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Catalytic Hydrodechlorination of 1,1-Dichlorotetrafluoroethane by Pd/Al_2O_3

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Palladium supported on γ-alumina displays high activity for the hydrodechlorination of 1,1-dichlorotetrafluoroethane. High H_2 partial pressures are needed to avoid deactivation, and steady state is obtained after ~5 h time on stream. Under these conditions (H_2/CFC feed ratio = 20) the reaction is zero order in H_2 partial pressure and positive (0.65) order in 1,1-dichlorotetrafluoroethane partial pressure. Three main products are formed: 1,1,1,2-tetrafluoroethane, 1-chloro-1,2,2,2-tetrafluoroethane, and 1,1,1-trifluoroethane, with approximately 85% selectivity toward the desired CF_3CFH_2. The apparent activation energies associated with the formation of each product range from 52 to 68 kJ/mol. All three major products have a nonzero rate of formation in the limit of zero conversion, the implication of which is that all are primary products. The kinetics results are consistent with a reaction mechanism involving a carbene intermediate. Variation of the temperature at which the catalyst is prereduced from 300 to 600°C results in an increase in particle size from 11–53 nm and in an increase in the hydrodechlorination TOF from 2.3 to 5.0 s^{-1}.

INTRODUCTION

Chlorofluorocarbons (CFCs) are industrially important compounds which are extremely stable. Because of their stability, CFCs emitted into the atmosphere do not react before reaching the stratosphere. Once in the stratosphere the CFCs photodissociate, producing Cl radicals which participate in ozone depletion reactions (1). This damaging behavior has resulted in the phase-out of their production and the creation of a market for alternative compounds (2). The development of CFC alternatives has focused on nonchlorinated compounds which have similar physical properties but will break down in the lower atmosphere. One such class of alternatives is the hydrofluorocarbons (HFCs) (3).

While there are a number of synthetic routes for the production of HFCs, one of the simplest methods involves the selective hydrodechlorination of CFCs. One potentially important industrial process is the hydrodechlorination of CF_3CFCl_2 to yield CF_3CFH_2, a replacement used in automobile air-conditioning units (2). Another, the hydrodechlorination of $CF_2ClCFCl_2$, produces $CF_2{=}CFH$, a monomer used in the production of Teflon-like polymers (4). Both of these reactions require selective cleavage of C–Cl bonds which in turn requires highly selective catalysts.

Numerous examples of hydrodechlorination catalysts are described in the literature (5–9), many of which emphasize the superior performance of palladium supported on various high surface area materials (2, 6, 10, 11). Several factors have been identified which influence the activity and selectivity of hydrodechlorination catalysts. These factors include support material, metal particle size, and reaction conditions. Coq *et al.* observed that increasing the Pd particle size from 1.5 to 8 nm resulted in higher activity for CF_2Cl_2 conversion of CF_2H_2 (11). Further, Pd supported on AlF_3 was found to have higher initial activity than Pd supported on either carbon or Al_2O_3. However, the catalytic activity of Pd supported on Al_2O_3 has been shown to increase as a function of time on stream for the conversion of CF_2Cl_2. As methane was observed as a product, Coq *et al.* suggested that the hydrogenolysis of C–F bonds results in surface fluorine species (11, 12, 17). These fluorine atoms were subsequently incorporated into the Al_2O_3 lattice, thus transforming it, at least partially, into the more active AlF_3 support. Finally, the reaction conditions also influence activity in the hydrodechlorination of CF_2Cl_2. For CFC/H_2 feed ratios in the range 0–3, the activity goes through a maximum (11).

Far less fundamental information is available on the hydrodechlorination of chlorofluoroethanes. Clear differences between the ethanes and methanes are illustrated by the study of CF_3CFHCl hydrodechlorination by Kellner and Rao (10). In contrast to the studies by Coq *et al.* with CF_2Cl_2 (11, 12), very high (nearly 100%) selectivity toward CF_3CFH_2 was achieved with palladium supported either on AlF_3 or fluorinated Al_2O_3. Important differences in reactivity have also been observed among the different ethanes. Gervasutti *et al.* found that over a Pd/C catalyst CF_3CFCl_2 is much more readily hydrodechlorinated than its structural isomer, CF_2ClCF_2Cl (6).

