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The catalytic transformation of chlorofluorocarbons in hydrogen on metal-based catalysts supported on inorganic fluorides

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Abstract

The use of metal halides as carriers for supported metal catalysts allows to obtain stable and selective materials for the hydrodechlorination of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) to hydrofluorocarbons (HFCs). The most used catalyst is Pd/AlF_3, but unexpected selectivities have been obtained with Pd on "ZrF_4" oxyfluoride materials or $KMgF_3$ perovskite-like structure. From a survey of the kinetics, mechanism and surface complexes occurring in the transformation of CFC on Pd, explanations of the beneficial use of metal fluorides as carriers are provided. It is proposed that the good hydrodechlorination selectivity observed on Pd/fluoride comes from an electronic modification of Pd by substoichiometric fluoride species, e.g. AlF_x ($x < 3$), in decoration onto the metal particles. The electron withdrawing effect of these species decreases the disponibility of Pd d electrons and favors the desorption of pallado-fluorocarbenes, e.g. $=CF_2$, CF_3–CF=, etc., to yield HFC compounds. It is also demonstrated that the dilution of the Pd surface by the decorating AlF_x species decreases the probability of occurrence of surface complexes exchanging multiple bonds with Pd, e.g. CF_3–C=, and leading to deeply hydrogenated compounds. Several methods, alloying, coprecipitation, etc. allow to prepare Pd/fluoride with enhanced interaction between Pd and these substoichiometric species.

Keywords: Chlorofluorocarbons; Hydrochlorofluorocarbons; Hydrofluorocarbons; Palladium; Metal fluorides; Hydrodehalogenation; Hydrodechlorination; Environmental catalysis

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1. Introduction

In this special issue dedicated to the conversion of halons and hydrochlorofluorocarbons (HCFCs), it is unnecessary to emphasize more about their noxious impact on the environment. On that account, CFC are banned from use and are replaced by hydrochlorofluorocarbons (HCFCs) in a first time, and finally by hydrofluorocarbons (HFCs). There is thus the need to find out methods for the synthesis of HCFC and HFC on the one hand [1], and to destroy or valorize banked CFC on the other hand. A first approach for CFC valorization is the F/Cl exchange from reaction with HF, but this is restricted to a few compounds. A more widely explored way from 20 years is the selective hydrodechlorination of CFC and HCFC, to HCFC and HFC, respectively [2–27]. Metal-based materials constitute most of the catalysts, mainly composed of Pd on various carriers. In comparison with other metals, the performances of Pd are superior in terms of stability, activity and selectivity for Cl removal. A special attention has been paid towards the

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use of supports chemically resistant to hydrogen fluoride released in the course of the reaction, and able to provide specific patterns of selectivity. Carbon-based materials and inorganic fluorides belong to this type of supports. Carbon-based catalysts exhibit attractive properties for the selective hydrodechlorination [14], and are described elsewhere in this special issue. Regarding metal fluorides as supports, their use gives stable catalysts and allows better control of the extent of hydrodehalogenation [4,5,8–10,12,13,19,20,23,24]. This aspect will be developed in this short review with emphasis on the studies carried out in our groups in Montpellier and Tarragona. In Section 2 we will provide a short outlook about the kinetics and mechanism of CFC hydrogenolysis on metal with the scope to understand the promotion effect of metal fluoride carriers. Some elements of interpretation of these effects will be thus proposed in Section 4. Section 3 will address to some examples of CFC hydrogenolysis on metals supported on simple and mixed fluorides, and will demonstrate that some reactions may occur on the fluoride support.

2. Mechanistic considerations

Most of the mechanistic studies regarding the hydrogenolysis of CFC and HCFC dealt with the catalytic transformation of CF_2Cl_2 and CF_3CFCl_2 over Pd-based catalysts. The main products appearing in the course of these transformations are those from Cl(F)/H exchange, i.e. hydrodehalogenation. Because the conversion level has generally only a little effect on the products distribution, one important question in the reaction network was to find out if this reaction is a serial or a parallel hydrogenation. From the reactivity of intermediate products, it was concluded that the reaction network is formally of the parallel type. Actually, it is better described by a rake scheme mechanism as illustrated for the history case of CF_2Cl_2 conversion (Fig. 1). Such kind of reaction scheme was early proposed by Weiss et al. [28] for the hydrodechlorination of CCl_4 to $CHCl_3$ and CH_4 on Pt/Al_2O_3 catalysts. Providing the reactivity of gaseous intermediate products is low, the product selectivity in such a mechanism is mainly determined by the fate of adsorbed intermediates to suffer either a reactive desorption from hydrogen addition, or further halogen/H exchanges in the adsorbed state. As compared to CF_2Cl_2, the reactivity of intermediates $CHFCl_2$ and CH_2F_2 was indeed demonstrated to be very low [4,14]. The difference of reactivity was even larger when comparing the rate of CF_3CFCl_2 hydroconversion with that of CF_3CHFCl and CF_3CHF_2 [22,29,30]. As a general rule, substituting F and/or H for Cl decreases the reactivity of halogenated alkanes.

