

Hydrodechlorination of polychlorobenzenes and polychlorinated aliphatic compounds under mild conditions by Pd and Rh ions or their complexes intercalated in γ -zirconium phosphate

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Received 12 July 2004; received in revised form 7 October 2004; accepted 8 October 2004
Available online 26 November 2004

Abstract

Polychlorinated aliphatic or aromatic compounds are hydrodehalogenated under mild conditions ($T=303\text{--}343\text{ K}$; $p_{\text{H}_2}=0.1\text{ MPa}$) in methanol containing an organic or inorganic base, using intercalated Pd(II) and Rh(III) as metal catalysts. Both “naked” ions inserted into γ -Zirconium phosphate ($\gamma\text{-ZrP-M}$) and their complexes with 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (phen), $\gamma\text{-ZrP-M-L}$ ($L = \text{bipy, phen}$) intercalated into the same matrix have been used. A recently prepared material containing intercalated octadecyltrimethylammonium ion, $\gamma\text{-ZrP-C}_{18}$ ($\text{C}_{18} = \text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3^+$), with an unusually large interlayer distance has been also used as support. The catalytic activity depends on the metal, the ligand and the base. The best results have been obtained upon using NEt_3 as the base. Pd-compounds are more active but less stable than the analogous Rh-compounds. Bipy and phen ligands play a dual role: in fact, they reduce the catalytic activity, but they increase the stability over time and the recycling possibility of the catalyst. Conversely, the catalyst based on naked metal ions inserted into $\gamma\text{-ZrP}$ charged with surfactant ions exhibits an initial catalytic activity comparable with that of the materials described above, but it loses more rapidly its activity.

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Keywords: Heterogeneous catalysis; Zirconium phosphates supports; Hydrodechlorination; Chlorobenzene; Polychlorinated compounds

1. Introduction

Chlorinated organic compounds are noxious and persistent pollutants owing to their inertness and, in general, low biodegradability. An efficient procedure for their abatement is the hydrodechlorination that can be performed upon reacting the chlorinated species with hydrogen at atmospheric or higher pressure in the presence of transition metal centres or their complexes, at 300–373 K. Noble metals supported on coal, silica or alumina have mostly been used as catalysts [1–21], but their practical application is limited by their poor

stability over the time. A review on the catalytic hydrodehalogenation by palladium catalysts in both liquid and gas phase did appear in 2001 [22]. It should be stressed that this metal-catalyzed technology is by far preferred to the thermo-oxidative—and/or chemical oxidation—destruction ones that may produce species more toxic than the reactants, particularly chloro-dioxins and/or phosgene [23–26].

In recent years, we have investigated the use of titanium and zirconium hydrogen phosphate, both as α - and γ -phase ($\alpha\text{-TiP}$ and $\gamma\text{-ZrP}$), as “heterogenizing” support. These inorganic zeolite-like ion-exchanger materials, with layered structure, are able to locate in their layers either “naked ions” or transition metal complexes. Remarkably, the inserted metals or complexes, sometimes, are more active than the

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non-supported compounds [27] and the intercalated catalysts can be easily recovered and reused, preserving in most cases their catalytic activity over several runs.

In this paper we report on the activity of some γ -zirconium-phosphate materials, containing either “naked ions” (γ -ZrP-Me; Me = Pd(II), Rh(III), or their N,N' -diamine complexes (γ -ZrP-Me-L; L = 2,2'-bipyridil, 1,10-phenanthroline), for the hydrodechlorination of chlorobenzenes, polychlorobenzenes and other polychlorinated aromatic and aliphatic compounds, which are converted into the relevant hydrocarbons. The preliminary results have been reported in 2002 [28].

The influence of the reaction conditions on the catalytic activity as well as on the stability over time and recycling of different materials is also reported and discussed.

2. Experimental

2.1. Chemicals and materials

Rh(III) nitrate, Pd(II) chloride, 2,2'-bipyridil (bipy), 1,10-phenanthroline (phen) and solvents were Aldrich products and were used as purchased. The precursor material γ -zirconium phosphate, γ -Zr(PO₄)(H₂PO₄)·2H₂O (γ -Zr-P) was prepared according to the literature procedure [29–31]. γ -Pd(II)-zirconium phosphate (γ -ZrP-Pd), γ -Rh(III)-zirconium phosphate (γ -ZrP-Rh), γ -Pd(II)-ligand-zirconium phosphate (γ -ZrP-Pd-L; Ligand = bipy or phen), and γ -Rh(III)-ligand-zirconium phosphate (γ -ZrP-Rh-L; Ligand = bipy or phen) were prepared as already reported [32–35]. γ -Pd(II)-octadecyltrimethylammonium-zirconium phosphate (γ -ZrP-Pd-C₁₈), γ -Rh(III)-octadecyltrimethylammonium-zirconium phosphate (γ -ZrP-Rh-C₁₈), were also prepared as recently described [36].

