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Hydrodechlorination of Dichlorodifluoromethane over Palladium Model Catalysts and a Comparison with the Hydrodechlorination of 1,1-Dichlorotetrafluoroethane

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The hydrodechlorination of dichlorodifluoromethane (CFC-12) was performed on small surface area model catalysts, including Pd(111) and Pd(110) single crystals and polycrystalline palladium foil. Reactions were performed in a batch reactor, at atmospheric pressure and in the temperature range of 423–523 K. The main products were CH_2F_2 and CH_4. Ethane could be detected at higher temperatures. Lower deactivation rates and a higher activation energy for CH_2F_2 formation were found for Pd(111). In a comparison to our previous results with dichlorotetrafluoroethane (CFC-114a), the hydrodechlorination rate of CCl_2F_2 was 2 orders of magnitude lower, the mono-dechlorinated product ($CHClF_2$) was not produced, and the bulk palladium hydrogen activity was not detected. An overview of the hydrodechlorination reaction is presented. © 2000 Academic Press

Key Words: **palladium model catalysts; Pd(111); hydrogen; CFC-12; dichlorodifluoromethane; CFC-114a; hydrodechlorination; dechlorination; chlorine.**

1. INTRODUCTION

Chlorofluorocarbons (CFCs) fulfilled an important societal need in the 20th century. Due to unique physical and chemical properties, they were used in a wide variety of applications, especially in the area of refrigeration.

Because of environmental concerns (1, 2) that led to regulations in recent years, a market of alternative compounds was created. The development of CFC alternatives has focused on nonchlorinated compounds with similar physical properties that would break down in the lower atmosphere. One such class of alternatives is the hydrofluorocarbons (HFCs). One of the simplest methods to obtain these alternatives involves the catalytic reaction of CFCs with hydrogen on metal surfaces with selective chlorine removal, which is called hydrodechlorination. The development of this technology has allowed the discovery of 1,1,1,2-tetrafluoroethane (HFC-134a), a good substitute for CCl_2F_2 in refrigerant applications. This compound has very similar properties to that of CCl_2F_2 (e.g., molecular weight and boiling point).

The hydrodechlorination of CCl_2F_2 on palladium catalysts yields CH_2F_2 (HFC-32) with a selectivity higher than 80%, thereby avoiding the need for its disposal. Besides, CH_2F_2 is a good replacement in heavy duty cooling applications and has a lower global warming potential than CF_3CH_2F, the current substitute of CCl_2F_2 (3, 4).

In recent years hydrodechlorination was an area of focus in catalysis science. Weiss *et al.* (5) has studied the hydrodechlorination of CCl_4 on platinum catalysts. Using a Pd/C catalyst, Gervasutti *et al.* (6) was one of the first groups to study the hydrodechlorination of CFCs (conversion of CFC-114a to HFC-134a). In the 90s, due to CFCs production restrictions, the hydrodechlorination reactions of CF_3CCl_2F (7–11), CCl_2F_2 (3, 4, 11–27), and CCl_2FCClF_2 (28, 29) have been studied. Our group has studied the hydrodechlorination of CF_3CCl_2F using palladium foil (7–9) and single crystals (8, 9). Our experimental system allows the study of the reaction under conditions of minimum contamination. The absence of support eliminates possible metal–support interactions, so that only the intrinsic catalytic behavior of palladium is analyzed. The use of well-defined structure single crystals is also very important to understand the role of surface structure in the reaction.

The present work aims to explore the kinetics and mechanism of the CCl_2F_2 hydrodechlorination on model catalysts. By comparing the present results with those obtained in the reaction with CF_3CCl_2F, we can elucidate some of the mechanistic details of the hydrodechlorination reaction on metals.

2. EXPERIMENTAL

The experimental apparatus has been described previously (7–9). It consists of a gold-coated high-pressure

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(1 atm) batch reactor (700 cm^3) attached to an ultrahigh vacuum (UHV) chamber with a base pressure of 8×10^{-10} Torr ($1\ Torr = 133.3\ N\ m^{-2}$). The chamber was equipped with four-grid electron optics for low-energy electron diffraction (LEED), a double-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), an argon ion gun for crystal cleaning, and a quadrupole mass spectrometer. Small surface area (ca. 1 cm^2) model catalysts can be transferred between the UHV chamber and the high-pressure reactor with a welded bellows assembly capable of maintaining an UHV environment during sample transfer. The sample was attached to a sample cart containing two pins for resistive heating and two pins (chromel and alumel) for thermocouple temperature readings, allowing heating and temperature measurement both in the UHV chamber and in the reactor. The type-K thermocouple was spotwelded to the center of the rear of the foil and to the side of the single crystals.

The palladium polycrystalline foil used in this study was 0.125-mm thick, with a surface area of about 0.50 cm^2 and a purity of 99.99+% (Goodfellow). Atomic surface structures for the single-crystal samples used in this research include the flat (111) and (110) surfaces, which are characterized by hexagonal and rectangular atomic arrangements, respectively. Both single crystals were about 0.7-mm thick and 0.5 cm^2 and were cut from bulk material (single-crystal rods, Goodfellow) with 0.5^0 precision and polished using standard techniques.