The selectivity patterns in CFC hydrogenation being determined by the fate of adsorbed species, the nature of these species is of utmost importance. Based on the products distribution analysis of the hydrodehalogenation of CF_2Cl_2 [4,14] and CF_3CFCl_2 [15,31], surface metallo-carbenes were postulated as a clue for selectivity. The occurrence of surface carbenes has been put in evidence through the reaction of adsorbed species, formed during the CF_2Cl_2 hydrodehalogenation, with the scavenging agent C_2H_4 [32]. This tran-

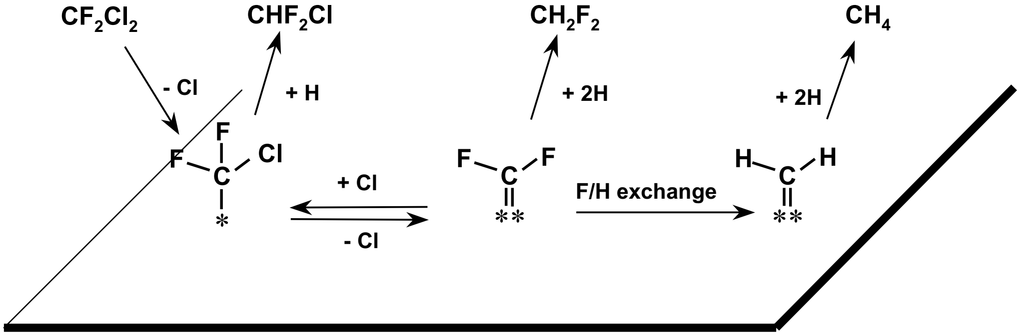

Fig. 1. Simplified reaction scheme for the hydroconversion of CF_2Cl_2 on a metallic Pd surface.

sient reaction yielded products typical of C_2H_4 addition on the surface carbene $=CH_2$ and fluorocarbene $=CF_2$. A FTIR investigation of CF_3CFCl_2 adsorption on Pd/Al_2O_3 has shown different types of adsorbed species [33]. The fluorocarbene CF_3–$CF=$ was identified in great proportion on the Pd surface upon contacting a $CFC+H_2$ mixture at 473 K; on the fresh catalyst the trifluoroethylidyne CF_3–$C\equiv$ was also present. The fluorocarbene yields CF_3CH_2F upon hydrogenation, whereas the fluoroethylidyne yields CF_3CH_3. IR spectroscopic evidence was also provided for the formation of $=CH_2$ carbene from CH_2Cl_2 on a Pd/SiO_2 catalyst [34].

So far, several mechanisms for the hydrodehalogenation have been proposed, and some general tendencies emerge. Many studies propose that the breaking of the first C–Cl bond is involved in the rate determining step [4,22,26,30,33]. In molecules containing several Cl atoms, after the first C–Cl has been broken the second C–Cl cleavage is very fast [26,33], reversible and this second chlorine may be exchanged with a pool of surface Cl atoms, as shown by isotopic labeling studies using ^{37}Cl [26]. The C–Cl bond cleavage is homolytic with very little charge redistribution, and occurs very early in the reaction coordinates [30,33]. Globally, the rate is dominated by the C–Cl bond strength [22,35], which increases upon substituting H and/or F for Cl. These features also explain why Cl is initially removed very selectively from CFC on account of the lower strength of the C–Cl bond in comparison with the C–F bond. Besides, XPS measurements indicate that activation of the catalyst occurs through the formation of “palladium chloride” [31]. In agreement with these general observations different reaction mechanisms were proposed:

1. An halogenation/dehalogenation-like mechanism, formally equivalent to the Mars and van Krevelen mechanism occurring in the selective catalytic oxidation of alkanes [3,4,36]. Basically, the halogenated compound and HCl react with the Pd surface (or surface Pd–H) to yield a chlorided surface which is in turn regenerated with hydrogen. A very similar mechanism was proposed later on, involving the associative adsorption of CFC followed by the C–Cl bond breaking as rate determining step [22,26,29,30].
2. A Langmuir–Hinshelwood kinetic model with dissociative adsorption of CF_2Cl_2 in competition with H_2 and HCl [13].

The rate laws derived often exhibit first-order dependence on CFC, 0.5-order dependence on H_2 and -1 on HCl, in general agreement with the experimental observations.

3. Metal on inorganic fluorides as catalysts for hydrodehalogenation

3.1. The fluoride supports

Inorganic fluorides are stable compounds, both at high temperature and towards reaction with HF. For this reason they can be used as supports and/or catalysts for reactions involving fluorine compounds as reactants or as products. Fluoride type materials, most as chromium or aluminum oxyfluorides or fluorides, have thus been employed in the synthesis of CFC from fluorination (in the absence of H_2) of their chloride precursors, e.g. CCl_2F_2 from CCl_4. Normally, activation of the surface of the oxide precursor by fluorine or fluoroalkane is required, suggesting that the active phase is of the CrO_xF_y oxyfluoride-type [37]. Hess and Kemnitz [38] reported that the activity in the exchange/fluorination reactions on AlF_3 materials is related to the presence of Lewis acid sites, and that the introduction of Mg^{2+} in low amounts increases the activity of the catalysts [39]. Therefore, the activity and selectivity may depend on their structural phases and surface areas.