2.2. Physical measurements

GLC quantitative analyses of reaction products were carried out with a Varian Chrompack CP 3800 gas chromatograph connected to a Varian “Star chromatograph workstation”, using a CP Sil 8 CB 30 m 0.53 i.d. capillary column and toluene as internal standard. GC–MS analyses were performed using a Hewlett-Packard instrument. X-ray photoelectron spectra were taken with a Leybold LHS 10 spectrometer: the experimental details were already described [37].

2.3. Catalyst pre-reduction

The catalyst was suspended in methanol in a glass reactor, under H₂ at atmospheric pressure, and allowed to react under stirring at 345 K for a fixed time (3, 5, and 7 h). Then, it was recovered by filtration dried in vacuo and used for catalytic reactions and XPS characterization.

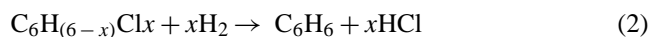
2.4. Substrate hydrodechlorination

All reactions were carried out in a 175 mL glass reactor. In a typical experiment, 20 mL of a methanol solution of C₆H₅Cl 0.25 M, 2 mL of NEt₃ and 60 mg of γ -Zr(PO₄)₂H_{1.8}Pd_{0.1}·2.5H₂O (C₆H₅Cl/Pd = 282 mol/mol) were introduced in the reactor under nitrogen atmosphere at 343 K. Hydrogen was bubbled for 2 min and then the reactor was closed at atmospheric pressure of H₂. The mixture was reacted under stirring at 343 K for 1 h. The reactor was then cooled at ambient temperature and the volume of H₂ consumed was calculated by a gas burette measuring the required gas to restore the initial pressure in the reactor. The reaction mixture was filtered and the solution was LGC analysed for reactants and products. The catalyst on the filter was washed with a 1:2 methanol–diethyl ether mixture and recovered. It was either directly used in another run, to test its catalytic stability, or for XPS analysis, to detect the oxidation state of the metal centres (see Tables 2–4 and 6).

The same procedure was used for all the reactions involving other catalysts, substrates and bases. Catalyst amount, H₂ uptake, halogenated compounds reacted and TOF, expressed as mole of dechlorinated compounds per mole of metal per hour, are reported in Tables 1–5.

3. Results and discussion

The Pd(II)- and Rh(III)-intercalated γ -zirconium phosphate catalytic systems (γ -ZrP-M), their corresponding materials in which the metal centres are coordinated to 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (phen) (γ -ZrP-Pd-L, γ -ZrP-Rh-L; L = bipy, phen), or the more recently prepared [36] derivatives that bear an intercalated octadecyltrimethylammonium ion, γ -ZrP-M-C₁₈ (M = Pd, Rh; C₁₈ = C₁₈H₃₇N(CH₃)₃⁺), that imposes a greater inter-layer distance, are effective in the hydrodechlorination of monochloro- and polychlorobenzenes (reactions (1)–(2)) and other polychlorinated aliphatic and aromatic compounds (tetrachloroethylene, esachloroethane, benzylchloride)



(1 ≤ x ≤ 6).

The dehalogenation reaction has been monitored by both a quantitative analysis of reagents and products by gas-chromatography and measuring the volume of reacted hydrogen. The titration of HCl developed, when the reaction is carried out without the addition of a base, has also been used as a means of controlling the course of the reaction.

All the catalysts, with the exception of those containing intercalated palladium ions exhibit an induction time and the rate of dehalogenation reaches a maximum within 3–5 h. Blank tests have shown that a methanol solution of a Pd(II)-salt, nitrate or acetate, treated with H₂ immediately produces

Table 1
Hydrodechlorination of C₆H₅Cl in presence of NEt₃ at 343 K under 0.1 MPa of H₂^a