The sample was cleaned by multiple cycles of Ar^+ bombardment at $P_{Ar} = 5 \times 10^{-5}$ Torr followed by annealing in UHV at 973 K. Due to the design of the chamber, only one side of the sample could be cleaned by Ar^+ bombardment. The surface cleanliness was checked by Auger electron spectroscopy (AES) and the single-crystal structure was examined by checking the LEED diffraction pattern.

Dichlorodifluoromethane (CFC-12) (Oakwood, 99%) and hydrogen (Airgas, ultrahigh purity) were the reactants used in this work. During the cleaning of the sample, the reactor was kept in high vacuum (10^{-7} Torr) by the use of a turbomolecular pump (80 liter s^{-1}). The clean sample was transferred to the reactor with a transfer arm. After the sample was mounted in the sample holder, the UHV chamber and the transfer arm were insulated from the reactor by closure of their respective gate valves. The reactor was immediately filled with 760 Torr of argon and flushed and recirculated with a metal bellows pump (Parker Model MB 21) with a flow rate of about 1 liter min^{-1}. After the argon was pumped out with sorption pumps and the turbomolecular pump, the reactants were introduced and recirculated in the reactor. The reaction rates were measured in the temperature range of 423–523 K and pressure ranges of 8–40 Torr CCl_2F_2 and 40–120 Torr H_2, with argon used as a make-up gas until a total pressure of 760 Torr was reached.

One important aspect of this work was the avoidance of palladium hydride formation. Previous experience has demonstrated that a combination of high pressure of hydrogen (e.g., 200 Torr) and low temperatures (R.T.) would warp the sample and destroy the surface structure of the crystals (7), probably due to the formation of the β-PdH_x bulk compound. To avoid this, the sample was kept at 383 K during the introduction of the reactants. At this temperature and at the hydrogen pressures used in this study, the palladium–hydrogen phase diagram is far from the β-PdH_x phase, and only soluble bulk hydrogen (solid state hydrogen) is present, which does not damage the structure of the crystal.

The reaction products were analyzed using an on-line gas chromatograph (Hewlett-Packard 5790A) equipped with a flame ionization detector and a 5% Krytox 143AC, 60/80 Carbopack B HT 20 ft × 1/8 in. column (Supelco). All the possible products and reactants were calibrated to have an accurate measurement of the reaction rates. The final conversion was kept lower than 2% to avoid side reactions and to consider the reaction pseudo zero order on H_2 and CFC. Selectivities are defined as $S_i = 100 \times TOF_i / \sum TOF_i$, where TOF_i is the turnover frequency (product molecules/Pd atom/s) of the detected product *i*. Heat and mass transfer limitations are of no concern in this type of experiment since all of the active area is exposed. At the end of the reaction-rate studies, the sample was cooled down to 373 K, the reaction mixture was pumped out, the sample was transferred back to the UHV chamber, and an Auger spectrum was immediately recorded.

Blank experiments using stainless steel foil were carried out under the same usual reaction conditions ($T = 473$ K; $P_{H_2} = 80$ Torr; $P_{CCl_2F_2} = 8$ Torr) to check if the background activity was significant. After 4 h in the reaction mixture, no reactivity could be detected, implying that the activity detected comes solely from the palladium samples.

We have previously reported (7) an inhibition effect of the product HCl in the hydrodechlorination of CF_3CCl_2F, with a reaction order close to −1. The same result was obtained for the reaction of CCl_2F_2. As a consequence, the turnover rate is a strong function of conversion. The product accumulation curve has a decrease in slope with time, which would not occur under the conditions of the experiments (low conversion, pseudo-zero-order reaction) and with no inhibition. As shown before (9), the turnover rate for a given HCl concentration can be obtained by integrating the rate equation. The integrated equation has a linear dependence between the square of the number of turnovers and time ($TON^2 \times$ time), where the number of turnovers is defined as the number of product molecules per palladium site. The slope of this plot is used to calculate the turnover frequency at a given HCl concentration.

We have also reported (9) the deposition of sulfur on the sample promoted by HCl, causing deactivation of the catalyst and some changes in selectivity. The sulfur surface concentration increases with conversion, and it was proven that the initial rates could be measured without interference from sulfur. Under the usual conditions of these experiments, this interference by sulfur contamination is negligible because the reactivity of CCl_2F_2 that is used in the present study is much lower than that of CF_3CCl_2F that was used in our previous study.

3. RESULTS

3.1. Catalytic Performance of Palladium Model Catalysts for the Hydrodechlorination of CCl_2F_2

For all the palladium catalysts used in this study (foil and single crystals) the main products were CH_2F_2 and methane. Ethane could be detected at higher temperatures (e.g., 513 K), with selectivity lower than 1%. Since its concentration is so low in the usual reaction conditions, it was not considered in selectivity calculations, except in the selectivity temperature dependence. Surprisingly, $CHClF_2$ was not a reaction product, even though other studies of CCl_2F_2 hydrodechlorination over supported palladium catalysts have reported its production (13–22, 25). The possible reasons for the differences in product distribution in our studies and those of others will be discussed later.

Table 1 presents catalytic results for all the samples corrected for the same reaction conditions, including HCl concentration. It should be emphasized that, as will be seen later, the samples had different activation energies. So the comparison of reactivity depends on the temperature analyzed. In general, palladium foil presented higher activity than both crystals. Pd(111) and Pd(110) have shown similar activities, within experimental error. Concerning selectivity, all the samples yielded similar results, with a slight trend for higher selectivity toward CH_2F_2 for the Pd(110) sample and a lower selectivity for the Pd(111) sample.

