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Conversion under Hydrogen of Dichlorodifluoromethane over Supported Palladium Catalysts

BERNARD COQ,*[1] JEAN MARIE COGNION,† FRANÇOIS FIGUÉRAS,*
AND DIDIER TOURNIGANT*

**Laboratoire de Chimie Organique Physique et Cinétique Chimique Appliquées, URA 418 du CNRS, ENSCM, 8 Rue de l'Ecole Normale, 34053 Montpellier Cedex, France; and †ATOCHEM, Centre de Recherche Rhône-Alpes, Rue Henri Moissan, B.P. 63, 69310 Pierre-Bénite, France*

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The conversion of difluorodichloromethane has been studied in the gas phase between 433 and 523 K at atmospheric pressure over Pd black and Pd supported on alumina, graphite, or AlF_3. In CF_2Cl_2 hydrogenation, CH_2F_2 and CH_4 represented more than 95% of the products. The catalytic properties of Pd/AlF_3 samples are unchanged with time, but Pd/graphite, Pd/Al_2O_3, and Pd black suffered changes of activity and/or selectivity during the first few hours on stream. This was ascribed to the diffusion of halide species into the bulk of palladium, and transformation of Al_2O_3 to AlF_3. At the steady state, the kinetics of CF_2Cl_2 hydrogenation can be described either by a halogenation/dehalogenation of the Pd surface by CF_2Cl_2 and H_2, respectively, or by a classical Langmuir–Hinshelwood mechanism. It was concluded that at 453 K the interaction between the Pd surface and CF_2Cl_2 or H_2 is of the same order of magnitude. The CH_2F_2/CH_4 selectivity ratio was the lowest on Pd/graphite and the highest on Pd/AlF_3. It is proposed that adsorbed, or absorbed, halide species are responsible for the loss of CH_2F_2 selectivity. The high selectivity ratio on Pd/AlF_3 is ascribed to a cooperative effect between Pd and AlF_3.

INTRODUCTION

Since 1974 much research has been devoted to the problem of redressing the destruction of the ozone in the stratosphere. Among several chemicals responsible for the ozone depletion, the chlorofluorocarbons (CFCs) are the most important. As a result "the Montreal Protocol on Substances that Deplete the Ozone Layer" was completed in September 1987. Agreement was reached, at first for a freeze, and further for a scaled reduction to 50% in the production of several CFCs by 1999. Moreover, a large reduction in allowed emission of CFCs will be introduced by legislation, and hence methods of collection, disposal and destruction will become important. Chemical processes for destruction or substitution of CFCs include pyrolysis, photochemistry, incineration, and catalytic conversion over oxides or supported metal catalysts. Among them, the catalytic conversion of CFCs by hydrogen to hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) is a challenging task for heterogeneous catalysis (*1*). Indeed, in order to speed up the phaseout of CFCs, the midterm transition compounds will be HCFCs, which have a limited effect on the ozone layer (*2*). However, the final goal is the use of HFCs, nonozone-depleting compounds, like CH_2F_2 (HFC32), CH_2FCH_3 (HFC114a), or CHF_2CF_3 (HFC115). In particular, CH_2F_2 appears as an excellent candidate for the low-temperature refrigeration applications (*3*).

Hydrogenolysis of the carbon–halogen bond over selected metal catalysts seems a promising way. The interaction between hydrogen and halogenated aliphatic compounds has long been studied over metals

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[1] To whom correspondence should be addressed.

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(*4–12*), but only a few studies have dealt with fluorine compounds (*4*, *10*) and chlorofluorocarbons (*11*, *12*). It appears that hydrogenolysis of the C–Cl bonds occurs more readily than hydrogenation of the C=C bonds, which in turn is faster than hydrogenolysis of C–F bonds. Moreover, the most efficient metals to achieve the hydrogenation are platinum and palladium, which offer a good compromise between activity and stability, as the literature of patents shows (*13–19*). For producing fluoroalkenes from CFCs, nickel or platinum deposited on a phosphate support are generally preferred (*13*, *15*, *16*, *19*). On the other hand, palladium supported on carbon or AlF_3 seems the best catalyst in order to obtain fluoroalkanes (*17*, *18*). Thus good yields, up to 76%, were claimed for the preparation of CH_2FCF_3 from $CHFClCF_3$ with 99% selectivity using Pd/AlF_3 as catalyst (*19*).

Neither influence of the support nor effect of the dispersion of the metallic phase on the catalytic properties were studied in detail in these works. It is well established now that these parameters are of a prime importance to tune the activity and the selectivity when processing hydrocarbons in petrochemistry. Keeping that in mind, our purpose was to study the effect of both Pd particle size and nature of the support on the conversion of dichlorodifluoromethane under hydrogen on the one hand, and the kinetics of this reaction on the other hand. Special attention will be paid to the selectivity to difluoromethane, the target compound.

EXPERIMENTAL

Reactants

Hydrogen of high purity grade (99.99%) was used for the catalytic experiments, and hydrogen of ultrahigh purity (99.9995%) for adsorption measurements. Dichlorodifluoromethane was obtained from ATOCHEM (purity > 99.95%). Palladium acetylacetonate ($Pd(acac)_2$, Aldrich, purity > 99%) was used as precursor for the supported catalysts. The precursor was dissolved in dehydrated toluene (purity > 99.5%). The carriers for the catalysts were γ-Al_2O_3 from Rhône–Poulenc (surface area 200 m^2 g^{-1}), AlF_3, $3H_2O$ from Rhône–Poulenc (surface area 75 m^2 g^{-1}, purity > 97%, no presence of aluminium oxyfluoride species was identified by XRD analysis), and graphite from LONZA (HSAG300, surface area 300 m^2 g^{-1}). Palladium black from Strem Chemical was used as unsupported catalyst.