On that account, in the hydrogenation of CFC and HCFC on Pd/metal fluoride catalysts, side Cl/F exchange reactions may occur. The possible extent of these side reactions can be estimated from a study about the conversion of CF_2Cl_2 and CHF_2Cl, in hydrogen atmosphere, on two different AlF_3 materials [40]. The thermodynamic analysis showed that the Cl/F exchange reactions are possible for both reactants. The α-AlF_3, prepared by calcination of β-$AlF_3\cdot 3H_2O$, is much more acidic than the γ-AlF_3, obtained by calcination of NH_4AlF_3. Acid sites are predominantly of the Brønsted type in α-AlF_3 and of the Lewis type in γ-AlF_3. Table 1 presents some results for the Cl/F exchange reactions of CCl_2F_2 and CHF_2Cl on these ma-

Table 1
Catalytic properties in the reaction of CF_2Cl_2 and CHF_2Cl in hydrogen on two AlF_3 phases (reactant/H_2 = 1)

Catalyst	CF_2Cl_2 conversion					CHF_2Cl conversion				
	Reaction temperature (K)	Rate (mol min^{-1} g^{-1}) × 10^5	Selectivities (mol%)			Reaction temperature (K)	Rate (mol min^{-1} g^{-1}) × 10^5	Selectivities (mol%)		
			$CClF_3$	CCl_3F	CCl_4			CHF_3	$CHCl_2F$	$CHCl_3$
α-AlF_3	548	11.5	62	13	25	573	2.6	59	23	18
γ-AlF_3	648	9.6	60	20	20	673	0.7	56	22	22

terials. As expected, different catalytic behaviors are observed. α-AlF_3 is much more active than γ-AlF_3 for both reactants, since the same conversion was reached on the former 100 K below [40]; this has been related to the difference in acidity of these materials. Moreover, CF_2Cl_2 exchanged faster than CHF_2Cl. This fact can be explained considering the higher C–Cl bond strength in $CHClF_2$.

In order to achieve high selectivity for hydrodechlorination on metal/fluoride catalysts, these Cl/F exchange reactions should be avoided. Fortunately, the Cl/F exchange reaction will occur to a very low extent for kinetic reasons in the conditions of hydrodechlorination, since they become rate significant at 100–300 K above (see Tables 1 and 2). Moreover, one has to take care with the surface acidity of fluorides, which may promote acid-catalyzed reactions leading to coke formation.

3.2. Metals on simple fluorides

Several metal fluorides have been used as supports for selective hydrodechlorination catalysts, mainly AlF_3, but also MgF_2, TiF_3 and ZrF_4. Table 2 presents some relevant examples of hydrogenolysis of CFC and HCFC on fluoride-supported metal catalysts. Pd is the most widely used active component because of its good stability and high selectivity to hydrodechlorination alone. This is illustrated by the respective behavior of Pd/MgF_2 and Ru/MgF_2 in the CF_2Cl_2

Table 2
Some examples of catalytic hydrogenolysis of CFC and HCFC on fluoride-supported metal catalysts

Reactant	Catalyst	Conditions	Catalytic properties	Reference
CF_2Cl_2	Pd/AlF_3 (dp_{Pd} = 10 nm) Pd/AlF_3 (dp_{Pd} = 6 nm)	453 K; CF_2Cl_2/H_2: 1/3	CH_4: 13.9%; CH_2F_2: 80.3%; CHF_2Cl: 1.7% CH_4: 17.2%; CH_2F_2: 78.4%; CHF_2Cl: 4.1%	[4]
CF_3CHFCl	Pd/AlF_3	473 K; CF_3CHFCl/H_2: 0.3–2	CF_3CH_2F: 99%	[8]
CF_3CF_2Cl	Pd/AlF_3	473 K; CF_3CF_2Cl/H_2: 1/2	CF_3CHF_2: 97%	[10]
CF_2Cl_2	Pd/TiF_3 Pd/ZrF_4 Pd/ZrF_xO_y	453 K; CF_2Cl_2/H_2: 1/3	CH_4: 13.1%; CH_2F_2: 81.8%; CHF_2Cl: 4.9% CH_4: 9.6%; CH_2F_2: 86.0%; CHF_2Cl: 3.8% CH_4: 7.1%; CH_2F_2:91.6%	[12]
CF_2Cl_2	Pd/AlF_3	463 K; CF_2Cl_2/H_2: 1/2	CH_4: 27%; CH_2F_2: 55%; CHF_2Cl: 6%	[13]
CF_3CFCl_2	Pd/AlF_3 Pd/30%F–Al_2O_S	473 K; CF_3CFCl_2/H_2: 1/3	CF_3CFH_2: 69%; CF_3CH_3: 24%; CF_3CHFCl: 6% CF_3CFH_2: 53%; CF_3CH_3: 37%; CF_3CHFCl: 9%	[19]
CF_2Cl_2	Pd/MgF_2 Pd–Au/MgF_2 Ru/MgF_2	453 K; CF_2Cl_2/H_2: 1/10	CH_4: 19%; CH_2F_2: 72%; CHF_2Cl: 8.5% CH_4: 9.3%; CH_2F_2: 86%; CHF_2Cl: 3.8% CH_4: 67.5%; CH_2F_2: 7.0%; CHF_2Cl:19.2%	[20]
CF_2Cl_2	Pd/MgF_2 (dp_{Pd} = 1 nm) Pd/MgF_2 (dp_{Pd} = 9 nm)	407 K; CF_2Cl_2/H_2: 1/2	CH_4: 7.4%; CH_2F_2: 88.1%; CHF_2Cl: 4.5% CH_4: 17.4%; CH_2F_2: 70.7%; CHF_2Cl: 11.9%	[23]