The reaction rate was zero order with respect to H_2 and close to 1 with respect to CCl_2F_2. Selectivities did not change appreciably as the partial pressures of the two reactants were altered.

Figure 1 shows the accumulation plot for all the palladium samples. The decrease in slope of the accumulation curves typical of inhibition can be seen. Pd(111) had a smaller decrease in slope with time on stream than Pd foil and Pd(110). For example, at the beginning of the reaction, CH_2F_2 production is much smaller on Pd(111) than on Pd(110), but it is almost the same at the end. This means a higher deactivation rate for Pd(110) and Pd foil compared to that for Pd(111). It is also clear that there is a higher selectivity toward CH_2F_2 on Pd(110).

TABLE 1

Turnover Frequency and Partial Pressure Dependence Comparison for the Hydrodechlorination of CCl_2F_2 over Palladium Model Catalysts (Conditions: $T = 473$ K; 80 Torr H_2; 8 Torr CCl_2F_2; 672 Torr Ar; 0.02 Torr HCl)

	TOF (molecules/ Pd atoms)		Selectivity (%)		Reaction Order			
					H_2		CCl_2F_2	
Catalyst	CH_2F_2	CH_4	CH_2F_2	CH_4	CH_2F_2	CH_4	CH_2F_2	CH_4
Pd foil	2.037	0.262	88.6	11.4	0.1	0.2	1.1	1.3
Pd(111)	0.528	0.087	85.9	14.1	0.2	−0.2	1.3	1.1
Pd(110)	0.519	0.046	91.9	8.1	0.3	0.1	0.9	0.8

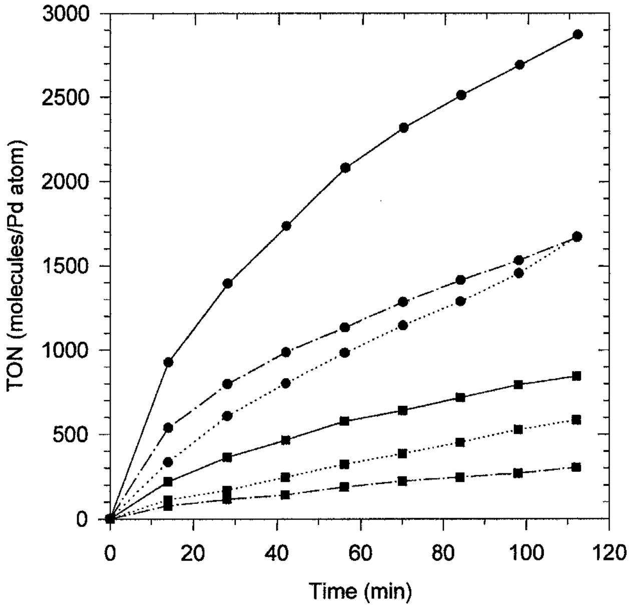

FIG. 1. Accumulation plot (number of turnovers versus time) for the hydrodechlorination of CFC-12 (CCl_2F_2). Conditions: $T = 473$ K; $P_{H_2} = 80$ Torr; $P_{CCl_2F_2} = 8$ Torr; $P_{Ar} = 672$ Torr. (—) Pd foil; (- - - -) Pd(110); (· · · ·) Pd(111); (●) CH_2F_2; (■) $2xCH_4$.

Figures 2A and 2B present (turnover number)^2 vs time plots for CH_2F_2 and CH_4 formation, respectively, on the different palladium catalysts. The slope of this graph was used to calculate the turnover frequency for a given HCl concentration. A good linear correlation between the square of the turnover number and time can be seen, as it should be according to the HCl inhibition model. Pd(111) shows concave curvature, which can be correlated to the smaller deactivation rate of this sample. This fact can also be seen in Table 2, which shows the percentage of initial and steady state deactivation for all the samples. It is clear that Pd foil and Pd(110) has similar deactivation rates, while Pd(111) differs from the others.

Figure 3 shows the selectivity behavior with time on stream. Selectivity toward CH_2F_2 has a slight initial decrease and then it is constant. This trend was observed for all the catalysts.

Figure 4 presents the integrated rate equation for CH_2F_2 formation over Pd(111) at a higher temperature (523 K). There is deviation of linearity that could be caused by the accumulation of sulfur or carbon on the palladium crystal surface. Auger spectroscopy detects higher carbon coverage at

