

Hydrogenolysis of organohalogen compounds over palladium supported catalysts

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Abstract

Catalytic hydrodehalogenation is one of the most promising methods for detoxification of organohalogen waste. A variety of catalytic systems has been used, although palladium catalysts are the best choice because of their optimal catalytic properties. Catalytic hydrodehalogenation on palladium catalysts is carried out in both the liquid and gas-phases. The experimental procedures for the catalytic hydrodehalogenation are reviewed; the hydrogen source can be either molecular hydrogen or a hydrogen donor in the so called hydrogen-transfer hydrogenolysis. A wide variety of hydrogen donors has been used, including inorganic salts (phosphinates) organic salts (formates), alcohols, proaromatic compounds, etc. Kinetics and mechanisms proposed for hydrodehalogenation are presented, and both agreements and disagreements on the mechanistic aspects are discussed. Catalysts modification (base addition, support modification, second metal addition, etc.) as well as its transformation during the hydrogenolytic process (i.e. deactivation) are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic hydrodehalogenation; Palladium catalysts; Hydrogen-gas hydrogenolysis; Hydrogen-transfer hydrogenolysis

1. Introduction

Chlorinated hydrocarbons are hazardous pollutants which are contained in various waste oils and other organic liquids. They constitute one of the most important kind of organic pollutants due to their environmental impact and noxious effects. Among this pollutants, polychlorobiphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF), chlorofluorocarbons (CFCs), and other chlorinated solvents, are included.

The PCBs possess a series of unique physical and chemical properties: exceptional thermophysical and electrical insulating characteristics, thermal stability, inertness to acids and bases, fire resistance, etc. All

these features are responsible for their wide-scale employment as dielectrics in transformers and capacitors, hydraulic liquids, as heat exchangers and refrigerants, lubricating oils, inks, etc. Although they were never intended for release into the environment, PCBs have become, perhaps more than any other chemical, the most widespread pollutant. Between 1929 and 1972, about 5,00,000 metric tons of PCBs were manufactured. In the seventies, these compounds were recognised as pollutants for the environment. In 1977, the EPA banned the direct discharge into waterways, and since 1979 their manufacture, processing, and distribution have been prohibited. For those compounds, such as PCBs, which can no longer be sold on the market, the problem remains of how to dispose of them. Incomplete combustion of PCBs lead to the formation of PCDDs and PCDFs.

The CFCs have been extensively used since their discovery in the thirties, mainly as refrigerants, foam

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blowing agents or solvents because of their unique properties (non toxic, non flammable, cheap). One of such properties, namely their stability, appears to be its main drawback. It has been found that CFCs accumulate in the troposphere and diffuse to the stratosphere, where they release chlorine atoms which catalytically destroy ozone. In addition to their ozone depletion potential, the emitted CFCs also have a relatively large impact on the greenhouse effect. The relative contribution of CFCs to man-induced global warming is estimated to be up to 25%. Recognising the global nature of the problem, the “Montreal Protocol” was initiated in 1987. This treaty required the signing nations to reduce their production and consumption of CFCs. On the basis of these reports, it has been decided that the world-wide production and consumption of CFCs should be terminated. The recovery of CFCs in use and the subsequent destruction is a logical step forward.

Other chlorinated solvents, such as perchloroethylene (PCE), 1,1,1-trichloroethane (TCE), carbon tetrachloride, and vinyl chloride (VC), are among the most prevalent contaminants in ground water.

2. Background on catalytic hydrogenolysis

The options for the disposal of such organohalogenated pollutants are based on thermal and catalytic combustion, gas-phase thermal and catalytic dehydrohalogenation as well as hydrodehalogenation or hydrogenolysis. Among them, hydrodehalogenation may be regarded as the most universal and promising method for the treatment and detoxification of organohalogen waste. It can be effected by thermal, catalytic and reactive procedures. The last involve the use of expensive hydrogen donors such as LiAlH_4 or NaBH_4 and are only of preparative significance. Catalytic hydroprocessing is now emerging as a promising non-destructive alternative technology whereby the chlorinated waste is converted to products with a commercial value. Catalytic hydrodechlorination is simple, safe, effective, and it ensures, in many instances, the regeneration of the initial raw material.

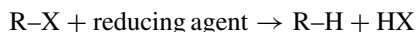
A detailed review [1] published in 1980 and devoted to hydrogenolysis of organic halides gives a good insight into the state of the problem up to that date. More recently, several reviews have been published in which

Table 1
Homolytic bond dissociation energies for C–X, C–H and C–C bonds [6]

Bond	kcal/mol	kJ/mol
$\text{CH}_3\text{-F}$	108	451
$\text{CH}_3\text{-Cl}$	84	349
$\text{CH}_3\text{-Br}$	70	293
$\text{CH}_3\text{-I}$	56	234
$\text{CH}_3\text{-H}$	105	439
$\text{CH}_3\text{-CH}_3$	88	368

the problem of the organohalogen wastes and the development of methods for their processing have been evaluated [2,3]. Besides, a review has been devoted to the study of catalytic hydrodehalogenation of organic compounds [4].

The hydrogenolysis of organic halides can be represented by the following equation:



The ease of C–X bond hydrogenolytic cleavage is dependent on the type of halogen involved, the presence of other functional groups and the catalysts and conditions used for the reaction. Alkyl halides are removed less readily than benzyl, aryl, or vinyl halides, and for all types of halogen compounds the reactivity order is $\text{R-I} > \text{R-Br} > \text{R-Cl} \gg \text{R-F}$ [5]. This order is parallel to the dissociation energy of carbon–halogen bonds as reproduced in Table 1 [6].

Catalytic hydrogenolysis is often inhibited by the release of hydrogen halide produced during the reaction and, therefore, the hydrogenolysis of organic halides is usually carried out in the presence of a base, specially in batch reactions. The role of the added base is to neutralise the acid and to keep the catalytic metal in a reduced state, free from halide ions. Sodium, potassium, calcium and barium hydroxides are generally employed, while sodium acetate, amines and ammonia are often used for base-labile compounds [5].

Amongst all Group VIII noble metal known for their C–Cl bond cleavage and hydrogenation ability, Pd is considered as the best catalyst to replace selectively chlorine atoms with hydrogen, since not only does it promote bond cleavage, but it is also the least affected by the catalyst poisoning properties of the halide ions released [5,7,8].

There is a large number of reported catalytic hydrogenolysis processes that are implemented in either the gas or the liquid-phase, and use a wide variety of catalysts. The hydrogen source can be molecular hydrogen or indeed any other hydrogen donor such as a formate salt, a hypophosphite salt, etc. Finally, the properties of the catalysts can be varied widely by fusing them with other metals, by adding promoting agents, and by selecting or modifying supports.

The progress of the knowledge of the catalytic hydrodehalogenation depends on the understanding of the reaction mechanism. However, since reaction conditions widely vary (aliphatic versus aromatic halides, gas-phase versus liquid-phase reaction, hydrogen gas versus hydrogen donors as reducing agent, etc.) the reaction mechanism may not follow an unified picture.

This review, is intended to report the last decade progress on the application of palladium supported catalysts to the hydrodehalogenation of organic halides. Kinetics and mechanistic aspects are to be discussed, as a function of the reaction conditions. In addition, several aspects dealing with the palladium catalyst (active sites, deactivation, support effect,

additives, etc.) are to be also reviewed. In order to help the researcher to find related references, Table 2 includes most of the references cited herein, organised by subjects. Finally, prospects for the development of catalysts with enhanced activity, selectivity and durability are to be addressed.

3. Hydrogen-gas hydrogenolysis

Catalytic hydrodehalogenation of halogenated compounds can be carried out by both hydrogen gas or by hydrogen transfer from a hydrogen donor. Although catalytic hydrogen transfer hydrogenolytic methods have been described so far, the main method to carry out the carbon–halogen breakage is hydrogen gas hydrogenolysis.