Entry	Catalyst	V _{H₂} (mL)	C ₆ H ₅ Cl (mmol) reacted	TOF ^b
1	γ-Zr(PO ₄) ₂ H _{1.8} Pd _{0.1} ·2.5H ₂ O (Pd% = 3.14), 60 mg	101	4.49	254
2 ^c	γ-Zr(PO ₄) ₂ H _{1.8} Pd _{0.1} ·2.5H ₂ O	104	4.51	255
3	γ-Zr(PO ₄) ₂ H _{1.46} Rh _{0.18} ·1.75H ₂ O (Rh% = 5.57), 50 mg	16	0.68	25
4 ^c	γ-Zr(PO ₄) ₂ H _{1.46} Rh _{0.18} ·1.75H ₂ O	41	1.84	68
5 ^d	γ-Zr(PO ₄) ₂ H _{1.46} Rh _{0.18} ·1.75H ₂ O	68	3.03	112
6 ^e	γ-Zr(PO ₄) ₂ H _{1.46} Rh _{0.18} ·1.75H ₂ O	67	2.97	110
7	γ-Zr(PO ₄) ₂ H _{1.64} Pd _{0.18} (bipy) _{0.27} ·1.9H ₂ O (Pd% = 5.06), 40 mg	45	2.02	106
8 ^c	γ-Zr(PO ₄) ₂ H _{1.64} Pd _{0.18} (bipy) _{0.27} ·1.9H ₂ O	77	3.42	180
9 ^d	γ-Zr(PO ₄) ₂ H _{1.64} Pd _{0.18} (bipy) _{0.27} ·1.9H ₂ O	91	4.05	212
10 ^e	γ-Zr(PO ₄) ₂ H _{1.64} Pd _{0.18} (bipy) _{0.27} ·1.9H ₂ O	90	4.01	210
11	γ-Zr(PO ₄) ₂ H _{1.44} Pd _{0.28} (Phen) _{0.28} ·1.75H ₂ O (Pd% = 7.55), 40 mg	21	0.91	32
12 ^d	γ-Zr(PO ₄) ₂ H _{1.44} Pd _{0.28} (Phen) _{0.28} ·1.75H ₂ O	99	4.41	155
13 ^e	γ-Zr(PO ₄) ₂ H _{1.44} Pd _{0.28} (Phen) _{0.28} ·1.75H ₂ O	92	4.10	144
14 ^d	γ-Zr(PO ₄) ₂ H _{1.4} Rh _{0.20} (bipy) _{0.22} ·2H ₂ O (Rh% = 5.51), 40 mg	44	1.93	90
15 ^e	γ-Zr(PO ₄) ₂ H _{1.4} Rh _{0.20} (bipy) _{0.22} ·2H ₂ O	42	1.88	88
16 ^d	γ-Zr(PO ₄) ₂ H _{1.16} Rh _{0.28} (Phen) _{0.40} ·2.6H ₂ O (Rh% = 6.70), 40 mg	40	1.80	69
17 ^e	γ-Zr(PO ₄) ₂ H _{1.16} Rh _{0.28} (Phen) _{0.40} ·2.6H ₂ O	40	1.77	68
18	γ-Zr(PO ₄) ₂ H _{1.46} Pd _{0.18} (C ₁₈) _{0.18} ·2H ₂ O (Pd% = 4.86), 40 mg	62	2.74	150
19 ^d	γ-Zr(PO ₄) ₂ H _{1.46} Pd _{0.18} (C ₁₈) _{0.18} ·2H ₂ O	78	3.47	190
20 ^d	γ-Zr(PO ₄) ₂ H _{0.6} Rh _{0.3} (C ₁₈) _{0.5} ·2H ₂ O (Rh% = 6.16), 40 mg	54	2.39	100
21 ^e	γ-Zr(PO ₄) ₂ H _{0.6} Rh _{0.3} (C ₁₈) _{0.5} ·2H ₂ O	51	2.27	95

^a In all experiments 20 mL of a methanol solution of C₆H₅Cl (0.25 M) and 2 mL of NEt₃ were used. The reaction time is 1 h.

^b Turnover frequency (TOF) expressed as mole of chlorobenzene reacted per mole of metal per hour.

^c Pre-reduced under H₂ at 343 K for 3 h.

^d Pre-reduced under H₂ at 343 K for 5 h.

^e Pre-reduced under H₂ at 343 K for 7 h.