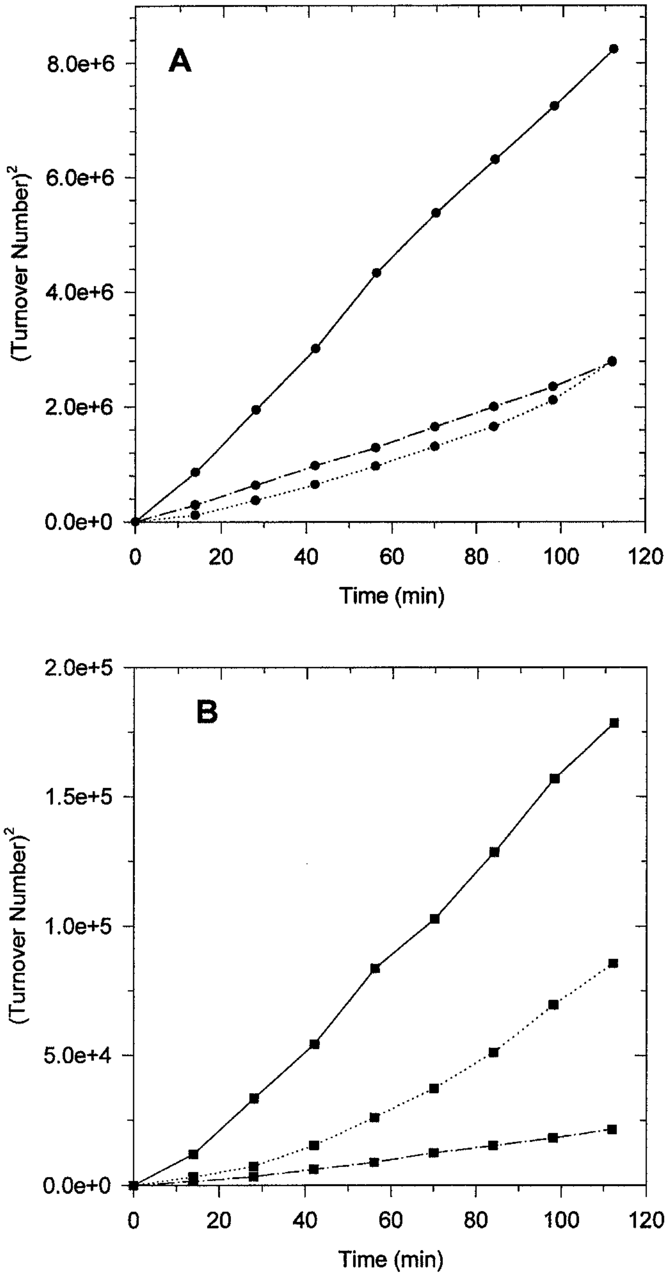

FIG. 2. Integrated equation plotted in linear form for the hydrodechlorination of CFC-12 (CCl_2F_2). Conditions: $T = 473$ K; $P_{H_2} = 80$ Torr; $P_{CCl_2F_2} = 8$ Torr; $P_{Ar} = 672$ Torr. (—) Pd foil; (-···) Pd(110); (····) Pd(111); (●) CH_2F_2; (■) CH_4.

higher temperatures in addition to the presence of sulfur. It appears that both sulfur and carbon depositions are responsible for deactivation under this reaction condition.

Table 3 shows activation energies for CH_2F_2 and CH_4 formation on the different palladium catalysts. The activation energy for CH_2F_2 formation is clearly higher for Pd(111), while Pd(110) and Pd foil have similar values. The activation energy for CH_4 formation is nearly the same for all of the samples.

TABLE 2

Deactivation Behavior for the Hydrodechlorination of CCl_2F_2 over Palladium Model Catalysts (Conditions: $T = 473$ K; 80 Torr H_2; 8 Torr CCl_2F_2; 672 Torr Ar)

	Initial deactivation (%)[a]		Steady state deactivation (%)[b]	
Catalyst	CH_2F_2	CH_4	CH_2F_2	CH_4
Pd foil	49	34	81	78
Pd(111)	14	18	57	34
Pd(110)	52	50	75	71

[a] [TOF($t = 14$ min)−TOF($t = 28$ min)]/TOF($t = 14$ min).

[b] [TOF($t = 14$ min)−TOF($t = 112$ min)]/TOF($t = 14$ min).

The effect of temperature on the product selectivity is shown in Fig. 5. Methane selectivity increases with temperature at the expense of CH_2F_2. C_2H_6 could be detected at higher temperatures, and the selectivity seems to increase with temperature. The same trends were observed for all the catalysts.

3.2. Comparing the Hydrodechlorination of Dichlorodifluoromethane (CCl_2F_2) and 1,1-Dichlorotetrafluoroethane (CF_3CCl_2F)

According to the HCl inhibition model, hydrodechlorination reaction rates are a strong function of conversion. Tables 1 and 4 show hydrodechlorination rates of CCl_2F_2 and CF_3CCl_2F, respectively, under the same reaction conditions ($T = 473$ K; $P_{H_2} = 80$ Torr; $P_{CFC} = 8$ Torr) and in the