Table 3
Hydrogenolysis of CF_2Cl_2 and CHF_2Cl on Pd supported on Mg(Al)O obtained from hydrotalcite (from [41]), and on $KMgF_3$ perovskite-like structure (from [24])[a]

Catalyst	CF_2Cl_2 conversion				CHF_2Cl conversion				
	Conversion (mol%)	Selectivities (mol%)			Conversion (mol%)	Selectivities (mol%)			
		CH_4	CH_2F_2	CHF_2Cl		CH_4	CH_2F_2	CH_3F	CHF_3
4% Pd/“Mg(Al)O”	16	20	76	4	2.5	29	68	–	8
2% Pd–$KMgF_3$ coprecipitated	1	3	22	75	1.2	20	80	–	–
6% Pd/$KMgF_3$ impregnated	13	20	35	44	1.5	26	28	43	–

[a] Conditions: 473 K, CF_2Cl_2/H_2: 1.

hydroconversion [20]; 72% CH_2F_2 selectivity was obtained on the former, but only 7% on the latter (Table 2). The reaction is generally carried out at atmospheric pressure around 473 K, and selectivities larger than 70% in HFC are usually achieved.

If several studies refer to catalysts prepared by deposition of metal precursor on the fluorides directly, most of the works actually concern catalysts initially prepared by deposition on oxides. The fresh metal/oxide material suffers chemical transformations by reaction with hydrogen halides in the course of the reaction, or during the activation step processed in CFC/H_2 mixture. The mineral oxides are transformed into complex mixtures of fluorides, oxyfluorides and/or hydroxyfluorides (see Section 4). Generally, this chemical transformation results in an increased selectivity to hydrodechlorination. In most cases, the catalytic properties of metal/fluoride and metal/“ex-oxide” materials look very similar at the steady state (Fig. 1).

3.3. Metals on mixed fluorides

We will see further on (Section 4) that the promotion of hydrodechlorination, thanks to the use of fluoride supports, was ascribed to the vicinity in mixed sites of Pd^0 and decorating substoichiometric fluoride species, e.g. AlF_x ($x < 3$). One can anticipate that this intimate interaction between Pd and AlF_x would depend on the preparation method and would be easier in coprecipitated materials. This speculation has prompted studies on catalytic materials elaborated from Pd/Mg/Al layered double hydroxides [41], and $KMg_{1-x}Pd_xF_3$ compounds with perovskite-like structure [24,42].

The layered double hydroxide Pd/Mg/Al after calcination and reduction in hydrogen transformed into Pd/Mg(Al)O [41]. These materials containing various amounts of Pd were evaluated in the hydrogenolysis of CF_2Cl_2 and CHF_2Cl. Mg(Al)O is actually transformed into fluorides in the course of the reaction and the catalytic properties stabilized after 20 h reaction (Table 3). After reaction, the formation of MgF_2 (or $Mg(Al)F_2$ maybe) phase was identified by XRD, with no presence of MgO. In contrast, no aluminum compound was detected indicating a high dispersion or the formation of an amorphous phase.

With the aims to (i) make the interaction between Pd and fluoride species stronger and (ii) prevent the Cl/F exchange reactions, the use of Pd catalysts supported on fluorides materials of low acidity has been studied. For that purpose new $KMgF_3$ perovskite-like materials were synthesized by soft-chemistry at low temperatures [24,42]. The Pd has been introduced by impregnation or coprecipitation in the early stages of the synthesis, and the catalysts evaluated in the hydrogenolysis of CF_2Cl_2 and CHF_2Cl. As shown in Table 3, the synthesis route (impregnation or coprecipitation) has a great influence on the catalytic behavior. The main products for the hydrodechlorination reaction of CCl_2F_2 are $CHClF_2$ (up to 75%) and CH_2F_2, and for $CHClF_2$ are CH_2F_2 (up to 80%) and CH_3F (only for the impregnated sample). The low loaded Pd coprecipitated material (2% Pd–$KMgF_3$) exhibited an exceptional high selectivity to CHF_2Cl in the hydrogenolysis of CF_2Cl_2. This is very surprising, since it was never observed with Pd-based catalysts other than trace amounts of CHF_2Cl (Table 2). This behavior can be put in parallel with the similar reactivity of CF_2Cl_2 and CHF_2Cl on this catalyst, which is also unusual. It was generally reported, and in particular on Pd/AlF_3 and Pd/carbon, a much faster rate with CF_2Cl_2 in comparison with CHF_2Cl [4,14]. Some explanation about all these behavior are proposed hereafter.

4. The origins of selectivity promotion when using metal/fluoride catalysts

As mentioned above, the use of inorganic fluorides as supports brings a lot of advantages in terms of stability, activity and selectivity in the selective hydrodechlorination of CFC and HCFC. It is noteworthy that the Pd/"AlF_3" catalyst reported to be selective for the hydrodechlorination of CF_3CFCl_2 was prepared by fluorination of Al_2O_3 by HF/N_2 at 723 K [8]. This is fully true in comparison with oxides, and even with some carbons such as graphite. However, it is worth noting that excellent catalytic properties were reported in the hydroconversion of CF_2Cl_2 over Pd-based catalysts on carbon supports after some specific treatments [14].