Table 2
Catalytic stability of Pd-materials^a

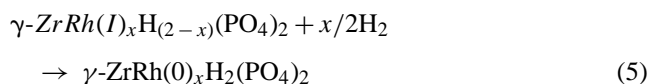
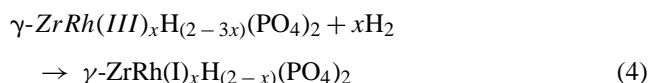
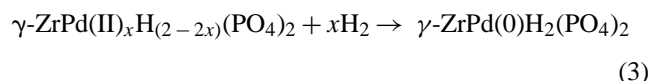
Entry	Cycles	Catalysts	C ₆ H ₅ Cl (mmol) reacted	TOF ^b
1	2	γ-Zr(PO ₄) ₂ H _{1.8} Pd _{0.10} ·2.5H ₂ O (Pd% = 3.14), 60 mg	8.85	250
2	4		7.86	222
3	6		6.13	173
4	7		3.89	110
5	2	γ-Zr(PO ₄) ₂ H _{1.64} Pd _{0.18} (bipy) _{0.27} ·1.9H ₂ O (Pd% = 5.06), 40 mg	7.60	200
6	4		7.00	184
7	6		5.93	156
8	7		4.56	120
9	2	γ-Zr(PO ₄) ₂ H _{1.44} Pd _{0.28} (Phen) _{0.28} ·1.75H ₂ O (Pd% = 7.55), 40 mg	7.95	140
10	4		7.43	131
11	6		6.53	115
12	7		5.39	95

^a In all experiments 20 mL of a methanol solution of C₆H₅Cl 0.5 M and 2 mL of NEt₃ were used. The catalyst were pre-reduced under H₂ before the use. Reaction conditions: T = 343 K; p_{H₂} = 0.1 MPa; time = 2 h.

^b Turnover frequency (TOF) expressed as mole of chlorobenzene reacted per mole of metal per hour.

a suspension of Pd black. Similarly, a methanol solution of RhCl₃·3H₂O produces a fine black suspension of reduced Rh, but with a slower kinetics. Moreover, the addition of either bipy or phen to the methanol solution of metal salts causes in all cases, a decrease of the reduction rate.

These features suggest that the catalytically active species are not the initial intercalated metal ions or complexes, but their reduced forms produced by interaction with molecular hydrogen (reactions (3)–(5)).



(0 ≤ x ≤ 1 for Pd-compounds, and 0 ≤ x ≤ 0.66 for Rh-compounds).

It is worth noting that the protons generated in the reductive process involving Pd(II), Rh(III) and Rh(I) for the electro-neutrality of the materials remain in the

Table 3
Catalytic stability of Rh-materials^a

Entry	Cycles	Catalysts	C ₆ H ₅ Cl (mmol) reacted	TOF ^b
1	2	γ -Zr(PO ₄) ₂ H _{1.46} Rh _{0.18} ·1.75H ₂ O (Rh% = 5.57), 50 mg	5.84	108
2	4		5.41	100
3	6		4.60	85
4	7		3.52	65
5	2	γ -Zr(PO ₄) ₂ H _{1.4} Rh _{0.20} (bipy) _{0.22} ·2H ₂ O (Rh% = 5.51), 40 mg	3.68	86
6	4		3.43	80
7	6		3.04	71
8	7		2.57	60
9	2	γ -Zr(PO ₄) ₂ H _{1.16} Rh _{0.28} (Phen) _{0.40} ·2.6H ₂ O (Rh% = 6.70), 40 mg	3.44	66
10	4		3.28	63
11	6		2.97	57
12	7		2.60	50

^a In all experiments 20 mL of a methanol solution of C₆H₅Cl 0.5 M and 2 mL of NEt₃ were used. The catalyst were pre-reduced under H₂ before the use. Reaction conditions: T = 343 K; pH₂ = 0.1 MPa; time = 2 h.

^b Turnover frequency (TOF) expressed as mole of chlorobenzene reacted per mole of metal per hour.

Table 4
Catalytic stability of Pd- and Rh-C₁₈ materials^a

Entry	Cycles	Catalyst	C ₆ H ₅ Cl (mmol) reacted	TOF ^b
1	2	γ -Zr(PO ₄) ₂ H _{1.46} Pd _{0.18} (C ₁₈) _{0.18} ·2H ₂ O (Pd% = 4.86), 40 mg	4.20	115
2	4		3.50	96
3	6		2.37	65
4	7		0.87	24
5	2	γ -Zr(PO ₄) ₂ H _{0.6} Rh _{0.3} (C ₁₈) _{0.5} ·2H ₂ O (Rh% = 6.16), 40 mg	3.40	71
6	4		3.02	63
7	6		1.91	40
8	7		1.34	28

^a In all experiments 20 mL of a methanol solution of C₆H₅Cl, 0.5 M and 2 mL of Net₃ were used. The catalyst were pre-reduced under H₂ before the use. Reaction conditions: T = 70 °C, pH₂ = 1 atm, time = 2 h.

^b Turnover frequency (TOF) expressed as mole of chlorobenzene reacted per mole of metal per hour.