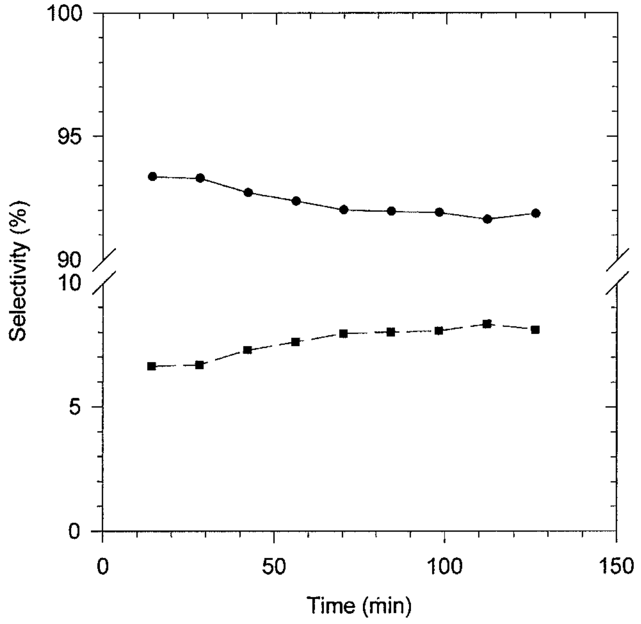

FIG. 3. Accumulated product selectivity with time on stream for the reaction of CCl_2F_2 on Pd (110). Conditions: $T = 473$ K; $P_{H_2} = 80$ Torr; $P_{CCl_2F_2} = 8$ Torr; $P_{Ar} = 672$ Torr. (●) CH_2F_2; (■) CH_4.

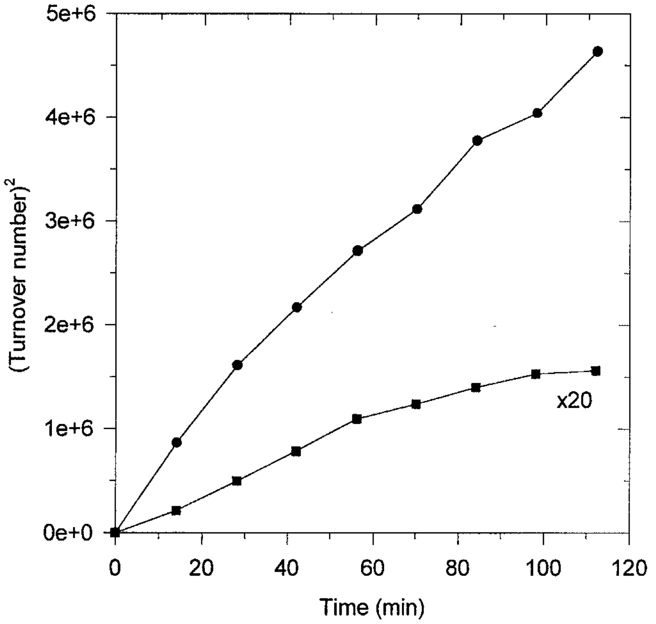

FIG. 4. Integrated equation plotted in linear form for the hydrodechlorination of CCl_2F_2 on Pd(110). Conditions: $T = 513$ K; $P_{H_2} =$ 80 Torr; $P_{CCl_2F_2} = 8$ Torr; $P_{Ar} = 672$ Torr. (●) CH_2F_2; (■) $20x CH_4$.

same HCl concentration (0.02 Torr). In a comparison of the reaction rates at the same degree of hydrodechlorination, CF_3CCl_2F reactivity is about 2 orders of magnitude higher. As a result, the accumulation of chlorine and sulfur was much greater compared to that of the reaction of CCl_2F_2, as found by AES studies. Another difference is the higher selectivity toward the formation of the mono-dechlorinated product (CF_3CHClF), while in the case of the CCl_2F_2 reaction no $CHClF_2$ production could be detected.

3.3. The Hydrodechlorination Activity of Solid State Hydrogen in Palladium

We have reported before (8) that the hydrodechlorination of CF_3CCl_2F occurs even in the absence of gas phase hydrogen due to the activity of solid state hydrogen, stored in the bulk of palladium single crystals. It was found that the reaction could be sustained for about 10^4 turnovers (molecules of products/Pd atom) before it stopped as the hydrogen in the palladium bulk is depleted. We had no difficulty in reproducing these experiments. The same studies were tried with CCl_2F_2.

The crystal was pretreated with 100 Torr of H_2 at 373 K for 30 min. The hydrogen atmosphere was removed, the crystal was kept at 303 K, and the reactor was flushed with argon several times followed by a pump out with a turbomolecular pump. Then 50 Torr of CCl_2F_2 was introduced and argon was used as a make-up gas to have a total pressure of 760 Torr. The crystal was heated to 473 K and the reaction was started. No activity was detected after 4 h of experiment. We have repeated the experiment using the same Pd single crystals but with CF_3CCl_2F as the reactant. We have found the same high hydrodechlorination

TABLE 3

Apparent Activation Energy for the Hydrodechlorination of CCl_2F_2 over Palladium Model Catalysts (Conditions: 80 Torr H_2; 8 Torr CCl_2F_2; 672 Torr Ar; 0.02 Torr HCl)

	Apparent activation energy (kJ/mol)	
Catalyst	CH_2F_2	CH_4
Pd foil	56 ± 10	113 ± 14
Pd(111)	92 ± 8	111 ± 15
Pd(110)	45 ± 3	104 ± 12

TABLE 4

Comparison of Reaction Rates for the Hydrodechlorination of CCl_2F_2 and CF_3CCl_2F over Pd(110) (Conditions: $T = 473$ K; 80 Torr H_2; 8 Torr CFC; 672 Torr Ar; 0.02 Torr HCl)

	CF_3CCl_2F reaction rates (molecules/Pd atom/s)			TOF ratio[a]	
				CF_3CH_3	CF_3CH_2F
Sample	CF_3CHClF	CF_3CH_2F	CF_3CH_3	CH_4	CH_2F_2
Pd(110)	4.61	67.1	3.54	77	129

[a] CCl_2F_2 reaction rates are reported in Table 1.