Preparation of Monometallic Palladium Catalysts

The requisite amount of $Pd(acac)_2$ was dissolved in toluene, then contacted with the support at room temperature for several hours. Afterwards, the solution was either evaporated or filtered. These solids were dried at 298 K under vacuum. Some samples were then subjected to a calcination step in air at 473 K for 4 h. Finally, all the samples were reduced under varying conditions. The requirements for preparing catalysts according to these procedures are given in Table 1.

Characterizations

The catalysts were characterized by hydrogen sorption, X-ray diffraction, and transmission electron microscopy. The chemisorption of hydrogen was carried out in a conventional volumetric apparatus, at 298 K in the 0–30 kPa pressure range. The sample was first reactivated in situ under flowing hydrogen at 523 K overnight, then evacuated to 1.2×10^{-4} Pa, at the same temperature, for 3 h. The double isotherm method proposed by Benson *et al.* (*20*) was used to measure the amount of hydrogen chemisorbed on the palladium surface as well as that absorbed as bulk β-palladium hydride. The first isotherm consists of both adsorbed and absorbed hydrogen; outgassing at room temperature for 30 min removes the absorbed hydrogen and completely destroys the β-PdH phase. The second (back-sorption) isotherm represents the amount of hydrogen absorbed into bulk palladium since hydrogen chemisorbed on the palladium surface has not been removed by evacuation

TABLE I

Characteristics of the Catalysts

Catalyst	Support	wt% Pd	Reduction step			$(H/Pd)_{irr}$	Mean particle size in nm determined by		
			Temp. (K)	Duration (h)	Gas		Chem.	TEM	XRD
Pd903	Al_2O_3	10	623	8	$H_2 + H_2O$ (97.5 + 2.5)	0.12	8	5.5	37
PdMFDI[a]	Al_2O_3	1.0	523	3	$H_2 + N_2$ (20 + 80)	0.65	1.5	2.7	—
CGF20[a]	Al_2O_3	0.25	573	3	$H_2 + N_2$ (10 + 90)	0.87	1.1	1.2	—
PdGIII	Graphite	10.0	773	3	$H_2 + H_2O$ (97.5 + 2.5)	0.01	100	—	73
PdGVIII	Graphite	2.5	523	3	$H_2 + N_2$ (20 + 80)	0.15	6	—	22
PdALF3I	AlF_3	3.0	523	3	$H_2 + N_2$ (10 + 90)	0.10	10	12	10
PdAlF3IV	AlF_3	0.39	523	2	$H_2 + N_2$ (10 + 90)	0.17	6	—	8

[a] Samples calcined at 573 K under dry air before reduction.

at room temperature *(20)*. The difference between the two curves represents the isotherm of adsorption of hydrogen. The extrapolated value at zero pressure was taken as the amount of irreversibly adsorbed hydrogen. Provided the surface stoichiometry of irreversibly adsorbed hydrogen is unity, we have the metal dispersion given by $D = (H/Pd)_{irr}$.

The size of the metallic particles was checked by transmission electron microscopy using a JEOL 100CX microscope.

X-ray diffraction (XRD) patterns were recorded on a CGR Theta 60 instrument using monochromatized CuK_{α_1} radiation.

Chemical compositions of the solids were determined by elemental analysis after dissolution, at the CNRS Service Central d'Analyse (CNRS, Solaize, France).

Table 1 summarizes the main characteristics of the catalysts. One may note the apparent disagreement between hydrogen chemisorption and TEM on the one hand and XRD on the other hand for determining the mean Pd particle size of Pd903 and PdGVIII samples. The larger values obtained from XRD for these samples are probably due to a broad particle size distribution (Pd903), in which the small particles were not taken into account by XRD analysis.

Catalytic Experiments

The reaction of dichlorodifluoromethane with hydrogen was carried out at atmospheric pressure in a microflow reactor. The flow rate of each reactant was checked by a mass flowmeter (ASM, model Qualiflow AFC260). The effluents were analyzed by sampling on line to a gas chromatograph equipped with a J & W capillary column (30 m × 0.5 mm i.d., GSQ bonded polymer phase) and a thermal conductivity detector. 500 mg of sample were reactivated *in situ* under flowing hydrogen at 523 K overnight. Usually Pd catalysts suffer changes of activity and selectivity with time on stream, therefore a protocol was determined which allowed to reach constant catalytic properties. The protocol used for catalytic tests was: (1) the reaction conditions were fixed at $T_R = 473$ K, $CF_2Cl_2/H_2 = 0.35$, space velocity = 2000 h^{-1} for 20 h, which corresponds to passivation of the catalysts (attainment of constant activity and selectivity); (2) the reaction temperature was varied in the sequence 473, 433, 453, 413 K with $CF_2Cl_2/H_2 = 0.3$ and a space velocity between 2000 and 13000 h^{-1}; (3) at a reaction temperature of 453 K, the feed composition was varied in the range $0.1 < CF_2Cl_2/H_2 < 3$ with a space velocity in the range between

2000 and 13,000 h^{-1}, and alternating high and low CF_2Cl_2/H_2 ratios. With these conditions of test, and after the passivation period, the catalytic activity was stable as a function of time on stream.