Table 5
Hydrodechlorination of chloro benzene in absence of base T = 343 K; time = 1 h^a

Entry	Catalyst	TOF ^b
1	γ -Zr(PO ₄) ₂ H _{1.8} Pd _{0.10} ·2.5H ₂ O (Pd% = 3.14), 60 mg	250
2 ^c	γ -Zr(PO ₄) ₂ H _{1.8} Pd _{0.10} ·2.5H ₂ O	247
3	γ -Zr(PO ₄) ₂ H _{1.46} Rh _{0.18} ·1.75H ₂ O (Rh% = 5.57), 50 mg	20
4 ^d	γ -Zr(PO ₄) ₂ H _{1.46} Rh _{0.18} ·1.75H ₂ O (Rh% = 5.57), 50 mg	90
5 ^d	γ -Zr(PO ₄) ₂ H _{1.64} Pd _{0.18} (bipy) _{0.27} ·1.9H ₂ O (Pd% = 5.06), 40 mg	175
6 ^d	γ -Zr(PO ₄) ₂ H _{1.4} Rh _{0.20} (bipy) _{0.22} ·2H ₂ O (Rh% = 5.51), 40 mg	75

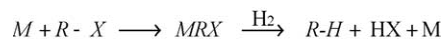
^a In all experiments 20 mL of a methanol solution of C₆H₅Cl 0.25 M were used.

^b Turnover frequency (TOF) expressed as mole of chlorobenzene reacted per mole of metal per hour.

^c Pre-reduced under H₂ at 343 K for 3 h.

^d Pre-reduced under H₂ at 343 K for 5 h.

matrix bonded to PO₄³⁻ moieties that are converted into monohydrogen- or dihydrogen-phosphate. However, the efficiency of the catalysts has been evaluated comparing the activity of materials after they were pre-reduced under H₂. Table 1 shows the activity of the materials used in the hydrodechlorination of monochlorobenzene expressed as the turnover frequency (TOF, mole of chlorobenzene reacted per mole of metal per hour). The materials containing palladium (entries 1–2; 7–10; 11–13) are much more active than the corresponding rhodium ones (entries 3–6, 14–15, 16–17). This different reactivity, already previously observed with other systems [6], can be ascribed to the greater ability of Pd(0)



Scheme 1.

to be oxidized by chlorobenzene (Scheme 1) [38]. The subsequent interaction with H₂ (Scheme 1) causes the reductive elimination of benzene and hydrogen chloride.

This mechanism has already been proposed by other authors through kinetic measurements [1], under comparable conditions. The presence of intercalated ligand such as bipy or phen causes a decrease of the catalytic activity for both the palladium- (Table 1, entries 2, 8, 12) and

rhodium-compounds (Table 1, entries 5, 14, 16). This effect can be rationalized on the basis of the steric hindrance: the presence of ligand makes more difficult the interaction between the substrate and the active metal centre. Quite different is the behaviour of materials with intercalated C_{18} ions. Their initial activity is in fact lower than that of the corresponding materials containing “naked” ions, but higher than that of catalysts loaded with intercalated bipy and phen ligands (Table 1, entries 1, 2, 9, 12, 18, and 19 for palladium-compounds and 5, 14, 16, 20 for Rh-compounds). We observe that the C_{18} ions are released during the catalytic runs as evidenced by GC and carbon and nitrogen elemental analysis on recovered catalysts.

4. Stability of the catalysts and demonstration of heterogeneous catalysis

Our previous studies on the catalytic activity in carbonylation processes of these and related materials [27,32,33] have shown that their efficiency and stability do mainly depend on the metal, its oxidation state and the substrate present in solution. Deactivation of catalysts can occur by elution of both oxidized and/or reduced active metal centres depending on whether the catalysis occurs under oxidative or reductive conditions. In general, the catalytic materials are more stable under oxidative than reductive conditions [33,39–40]. To check the stability of catalytic systems over time and after recycling, they have been separated from the reaction mixture after 2 h and re-used. After each run, the solution has been analysed and the TOF calculated as moles of halocarbons converted per mole of metal. At least seven runs have been performed per each material.

In Tables 2–4, the TOF values for different compounds are reported. The results show that within the first two or three runs the catalytic activity of our systems remains almost constant, and then a decrease is observed, the entity of which depends on the metal and the intercalated ligand. After seven cycles, the TOF value is about 55% lower than the initial one for materials containing “Pd-naked” ions (Table 2 entries 1–4) and 40% lower for the corresponding Rh-materials

(Table 3, entries 1–4). The presence of intercalated nitrogen ligands, such as bipy or phen, improves the performance of the catalysts and the observed decrease of activity was 40% for γ -ZrPPd-bipy (Table 2, entries 5–8), and 30% for γ -ZrPPd-phen (Table 2, entries 9–12). For the corresponding Rh-containing materials the decrease ranges around 30% for γ -ZrPRh-bipy (Table 3, entries 5–8), and 20% for γ -ZrPRh-phen (Table 3, entries 9–12).