It is difficult to claim that the superior behavior of fluorides as supports has been fully explained, some pieces of information can be found in the evolution of the catalytic properties which occurs in the first stage of the transformation of CFC on metal/oxide catalysts. During this period the inevitable transformation of the oxide to a "fluoride"-like material takes place due to the release of HF. The transformation of oxide to fluoride, naturally occurring in the course of the CFC transformation or realized on purpose before the reaction by treatment with HF, has been evoked or studied in details in several reports [3,4,12,17–19,21,25]. In the hydrodehalogenation of CF_2Cl_2 on Al_2O_3-, TiO_2-, MgO- and CaO-supported Ni catalysts, XRD analysis of the materials after the reaction showed that Al_2O_3, MgO and CaO were converted to fluorides, whereas TiO_2 was not modified after 10 h reaction [3]. The transformation of crystalline ZrO_2 to ZrF_4-like species was also reported as difficult [12]. In contrast, the transformation of Pd/MgO to Pd/MgF_2 during the hydrodehalogenation of CF_2Cl_2 was found easier than that of Pd/Al_2O_3 to Pd/"AlF_3" [25], though the latter transformation was reported easy at lower H_2/CF_2Cl_2 ratio and 473 K [4]. Anyway, this transformation of the supports from oxides to fluorides is always associated with an increase of the selectivity to hydrodechlorination. This was well demonstrated in a report specifically dedicated to the comparative behavior of Pd-based catalysts on oxides and fluorides supports in the hydrodehalogenation of CF_2Cl_2 at 453 K and $CF_2Cl/H_2 = 0.35$ [12]. It emerges very clearly that the fluoride supports (AlF_3, ZrF_4, TiF_3) favor both the selectivity to CH_2F_2, generally larger than 80%, and the specific activities per surface Pd atoms. The fresh Pd catalysts supported on oxides exhibit lower CH_2F_2 selectivity, from 25% for Pd/ZrO_2 to 60% for Pd/Al_2O_3, but this selectivity increases for Pd/TiO_2 and Pd/Al_2O_3 in the course of the reaction. In contrast, the CH_2F_2 selectivity on Pd/ZrO_2 does not change very much, after a slight initial increase. The fluorination did not occur for crystalline zirconia. Indeed, X-ray diffraction patterns provided evidence that the tetragonal ZrO_2 phase was altered very little at the end of the reaction, and only traces of hydrated ZrF_4 phases appeared. Conversely, alumina was transformed to a large extent into AlF_3 and $AlF_{1.96}(OH)_{1.04}$ phases. TiO_2, which is a mixture of anatase (85%) and rutile (15%) is transformed in part to $TiOF_2$. It is worth noting that only anatase underwent this bulk transformation, while rutile remained unmodified.

The effect of fluorination of Al_2O_3 by aqueous HF treatment on the catalytic behavior of Pd in the hydrodehalogenation of CF_3CFCl_2 and CF_2Cl_2 has been studied by Early et al. [19]. By varying the fluor content from 5 to 30%, the selectivity towards selective hydrodechlorination was improved. In the CF_3CFCl_2 transformation, the stability is optimum at 10% F, then declines at higher fluor content and with AlF_3 as support. This is not true in the case of CF_2Cl_2 transformation. Actually, the activity decay comes from the deposition on the metal of both Cl (and F to a lower extent) and a carbonaceous residue. The carbonaceous deposit forms more rapidly as the acidity of the support goes up, and both 30% F–Al_2O_3 and AlF_3 indeed possess the higher acidity as demonstrated by IR spectroscopy of CO [19]. Otherwise, it is noteworthy that the more carbon atoms in the molecule, the easier the molecule undergoes coking on acid sites of a catalyst [43]. Moreover, it was suggested that the presence of a "fluoride"-like support limits the extent of Cl(F) deposition onto the metal particles [4,19]. For these reasons, an optimum in fluor content of the support may exist for which the decrease of halogen deposition counter-balances the extent of "coke" building. Obviously, this optimum fluor content, which determines the acidity of the carrier, does depend on the molecule to be converted, and will be larger on shorter molecules. In the case of CF_2Cl_2, which can hardly lead to coke formation even on highly acidic materials, supports of high F content such as AlF_3 can be used.

It is clear that in the course of fluorination of Al_2O_3 before or during the CFC transformation, a complex mixture of fluorides, oxyfluorides and hydroxyfluorides can be formed. This point was addressed in the hydrodehalogenation of CF_2Cl_2 on Pd supported on various "fluoride" phases of zirconium [12]. By varying the thermal treatment with N_2 and HF/N_2 of ZrO_2 and a commercial ZrF_4, different materials containing fluorides, hydrated fluorides, oxyfluorides and hydroxyfluorides phases were prepared and used as support of Pd catalysts. The catalyst exhibiting the lowest CH_2F_2 selectivity (78%) is the one which is free of hydrated fluoride, oxyfluoride and hydroxyfluoride phases. By contrast, all the catalysts that are very selective for CH_2F_2 formation (89–92%) contain some hydrated, oxy- or hydroxyfluoride phases. It is worth noting that Kellner and Malikarjuna Rao [44] suggested that the Re/AlF_3 catalyst selective for the hydrodechlorination of CFCs contained oxy- and hydroxyfluoride phases. However, we have not yet any rational explanation for the specific properties introduced by oxygen containing fluoride phases.