3.1. Gas-phase reactions

Most of the hydrogen-gas catalytic hydrogenolysis of organic halides is carried out on the gas-phase. They mainly deal with light aliphatic halocarbons

Table 2
References cited organised by subject

Subject studied	References
General reviews	[1–4]
Gas-phase reactions	Aryl halides: [9–13,32] CFCs: [8,18–24,29–34] Mechanism: [20–23,25,26,28–32] Selectivity: [8,18–20,31,32] Reaction conditions: [14,18,33,34]
Liquid-phase reactions	General: [22,47–61] Solvent effect: [52,57,58] Multiphase system: [54–56,61]
Hydrogen-transfer hydrogenolysis	[60,63–69]
Base addition	[5,49,50,52,53,58,59]
Catalyst deactivation	Poisoning by HX: [8,9,13,24,31,49,50,53,58,75,80–83] Carbonaceous deposits: [19,23,28,30,31,34,71] Sintering: [13,18,31,72] Catalyst degradation: [50,74,82]
Catalyst	Metallic precursor: [50] Support effect: [13,14,20,32,34–36,39,50,63,70–74] Metal support interactions: [20,32,35,37,39,70] Bimetallic catalysts: [10,11,17,20,38,39,76,77,78] Structure sensitivity: [7,9,24,28,37,41,49,50,75]

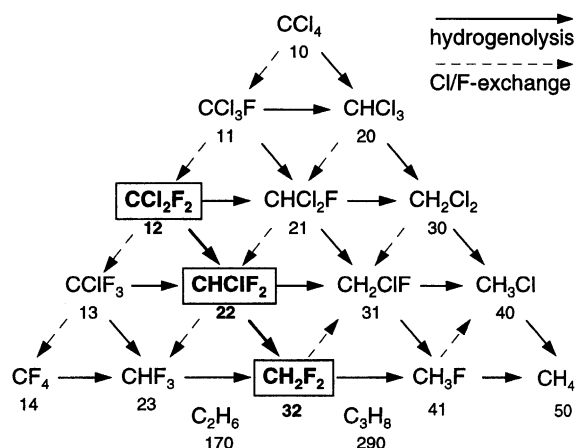


Fig. 1. CFC reaction scheme. The bold formulas and arrows are the reaction aimed at. The direction represents the thermodynamic driving force at 298 K and atmospheric pressure. Reprinted from [14] with permission from Elsevier.

(CFCs and halogenated solvents). However, there are also several works dealing with the gas-phase catalytic hydrodehalogenation of aryl halides [9–13].

3.1.1. Aliphatic halides

Among CFCs, dichlorodifluoromethane (CFC-12) is, by far, the most studied compound. Fig. 1 shows a reaction scheme for C1-type CFCs in which hydrodehalogenation and halogen exchange reactions are presented [14]. The main product of the hydrogenolysis of CCl_2F_2 over palladium supported catalysts is CH_2F_2 (HFC-32). Secondary products are CHClF_2 and CH_4 . Other by-products to a minor extent are CH_3F , CH_3Cl , and CH_2ClF . Coupling products such as ethane and propane are also sometimes detected on palladium [8] although they are important over ruthenium [15] and iron [16,17] catalysts. Products from Cl/F exchange (CHF_3) are also eventually detected but are usually formed at the support [18,19]. From a practical point of view, CH_2F_2 (HFC-32) is the desired product since it is a good replacement for CFCs because of its excellent cooling properties, being more environmental benign. Therefore, the selectivity towards CH_2F_2 is one of the main points studied by the researchers. To visualise the way by which selectivity towards CH_2F_2 can be improved, the understanding of the reaction mechanism is needed.

Coq et al. [20] working with $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts showed that, at the steady-state, the kinetics of CCl_2F_2 hydrodechlorination can be described by two kinetic models: (i) a classical Langmuir–Hinshelwood model with competitive adsorption of the reactants and (ii) an halogenation/dehalogenation mechanism, in which the Pd surface is halogenated by CCl_2F_2 dissociative adsorption and subsequently dehalogenated by hydrogen. This chlorination/dechlorination of the metallic surface is the key step controlling the reaction rate and selectivity. The last approach has been supported by most of the researchers working on the gas-phase hydrogenolysis of aliphatic halocarbons.

Solymosi and Rasko [21] studied the adsorption and dissociation of CH_2Cl_2 on Pd/SiO_2 by FTIR. They reported that CH_2Cl_2 adsorbed molecularly (non-dissociative adsorption) on Pd/SiO_2 at low temperature (-80 to -60°C) but dissociation was observed at -40 to -30°C . Dissociative adsorption was also reported for chlorinated methanes at 300°C [22] and CCl_2F_2 at 150 – 300°C [23]. Generally, the order of the bonding strengths is $\text{C}-\text{Cl} < \text{C}-\text{H} \ll \text{C}-\text{F}$ (Table 1), and therefore, the dissociation would preferably include breakage of the carbon–chlorine bond. However, Ribeiro et al. [24], based on their kinetic results, proposed a non-dissociative adsorption for CF_3CFCl_2 over a polycrystalline Pd foil in the temperature range of 80 – 200°C .

Surface science studies on $\text{Pd}(111)$ surfaces carried out by Gellman and co-workers [25,26] revealed a homolytical cleavage (formation of radical species) of the $\text{C}-\text{Cl}$ bond as it is generally accepted. They established linear free energy relationships (LFER) correlating the dechlorination rate constants [25] or the activation energies [26] to the degree of fluorination of the alkyl chlorides with varying degrees of fluorine substitution (CF_3CFCl_2 , CH_3CFCl_2 , $\text{CH}_2\text{FCFCl}_2$, CH_3CHCl_2). The LFERs have been applied in physical organic chemistry to prove changes in charge distribution occurring during the reaction [27]. For example, if the carbon atom in the transition state is cationic, then an electronegative substituent such as fluorine would increase the activation barrier by destabilising the electron-deficient transition state. Alternatively, if the carbon atom in the transition state is anionic with respect to the initial stage, adding an electronegative substituent would lower the barrier by stabilising the electron-rich transition state. Gellman

and co-workers found that the barriers were insensitive to inductive substituent effects. This implies that the transition state for dehalogenation is homolytic and occurs early in the reaction co-ordinate [25,26].

The result of a dissociative adsorption of the CFC molecule with homolytic cleavage of the carbon–halogen bond is the formation of adsorbed radicalary species. The most important radical intermediate in the hydrodehalogenation of geminal dihalocarbons catalysed by Group VIII metals are carbene species [20,21,23,28–31]. This carbene species, usually difluorocarbenes, would be formed by two sequential dechlorination steps.

Direct evidence for the metal-carbene species was reported by Deshmukh and d'Itri [29]. Based on transient kinetics trapping experiments, the authors provided an insight into the stability and reactivity of the surface carbenes and fluorocarbenes at temperatures and pressures used for catalytic CFC hydrodechlorination. The authors concluded that parallel hydrogenation pathways starting from a common intermediate $:\text{CF}_2$ species, can explain the formation of the products CH_2F_2 and CH_4 for the hydrodechlorination of CCl_2F_2 over Pd/AlF_3 . The formation of the coupling product C_2H_6 also suggests the presence of $:\text{CH}_2$ carbene species as a reaction intermediate. Transient kinetics experiments using ethylene as trapping agent for surface carbenes have provided additional support for the presence of $:\text{CH}_2$ intermediate species. The absence of either coupling products or trapped products containing F suggests that the rate of hydrogenation of surface $:\text{CF}_2$ species is faster than

that of surface $:\text{CH}_2$ species. Such a reactivity trend is consistent with the observed selectivities for the hydrodechlorination products [29]. Solymosi and Rasko [21] also reported the formation of $:\text{CH}_2$ carbene species, characterised by FTIR, upon the dissociation of CH_2Cl_2 on Pd/SiO_2 .