Activities are expressed both as mole of reactant converted per unit time and mass of catalyst and as turnover numbers (TON), or number of molecules of reactant converted per surface metal atom and per hour. Selectivities are defined as $S_i = 100\, C_i/\Sigma C_i$, where C_i is the molar concentration of the detected product *i*. Selectivities were measured at low conversions, usually less than 5%, in order to avoid secondary reactions. They thus represent initial selectivities. Hydrogen chloride and hydrogen fluoride formed during the reaction were not taken into account as reaction products. They were adsorbed on a precolumn filled with NaF, Cu, and $ZnCl_2$.

RESULTS

In the course of CF_2Cl_2 conversion under hydrogen over supported Pd catalysts two main organic compounds are formed, namely, CH_2F_2 and CH_4, which usually represent more than 95% of the products. Besides these compounds, small amounts of CHF_2Cl (2–5%) were found. The concentration of CHF_2Cl decreased usually with time on stream during the passivation of the catalyst. Traces lower than 1% of various compounds such as CH_3F, $CHFCl_2$, or CF_3Cl were detected. This last product is only formed on Pd/AlF_3 catalysts by F/Cl exchange between CF_2Cl_2 and HF. Very probably, this reaction took place on the carrier, since AlF_3 was claimed as a good catalyst to prepare CF_3CFCl_2 from $CFCl_2CF_2Cl$ at 673 K (*21*).

During the passivation period, different behaviours were observed:

(i) Pd black and Pd/AlF_3 did not deactivate, while Pd catalysts supported on alumina or graphite suffered a 20–50% activity loss;

(ii) the selectivity to methane increased with time on stream for Pd/graphite and Pd black, remained constant for Pd/AlF_3, but decreased for Pd/Al_2O_3 (Fig. 1 and Table 2).

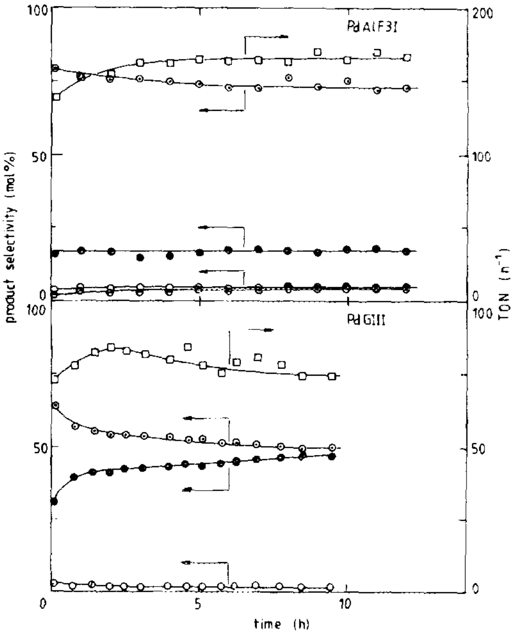


FIG. 1. Turnover number (TON) and product selectivities for the hydroconversion of CF_2Cl_2 over Pd catalysts as a function of time during the first hours on stream: (□) TON, (⊙) CH_2F_2, (●) CH_4, (○) CHF_2Cl, (◒) $CHFCl_2$. T_R = 473 K.

These changes in properties of the catalysts will be discussed further.

At the steady state, the catalytic properties were studied as a function of the reaction temperature, feed composition, and conversion level. In order to reach high conversions the reaction temperature was raised to 523 K for one experiment on the PdAlF3I sample (Fig. 2). When the CF_2Cl_2 conversion increases the ratio CH_4/CH_2F_2 increases also, suggesting that a formal consecutive reaction scheme applies: $CF_2Cl_2 \rightarrow CH_2F_2 \rightarrow CH_4$.

Figure 3 illustrates the dependence of the reaction rate on the feed composition ($P_{CF_2Cl_2}/P_{H_2}$) for different Pd catalysts. The activity goes through a maximum, then decreases. This general behaviour observed

TABLE 2

Change of Catalytic Properties of Pd Catalysts during the Passivation Period; T_R = 473 K; CF_2Cl_2/H_2 = 0.3

Sample	Time on stream ≅ 10 min		Time on stream ≅ 10 h	
	TON (h^{-1})	CH_2F_2/CH_4	TON (h^{-1})	CH_2F_2/CH_4
Pd903	98	2.6	61	3.7
PdMFDI	45.2	1.4	28.2	3.5
PdGIII	151	2.8	116	1.9
PdGVIII	73	2.1	72	1.1
PdAlF3I	138	4.9	166	3.6
PdAlF3IV	283	3.6	307	3.8
Pd black	89	2.8	89	0.9

for all the cataysts led us to speculate that there is a competition of adsorption between hydrogen and CF_2Cl_2 for the active sites. At low CF_2Cl_2 pressure the reaction order versus the organic reactant tends to one. A similar dependence was reported earlier for the hydrodefluorination of $CH_3CH_xF_{3-x}$ over Pd/C at reactant pressures lower than 2 kPa (*10*). At variance with this, Gervasutti *et al.* (*11*), studying the hydroconversion of CF_3CFCl_2 over a Pd/C catalyst, reported a zero-order dependence against CF_3CFCl_2 pressure in the range of composition $2 < H_2/CF_3CFCl_2 < 4$.