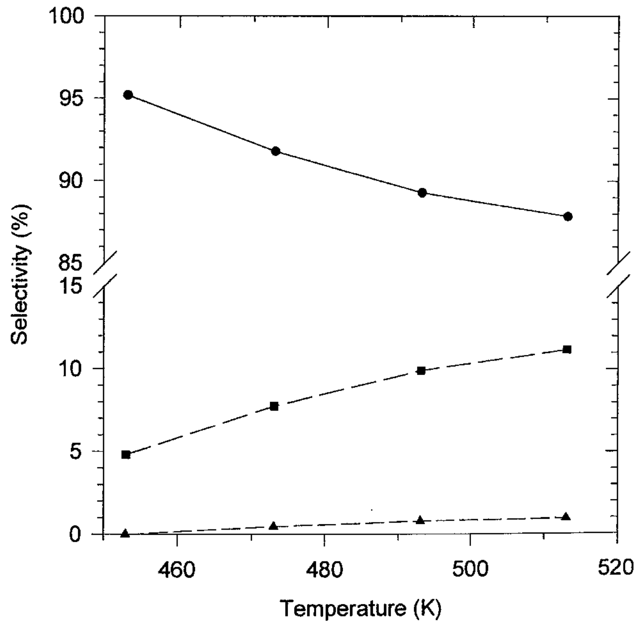

FIG. 5. Selectivity as a function of temperature for the hydrodechlorination of CCl_2F_2 on Pd(110). Conditions: $P_{H_2} = 80$ Torr; $P_{CCl_2F_2} = 8$ Torr; $P_{Ar} = 672$ Torr; 0.02 Torr HCl. (●) CH_2F_2; (■) CH_4; (▲) C_2H_6.

reactivity as we have reported before. This might be explained by the difference in reactivity of both molecules (2 orders of magnitude).

4. DISCUSSION

4.1. *Product Distribution in the Hydrodechlorination of CCl_2F_2*

The major contribution of this work is the opportunity to employ model catalysts under controlled conditions, avoiding the influence of contamination and the effects of interaction between the metal and the support. In this way, all the results obtained can be considered as due to intrinsic palladium hydrodechlorination activity. Concerning the product distribution, some products could not be detected in this work, implying that their formations are catalyzed by the metal–support interface, the support, or the impurities that are absent in our system.

For example, Coq *et al.* (13), using Pd/graphite and Pd/AlF_3, attributed the production of CF_3Cl to a fluorine/chlorine exchange between CCl_2F_2 and HF on the AlF_3 support. Öcal *et al.* (17) reached the same conclusion. In another work, Coq *et al.* (14) detected production of C_2F_4 up to 26% under certain conditions using bimetallic systems (Pd–Fe and Pd–Co). They explained this fact by a higher $^*CF_2$ surface concentration on these catalysts. Wiersma *et al.* (3), using palladium-supported catalysts, detected production of $CHClF_2$, up to 20%. They also reported that the chlorine/fluorine exchange reaction (producing CHF_3) and the coupling reaction (producing C_2H_6 and C_3H_8) were promoted by impurities on the activated carbon support, such as iron, aluminum, and copper (22). Juszczyk *et al.* (24) reported that the Al_2O_3 support exhibits some, although low, activity in the CCl_2F_2 hydrodechlorination reaction, producing $CClF_3$ (major product), CH_2F_2, CH_4, ethane, and ethylene, indicating that Al_2O_3 also promotes the chlorine–fluorine exchange.

All these previous results show the influence of supports, impurities, and bimetallic systems since we produce only CH_2F_2, CH_4, and very small amounts of C_2H_6 at higher temperatures on palladium model catalysts. However, it is surprising that $CHClF_2$ was not produced in our system. The main reason might be because our reactions were performed in excess of hydrogen. Wiersma *et al.* (22) proposed that the amount of chlorine adsorbed would determine selectivity toward $CHClF_2$ and CH_2F_2. Auger spectroscopy has detected low chlorine coverage after the hydrodechlorination of CCl_2F_2. We proposed (7) that the catalyst surface was equilibrated with H_2 and HCl in the gas phase. A higher H_2 concentration would be responsible for a lower concentration of chlorine on the surface. Sinfelt also proposed equilibrium between atomic chlorine and hydrogen surface species and HCl in the gas phase in the reaction of methyl chloride on metals (31). This way, $^*CF_2$ would be the most reactive intermediate on the surface, instead of $^*CF_2Cl$, which could explain the absence of $CHClF_2$ production. The support could also have an important role in storing chlorine atoms, yielding $CHClF_2$ in higher amounts on supported catalysts than on palladium that is used as a catalyst without support.