In short, regarding stability and activity the contribution of "fluoride"-like materials as support of metal-based catalysts in the hydrodehalogenation of CFC is quite difficult to appreciate. This is mainly due because the highly corrosive nature of halogenated species which are formed in the reaction contributes to the highly dynamic behavior observed in these systems. However, the increase of selectivity towards hydrodechlorination is the constant behavior on these catalytic materials. Different proposals can be put forward for explaining the promoting effect of "fluoride"-like supports for hydrodechlorination:

1. a geometrical effect based on the size and/or the morphology of the Pd particles,
2. an electronic influence at the metal/insulator interface,
3. a peculiar metal/support interaction with formation of a mixed site.

In relation with the first point, no significant difference in selectivity was reported in the hydrodehalogenation of CF_2Cl_2 on fresh Pd black, Pd/Al_2O_3 and Pd/graphite catalysts (CH_2F_2/CH_4 = 2.8–2.9) with sizes of Pd particles larger than 8 nm [4]. It is generally considered that little change in morphology occurs for particles larger than 5 nm. On smaller Pd particles there is a small decrease of the selectivity to CH_2F_2 [4]. Very small changes of selectivity to CF_3CH_2F and CF_3CH_3 were also reported in the conversion of CF_3CFCl_2 on Pd/Al_2O_3 with sizes of Pd particles varying from 11 to 53 nm [15]. In these two studies the TOF, expressed per surface Pd atom on the fresh catalysts, exhibited only a twofold increase with the particle size. It is worthy to note that when the same reactions were performed on small surface area model catalysts, including Pd(1 1 1), Pd(1 1 0) and polycrystalline foil, the variations of selectivity were also found very small [35,45], e.g. from 88 to 91% in CH_2F_2 [35]. Regarding that point, from IR spectroscopy of adsorbed CO on Pd/Al_2O_3 catalysts, Binet et al. [46] have shown that the proportion of (1 0 0) facets increases, whereas that of (1 1 1) facets decreases when the size of Pd particles is larger than 10 nm.

In order to identify any difference in morphology of Pd particles when supported on oxides or fluorides, several studies have carried out the IR spectroscopy of CO [12,18,42]. Fig. 2 shows typical IR spectra, in the 2100–1800 cm^{-1} region, of CO adsorbed on Pd/Al_2O_3 and Pd/AlF_3 composed of similar size of Pd particles (ca. 10 nm). The IR spectra do not differ markedly; this is an indication of Pd particles being not very different in size and morphology. However, a higher intensity of the low frequency band is observed on Pd/AlF_3. To obtain more details on this feature, the spectra were deconvoluted according to the procedures described by Binet et al. [46]. Five elementary bands were extracted from the raw spectra. These bands, labeled A_1, A_2, B, C and D in a decreasing wavenumber order were assigned to the following adsorbed CO species: (i) A_1 (ca. 2075 cm^{-1}) and A_2 (ca. 2050 cm^{-1}) bands correspond to linearly adsorbed CO on low coordination sites, such as edges and corners; (ii) the band B (ca. 1980 cm^{-1}) corresponds to bridged CO in C_{2v} symmetry on (1 0 0) faces; (iii) C (ca. 1935 cm^{-1}) and D (ca. 1850 cm^{-1}) bands correspond to bridged CO in C_{2v} and C_{3v} symmetry on (1 1 1) facets. respectively. The deconvoluted spectra allowed to estimate the proportion of (1 1 1) and (1 0 0) facets, and low coordination sites in the two catalysts. The main difference which appears between Pd/Al_2O_3 and Pd/AlF_3 is a higher

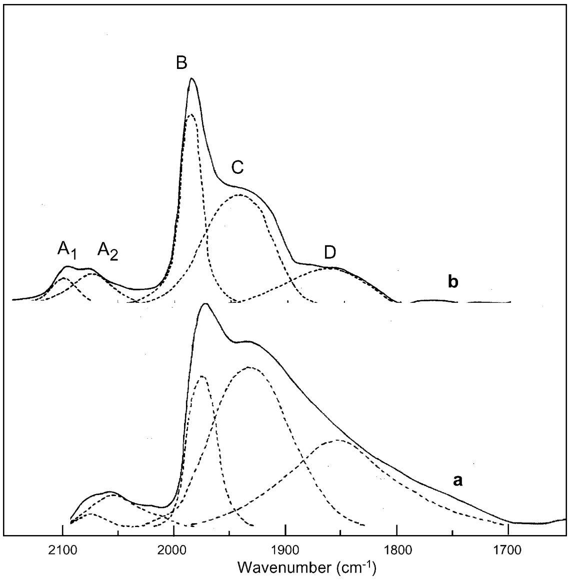

Fig. 2. Infrared spectra of CO adsorption on Pd/Al_2O_3 (a) and Pd/AlF_3 catalysts at full CO coverage; (—) experimental profile, (- - -) decomposition of the experimental profile into ν_{CO} elementary bands (from [12]).