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The present investigation was motivated by the lack of information on the hydrodechlorination of chlorofluoroethanes. This study focuses on the hydrodechlorination of CF_3CFCl_2 catalyzed by Pd/Al_2O_3. The reaction rates were measured to establish the dependence of reaction kinetics on reactant concentrations and temperature. In addition, the effect of time-on-stream on catalytic activity and selectivity was considered. As this initial investigation was focused on the reaction kinetics, experiments were conducted under high excess of hydrogen to limit self-poisoning. Finally, in order to modify our Pd/Al_2O_3 catalysts, different catalyst pretreatments were used. The effect of such modifications on both C−Cl and C−C bond hydrogenolysis was determined by studying hydrogenolysis of CF_3CFCl_2 and ethane.

EXPERIMENTAL

Catalyst Preparation

The catalyst, a 2 wt% Pd/γ-Al_2O_3, was prepared by incipient wetness impregnation of γ-Al_2O_3 (Vista-B, surface area 300 m^2/g, pore volume 1.7 ml/g) with a 0.86 *M* aqueous solution of $Pd(NO_3)_2$ (Alfa Products, purity 99.9%). After drying overnight at 90°C, the material was calcined in a 2% O_2/He stream (30 ml/min) while heating at a rate of 1°C/min to 300°C and then holding at this temperature for 10 h. After cooling to room temperature the catalyst was stored in a closed vessel.

Catalyst Characterization

Metal dispersions were measured by chemisorption of CO at room temperature in a conventional glass system capable of achieving a vacuum of less than 2×10^{-6} Torr. The system was equipped with a turbomolecular pump backed by a mechanical pump, and approximately 1 g of catalyst was used for each experiment. The catalyst was reduced in flowing H_2 (30 ml/min) during heating from room temperature to 300°C (unless otherwise stated) at a rate of 1°C/min and then maintaining this temperature for 10 h. The catalyst was then outgassed at 300°C by evacuating to less than 2×10^{-6} Torr for 2 h. The sample was cooled to room temperature and the irreversible uptake of CO was determined using the dual isotherm method described by Yates and Sinfelt (13). The metal dispersion was calculated as a CO/Pd ratio with the assumed surface stoichiometry of one adsorbed CO molecule per Pd atom. Table 1 summarizes metal dispersion data for samples reduced at different temperatures. For samples reduced at 300°C the metal particle size determined from TEM (10 nm) agreed reasonably well with the value obtained from CO chemisorption (11 nm).

TABLE 1

Characteristics of 2 wt% Pd/γ-Al_2O_3 Catalyst

Reduction temperature (°C)	Palladium dispersion (CO/Pd)	Metal particle size from CO/Pd[a] (nm)
300	0.10	11
450	0.06	18
600	0.02	53

[a] According to the formula $d_{Pd} = 1.12/D$ (25), where *D* denotes metal dispersion (fraction exposed).

Catalytic Experiments

The hydrodechlorination of 1,1-dichlorotetrafluoroethane was conducted in a stainless-steel flow system at atmospheric pressure. A constant flow of each reactant (CF_3CFCl_2 preblended with He, H_2, and N_2) was maintained by mass flow controllers (Brooks). The effluent was analyzed by gas chromatography (Varian Model 3300 with FID) using a 5% Fluorocol/carbosieve column (10 ft) from Supelco.

Prior to each reaction the catalyst (0.05–0.17 g samples) was pretreated in flowing H_2 (30 ml/min) while being heated at a rate of 1°C/min to the desired temperature (300, 450, or 600°C) and then was held at this temperature for 10 h. After reduction the catalyst was cooled in H_2 to the desired initial reaction temperature, usually 140°C. The reduction temperature was varied in order to control the Pd particle size on the alumina support. Variation of the prereduction temperature from 300 to 600°C resulted in Pd particle sizes in the range 11–53 nm.

For a standard reaction experiment the total flow of the reactant mixture was 100 ml/min and consisted of 1,1-dichlorotetrafluoroethane (2 ml/min), H_2 (40 ml/min), and $He + N_2$ (58 ml/min). The CF_3CFCl_2 was obtained from DuPont and analysis by GC (gas chromatography) determined that the purity was greater than 99.9%. Hydrogen, N_2, and He were of 99.999% purity (Liquid Carbonic). The reaction was carried out at 140°C until steady state was achieved (∼5 h). Then, the reaction temperature was varied between 100 and 200°C. Upon returning the temperature to 140°C the reaction rate returned to the steady-state value measured prior to varying the temperature. All results shown were at steady state unless otherwise noted. For partial pressure and contact time studies the flows of relevant gases were appropriately adjusted.