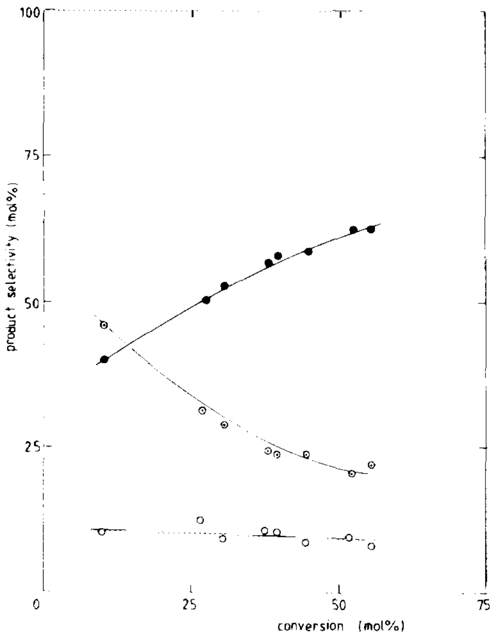


FIG. 2. Product selectivities for the hydroconversion of CF_2Cl_2 over PdAlF3I as a function of reactant conversion. T_R = 523 K; $P_{CF_2Cl_2}/P_{H_2}$ = 0.35. Same symbols as in Fig. 1.

In the range studied the feed composition had little influence on the product selectivity, as shown for PdAlF3I catalyst in Fig. 4. For the conversion of CF_3CFCl_2 over a Pd/C catalyst no effect of reactant pressure was observed either, and the selectivity ratio CF_3CH_2F/CF_3CH_3 between the products remained around six (*11*). However, for the same reaction Kellner and Mallikarjuna (*19*) claimed a 99% selectivity for CF_3CH_2F when CF_3CFCl_2 was processed over a Pd/AlF_3 catalyst between 523 and 573 K and under 10^6 Pa total pressure. An effect of the nature of the support appears from these two reports, and aluminium trifluoride seems a better carrier than graphite to lower the removal of fluorine atoms. The same behaviour applied for the hydrodehalogenation of CF_2Cl_2, as Table 3 points out. Methane formation is the highest when graphite is used as carrier.

The value of the activation energy (Table 3) varies from catalyst to catalyst but with a general trend between 60 and 70 kJ mol^{-1}. Increasing the reaction temperature always

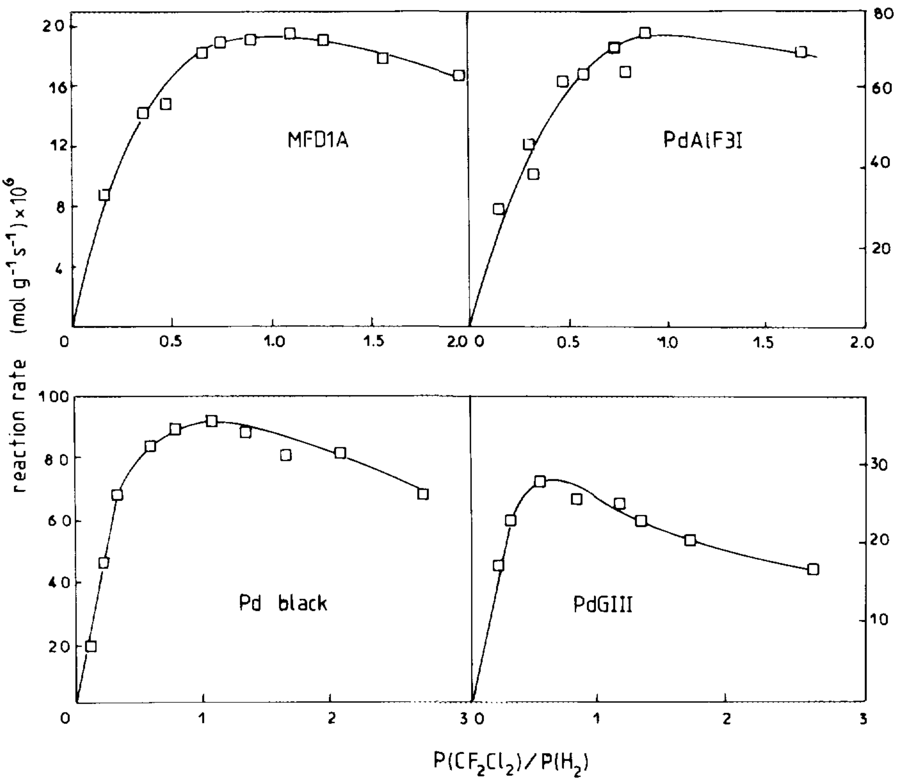


FIG. 3. Reaction rate for the hydroconversion of CF_2Cl_2 over Pd catalysts as a function of feed composition. T_R = 453 K.

results in a higher selectivity to methane for most of the catalysts. Figure 5 illustrates this temperature dependence of the selectivity for PdAlF3I. This is not due to an effect of the conversion level which was maintained less than 5%. This behaviour probably arises from differences in activation energies for the formation of CHF_2Cl (70.0 kJ mol^{-1}), CH_2F_2 (55.5 kJ mol^{-1}), and CH_4 (90.0 kJ mol^{-1}). Gervasutti *et al.* (*11*) also reported that the selectivity ratio CF_3CH_3/CF_3CH_2F, in the conversion of CF_3CFCl_2 over a Pd/C catalyst, increases with the reaction temperature.

DISCUSSION

The first point was to check that under the experimental conditions the removal of halogen was a reaction specific to the Pd surface and not catalyzed by the carrier. Indeed, it was reported that some acidic supports can remove chlorine or fluorine atoms from CFCs (*22*). For this purpose, Pd black and two mechanical mixtures between Pd black and AlF_3 on the one hand, and PdALF3I and AlF_3 on the other hand, were tested for the reaction. It appears (Table 4) that adding AlF_3 either to Pd black, or to PdAlF3I does not modify deeply the activity of pure Pd black or PdALF3I catalysts, respectively. Therefore, we can reasonably assume that the hydrodehalogenation of CF_2Cl_2 takes place for the main part on the Pd surface.