density of the low coordination sites and the (1 0 0) faces on the latter. This means that the average coordination number of surface Pd atoms will be lower on Pd/AlF_3. On the other hand, the wavenumbers for A_1, A_2, B, C and D bands on Pd/Al_2O_3 are in good agreement with the values found on a Pd/Al_2O_3 catalyst of similar mean Pd particle size [46]. It was reported that decreasing the size of Pd particles in Pd/AlF_3, which results in a higher proportion of the low coordination sites, decreases the CH_2F_2 selectivity [4]. We can therefore conclude that the higher CH_2F_2 selectivity found on Pd/AlF_3 compared to Pd/Al_2O_3 can be hardly assigned to a morphology change of Pd particles.

We have seen above that in a rake scheme mechanism, the selectivity is mainly determined by the fate of adsorbed intermediates to suffer either a reactive desorption or further surface reactions. This is for instance the case of $=CF_2$ in the conversion of CF_2Cl_2 on Pd-based catalysts. The desorption of $=CF_2$, assisted by hydrogen, will be easier as the bond between $=CF_2$ and Pd will be weaker. In the metallocarbene $Pd{=}CF_2$ bond, the $=CF_2$ radical is electron withdrawing due to the inductive effect of fluorine atoms. Therefore, this metallocarbene bond will be weaker if Pd becomes electron-deficient. However, the adsorbed species may exchange various bond multiplicity with the metal surface which leads to different ensemble size requirements [47]. It was thus shown that triply bonded $\equiv C{-}CF_3$ species exists in larger proportion on fresh Pd/Al_2O_3 than on the passivated one [33]. One might also anticipate that the C_{3v} symmetry of Pd(1 1 1) facet would favor the formation of $\equiv C{-}CF_3$. Nevertheless, upon the reaction goes on, the deposition of Cl(F) and/or carbonaceous residues would dilute the Pd surface and the probability to encounter three free Pd atoms in C_{3v} symmetry will decrease; this is an ensemble size effect. It was indeed shown that after reaction of Pd with CF_2Cl_2/H_2 (ca. 0.35/1) at 453 K, the hydrogen taken up irreversibly (H_{irr}/Pd) of a Pd/Al_2O_3 decreased from 0.12 on the fresh catalyst to 0.04 on the passivated one [4]; in parallel only a small sintering of Pd was identified from TEM examinations. Moreover, hydrodehalogenation studies on Pd(1 1 1) and Pd(1 1 0) monocrystals have shown only small differences of selectivity depending on the facet [35,45]. On that account, one can postulate that the selectivity pattern would be mainly determined by electronic factors.

Some pieces of information about the electron-deficient character of the metal surface can be derived from IR spectroscopy of adsorbed CO in the case of Pd supported on fluorides [12,18,42]. Comparing the IR spectra of CO adsorbed on Pd/Al_2O_3 and Pd/AlF_3 (Fig. 2), a clear feature is the upward shift (10–20 cm^{-1}) of all vibrational frequencies for CO adsorbed on Pd/AlF_3 [12]. This upward shift was even larger when CO was adsorbed on $Pd/KMgF_3$ prepared from hydrothermal synthesis of $KMg_{1-x}Pd_xF_3$ [42]. There is a general agreement that the higher the stretching frequency of the $C{\equiv}O$ bond, the lower the bond strength between the carbon and the metal atoms [48,49]. That behavior is usually ascribed to a lower back donation of metal d electron in the $2\pi^*$ antibonding orbital of the CO bond. In the present work, when the support is changed from Al_2O_3 to AlF_3, the shift of the ν_{CO} by 10–20 cm^{-1} may be related to the variation of the electron density at the Pd atoms, this electron density is lower when Pd is supported by AlF_3. This behavior is certainly due to the strong Lewis acidity of AlF_3 [38]. The electron-deficient character of Pd supported on fluorides supports

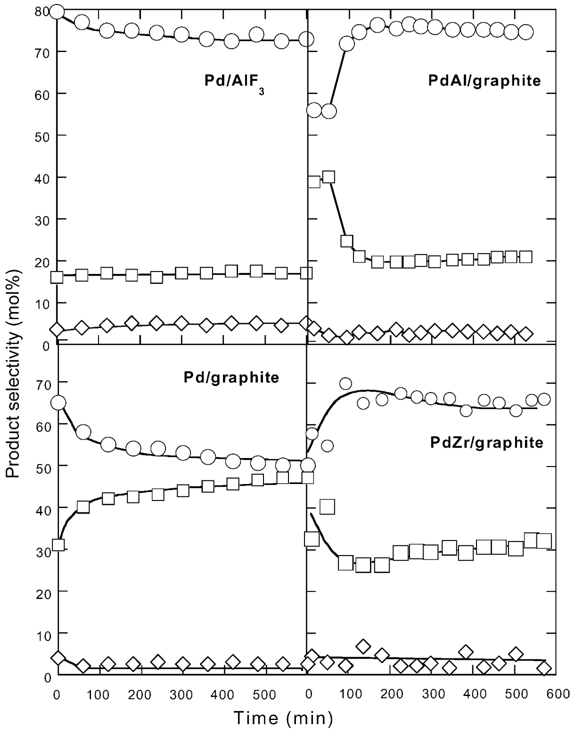

Fig. 3. Product selectivities for the hydroconversion of CF_2Cl_2 over Pd/AlF_3, Pd/graphite, PdAl/graphite and PdZr/graphite catalysts as a function of time during the first hours under stream: (○) CH_2F_2, (□) CH_4, (◇) CHF_2Cl; reaction temperature: 473 K (from [12]).

will then favor the desorption of $=CF_2$ adsorbed species.

