choi, O.B. Yang, K.H. Lee, J.S. Lee, Y.G. Kim, Chem. Commun. (1995) 2165.
[10] H.C. Choi, S.H. Choi, O.B. Yang, J.S. Lee, K.H. Lee, S.Y. Kim, J. Catal. 161 (1996) 790.
[11] Z. Karpinski, K. Early, J.L. d'Itri, J. Catal. 164 (1996) 378.
[12] B.S. Ahn, S.C. Lee, J.D. Moon, B.G. Lee, J. Mol. Catal. 106 (1996) 83.
[13] B. Coq, J.M. Coignon, F. Figuéras, D. Tournigant, J. Catal. 141 (1993) 21.
[14] M. Makkee, E.J.A.X. van de Sandt, A. Wiersma, J.A. Moulijn, J. Mol. Catal. A 134 (1998) 191.
[15] W. Juszczyk, A. Malinowski, Z. Karpiński, Appl. Catal. A 166 (1998) 311.
[16] A. Malinowski, D. Łomot, Z. Karpiński, Appl. Catal. B 19 (1998) L79.
[17] M. Bonarowska, A. Malinowski, W. Juszczyk, Z. Karpiński, Appl. Catal. B 30 (2001) 187.
[18] S. Ordóñez, F.V. Díez, H. Sastre, Appl. Catal. B 31 (2001) 113.
[19] P. Forni, L. Prati, M. Rossi, Appl. Catal. B 14 (1997) 49.
[20] L. Perrone, L. Prati, M. Rossi, Appl. Catal. B 15 (1998) 241.
[21] J.L. Benitez, G. Del Angel, React. Kinet. Catal. Lett. 70 (1) (2000) 67.
[22] M.A. Aramendía, V. Boráu, I.M. García, C. Jiménez, J.M. Marinas, F.J. Urbano, Appl. Catal. B 20 (1999) 101.
[23] Gmelin Handbuch der Anorganischer Chemie, Palladium, Verlag Chimie, Weinheim, 1947, p. 302.
[24] A.M. Venezia, M.A. Floriano, G. Deganello, A. Rossi, Surf. Interf. Anal. 18 (1992) 619.
[25] T.E. Holt, A.D. Logan, S. Chakraborti, A.K. Datye, Appl. Catal. 34 (1987) 199.
[26] E. Guglielminotti, S. Coluccia, E. Garrone, L. Cerruti, A. Zecchina, J. Chem. Soc., Faraday Trans. 75 (1979) 96.
[27] G. Leofanti, M. Solari, G.R. Tauszik, F. Garbassi, S. Galvagno, J. Schwank, Appl. Catal. 3 (1982) 131.
[28] C. Dossi, S. Recchia, A. Fusi, Fresenius J. Anal. Chem. 367 (2000) 416.
[29] A. Michalowicz, J. Phys. IV France 7C2-235 (1997).
[30] B. Lengeler, E.P. Eisenberger, Phys. Rev. B. 21 (1980) 4507.
[31] F. James, M. Roos, Comput. Phys. Commun. 10 (1975) 343.
[32] V. Dal Santo, L. Sordelli, C. Dossi, S. Recchia, E. Fonda, G. Vlaic, R. Psaro, J. Catal. 198 (2001) 0.
[33] M. Kappers, C. Dossi, R. Psaro, S. Recchia, A. Fusi, Catal. Lett. 39 (1996) 183.
[34] E.S. Lokteva, V.I. Simagina, E.V. Golubina, I.V. Stoyanova, V.V. Lunin, Kinet. Catal. 41 (6) (2000) 855.
[35] A.G. Somorjai, Introduction to Surface Chemistry and Catalysis, Wiley, New York, 1994, p. 495.
[36] P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, 1953.
[37] J.W. Bae, E.D. Park, J.S. Lee, K.H. Lee, Y.G. Kim, S.H. Yeon, B.H. Sung, Appl. Catal. A 217 (2001) 79.
[38] L. Urwongse, C.A. Sorrel, J. Am. Ceram. Soc. 63 (1980) 501.
[39] C.A. Sorrel, C.R. Armstrong, J. Am. Ceram. Soc. 59 (1976) 51.
[40] H.G. Fritsche, R.E. Benfield, Z. Phys. D. At., Mol. Clusters 26 (Suppl.) (1993) 15.