However, the presence of double bond in the aliphatic halide hinders the formation of radicals [22]; what is more, unsaturated molecules are easily adsorbed and hydrogenated onto palladium surfaces. In addition, at temperatures $>200^\circ\text{C}$, pyrolytic (non-catalytic) dehydrochlorination of polychloroethanes is favoured [22].

Based on the above described considerations a number of mechanistic pathways have been proposed for CCl_2F_2 [20,23,29–32] and other CFCs [28] hydrodehalogenation over palladium catalysts, most of which are coincident or, at least, are rather similar. One of the first, and most complete mechanisms, was that proposed by Coq and co-workers [20,32] for the hydrodechlorination of CCl_2F_2 over Pd/AlF_3 (Fig. 2). In this mechanism, CCl_2F_2 would interact with the Pd surface by two parallel ways to yield radical adsorbed species. A serial pathway is ruled out since the initial CH_4 selectivity was about 10–20%, depending on the catalyst, and only smoothly increased with conversion.

A similar reaction mechanisms, but simplified, have been also proposed by Wiersma and co-workers [23,30] and Deshmukh and d'Itri [29]. Fig. 3 shows the reaction mechanism for the hydrodechlorination of CCl_2F_2 over Pd/AlF_3 proposed by Deshmukh and d'Itri. The first step is the dissociative adsorption of

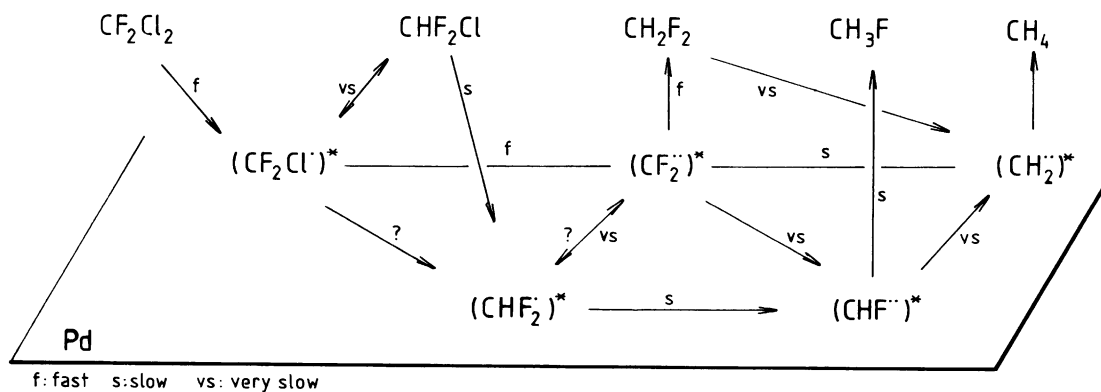


Fig. 2. Reaction scheme for CCl_2F_2 hydrodechlorination. Figure from [20], with permission from publisher.

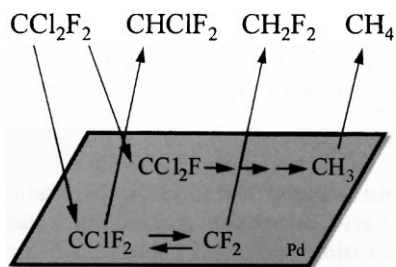


Fig. 3. Reaction pathways and intermediates for the hydrodechlorination of CCl_2F_2 over Pd/AlF_3 . Reprinted from [29] with permission from Elsevier.

CCl_2F_2 to yield adsorbed CClF_2 . This radical could be hydrogenated to CHClF_2 or dechlorinated on the surface to form $:\text{CF}_2$ carbene species. Adsorbed fluorocarbene could then be hydrogenated to yield CH_2F_2 (the main product) or hydrodefluorinated to $:\text{CHF}$ and subsequently to $:\text{CH}_2$ carbene. Finally, $:\text{CH}_2$ carbene can yield CH_4 , or CH_3Cl , or coupling products (i.e. C_2H_6).

Recently, Wiersma et al. [31] proposed a mechanism consisting of two parallel pathways on the palladium surface (Fig. 4). One route is coincident to the mechanism by Deshmukh and d'Itri and leads to CHClF_2 or CH_2F_2 through a $:\text{CF}_2$ carbene intermediate. The rate determining step is the dissociative adsorption of CCl_2F_2 while the selectivity is determined by the reactions on the catalyst surface. A second parallel pathway, accounts for the formation of the fully hydrogenated and coupling products. This pathway starts with the breakage of the C–F bond on the most active sites of the catalyst. Deshmukh and d'Itri proposed that, since the cleavage of the C–F bond is more energetically demanding than the C–Cl cleavage, it

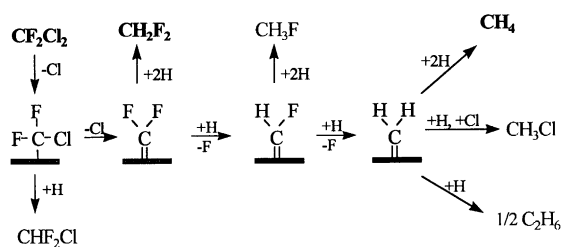


Fig. 4. Mechanism of the CCl_2F_2 hydrogenolysis over palladium. Figure from [31] with permission from publisher.

would be more likely to occur at sites on which the molecule adsorbs more strongly or sites which are intrinsically more active [29]. Then, as the most active sites become blocked by carbonaceous deposits, the hydrogenolysis of the C–F bond decays, and therefore, the formation of fully hydrogenated and coupling products (CH_4 , C_2H_6) is suppressed, and the selectivity towards CH_2F_2 increases, in agreement to their experimental data [31].

3.1.2. Selectivity

From a practical point of view, the selectivity towards CH_2F_2 in the gas-phase hydrodechlorination of CCl_2F_2 over palladium catalysts has to be as high as possible. Palladium is among the Group VIII noble metals the most selective one [8,31] with selectivity towards CH_2F_2 ranging from 30 to 90%.

The selectivity for the main products, CH_2F_2 and CH_4 , is mainly determined by the ratio between the desorption rate of the $:\text{CF}_2$ radical and the rate of the surface reaction leading to CH_4 . Indeed, the readsorption of the product CH_2F_2 can by no means explain the formation of CH_4 , due to the very low reactivity of CH_2F_2 in the gas-phase [20,32].

On the other hand, the selectivity for CHClF_2 and CH_2F_2 is determined by the amount of chlorine present on the catalyst surface and the ease of chlorine removal from the catalyst surface by means of hydrogen [20,31]. The higher the Cl coverage, the lower the driving force for C–Cl bond dissociation [8].

As for products resulting from C/F exchange (CHF_3), they are minor, since exchange activity of the different noble metal catalysts is in the order $\text{Ru} > \text{Ir} > \text{Pt} > \text{Rh} > \text{Pd}$ [31]. When exchange products are obtained in a detectable amount, these are usually due to exchange reactions carried out by the support [18,19].

Finally, selectivity is also affected by the reaction conditions. Thus, CH_2F_2 selectivity is higher at low reaction temperature [18], high time on stream [14,33] and high H_2/CFC feed ratio [33,34]. Other variables such as the catalytic support [34–36], the metal dispersion [37] and the presence of a second metal [38,39] are discussed far below.

3.1.3. Aryl halides

The disposal of aromatic organic wastes containing halogen atoms such as polychlorobiphenyls is a problem

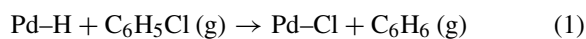
of great urgency. Conventional incineration of these wastes has been recognised to be associated with the unexpected formation of more harmful compounds such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). The removal of halogen from aryl halides by hydrodehalogenation treatment is an effective procedure for diminishing the toxicity and by this way dehalogenated organic wastes can be incinerated without formation of the dioxin-like compounds. Chlorobenzene is often chosen as a model compound in studying the hydrodechlorination reaction since it represents the halogenated species found in many organic wastes [9–12].