During the initial step of passivation, we thought that the logical behaviour was a decrease of activity coming from an adsorption of chloride or fluoride species on the Pd surface, as reported previously during the conversion of chlorobenzene over alumina-

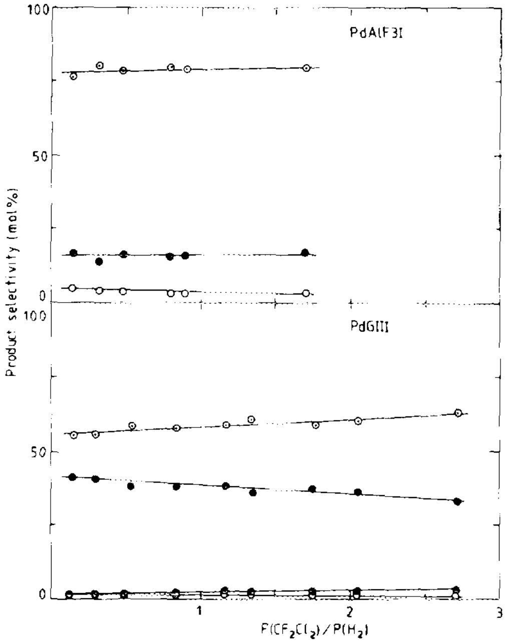


FIG. 4. Product selectivities for the hydroconversion of CF_2Cl_2 over Pd catalysts as a function of feed composition. T_R = 453 K. Same symbols as in Fig. 1.

supported Pd and Rh catalysts (*23*). Actually, the main point is the change of selectivity during the passivation period. Two opposite behaviours took place: on the one hand, a decrease of CH_2F_2 selectivity with time for Pd black and Pd/graphite, on the other hand for Pd/Al_2O_3 an increase of CH_2F_2 selectivity which reached at the steady state the mean values obtained with Pd/AlF_3. Characterizations of the fresh and passivated Pd903 sample were carried out by hydrogen chemisorption, transmission electron microscopy and X-ray diffraction. After reaction, the hydrogen uptake has decreased from H/Pd_{irr} = 0.12 to H/Pd_{irr} = 0.04, and only a small sintering of Pd particles appeared from TEM examinations. The main change observed by X-ray diffraction was the disappearance of the bands characteristic of alumina and the appearance of those of AlF_3. Very probably this transformation occurred by means of the released hydrogen fluoride. It is worth noting that the Pd/AlF_3 catalyst claimed for the selective hydrodechlorination of CF_3CFCl_2 (*19*) was prepared by fluorination of Al_2O_3 by HF at 723 K. Moreover, no change of the width of the Pd(111) line was observed on the passivated catalyst, which confirms that the mean size of Pd crystallites remained the same during this period, as for the other catalysts. In other respect, the Pd(111) and Pd(220) lines of Pd black and Pd/graphite samples after passivation did not suffer any broadening, but were shifted to smaller diffraction angles, which shows an increase by 3% of the interplanar distances. This phenomenon could be accounted for by the diffusion of fluorine or chlorine into the bulk of Pd particles. The passivated Pd black contains 0.3 and 0.2% of chlorine and fluorine, respectively. Nevertheless, the lines characteristic of PdF_2 or $PdCl_2$ did not appear. Keeping in mind the decrease of CH_2F_2 selectivity during the passivation step, we conclude that adsorbed or absorbed halogen species could be responsible for this loss of selectivity.

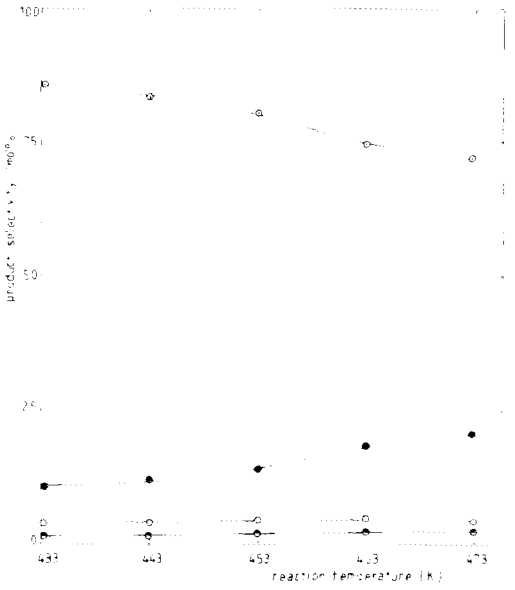


FIG. 5. Product selectivities for the hydroconversion of CF_2Cl_2 over PdAlF3I as a function of reaction temperature; $P_{CF_2Cl_2}/P_{H_2}$ = 0.35. Same symbols as in Fig. 1.

TABLE 3

Distribution of the Products and Activation Energies for Hydrogenation of CF_2Cl_2 at 453 K over Pd-Based Catalysts (CF_2Cl_2/H_2 = 0.3–0.35)

Catalyst	Conv. (%)	E_a (kJ mol^{-1})	Product selectivity (mol%)			
			CH_4	CH_2F_2	CHF_2Cl	Others[a]
Pd black	4.7	61.5	45.0	52.8	1.6	0.6
Pd903	6.4	60.5	16.5	79.1	3.2	1.0
PdMFD1	1.4	66	18.6	76.7	4.0	0.6
CGF20	0.1	—	24.5	68.6	—	6.8
PdGIII	1.4	67.0	32.5	63.7	1.0	2.7
PdGVIII	5.9	61.5	40.5	56.1	1.7	1.7
PdAlF3I	8.8	63.5	13.9	80.3	1.7	4.0
PdAlF3IV	2.0	75	17.2	78.4	4.1	0.3

[a] $CH_3F + CHFCl_2 + CF_3Cl$.