So, according to the trend of TOF values the stability order of the two series of materials results to be: ZrPPd-(phen) > ZrPPd-(dipy) > ZrP-Pd; ZrPRh-(phen) > ZrPRh-(dipy) > ZrP-Rh. It is worth noting the contrasting effect of the intercalated ligand, which if on one hand causes a decrease of the specific activity (lower TOF), on the other hand it improves the stability over cycles (higher turnover number, TON). The observed reduction of activity over the time and with recycling of the catalyst is higher for materials containing intercalated C_{18} ions (Table 4, entries 1–8). This trend can be perhaps related to larger interlayer distance imposed by the bulky surfactant C_{18} ion that makes easier the elution of the active metal centres.

The whole of these findings suggest that the dehalogenation process is promoted by the heterogeneous catalysts and not by the reduced metal eluted, which produces a metallic film on the walls of the reactor. This, if recovered, shows a poor catalytic activity. Also, the fact that the intercalation of large ions makes less effective the dehalogenation reaction suggests that the increase of the interlayer distance reduces the efficacy of the catalysts.

5. Modification of the catalysts during the hydrodechlorination catalysis

In an attempt to explain the course of activity with time and to evidence the nature of the active species, we have recorded the XPS-spectra of materials before and after their use. The binding energy values of signals are summarized in Table 6. As we have already shown [32,41] palladium-compounds before the use display signals at 338.5 and 338.6 eV, attributed to γ -ZrPPd(II), γ -ZrPPd(II)-L (L = bipy,

Table 6
XPS characterization of materials under different conditions: signals eV and assignment

Entry	Pd-compounds	Conditions	Pd (II)	Pd(0)	
1	γ -Zr(PO ₄) ₂ H _{1.8} Pd _{0.10} ·2.5H ₂ O	Before reaction	338.5	–	
2	γ -Zr(PO ₄) ₂ H _{1.64} Pd _{0.18} -L (L = bipy, phen)	Before reaction	338.6	–	
3	γ -Zr(PO ₄) ₂ H _{1.8} Pd _{0.10} ·2.5H ₂ O	After first cycle	–	335.4	
4	γ -Zr(PO ₄) ₂ H _{1.64} Pd _{0.18} -L(L = bipy, phen)	After first cycle	338.5	335.5	
5	γ -Zr(PO ₄) ₂ H _{1.64} Pd _{0.18} -L (L = bipy, phen)	Pre-reduced	–	335.5	
	Rh-compounds		Rh(III)	Rh(I)	Rh(0)
6	γ -Zr(PO ₄) ₂ H _{1.46} Rh _{0.18} ·1.75H ₂ O	Before reaction	309.6	–	–
7	γ -Zr(PO ₄) ₂ H _{1.4} Rh _{0.20} -L (L = bipy, phen)	Before reaction	309.5	–	–
8	γ -Zr(PO ₄) ₂ H _{1.46} Rh _{0.18} ·1.75H ₂ O	After first cycle	309.5	308.8–308.5	307.3–306.9
9	γ -Zr(PO ₄) ₂ H _{1.46} Rh _{0.18} ·1.75H ₂ O	Pre-reduced for 5 h	–	308.8–308.5	307.3–306.9
10	γ -Zr(PO ₄) ₂ H _{1.4} Rh _{0.20} -L (L = bipy, phen)	Pre-reduced for 5 h	–	308.5	306.9

phen), respectively, (Table 6, entries 1, 2). After one cycle the compounds loaded with “Pd-naked ions” do not show any Pd(II) signal, while a signal at 335.4 eV appears, attributed to Pd(0) (Table 6, entry 3). Conversely, materials loaded with the intercalated ligand bipy or phen display both Pd(II) and Pd(0) signals at the same reaction time (Table 6, entry 4). After the first run the signal intensity of Pd(II) decreases until to disappear after the third run, whereas that of Pd(0) increases. Materials pre-treated with H₂ for 5 h show only a XPS signal related to Pd(0) (Table 6, entry 5). Over the time all catalysts show a slow but steady decrease of the Pd(0) signal, which disappears after about 40 h. Apparently, a gradual total release of Pd occurs.