In the course of chlorobenzene gas-phase hydrogenolysis, three products could be observed, benzene, chlorocyclohexane and cyclohexane. However, the selectivity towards chlorocyclohexane on palladium supported catalysts is very low whatever the reaction conditions [9]. Moreover, benzene hydrogenation to cyclohexane is expected to occur on platinum catalysts but not on palladium [12].

One of the first studies dealing with the gas-phase chlorobenzene hydrodechlorination over Pd/Al₂O₃ catalysts was carried out by Coq et al. [9]. Their kinetic study indicated that the reaction order relative to chlorobenzene varied from 1 at low partial pressures to 0 at high pressure of the halogenated compound. The reaction order for hydrogen was close to 0.5. Moreover, a reaction order of –1 was found for HCl, although it changed at higher ClBz partial pressure to reach zero-order. From these results, the authors conclude that [9,32]:

1. In the rate determining step, hydrogen reacts in a dissociated form, which rule out the interaction of hydrogen gas with adsorbed organohalogen.
2. Chlorobenzene and HCl compete for the adsorption on the active sites and both are strongly adsorbed.

Based on these kinetic data, Coq et al. proposed a chlorination/dechlorination process similar to that described by Mars and van Krebelen [40] for the selective oxidation of hydrocarbons



Steps (1) and (2) involve the oxidative formation of surface palladium chloride either by chlorobenzene or by HCl (both are strongly adsorbed on the Pd), and step (3) regenerates the reduced Pd from hydrogen gas. A similar mechanism has also been applied to the gas-phase hydrodechlorination of chlorobenzene over other metals such as nickel [41]. This mechanism indicates that hydrodechlorination and deactivation processes take place simultaneously. Poisoning of the metal surface depends on the equilibrium between poisoning and regeneration of the Pd surface. An additional work by Coq and co-workers [10] dealing with the gas-phase chlorobenzene hydrodechlorination over Pd–Rh and Pd–Sn bimetallic catalysts was carried out and will be discussed below, in the bimetallic catalysts subsection.

However, more detailed works on the gas-phase hydrodechlorination of chloroaromatic compounds on palladium catalysts are lacking. Whether, the mechanism is radicalary such as in the gas-phase CFCs hydrodechlorination or ionic, including nucleophilic or electrophilic attack, it is not clear. Indeed, an electrophilic attack has been proposed to explain the gas-phase hydrodechlorination of chloroaromatics over nickel catalysts [42–46].

On the other hand, basic research on the liquid-phase hydrodehalogenation of aryl halides over palladium catalysts is discussed in the next section.

3.2. Liquid-phase reactions

Although to a lesser extent than those to the gas-phase reactions, several papers devoted to the palladium catalysed liquid-phase hydrodehalogenation of aliphatic [22,47,48] and aromatic halides [49–58] have been recently published. Some of these works deal with the treatment of contaminated water with chlorinated compounds [47,48,51]. However, others are focused on theoretical aspects of the reaction, i.e. kinetics, mechanism, catalysts, influence of the solvent, addition of base compounds, etc.

The choice of solvent for a liquid-phase hydrodehalogenation is of importance. The following aspects are to be considered in the selection of a solvent [57]: (i) dissolvability of the reactants, (ii) influence on catalytic reaction mechanism, (iii) recovery, high availability and fair price and (iv) toxic effects and environmental aspects. For example, some solvents,

such as DMF, inhibit the hydrodechlorination of chloroaniline [57] while others such as ethanol may also play a role as a hydrogen donor [52]. Alcohols (mainly methanol and ethanol) are the most usual choice as solvent for the liquid-phase hydrodehalogenation of organic halides. Aging experiments carried out by Hoke et al. [58] with 4-chlorophenol on Pd/C showed that solvent critically affects catalysts lifetime. When a 50/50 mixture of ethanol/water was used as the reaction solvent, a dramatic improvement in catalysts lifetime was observed. Clearly the poisoning effects of either reactants or products were minimised by the mixed solvent system.

The most important fact in the liquid-phase hydrodehalogenation of organic halides is the strong deactivation of the catalysts, specially in those processes carried out in a batch reactor, due to the hydrogen halide formed as by-product in the reaction.

It has been reported that a better resistance to chlorine is observed when the size of the metallic particle increases. Thus, the highest conversions were obtained for low-dispersed catalysts. This seems to indicate that this inhibitory effect is not a surface phenomenon but one directly related to the bulk of the metallic particle instead [50].

This deactivation, however, can be minimised through the addition of a base compound to the reaction medium. In this sense, some researchers have reported that in the absence of such base compound the reaction does not take place [58] or that if proceeds, it stops at low conversions of halogenated compounds. [49,50,53].

Although the exact function of the base in the catalytic hydrodechlorination is not completely understood, it serves, at least, as a proton scavenger for hydrogen halide liberated in the reaction [52,58]. Aramendia et al. [49] reported that the added base does not influence the catalytic activity in a direct manner, but it clearly helps the reaction to complete by avoiding passivation of the catalysts.

The rate and performance of catalytic hydrodechlorination depend on the type of base utilised. In this sense, ammonium hydroxide was found superior to sodium hydroxide, sodium acetate and triethylamine [58]. It seems that sodium hydroxide dissolves palladium when it is used as proton acceptor [53]. However, other authors found NaOH as the most suitable base for the reaction, as it allows a suitable catalyst stability

and a fast reaction rate [52]. This anomalous behaviour of NaOH has been studied by Marinas and co-workers in the liquid-phase hydrodechlorination of chlorobenzene over Pd/AlPO₄-SiO₂ catalysts. Their results show that the introduction of sodium compounds can play significant roles on activity and Cl-tolerance. However, both the nature of the sodium precursor and the incorporation method of such species can determine the degree of promotion or indeed adversely affect activity. For example, NaOH addition to the reaction mixture to neutralise the HCl formed during the reaction is ineffective due to the strong alkaline medium formed that destroys the porous system of the support and dissolves the palladium metal [59].

Alternatively, doping of the support with NaOH prior to the impregnation with the palladium precursor promotes performance, although the results depend to a great extent on the metal precursor used in the catalyst synthesis. When PdCl₂ is used as metal precursor, a catalyst with enhanced hydrodechlorination catalytic properties is obtained. This catalyst has large chloride free Pd⁰ particles, which are resistant to HCl poisoning. Moreover, due to the NaOH-PdCl₂ interaction, this material has NaOH moieties close to the Pd⁰ particles which facilitate chlorobenzene adsorption and reaction by capturing the chlorine atoms as NaCl. Conversely, the use of palladium acetylacetonate precursor leads to a highly dispersed catalyst, and therefore no NaOH beneficial effect for this solid is observed. Finally, the subsequent modification of the catalyst with sodium salts (NaOH and NaNO₃) results in catalysts which are more resistant to deactivation, although catalytic activity only improves slightly [59].

Aramendia et al. reported that the initial catalytic activity obtained in the liquid-phase hydrodehalogenation of halobenzenes over Pd/AlPO₄-SiO₂ decreased in the following order: BrBz > ClBz > IBz ≫ FBz [60]. These results were discussed as the combination of two opposite factors; (i) the carbon-halogen bond energies and (ii) the adsorption strength of the halobenzene on the catalysts. As far as the C-X bond energy is concerned, it decreases in the order: $D_{C-F} > D_{C-Cl} > D_{C-Br} > D_{C-I}$ (Table 1). However, the adsorption of aryl halides is rather selective. In this sense, competitive hydrodehalogenation experiments of pairs of halobenzenes led to the evaluation of differences in the adsorption of such pairs of substrates. Thus, the adsorption strength of halobenzenes over

Pd/AlPO₄-SiO₂ was determined to be in the decreasing order: IBz ≫ ClBz ≅ BrBz [60].