To sum up, for the catalysts supported on alumina the increase of CH_2F_2 selectivity in the course of the reaction very probably comes from the appearance of the AlF_3 phase.

With respect to these comments the Pd/AlF_3 catalysts behaved like stabilized Pd/Al_2O_3 catalysts. Indeed, very small changes of the catalytic properties appeared during the passivation step.

As stated previously, CH_4 and CH_2F_2 are the main products formed during CF_2Cl_2 conversion. Moreover, the selectivity in CH_2F_2 decreases when the conversion increases (Fig. 2), which suggests a possible consecutive reaction scheme. To obtain more detail about that point, the reactivities of CHF_2Cl and CH_2F_2 relative to that of CF_2Cl_2 were determined over the PdAlF3I catalyst. The data reported in Table 5 show that these two molecules exhibit a much lower reactivity for the Pd surface with respect to CF_2Cl_2. This behaviour parallels that reported for the hydrodechlorination of CCl_4, $CHCl_3$, and CH_2Cl_2 over supported Pt catalysts (*8*, *24*). Weiss *et al.* (*8*) found $CHCl_3$ and CH_4 as main products with a $CHCl_3/CH_4$ ratio remaining roughly the same, four to six depending on the catalyst, whatever the conversion level of carbon tetrachloride. Moreover, $CHCl_3$ and CH_2Cl_2 exhibited very low reactivities under the same conditions of reaction. For the hydrodechlorination of CCl_4, Weiss *et al.* (*8*) proposed a consecutive rake scheme mechanism: $CCl_4 \rightarrow CHCl_3 \rightarrow CH_4$.

In such a mechanism, the product selectivity is mainly determined by the ratio be-

TABLE 4

Catalytic Properties for the Hydrogenation of CF_2Cl_2 at 453 K over Pd Catalysts (CF_2Cl_2/H_2 = 0.3–0.35)

Catalyst	Reaction rate (mol/min/g) × 10^6	TON (h^{-1})	E_a (kJ mol^{-1})	Product distribution (mol %)		
				CH_4	CH_2F_2	CHF_2Cl
Pd black	70	44	61.5	45.0	52.8	1.6
Pd black + AlF_3 (1 + 4)	58	37	68.5	32.4	64.5	2.8
Pd/AlF_3 + AlF_3 (1 + 10)	60.5	135	58.5	12.0	84.4	3.6

TABLE 5

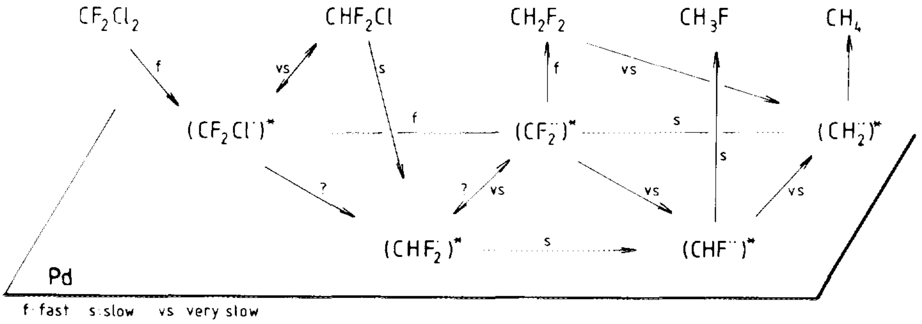
Catalytic Properties for the Hydrogenation of CF_2Cl_2, CHF_2Cl, and CH_2F_2 at 473 K over Pd/AlF_3 (CFC/H_2 = 0.3–0.35)

Reactant	Reaction rate[a]	E_a (kJ mol^{-1})	Product distribution (mol%)				
			CH_4	CH_3F	CH_2F_2	CHF_2Cl	Others[b]
CF_2Cl_2	74	63.5	20.8	0.1	71.7	2.9	4.5
CHF_2Cl	22.7	71.0	27.5	69	3.5	—	—
CH_2F_2	3.6	50.0	94.3	2.7	—	—	3.0

[a] Expressed in (mol min^{-1} g^{-1}) × 10^6.
[b] CHF_3, CF_3Cl, $CHFCl_2$.

tween the rate of desorption of the adsorbed ·CCl_3 radical to its direct reaction to CH_4 in the adsorbed state. A similar behaviour was observed in the conversion of CF_3CFCl_2 over Pd/C (*11*), where CF_3CH_2F and CF_3CH_3 only were detected, in a constant ratio of six, and the monohydrodechlorinated product CF_3CHFCl could not desorb apparently. In the same way, CH_3CHF_2 did not yield CH_3CH_2F but only C_2H_6 (*10*). Similar conclusions apply for the conversion of CF_2Cl_2. The selectivity for the two main products, CH_2F_2 and CH_4, is mainly determined by the ratio between the desorption rate of the :CF_2 radical and the rate of the surface reaction leading to CH_4. Indeed, the readsorption of the product CH_2F_2 by no means can explain the formation of CH_4, due to the very low reactivity of CH_2F_2 in the gas phase (Table 5).