4.2. *Comparison of Catalytic Performance of the Palladium Model Catalysts in the Hydrodechlorination of CCl_2F_2*

After 2 decades of research, some of the elementary reaction steps of the CFC hydrodechlorination mechanism have been clarified. Concerning the rate-determining step (RDS), there is evidence (5, 32, 33) that it is likely to be the removal of the first chlorine atom from the chlorinated molecule. Gervasutti *et al.* (6), studying the hydrodechlorination of CF_3CCl_2F, proposed rapid dissociative adsorption–associative desorption, with the removal of both chlorine atoms, as the initial step. Experimental gas phase and theoretical work by Kumaran *et al.* (30) showed that the ClH_2C–Cl bond strength is 85 kcal/mol, but once broken, it leaves a radical with H_2C–Cl bond strength of 49 kcal/mol, substantially lower. Karpinski *et al.* (10) used this result to propose that the removal of the first chlorine atom was the RDS in the hydrodechlorination of CF_3CCl_2F. Zhou *et al.* (32) and Chan and Gellman (33) studied the dissociative adsorption of four fluorinated 1,1-dichloroethanes on the Pd(111) surface. Dosing the crystal with a constant background pressure of the CFC and using X-ray photoemission spectroscopy (XPS) to monitor the uptake of chlorine on the surface, they obtained the rate of dissociative adsorption of the CFCs. They found similar reactivity trends as in the hydrodechlorination reaction at high pressure (1 atm): the rate constant decreases with the increase of fluorine content on the molecule and the presence of only one chlorine atom on each carbon atom (CH_2ClCH_2Cl vs CH_3CHCl_2) also reduces the rate constant. By these observations, they concluded that the dechlorination either is the rate-determining step or at least contributes significantly to the overall rate constant.

Concerning the CH_2F_2/CH_4 selectivity ratio, there are few data that would elucidate the steps that determine selectivity. Due to considerable differences in reactivity (at least 1 order of magnitude) among the homologous series (e.g., CCl_2F_2, $CHClF_2$, and CH_2F_2), a series mechanism was completely discarded (5, 7, 13). It is widely accepted, however, that $^*CF_2$ is the most reactive surface species during the hydrodechlorination reaction. The selectivity would be determined by the associative desorption of this species helped by hydrogen and the removal of fluorine atoms by adsorbed hydrogen, yielding $^*CH_2$, which would produce CH_4 further. Some authors have proposed that CH_4

might come from the hydrogenation of bare surface carbon species (*C) (26) or interstitial carbon (17). Then, it appears that CH_2F_2 and methane are produced by parallel routes. Generally, selectivity toward CH_2F_2 is high because it is much easier to break the carbon–chlorine bond than to break the carbon–fluorine bond. But selectivity toward methane would be favored in catalysts where this difference is smaller, increasing the concentration of dehalogenated intermediates on the surface.

We showed that polycrystalline palladium had higher activity than the single crystals. This might be explained by the higher activity of surface defects and kinks to bind chlorine and help the dissociation of CCl_2F_2. Pd(111) and Pd(110) had different activation energies, which makes the comparison of reactivity dependent on the temperature, which will be done later.

There is different behavior with Pd(111) than with Pd(110) and Pd foil in the accumulation plots. The smaller decrease in slope in the TON vs time graph and the concave curvature in the $(\mathrm{TON})^2$ vs time graph might show the same reason, a lower inhibition by HCl. This is a surprising result since most of the sites in the palladium foil are (111) sites. However, it was observed that the Pd foil had a 3-fold higher activity than the crystal samples. So it is possible that the steps and kinks were dominating the chemistry in this sample, and these sites would have behavior similar to that of the (110) sites, concerning inhibition by HCl. It also means that the more closed surface (111) has a weaker interaction with chlorine. Erley has studied chlorine adsorption at 300 K on Pd(111) and Pd(110) faces (34, 35). He has measured desorption energies of 60.5 and 65 kcal/mol, respectively. Besides, he has reported working function increases of 0.57 eV for Pd(111) and 1.23 eV for Pd(110) when the chlorine coverage varied from zero to saturation coverage ($\theta_{\mathrm{sat}} \cong 0.5$ for both crystals). These results confirm a stronger chlorine adsorption and interaction on the (110) sites. Then, it is reasonable to propose that the inhibition effect on (111) sites is less pronounced, giving rise to less deactivation.

Pd(111) showed a slightly lower selectivity toward CH_2F_2 than the other catalysts. It should be emphasized that this catalyst also had smaller HCl inhibition. The literature data show a weaker chlorine interaction with the Pd(111) surface (34, 35). Both results imply a greater difficulty in breaking the C–Cl bond on this surface. Then, the energy to break the C–Cl and C–F bond on this surface would be closer than on the others, implying a lower $^*CF_2/^*CH_2$ surface intermediate ratio. This might explain the lower CH_2F_2 selectivity on the Pd(111) surface. Our activation energy results (similar activation energy of formation for CH_2F_2 and CH_4 on the Pd(111) surface) confirm this assumption. Another possibility is that the intermediate $^*CF_2$ would be rather strongly bound to the Pd(111) surface compared to the others. This way, their further reaction to methane would be easier.

Despite this difference, the selectivity range (86–92%) is small compared to the differences between the supported catalysts in the literature. For example, Coq *et al.* (15) reported that the selectivity toward CH_2F_2 ranged from 24% (Pd/ZrO_2) to 89% (Pd/ZrF_4) using different supports. Using different pretreatments for the activated carbon support, van de Sandt *et al.* (20) showed that the selectivity toward CH_2F_2 varied from 40% to 74%. The small difference found in this work shows that this wide range in selectivity does not come from a different coordination of surface palladium atoms but from metal–support interaction.