Therefore, the low initial catalytic activity found for the iodobenzene could be explained as a result of its very high adsorption strength over palladium catalysts, since it is accepted that an excessive adsorption strength has a negative influence on the final activity. On the other hand, the high reaction rate found for the bromobenzene is to be explained as a result of the adequate combination of a moderate adsorption strength, together with a relatively low bond energy. For the chlorobenzene, the adsorption strength would be adequate. However, its high C–Cl dissociation bond energy would make it less reactive than bromobenzene.

On the other hand, Marques et al. found that by operating in a multiphase system composed by a concentrated aqueous alkaline phase, an insoluble hydrocarbon and a phase transfer agent (a quaternary onium salt), a facile hydrodehalogenation of aromatic halides occurs at low temperatures and H₂ at atmospheric pressure over Pd/C. The onium salt, insoluble in both the organic and aqueous phases, is localised in the interfaces, coats the Pd/C catalysts, and constitutes the phase in which the reaction takes place. This new environment may change the rate of the removal of the different halogen atoms, resulting in selectivity changes in the hydrodehalogenation. During the reactions in the presence of the phase transfer agent (i.e. Aliquat 336) the regeneration of the Pd/C catalyst poisoned by the byproduct HCl occurs via neutralisation with the concentrated aqueous alkaline solution. The phase transfer agent may help to transfer the alkaline ions from the aqueous phase forward to the catalysts by a phase-transfer process. This multiphase system has been successfully applied to the hydrodehalogenation of polyhalogenated benzenes [54,61], chloroalkylbenzenes [54,55], polychlorinated biphenyls [55], and halogenated aryl ketones and benzyl alcohols [56].

4. Hydrogen-transfer hydrogenolysis

In comparison with catalytic reduction using molecular hydrogen, transfer reduction using hydrogen donors has real and potential advantages [62]. Hydrogen transfer methods could potentially afford enhanced selectivity in reduction and, moreover, with

hydrogen donors, a new dimension is opened up because the choice of the hydrogen donor can affect the reaction through its competitive adsorption onto the catalyst surface.

Hydrogen transfer mechanism is not fully understood. In terms of electronegativity, hydrogen occupies a central position in the periodic table. Therefore, in reactions involving its transfer, hydrogen may appear as a proton, atom, or hydride depending on reagents and conditions. In many reductions with hydrogen donors, it may not be easy to decide just how hydrogen is transferred.

Some of the used hydrogen donors for heterogeneous hydrogen transfer hydrodehalogenation are simple molecules such as formic acid and formates [60,63–65], phosphorous acid and phosphites [66], alcohols [60,67,68], metal hydrides [69], etc. With noble metals, particularly Pd, Pt and Rh these hydrogen donors give up hydrogen to the substrate under mild conditions with reaction temperatures rarely exceeding 100°C.

Aramendia et al. studied the hydrogen-transfer hydrodehalogenation of halobenzenes using HCOOK as donor over palladium catalysts [60]. They found that the dehalogenation rate follows the order of C₆H₅Cl > C₆H₅Br ≫ C₆H₅F. This reaction order does not agree with the increasing C–X bond strength. Thus, the weakest bond, C–I (iodobenzene) remained intact under the reaction conditions. Additional experiences, in which they followed by mass spectrometry the evolution of free hydrogen, indicated that iodobenzene inhibits the donor adsorption over the catalyst active sites, while fluorobenzene was not adsorbed, the active sites being mainly occupied by the donor. Competitive reactions confirmed the strong adsorption of iodobenzene over the catalyst which inhibited the adsorption of the other aryl halides [60]. It is followed that it is the relative adsorption coefficient between hydrogen donor and acceptor that determines the course of the reaction.

Similar results were presented by Wiener et al. [64] that reported the affinity of various hydrogen acceptors for the Pd/C catalysts, determined by competitive kinetic experiments, to be in the decreasing order: iodobenzene > bromobenzene > chlorobenzene > fluorobenzene. Moreover, they stated that the rate-determining step in the overall process is the adsorption of the donor on the catalyst.

Thus, it is of great importance the order of addition of reagents when the substrate is strongly adsorbed on the catalysts as reported by Anwer et al. [63].

On the other hand, Ukisu and Miyadera [67] studied the hydrogen transfer hydrogenolysis of carbon–halogen bond in aryl halides over noble metal catalysts. They used alcohols as hydrogen source and found that the best donors are secondary alcohols. After the results obtained working with deuterium-labelled 2-propanol, they proposed that the mechanism included a hydride transfer from an α -hydrogen of the alcohol to the aryl halide. The hydrodechlorination process does not proceed without the addition of a base (NaOH) and a molar excess of the base compound is required to achieve complete hydrodechlorination. The authors also suggested that the role of the base compound is not limited to the neutralisation of HCl formed. It has been suggested that NaOH promotes the dehydrogenation of 2-propanol with noble metal catalysts and that base compounds facilitate the catalytic dehalogenation of organic halides in some way [67].

Results presented by Aramendia et al. [60] in the hydrogen transfer hydrodehalogenation of aryl halides from 2-propanol over palladium catalysts are consistent with those discussed above. For individual reactions, the reactivity order (iodobenzene > bromobenzene > chlorobenzene > fluorobenzene) follows the same tendency than the C–X bond dissociation energy (Table 1). Competitive experiences of the four aryl halides showed that the reaction took place at a high rate, despite the presence of iodobenzene, in contrast with the result obtained when HCOOK was used as donor. This seems to indicate that there is no competition between the 2-propanol and the acceptor for the same active sites and, therefore, the aryl halides are hydrodehalogenated following the affinity for the catalyst, $C_6H_5I > C_6H_5Br > C_6H_5Cl > C_6H_5F$ as determined by Wiener et al. [64].

Finally, the hydrogen transfer hydrodehalogenation was also carried out in multiphase conditions by Marques et al. [66]. Polyhalogenated benzenes were hydrodehalogenated in the presence of Pd/C with sodium hypophosphite as donor, in a multiphase system consisting of a hydrocarbon solvent, concentrated aqueous alkali and a quaternary onium salt (phase-transfer agent). The strong alkaline medium and the phase-transfer agent were synergic. The authors

suggested that the observed enhancement of the reaction rate was due to the transfer of the phosphite anion from the aqueous phase to the catalyst surface, to the partition of the halogenated compound between the hydrocarbon solution and the liquid-phase and the rapid removal of HCl adsorbed on the Pd/C catalyst by the alkaline medium.

5. The catalysts

There are many variables involving the catalysts synthesis and composition that can affect in a significant way to the activity and selectivity of the catalytic hydrodehalogenation of organic halides. The main parameters that determine the catalyst performance are the metallic precursor, the catalytic support, the metallic dispersion and the presence of additives. These are to be reviewed in order to better understand the role of palladium catalysts and how the catalytic performance can be improved.

5.1. The metallic precursor

The palladium precursor influences the properties of the final catalysts. First of all the interaction of the precursor with the catalytic support determines the final metallic dispersion of the catalyst and, therefore, the catalytic activity and selectivity as discussed below.

On the other hand, the self-poisoning effect of ions coming from the precursor is also to be considered. Aramendia et al. [50] reported the self-poisoning effect of chloride ions coming from the precursor ($PdCl_2$) on the activity of a Pd/SiO₂-AlPO₄ catalyst on the liquid-phase hydrodechlorination of chlorobenzene. They compared the performance of catalysts prepared from palladium chloride and palladium acetylacetonate to conclude that the very low activity and final conversion of the ex-PdCl₂ catalyst was due to the poisoning of the Pd with chloride ions coming from the metal precursor. Moreover, when a sodium doped support was used, the chloride ions of the precursor did not deactivate the catalysts since they were associated to sodium atoms by forming NaCl, as detected by XRD. The authors concluded that the correct choice of the metallic precursor (free of chloride ions) is crucial for the optimum performance of the final catalyst [50].