Rh(III)-based materials show signals at 309.6 and 309.5 eV for γ -ZrP-Rh(III) and γ -ZrP-Rh(III)-L, respectively, (Table 6, entries 6, 7). After the first run, they display besides the signal of Rh(III), two new signals, one in the range 308.8–308.5 eV, that we attribute to a Rh(I)-species, and the other in the range 307.3–306.9 eV, relevant to a Rh(0) species (Table 6, entry 8). These values are in agreement with our previous findings [27,32,33,40]. Over the time during the catalytic runs, the intensity of the signals decreases as follows: Rh(III), Rh(I), Rh(0). Materials pre-treated for 5 h with H₂ do not show the signals of Rh(III) (Table 6, entries 9, 10) and under these conditions they show the highest catalytic activity (Table 1, entries 5, 16, 18). The activity is preserved until the materials display at least the Rh(0) signal.

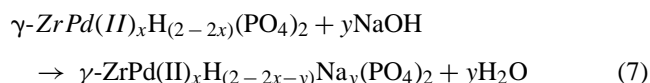
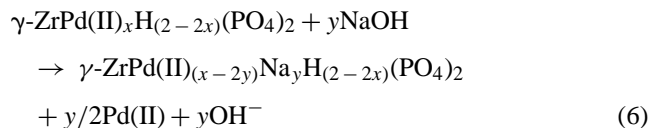
These data are in agreement with what discussed above for Pd and confirm that the catalytic active sites are the metal centres in their reduced state, namely, Pd(0) for Pd-compounds and Rh(I) or Rh(0) for the Rh-analogues. The higher stability of Rh-materials with respect to Pd, that we have already observed in previous works under reductive conditions [27,33,40], can be explained considering the fact that for Pd-catalysts only Pd(0) is active, whereas for Rh-compounds both Rh(I) and Rh(0) species are reasonably active.

6. Effect of the base on the hydrodechlorination of monochlorobenzene

The hydrodechlorination of monochlorobenzene is affected in different ways by the absence or presence of bases.

When the chlorobenzene is hydrodechlorinated in the absence of a base, the catalytic activity (TOF) is quite similar to that obtained in presence of NEt₃ for palladium materials and almost lower for Rh-compounds. We tentatively ascribe this behaviour to their different reactivity towards HCl produced in the hydrodechlorination process as in reactions (1)–(2). In fact, HCl may cause a release of Rh ions from the catalyst following the exchanges H⁺/Rh(III) and H⁺/Rh(I). Leaching of active species determines a decrease of catalytic activity. The same occurs at much less extent with Pd-materials because of their faster reduction to Pd(0).

Monochlorobenzene is hydrodechlorinated also in the presence of inorganic bases (NaOH, Na₂CO₃ and CaO). With NaOH, both Pd- and Rh-materials exhibit a good initial activity that ceases within 2–3 cycles, whereas with other bases (Na₂CO₃ and CaO) the activity decay is more rapid. Such worse performance of inorganic bases with respect to organic ones, can be explained in terms of increased leaching of Pd(II) or Rh(III) and Rh(I) from the catalyst by exchange with Na-cations (see Eq. (6), for Pd), or because an extended change of the surrounding of the active centre due to proton loss (Eq. (7)).



As a matter of fact, the protons play an important role in the stabilization of the structure of the catalyst as a whole. We have also found that Pd- or Rh-materials, pre-reduced with H₂ and subsequently allowed to react with a NaOH methanol solution under N₂, show a lower catalytic activity than that of materials not treated with NaOH. Reaction (8) could explain the decrease of activity in term of destabilization of the structure of the matrix upon deprotonation.

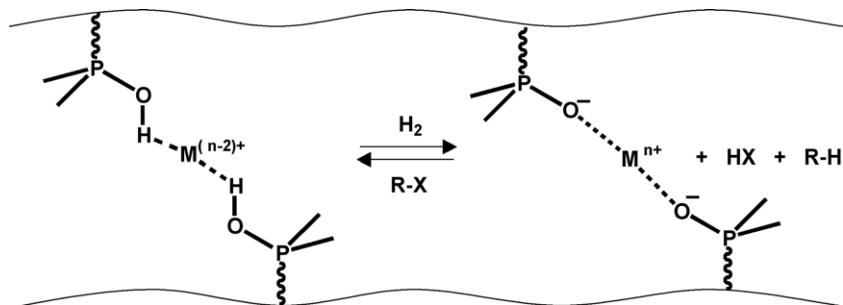
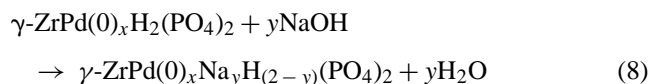


Fig. 1.