Concerning time-on-stream selectivity behavior (Fig. 3), we observed a slight decrease of CH_2F_2 selectivity with time on stream, which means a higher deactivation rate for CH_2F_2 formation. This change is very small compared to that reported in the literature for supported palladium catalysts (15, 16, 18, 23, 24).

The reaction orders observed for the hydrodechlorination of CCl_2F_2 are the same as those for CF_3CCl_2F (7). In the reaction conditions applied, the reaction is close to zero order for H_2 and first order with respect to CCl_2F_2. Karpinski *et al.* had the same result using supported palladium catalysts (10). This implies that the surface is saturated with hydrogen under the reaction conditions that were employed.

From Table 3, it is clear that methane formation has higher apparent activation energy than CH_2F_2 formation for all the palladium catalysts. The reason for this is well discussed in the literature and can be explained by the higher bond strength of the $F–CFCl_2$ bond compared to that of the $Cl–CF_2Cl$ bond (462 and 346 kJ/mol, respectively, in the gas phase) (36). This explains the increase of selectivity toward methane with temperature (Fig. 5).

In a comparison of the different palladium samples, the activation energy for methane formation was similar for all the samples, but Pd(111) had higher activation energy for CH_2F_2 formation. This may be explained by the same arguments used to explain the lower selectivity toward CH_2F_2 on this catalyst, that is, greater difficulty in breaking the C–Cl bond on this surface due to a weaker Pd–Cl interaction.

4.3. *Comparison of CCl_2F_2 and CF_3CCl_2F Hydrodechlorination*

The CF_3CCl_2F hydrodechlorination activity was 2 orders of magnitude higher than that for CCl_2F_2. Considering that the removal of the first chlorine atom from the CFC molecule is the rate-determining step, this result is very reasonable. The bond strength energy of the $Cl–CF_2Cl$ bond is 346 kJ/mol in the gas phase (36). The $Cl–CFClCF_3$ bond strength was not reported, but when compared to the bond strength energy of its isomer, the $Cl–CF_2CF_2Cl$ bond has an energy of 326 kJ/mol (36); this difference would be enough to explain the difference in reactivity. Weiss *et al.* attributed a 100-fold difference in reactivity between CCl_4 and $CHCl_3$ to a 21 kJ/mol difference in the C–Cl dissociation energy (5). Furthermore, Gervasutti *et al.* reported that this isomer is 10 times less reactive than CF_3CCl_2F (6). Then, it should be expected that the Cl–$CFClCF_3$ bond strength would be even lower than 326 kJ/mol. Additional evidence that it is easier to break this bond than the same bond in CCl_2F_2 is the higher chlorine surface concentration after hydrodechlorination of CF_3CCl_2F.

An interesting point should be highlighted here. In the CF_3CCl_2F hydrodechlorination, palladium polycrystalline foil was about 1.8-fold more active than Pd(111) and Pd(100) (9), while in the CCl_2F_2 reaction this difference was about 3.9-fold. This difference might be associated with the rate-determining step proposed for this reaction, that is, the removal of the first chlorine atom from the CFC molecule. Since this removal is more difficult in the CCl_2F_2 molecule than in CF_3CCl_2F due to a higher C–Cl bond strength energy, a higher facility of the steps and kinks to break this bond would influence much more the rate of CCl_2F_2 hydrodechlorination than that of CF_3CCl_2F.

The higher chlorine surface concentration can also explain the higher selectivity toward the monochlorinated product CF_3CHClF, while in the case of CCl_2F_2, $CHClF_2$ was not produced. Wiersma *et al.* (22) proposed that the amount of chlorine adsorbed would determine selectivity toward $CHClF_2$ and CH_2F_2 in the CCl_2F_2 reaction. Higher chlorine coverage would favor selectivity toward $CHClF_2$. The same explanation can be used to explain our results. Since chlorine accumulation during CCl_2F_2 reaction is much smaller than that during CF_3CCl_2F reaction, as was found by AES, production of $CHClF_2$ from CCl_2F_2 would not be favored, while CF_3CHClF production from CF_3CCl_2F would be.

5. CONCLUSION

The use of model catalysts allowed us to determine the intrinsic palladium activity for the hydrodechlorination of CCl_2F_2. CH_2F_2 and CH_4 were the main reaction products. Ethane could be detected at higher temperatures in small concentrations. Several by-products reported in the literature were not produced on model catalysts, implying that their formation is catalyzed by metal–support interfaces, supports, or impurities. The absence of $CHClF_2$ among the products was attributed to the low chlorine surface concentrations under our reaction conditions.

Pd foil was more active than the single crystals, probably due to a higher activity from the steps and kinks. Selectivity changes between the palladium catalysts and with time on stream were small, showing that wide ranges reported in the literature might come from the metal–support interaction. Pd(111) showed a lower deactivation rate, lower selectivity toward CH_2F_2, and higher activation energy for CH_2F_2 formation than the other catalysts, indicating a weaker Pd–Cl interaction on this surface, resulting in greater difficulty in breaking the C–Cl bond.

CCl_2F_2 was 2 orders of magnitude less reactive for hydrodechlorination than CF_3CCl_2F, probably due to the higher C–Cl bond strength in the molecule. The chlorine surface concentration is important in determining the selectivity toward the monochlorinated product. Solid state hydrogen in palladium was not active for the hydrodechlorination of CCl_2F_2.

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