5.2. The catalytic support

It has been shown in a number of works that the catalytic behaviour of Pd depends not only on the metal, but also on the type of support. The hydrodechlorination selectivity [20,32,70], the catalytic activity [13,70] and the catalyst stability [13,20,35] are strongly influenced by the catalytic support.

Van de Sandt et al. [36] reported the properties of a good support for palladium in the hydrogenolysis of halogenated organic compounds. It has to be stable under corrosive reaction conditions, which involve high concentration of HCl and HF and high temperatures. Also, secondary reactions such as Cl/F exchange or coupling reactions should be avoided since they would lead to a selectivity loss. In principle, inorganic and organic materials could be selected as support.

The main inorganic supports are alumina, silica, zeolites and other metal oxides such as TiO₂, MgO, ZrO₂, etc. The main disadvantage of this kind of supports is that they are readily attacked by the HCl and HF acids formed in the reaction, leading to the degradation of the catalyst. Moreover, they can catalyse unwanted reactions such as the chlorine/fluorine exchange one leading to a selectivity loss. However, they are widely studied since interesting conclusions can be obtained dealing with reaction mechanism, selectivity and catalyst deactivation.

The main organic supports are the activated carbons. They are very suitable for this kind of reactions since they are relatively inert to the HCl and HF formed in the reaction. However, the performance of activated carbon is dependent on variables, such as pore-size distribution, surface oxygen groups and amount of impurities. It is still very complicated to relate only one of these properties to the performance of the catalysts.

In the literature, the role of the support in the hydrodehalogenation of organic halides has been analysed from various points of view such as the support porous structure, metal–support interactions, the effect of the support on catalyst deactivation, support acid–base properties, etc.

Juszczyk et al. [71] examined the effect of the porous structure of the support on the hydrodechlorination of CFC-12 over Pd supported over α -Al₂O₃ and γ -Al₂O₃ and concluded that the catalytic activity was not affected by this factor. However, they suggested that the presence of smaller pores in γ -Al₂O₃

could be important in controlling the selectivity towards CH₂F₂; if Pd particles are located in small pores, a consecutive (excessive hydrodehalogenation) of CH₂F₂ leads to methane. When Pd/ γ -Al₂O₃ catalyst was calcined at high temperature (600°C) the pore structure collapsed and a portion of the small pores was eliminated. This high-temperature calcined catalysts presented a selectivity level similar to the Pd/ α -Al₂O₃ solid which was a solid characterised by the absence of small pores [71].

The effect of the support has also been analysed in terms of the metal–support interface. In this respect, Coq et al. [20] and Juszczyk et al. [37], using Pd/Al₂O₃, suggested the migration of fluoride and chloride species from the metal to the interface to form halogenated species with the support, thereby refreshing the metal surface and avoiding the gradual passivation of the catalyst. Moreover, Early et al. [35] also reported the alumina fluorination by direct interaction between the CFC molecule and the support, as followed by the consumption of surface hydroxyl groups by FTIR.

On the other hand, the electronic state of the palladium particles can be drastically modified by their interaction with electron-acceptor sites of the support. Coq and co-workers [20,32,70] reported that partially fluorinated Pd/Al₂O₃ catalysts showed an enhanced selectivity towards CH₂F₂ in the gas-phase hydrodechlorination of CCl₂F₂. Pure fluorinated supports such as MgF₂ [39], AlF₃ [20,35,70] and TiF₄ [70] were also studied in order to understand this increase in the selectivity towards CH₂F₂. These partially fluorinated species (AlF_x) would be formed at the periphery of palladium particles and could promote the appearance of Pd^{δ+} species. These electron-deficient Pd species could bind :CF₂ carbene radical less strongly, so a hydrogenative desorption of these radicals to CH₂F₂ would prevail leading to a high selectivity [20,37]. Moreover, AlF_x species prevent the diffusion of fluorine and chlorine into the Pd bulk, being this last phenomenon responsible for the loss of selectivity to CH₂F₂ which occurred with Pd/graphite and Pd-black catalysts [20,32,70].

The support has also been related to the catalysts deactivation. Thus, Early et al. [35] studied the gas-phase hydrodehalogenation of CCl₂F₂ and CF₃CFCl₂ over Pd supported on Al₂O₃, a series of fluorinated Al₂O₃ and AlF₃ and reported that the more acidic the support

(AlF₃), the more intense the deactivation suffered by the catalyst. Carbonaceous deposits form more rapidly on the more acidic supports (AlF₃) and can migrate onto the surface of metal particles, making it inaccessible for reactant adsorption [35].

However, Moon et al. [72] reported that Pd/AlF₃ catalysts present a low but fairly stable catalytic activity in the hydrodechlorination of CF₃CF₂Cl, in comparison with oxide-supported Pd catalysts (Pd/Al₂O₃, Pd/ZrO₂). The authors believe that deactivation is due to Pd sinterisation, favoured by support corrosion (fluorination). Alumina and zirconia supports fluorinated readily in comparison to AlF₃. Thus, Pd particles on oxide supports agglomerate and catalysts deactivate.

Hydrophobic supports such as carbon have been found to have a favourable effect on the liquid-phase hydrogen transfer hydrogenolysis by facilitating adsorption of the also hydrophobic organic halide [63]. Van de Sandt et al. [14] and Makkee et al. [34] discussed the importance of the removal of the impurities of the activated carbon used as support in the gas-phase hydrodechlorination of CCl₂F₂. They found that the selectivity towards the desired product CH₂F₂ increases after the amount of impurities of the support were lowered by washing it with HCl. Thus, the unwanted side reactions as chlorine/fluorine exchange and coupling reactions were suppressed since they were supposed to be catalysed by aluminium and iron [16] impurities, respectively.

On the other hand, in order to obtain supports with enhanced resistance to corrosion giving, at the same time, to the final catalyst both high activity and stability Gampine and Eyman [13] prepared modified supports by coating Al₂O₃ and SiO₂ with zirconium and titanium obtaining ternary oxides of Ti–Zr–Al and Ti–Zr–Si. Such oxides were used as support for palladium and the catalysts obtained tested for the gas-phase hydrodechlorination of *o*-dichlorobenzene. They found that the ternary-oxide-based catalyst, Pd/TiZrAlO_x exhibited an improved stability and activity much higher than the arithmetic sum of the activities of the component single oxide-based palladium catalysts. They suggest that TiZrAlO_x supports assist in the activation of chlorinated hydrocarbon and/or modify the electronic properties of palladium and thereby its adsorption properties. The authors suggest that by optimising the Ti/Zr ratio the metal–support interactions could be

modified thereby preventing the metal particles from agglomerating.

Finally, the potential influence of the acid–base properties of the support on the process has been studied. Schoonenboom et al. [73] studied the dechlorination of dioxins and furans over alumina supports with different acid–base properties and found basic supports to exhibit an increased catalytic activity that they ascribed to the capture of the halogen atoms by the basic sites of the alumina, which thus favoured their removal from the organic molecule. Aramendia et al. [50] studied the effect of the acid–base properties of the catalytic support on catalytic activity and deactivation of the liquid-phase hydrodechlorination of chlorobenzene. They concluded that basic supports such as ZrO₂ can neutralise the HCl formed in the reaction, allowing the reaction to proceed up to higher conversions. However, a basic support such as MgO dissolves as the pH of the reaction medium lowers due to the effect of the HCl formed, and the reaction ends prematurely [50]. Choi et al. [74] also observed this phenomenon (viz. a drastic drop in specific surface area in Pt/MgO catalysts), which they found to occur to a lesser extent, however, because their experiments were conducted in the gas-phase.