Table 7

Hydrodechlorination of polychlorinated compounds at 343 K and $p_{H_2} = 0.1$ MPa, in the presence of γ -Zr(PO₄)₂H_{1.8}Pd_{0.1}·2.5H₂O as catalyst^a

Entry	Substrates ^b	Time (h)	V _{H₂} (mL)	Products C ₆ H _(6-x) Cl _x						
				x = 6	x = 5	x = 4	x = 3	x = 2	x = 1	x = 0
1	1,2-Dichlorobenzene (4.89)	1	83	–	–	–	–	2.89	0.40	1.6
		2.5	197 ^c	–	–	–	–	0.34	0.55	4.1
2	1,2,3-Trichlorobenzene (1.43)	1	87	–	–	–	–	0.14	0.01	1.28
3	Esachlorobenzene (0.72)	1	52 ^d	0.035	0.17	0.10 ^e	0.10 ^f	0.085	0.02	0.17
4	4-Chloro-C ₆ H ₄ Br (1.86)	1	55	Br-C ₆ H ₅ trace		Cl-C ₆ H ₅ 1.36 (73%)			C ₆ H ₆ 0.5	
5	4-Cl-C ₆ H ₄ NO ₂ (2.99)	1	72	2-Cl-C ₆ H ₅ NO ₂ (0.38)		C ₆ H ₅ NO ₂ 2.31 (84%)			C ₆ H ₅ NH ₂ 0.30	
		2	150 ^c	Absent		C ₆ H ₅ NO ₂ 2.31 (1.96)			C ₆ H ₅ NH ₂ 1.03	
6	C ₆ H ₅ CH ₂ Cl (4.1)	1	75	C ₆ H ₅ CH ₂ Cl 0.9		C ₆ H ₅ CH ₃ 3.2				

^a Unless otherwise stated, all the experiments were carried out in methanol using NEt₃ as base. The amount of substrates and reaction products are expressed in mmol.

^b In parenthesis mmol of substrate.

^c Total H₂ volume consumed.

^d For solubility reason THF was used.

^e The amount is related to the 1,2,4,5 isomer, which is the main product.

^f The amount is related to the 1,2,3 isomer, which is the main product.

Fig. 1 shows the possible role of $\equiv P-OH$ and $\equiv P-O^-$ moieties in stabilizing reduced and oxidized forms of metal, respectively, which are implied into the H-transfer reaction. As XPS shows only reduced forms of the metals, most probably the H₂ to 2H⁺ conversion is quite fast and the rate-determining step is the H-transfer to RX.

7. Hydrodechlorination of poly-chlorinated compounds

In Table 7 we have summarized the results of the dehydrochlorination of poly-chlorinated substrates and listed the relevant reaction products. All the reactions have been carried out at 343 K under atmospheric pressure of H₂ using γ -Zr(PO₄)₂H_{1.8}Pd_{0.1}·2.5H₂O as catalyst.

The uptake of H₂ shows that the catalytic activity is almost independent of the chlorine content of the substrate (Table 7, entries 1–3), even though the distribution of reaction intermediates suggests that they occur at different dechlorination rates, the monochlorobenzene being the most reactive.

As expected on the basis of the bond strength, the 4-chlorobromobenzene (Table 7, entry 4) is de-halogenated almost selectively to chlorobenzene, that is subsequently reduced to benzene. Also of interest is the behaviour of 4-chloronitrobenzene (entry 5), which is converted into nitrobenzene before undergoing the reduction of the nitro group to give aniline.

Finally, the catalysts are also effective for the hydrodechlorination of chloro-aliphatic compounds. For instance, benzyl chloride (Table 7, entry 6) is easily converted into toluene. Likewise, esa-chloro-ethane is gradually converted into less chlorinated compounds and eventually to ethane.

8. Conclusions

This work has shown that the use of zirconium hydrogen phosphate as heterogenizing support of Pd(II), Rh(III)

and Rh(I) ions or their complexes with di-nitrogen ligands allows to prepare catalytic systems active for the hydrodehalogenation of per-halogenated organics. An organic base can assist the process. The higher stability of catalysts when the hydrodechlorination process is carried out in the presence of NEt₃ rather than of an inorganic base (NaOH, CaO), is explained, also taking into account our previous findings [32,33,40], in terms of the fact that protons of phosphate groups can play an important role in stabilizing metal species in a reduced oxidation state as shown in Fig. 1.

Acknowledgement

The authors wish to thank MURST, (Prin Cofin, 2003 prot. 2003039774) for financial support.

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