The electron-deficient character of the metal particles comes from the interaction with fluorides supports. Two studies aimed to identify more precisely if the effect of fluoride supports on the enhancement of CH_2F_2 selectivity is a short range or a long range one [12,17]. For that purpose, graphite-supported “bimetallic” PdAl and PdZr catalysts were prepared by coimpregnation of graphite with $Pd(acac)_2$ and $Al(acac)_3$ or $Zr(acac)_4$ and evaluated in the hydrogenation of CF_2Cl_2 [12]. At steady state, the behavior of the bimetallic PdAl/graphite catalyst agrees very nicely with that of Pd/AlF_3 (Fig. 3). However, the more interesting point deals with the passivation period. In the passivation step, during the first 10 h on stream, the behavior of PdAl- and PdZr/graphite greatly differs from that of the pure Pd on graphite catalyst. On the latter, the CH_2F_2 selectivity decreases from 66 to 50%. In contrast, the CH_2F_2 selectivity on PdAl- and PdZr/graphite increases (Fig. 3). A parallel decrease of CH_4 selectivity is then observed. This “bimetallic” effect is really specific to Al and Zr since the addition of Co, Ag, Fe or K did not increase at all the CH_2F_2 selectivity [50]. It was proposed that Al, and to a lower extent Zr, were fluorinated in PdAl- and PdZr/graphite; the intimate contact between Pd and AlF_x or ZrF_x species ($x \leq 3, 4$) being responsible for the large decrease of CF_2Cl_2 hydrodefluorination. However, it was impossible to detect the presence of any kind of AlF_x or ZrF_x species in these catalysts, due to the low amount of aluminum and zirconium, 0.49 and 1.52 wt.%, respectively, for 1.8 wt.% Pd [12].

A very similar interpretation has been proposed in the CF_2Cl_2 hydrogenation for the behavior of Pd/Al_2O_3 reduced at high temperature [17]. The reduction at 600 °C caused an increase of the selectivity to CF_2Cl_2, from ca. 4 to 65%, for samples exhibiting the smaller Pd particles; this was ascribed to an extended presence of AlF_x species at the $Pd–Al_2O_3$ interface. Earlier works have shown that the Pd/Al_2O_3 system transforms partially into a Pd–Al alloy after high-temperature reduction (at 600 °C) [51]. It seems that at corrosive conditions caused by evolution of HF, the PdAl “alloy” is destroyed, leading to a considerable fluorination of alumina species at the Pd–“Al” interface. Indeed, Pd/Al_2O_3 catalysts which passed high-temperature reduction, acquired higher selectivity to CH_2F_2 much faster than the Pd/Al_2O_3 catalysts subjected to a low-temperature reduction [17].

Finally, the partial coverage of Pd with migrating “sub-fluoride” species is in agreement with the decrease of hydrogen uptake of Pd/Al_2O_3, from $H_{irr}/Pd = 0.12–0.04$, in the course of the $CF_2Cl_2+H_2$ reaction [4].

One can then propose that the promoting effect of fluoride supports on the catalytic behavior of metal catalysts for the selective hydrodechlorination of CFC can be mainly ascribed to the presence of migrating substoichiometric fluoride species onto the surface of metal particles. These species are responsible for (i) a faster desorption of intermediates, e.g. $=CF_2$, by making the metal surface more electron-deficient, and (ii) a larger proportion of intermediates exchanging less bonds with the metal surface, e.g. $CF_3–CF=$ rather than $CF_3–C\equiv$. The unusual and exceptional high selectivity to CHF_2Cl (ca. 75%, Table 3), in the hydrogenation of CF_2Cl_2 on the Pd–$KMgF_3$ catalysts has been interpreted by a strong cooperation between these two phenomena on this material prepared by soft-chemistry in a one-step coprecipitation [24]. A very large covering and dilution of the Pd surface dilution was concluded from XRD analysis and chemisorption measurements [42].

5. Concluding remarks

The selective hydrodechlorination of CFC and/or HCFC is a fair method for the synthesis of HFC from these banked and banned compounds. Fluoride-supported metal (Pd essentially) are very efficient catalysts for this reaction. Actually, in many cases the starting fresh materials are Pd/oxide which suffer chemical transformations by HF released in the course of the reaction. It seems even better, for the achievement of high selectivity, to start from these materials, because the chemical transformation of oxides by HF yields fluorides, but also oxyfluorides and hydroxyfluorides which are better promotor for the selective hydrodechlorination. The origin of selectivity is well explained by modification of the Pd d band which makes the desorption of intermediates of interest (Pd fluorocarbenes) faster. An intimate interaction between Pd and fluoride species in a mixed site is the clue to achieve this electronic modification.

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