An interesting point deals with the product distribution during CHF_2Cl conversion. Surprisingly, a very low selectivity to CH_2F_2 is observed and CH_3F was the main product. In this respect, the reactivity of CHF_2Cl does not conform simply to the consecutive scheme: $CF_2Cl_2 \rightarrow CHF_2Cl \rightarrow CH_2F_2 \rightarrow CH_3F \rightarrow CH_4$. The formal reaction scheme is probably much more complicated, as tentatively proposed in Scheme 1. Chlorodifluoromethane would interact with the Pd surface by two parallel ways to yield ·CF_2Cl or ·CF_2H adsorbed species. The latter will be the most abundant if one considers that in halomethane the halogen–metal exchange is usually more rapid than hydrogen–metal exchange (*25*). Moreover, only low interconversion would exist between these species. In conclusion, the reactions favoured are those allowing the removal of two halogen atoms during one sojourn at the surface: $CF_2Cl_2 \rightarrow CH_2F_2$; $CHF_2Cl \rightarrow CH_3F$; $CH_2F_2 \rightarrow CH_4$.



(1)

SCHEME 1

With respect to the hydrodechlorination of CCl_4 (*8*), the hydrodehalogenation of CF_2Cl_2 differs in the sense that the ratio CH_2F_2/CH_4 decreases when the conversion level increases (Fig. 2), whereas the ratio $CHCl_3/CH_4$ does not (*8, 24*). This phenomenon cannot be accounted for by readsorption of CH_2F_2, owing to the very low reactivity of that compound under these conditions (Table 5). In this respect, different kinetic dependences, of the reactions leading either to CH_2F_2 or to CH_4, to the surface coverage in $:CF_2$ species (Scheme 1) could be suggested. Very probably, when CF_2Cl_2 conversion increases, the surface coverage in $:CF_2$ is changed. However, due to the high exothermicity of the halogen removal (*4*), some heat-transfer limitation can occur which modifies the selectivity between reactions exhibiting different Arrhenius parameters, namely, 55.5 and 90.0 kJ mol^{-1} for CH_2F_2 and CH_4 formation, respectively.

According to the dependence of the reaction rate on reactant pressure (Fig. 3), a competition between the reactants for the active surface is likely. The kinetics of such a reaction have not been studied in detail previously. Several mechanisms which differ only slightly have been postulated. For the conversion of carbon tetrachloride over Pt/Al_2O_3, Weiss *et al.* (*8*) proposed a dissociative adsorption of CCl_4 as the rate-controlling step, followed by a rapid reaction between the $\cdot CCl_3$ radical and hydrogen. The adsorbed chlorine species were assumed to be scavanged easily from the metallic surface. Campbell and Kemball (*6*), however, provided evidence for an inhibiting effect of chlorine during the reaction between alkyl chlorides and hydrogen. The setting up of the steady state, i.e., regeneration of the active surface, is reached by removal of adsorbed chlorine by hydrogen. This chlorination/dechlorination of the metallic surface could be the key step controlling the reaction rate as proposed recently for the hydrodehalogenation of $CFCl_2CF_2Cl$ over different metal catalysts (*12*b). We proposed earlier a similar kinetic model for the hydroconversion of chlorobenzene over supported Pd and Rh catalysts (*23*) and their alloys (*26*). On similar basis, Gervasutti *et al.* (*11*) proposed a rapid dissociative–adsorption/associative–desorption for CF_3CF_2Cl of the type

$$CF_3CF_2Cl + H^* \rightarrow CF_3CF_2^* + HCl, \quad (2)$$

where the asterisk (*) refers to an adsorbed species.

By considering the state of the art in the literature, and our experimental results, two kinetic models can be tentatively proposed:

(1) a classical Langmuir–Hinshelwood model with competitive adsorption of the reactants,

$$CF_2Cl_2 + S^* \overset{\lambda_R}{\longleftrightarrow} CF_2Cl_2^* \quad (3)$$

$$H_2 + 2S^* \overset{\lambda_H}{\longleftrightarrow} 2H^* \quad (4)$$

$$CF_2Cl_2^* + H^* \xrightarrow{k} \text{products}, \quad (5)$$

where λ_R and λ_H are the adsorption constants, and k the rate constant for the surface reaction. Assuming a first-order dependence of the surface reaction versus the coverages in CF_2Cl_2 and hydrogen, and a Pd surface totally covered by CF_2Cl_2 and hydrogen, the rate law can then be derived,

$$r = k\lambda_R P_R(\lambda_H P_H)^{0.5}/(\lambda_R P_R + (\lambda_H P_H)^{0.5})^2, \quad (6)$$

where P_R and P_H are the pressure of CF_2Cl_2 and H_2, respectively.

(2) a halogenation/dehalogenation mechanism,

$$CF_2Cl_2 + H^* \xrightarrow{k_R} \text{products} + Cl^*, F^* \quad (7)$$

$$Cl^*, F^* + H_2 \xrightarrow{k_H} H^* + HCl, HF, \quad (8)$$

where k_R is the rate constant for the halogenation of the Pd surface, and k_H the rate constant for the regeneration of the Pd surface. The expression of the rate equation is

$$r = k_R P_R k_H P_H / (k_R P_R + k_H P_H), \quad (9)$$

assuming a first-order dependence with respect to CF_2Cl_2 and H_2 pressures for the halogenation and regeneration of the Pd surface. As we worked at atmospheric pressure (10^5 Pa), the rate law takes the form

$$r = 10^5 k_R k_H (P_R/P_H) / [k_R (P_R/P_H)^2 + (k_R + k_H)(P_R/P_H) + k_H]. \quad (10)$$

When fitting the experimental data to the two rate expressions (Eqs. (6), (10)) it appears that very little difference exists between both models in the range of reactant pressures investigated, $0.1 < P_{CF_2Cl_2}/P_{H_2} < 3$. Therefore, the kinetic parameters were only determined for the halogenation/dehalogenation mechanism.