5.3. Structure sensitivity

There is no general consensus about the structure-sensitivity of the hydrodechlorination reaction. Thus, some authors present data that indicate that the reaction is structure-sensitive [9,28,37,41,50] while others have suggested that the reaction is structure-insensitive [7,24,75]. The results reported in the literature are difficult to compare. The reaction conditions, including gas or liquid-phase reaction, catalyst support, reactants for which the hydrodechlorination is studied, etc. vary from one study to another, making it difficult to obtain a unified picture of the chemistry involved. Moreover, the inhibitory effect of HCl formed during the reaction also makes it difficult to compare data since, as a consequence of such inhibition, the turnover rate will be a strong function of conversion [24,75].

Karpinski and co-workers studied the gas-phase hydrodechlorination of CF₃CFCl₂ [28] and CCl₂F₂ [37] over Pd/Al₂O₃ catalysts and reported an increase in the TOF when the Pd particle size increased. The authors suggested that the hydrodechlorination

reaction requires relatively large ensembles, the number of which would increase with increasing the particle size. In addition, the Pd/Al₂O₃ catalysts characterised by the lowest dispersions were also the most selective towards CH₂F₂. They suggest that larger Pd particles are more easily transformed into Pd carbide since it contains higher proportion of surface plane sites, which should bind C1 species more strongly than highly unsaturated surface sites of lower co-ordination. Carbided Pd plane surfaces are sites of high activity and selective towards CH₂F₂. The same authors, by comparing the features of the CCl₂F₂ and CCl₂H₂ hydrodechlorination reactions on Pd/Al₂O₃ concluded that the most Pd particle size-dependent reaction is the hydrogenation of adsorbed :CF₂ species, leading selectively to CH₂F₂, that proceeds more efficiently on large Pd particles. On the other hand, CH₄ formation appears to be associated with hydrogenation of bare C1 adspecies. The presence of such species is suggested by XRD, and are responsible for the loss of selectivity towards CH₂F₂. This reaction seems to be less particle size dependent than the selective formation of CH₂F₂ from :CF₂ species.

Moreover, sensitivity to the structure has been also reported for the liquid-phase hydrodechlorination of chlorobenzene and bromobenzene by Marinas and co-workers [49,50]. They reported that the initial catalytic activity (TOF) is inversely related to metal dispersion (%D), as shown in Fig. 5 for the liquid-phase chlorobenzene hydrodechlorination over Pd/SiO₂-AlPO₄ catalysts. A decrease in the dispersion from 54 to 7% was accompanied by an increase in the catalyst activity (TOF) by a factor of 20.

However, Ribeiro et al. [75] reported that hydrodechlorination of CF₂CFCl₂ on Pd(111) and Pd(100) surfaces is structure insensitive, and therefore the rates of hydrodechlorination are proportional to the total Pd surface area. For all the catalysts used in that study, the reaction order in HCl was -1. The immediate consequence of this is that the turnover rate is a strong function of the conversion. Therefore, great care was taken to obtain the reaction rates free of the negative effect of HCl. Otherwise, misleading results would be obtained.

The central roles of the catalyst preparation procedure and modification warrant in-depth investigation

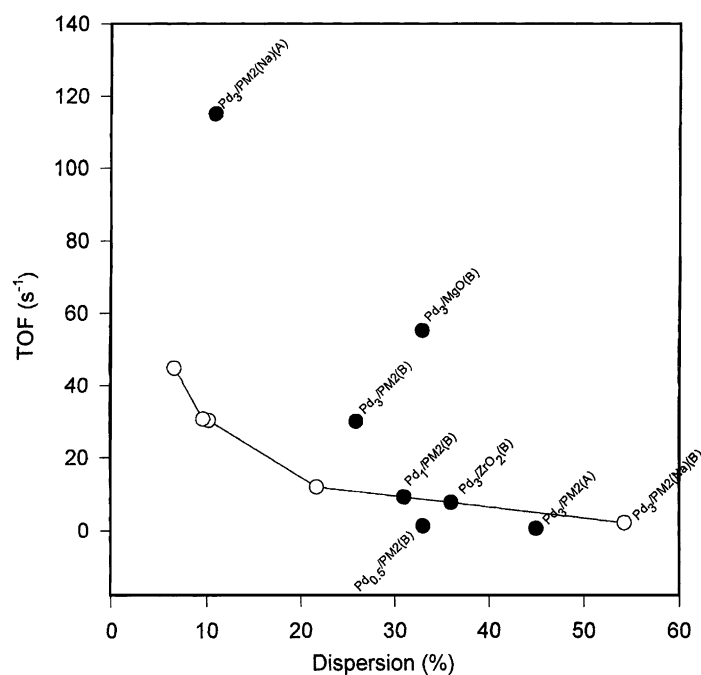


Fig. 5. Influence of the metal dispersion on catalytic activity in the liquid-phase hydrodechlorination of chlorobenzene over palladium catalysts. Figure from [50] with permission from publisher.

with a view to acquiring a better understanding of the actual effect of particle size on catalytic activity.

5.4. Bimetallic catalysts

One of the most important challenging tasks in carbon–halogen bond hydrogenolysis is to obtain highly stable and active catalysts. In this sense, more attention has been recently focused on bimetallic catalysts in order to improve both longevity and activity. This may be achieved by alloying Pd with an inactive metal. The dilution of the active Pd sites would alter the rates of different reaction steps, leading to different products distribution.

Most of the works dealing with bimetallic catalysts were carried out in the gas-phase hydrodechlorination of CFCs. In addition to palladium, the second metal added has been iron [11,17,76], rhenium [38,77], silver [17,78], gold [39], cobalt [17] and potassium [20].

When preparing bimetallic catalysts there are two aspects that need to be pointed out in order to understand the bimetallic effect. These are the degree of interaction between both metals and the distribution of the metal components on the catalyst (random distribution, segregation of one component, etc.). The effect of adding of a second metal is generally related to geometric and/or electric factors.

A close contact between Pd and the second metal seems to be essential in order to obtain a positive effect in the bimetallic catalysts as reported by Malinowski et al. [39] for Pd–Au/MgF₂ catalyst in the gas-phase hydrodechlorination of CCl₂F₂. The authors reported an increase in the selectivity towards CH₂F₂ for the bimetallic catalysts that showed two Pd–Au solid solutions by XRD. The results reported by Coq et al. [17] in which no increase in the selectivity was found for Pd–Ag/graphite catalysts were supposed to be due to an absence of Pd–Ag interaction in the catalysts.

In addition, Coq et al. [17] also studied the behaviour of palladium when alloyed with Fe, Co or K and they observed that those bimetallic catalysts presented a selectivity to CH₂F₂ fairly constant on stream. Since Pd/Graphite catalyst exhibited a progressive decay in selectivity due to the diffusion of halide species into the bulk palladium, they concluded that the presence of Fe, Co or K prevents the diffusion of these species in bulk palladium, thus keeping the selectivity value.

The second metal distribution seems to be important as reported by Lingaiah et al. [11] studying the gas-phase chlorobenzene hydrodechlorination over Pd–Fe/C catalysts. They reported that the addition of Fe–Pd leads to a substantial increase in the activity (87% conversion) in comparison to a Pd/C catalyst (<5% conversion at steady-state). This increase in activity is related to the presence of the Pd on the surface of the particles whereas most of the iron is dispersed inside the catalyst particle. The authors relate this catalyst structure to the novel preparation method in comparison to the conventional one that lead to bulk palladium particles with most of the iron migrated to the surface.

A bifunctional mechanism has been proposed to explain differences in activity and selectivity on the hydrodechlorination reaction. Thus, Coq et al. [17] reported an increase in the hydrodechlorination activity per surface Pd atom on Pd–Fe catalysts. They proposed that hydrogen is activated on the palladium surface, but the conversion of CCl₂F₂ mainly occurs at the boundary between palladium and iron ensembles, or between palladium and iron atoms (mixed ensembles). On the other hand, Heinrichs et al. [78] reported, for the gas-phase hydrodechlorination of 1,2-dichloroethane on Pd–Ag/SiO₂, an increase in the selectivity to ethylene. They propose a mechanism in which Ag interacts with 1,2-dichloroethane and picks up chlorine atoms but does not hold the rest of the molecule (CH₂–CH₂) firmly enough, this fragment being released as ethylene; Ag alone is inactive because AgCl covers the surface and deactivates it; the AgCl surface can not adsorb hydrogen but Pd can supply hydrogen atoms for its reduction into Ag; Pd splits the C–Cl bond too, but CH₂–CH₂ can be removed by hydrogen as ethane.