When the P_R/P_H ratio varies from zero to infinity, the reaction rate goes through a maximum value r_m for $\delta r / \delta (P_R/P_H) = 0$. The two rate constants k_R and k_H can then be determined from the values of the coordinates r_m and $(P_R/P_H)_m$ of that point:

$$(P_R/P_H)_m = (k_H/k_R)^{0.5} \quad (11)$$

$$r_m = 10^5 k_H / [1 + (k_H/k_R)^{0.5}]^2. \quad (12)$$

The values of k_R and k_H were then determined for all the catalysts and are reported in Table 6. Whatever the catalyst, it appears that the ratio between the two rate constants k_H and k_R does not change greatly, from 0.3 to 1.25 approximately. Hence, the strength of interaction between the Pd surface and CF_2Cl_2 or H_2 is of the same order of magnitude, and little affected by the nature of the support. We can only point out that k_R is larger than k_H for Pd supported on graphite.

As far as the specific activity per Pd surface atom is concerned, it appears that the TON is lower when graphite or alumina are used as carriers, and for small Pd particles. This last point is less obvious due to the possible transformation of alumina, and the deposit of chlorine and fluorine in the course of the reaction. Thus, the clearest influence on catalytic properties, and especially on selectivity, arises from the nature of the support.

TABLE 6

Estimated Values of the Kinetic Parameters in the Halogenation/Dehalogenation Mechanism for the Conversion of CF_2Cl_2 at 453 K over Pd-Based Catalysts

Catalyst	$(P_R/P_H)_m$	r_m[a]	k_H[b]	k_R[b]	TON[c] (h^{-1})
Pd black	1.1	92	405	335	58
Pd903	1.1	90	397	328	47
PdMFD1	1.1	7	31	25.5	19
CGF20	—	—	—	—	3
PdGIII	0.65	11.0	30	71	72
PdGVIII	0.60	28	72	200	52.5
PdAlF3I	0.9	74	267	330	165
PdAlF3IV	1.10	20	88	73	176

[a] Expressed in (mol min^{-1} g^{-1}) × 10^6.

[b] Expressed in (mol min^{-1} g^{-1}) × 10^{11}.

[c] Specific activities calculated from r_m values at 453 K.

Different proposals can be put forward for explaining the promoting effect of AlF_3 on Pd for CH_2F_2 formation:

(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 particular metal/support interaction between Pd and AlF_3.

In relation with the first point, there is no significant difference in selectivity on the fresh Pd black, Pd903, and PdGIII samples ($CH_2F_2/CH_4 = 2.8$–2.9) with sizes of Pd particles larger than 8 nm. It is generally considered that little change in morphology occurs for particles larger than 5 nm. On smaller Pd particles (PdMFD1, PdGVIII) there is a small decrease of the selectivity to CH_2F_2. Consequently, it seems difficult to link the increase in CH_2F_2 selectivity obtained over Pd/AlF_3 catalysts to a geometrical effect.

No report was found dealing with a direct modification of the Pd *d*-band by AlF_3, or other similar solids. However, some preliminary studies concerning the infrared spectroscopy of adsorbed CO on Pd903 and PdAlF3I (*27*) showed a shift of all the CO stretching frequencies to higher values on the latter solid. This can reflect a lower backdonation into the antibonding π^*-orbitals of CO. This behaviour is often ascribed to a lower density of Pd 4*d* states at the surface sites. Such an electronic influence can be induced by both AlF_3, through its acidic character, or by fluorine, as an electron withdrawing element. It is clear that adsorbed, or absorbed, fluorine can promote the appearance of $Pd^{\delta+}$ species. Nevertheless, the sole occurrence of these species does not allow one to explain the increase of both TON and CH_2F_2 selectivity obtained on Pd/AlF_3 samples. Indeed, after the passivation step, Pd/graphite and Pd black which contain fluorine in close interaction with Pd are less active and much less selective to CH_2F_2 than Pd/AlF_3.

Finally, therefore, it seems necessary to invoke a particular interaction, or cooperation, between Pd particles and the AlF_3 carrier. When preparing Pd/AlF_3 catalysts, hydrogen fluoride was released during the final step of reduction. We could speculate that AlF_x species ($x < 3$) were formed at the periphery of the Pd particles. In the course of CF_2Cl_2 hydrogenation, these species would withdraw adsorbed fluorine atoms, hence scavenging the surface, and protecting the Pd particles against the diffusion of fluorine into the bulk. Indeed, as considered above for Pd black and Pd/graphite, fluorine atoms occluded into Pd would be responsible for the lack of selectivity to CH_2F_2.

CONCLUSION

The conversion under hydrogen of CF_2Cl_2 over supported Pd catalysts yields two main products, CH_2F_2 and CH_4. The distribution of products, obtained from CF_2Cl_2 and CH F_2Cl conversions, can be explained by the formation of carbenoid surface species. The kinetics of the reaction show evidence for a competition of adsorption between CF_2Cl_2 and hydrogen for the active sites; the interactions between Pd and CF_2Cl_2 or hydrogen are of the same order of magnitude. The selectivity of the reaction slightly depends on the size of the Pd particles, large particles favouring CH_2F_2 formation. By contrast, the nature of the support has a great influence on selectivity. The use of AlF_3 as carrier allows one to reach the highest selectivity, up to 81%, in CF_2H_2. This behaviour is interpretated tentatively in terms of a metal–support cooperation. When palladium is supported on AlF_3, some AlF_x species ($x < 3$) would be formed at the periphery of the Pd particles; these species thereby prevent the diffusion of fluorine, or chlorine, into bulk palladium. This last phenomenon could be responsible for the loss of selectivity to CH_2F_2 which occurred with Pd/graphite and Pd-black catalysts.

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