Malinowski et al. [38] and Bonarowska et al. [77] reported that Pd–Re/Al₂O₃ bimetallic catalysts strongly deactivated with time on stream, whereas the activity of Pd/Al₂O₃ was fairly stable. However, while Malinowski et al. associated the deactivation to chlorine poisoning due to the strong Re–Cl interaction [38], Bonarowska et al. related the deactivation to the appearance of large amounts of carbon on the catalysts. This carbonaceous deposits formed on the Pd–Re catalysts are hydrogenated off at higher temperatures than in the case of Pd/Al₂O₃. In addition, they reported that retention of Cl by the metal seems

negligible. It has to be pointed out that Re cannot be regarded as an inert diluting element, such as, e.g. gold. ‘Inactivity’ of rhenium does not result from its inertness towards the species involved in CH_2Cl_2 hydrodechlorination. Rhenium is certainly more reactive towards chlorine and carbon, than palladium, so its inactivity in this reaction should, in fact, follow from too strong binding of the reaction intermediates [77].

5.5. Catalyst deactivation

One of the main drawbacks of catalytic hydrodehalogenation of organic halides is the catalyst deactivation. Such a deactivation has been related to several processes, i.e. the inhibitory effect of hydrogen halide formed as by-product, formation of carbonaceous deposits, sintering of the active phase and degradation of the catalysts by the corrosive acid formed in the reaction.

Based on thermodynamics data for Group VIII noble metal chloride reduction with hydrogen [79] and the general trend of increasing ‘nobility’ of the metal from left to right in the Periodic Table, it can be concluded that the chlorine coverage under hydrodechlorination conditions decreases towards the right in the series $\text{Ru} > \text{Rh} > \text{Pd}$ and $\text{Os} > \text{Ir} > \text{Pt}$. Thus, the activity of Pd and Pt catalysts is most likely attributed to the relatively low coverage on their surface, whereas the activity of the Ru, Rh, Os, and Ir catalysts is significantly suppressed by strongly adsorbed Cl and F atoms.

In a pioneering work, Campbell and Kemball [80] investigated the gas-phase dehalogenation of ethyl chloride on evaporated films of Pd, Pt and Ni and reported the poisoning effect of HCl produced on the reaction rate. Nowadays, there is a general agreement on the inhibition of palladium metal-supported catalyst by the HX formed in the hydrodehalogenation of organic halides for both gas-phase [8,9,13,24,31,75] and liquid-phase processes [49,50,53,58]. However, the batch processes suffer from the strong poisoning effect of HCl [81], while the use of reactants flowing through a fixed bed reactor avoids local excess of HCl on the catalyst [82]. This inhibition by the reaction product HCl, is manifested in a negative reaction order (−1), as reported by Somorjai and co-workers [24,83] working with model catalysts.

Moreover, Aramendia et al. studying the liquid-phase hydrodechlorination of aryl benzenes, reported a better resistance to chlorine as the size of the metallic particle increases. This results seem to indicate that this inhibitory effect is not a surface phenomenon but one directly related to the bulk of the metal particle instead. Besides, support and additives play also an important role in this subject [49,50].

Another source of deactivation is the formation of carbonaceous deposits, specially in the gas-phase hydrodechlorination processes. Coke deposition during the initial stages of the hydrogenolysis of CCl_2F_2 was reported by several researchers working with Pd/ Al_2O_3 [19,71] and Pd/C [23,30,31,34]. These carbonaceous species are responsible for the loss of activity detected with time on stream, but also for an increase in the selectivity towards CH_2F_2 , suggesting that Pd carbide is the active phase for a stable selectivity to CH_2F_2 and that clean Pd surfaces are very active in a deep dehalogenation of CCl_2F_2 molecules to CH_4 [71]. However, interstitial carbon could be an alternative source for CH_4 formation and thus for a selectivity loss. In any case, the greatest deactivations have been observed at the lowest H_2/CFC ratios and excess hydrogen is needed to minimise the coverage of strongly adsorbed species which block active sites [23,28,30,34].

The third mechanism of deactivation is sintering of the active metal as reported by several researchers [13,18,72]. Thus, Van de sandt et al. [18] reported the sintering of Pd black catalyst in the gas-phase hydrodechlorination of CCl_2F_2 . However, the absence of support could facilitate this process.

Moon et al. [72] also reported the sintering of Pd catalysts as the primary cause of deactivation in the gas-phase hydrodechlorination of CClF_2CF_3 . It was found that deactivation of the Pd catalysts on oxide supports was promoted by the reaction of HF produced during the hydrodechlorination of CFC-15 with the support of the Pd catalysts. The fluorination of the support would facilitate the migration of the Pd particles. Palladium on AlF_3 was found to be more stable than the oxide supported Pd catalysts. This points to the support reaction with the formed hydrogen halides as the starting point to the Pd particles sinterisation. On the contrary, Wiersma et al. [31] observed redispersion for Pd at a temperature of 263°C using a pure CCl_2F_2 feed, but with active carbon as support.

Finally, it should be also taken into account the catalysts degradation due to the corrosive environment, i.e. Formi et al. [82] detected a 25% loss of the BET area and a 20% leaching of the active metal, palladium, after 20 h on stream on the hydrodechlorination of PCBs on Pd/C. Similar results were reported by Aramendía et al. [50] on the liquid-phase hydrodechlorination of chlorobenzene over Pd/MgO. The support dissolves as the pH of the reaction medium lowers due to the effect of the HCl formed, and the reaction ends prematurely. Choi et al. [74] also observed this phenomenon (viz. a drastic drop in specific surface area in Pt/MgO catalysts), which they found to occur to a lesser extent, however, because their experiments were conducted in the gas-phase. Hoke et al. [58] working in the liquid-phase hydrogenolysis of chlorophenols over Pd/C also detected palladium solubilisation by the HCl formed in the reaction medium. They showed that Pd solubilisation can be minimised by selecting the appropriate solvent.

6. The future

Although intense research has been carried out in the last decade on the hydrodehalogenation of organic halides over palladium catalysts, there are still some aspects of the process that are not completely understood. Some of these points are outlined below.

First of all, the mechanistic aspects must be considered. Although the mechanism of the gas-phase hydrodehalogenation of CFCs and related compounds seems to be rather clear, the reaction mechanism of the hydrodehalogenation of aryl halides, specially in the liquid-phase processes, needs to be clarified. Whether the mechanism is radicalary or, on the contrary, ionic (nucleophilic or electrophilic) needs to be clarified. In this sense, the application of linear free-energy relationships (LFER) could give valuable information.

Moreover, the structure sensitivity or insensitivity of this reaction should be clarified. Investigations have to be carried out carefully in order to avoid the influence of secondary factors such as the poisoning effect of the hydrogen halide produced. The key roles of the catalyst preparation procedure and modification warrant in-depth investigation with a view to acquiring a better understanding of the actual effect of particle size on catalytic activity.

As far as the catalytic system is concerned, the research has to be aimed at obtaining supports with enhanced resistance to corrosion giving, at the same time, to the final catalyst both high activity and stability. In this sense, the modification of usual supports with base compounds could be an interesting way to obtain poison-resistant catalyst.

Finally, the search for new types of hydrogen sources and experimental devices are also interesting aspects to research on. For example Rupprechter et al. [83] reported the use of solid-state hydrogen as a powerful hydrogenating source with some advantages.

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