Similar reaction system and procedure were used for studying ethane hydrogenolysis on the 2 wt% Pd/γ-Al_2O_3. The catalyst was subjected to the same reduction conditions as in the case CF_3CFCl_2 hydrodechlorination, i.e., after reduction at 300, 450, and 600°C for 10 h. The reactant stream consisted of C_2H_6 (3 Torr) and H_2 (27 Torr) balanced with He to a total flow of 61.5 ml/min. Reactions were conducted at atmospheric pressure and the reaction temperature ranged between 279 and 321°C. Higher reaction

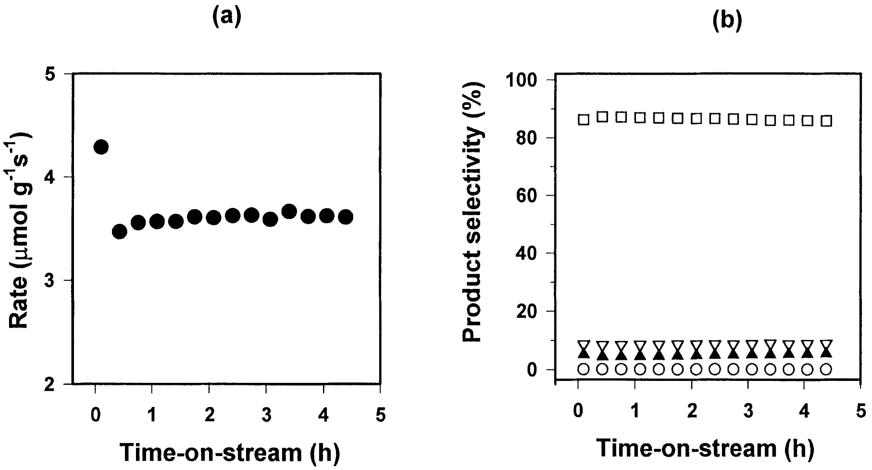

FIG. 1. Time-on-stream behavior in the reaction of hydrodechlorination of CF_3CFCl_2 on 2 wt% Pd/γ-Al_2O_3 reduced at 300°C. Reaction conditions: 140°C, H_2/CF_3CFCl_2 ratio = 20. (a) Overall conversion rate, (b) selectivities (squares, formation of 1,1,1,2-tetrafluoroethane; reversed triangles, 1-chloro-1,2,2,2-tetrafluoroethane; upright triangles, 1,1,1-trifluoroethane; circles, hydrocarbons).

temperatures were required because of the lower reactivity of the catalyst for ethane hydrogenolysis.

RESULTS

The hydrodechlorination of 1,1-dichlorotetrafluoroethane (CF_3CFCl_2) catalyzed by Pd/Al_2O_3 resulted in the formation of three main products: 1,1,1,2-tetrafluoroethane (CF_3CFH_2, the desired product), 1,1,1-trifluoroethane (CF_3CH_3), and 1-chloro-1,2,2,2-tetrafluoroethane (CF_3CHFCl). These accounted for more than 99% of the products. Trace amounts of methane, ethane, and ethene were detected and will be grouped cumulatively as "hydrocarbons" in selectivity considerations. Figure 1 shows the time-on-stream behavior at 140°C for Pd/Al_2O_3 prereduced at 300°C in (a) overall activity and (b) selectivities. The activity of the catalyst decreased by approximately 20% during the first 30 min of time on stream, whereas the selectivities toward formation of major products showed only insignificant variations.

Figure 2 shows the effect of contact time on the steady-state conversion of CF_3CFCl_2. The H_2/CF_3CFCl_2 ratio was 20/1. Conversion over the range 0–20% varied linearly with contact time, demonstrating that the reaction is not limited by mass transport in this range. Accordingly, reactions conducted at conversions of less than 20% were used to establish kinetics parameters. At higher conversions the relationship between contact time and conversion was nonlinear. Because it was possible to obtain conversions approaching 100% at sufficiently long contact times, the deviation from proportionality is due to the "integral" nature of the reactor rather than a thermodynamic limitation.

The effect of reactant partial pressure on the turnover frequency is shown in Fig. 3 [(a) for H_2 and (b) for CF_3CFCl_2]. The H_2 partial pressure was varied from 152 to 456 Torr, whereas the CFC pressure was varied between 7.6 and 45.6 Torr. At these conditions, the reaction is zero order (±0.02) in H_2 and 0.65 (±0.02) order in CF_3CFCl_2. Measurements were not made at lower H_2 partial pressures because of the appreciable rate of catalyst deactivation.

Figure 4 shows the effect of CF_3CFCl_2 partial pressure on turnover frequencies for the formation of individual products. The reaction orders obtained from the respective

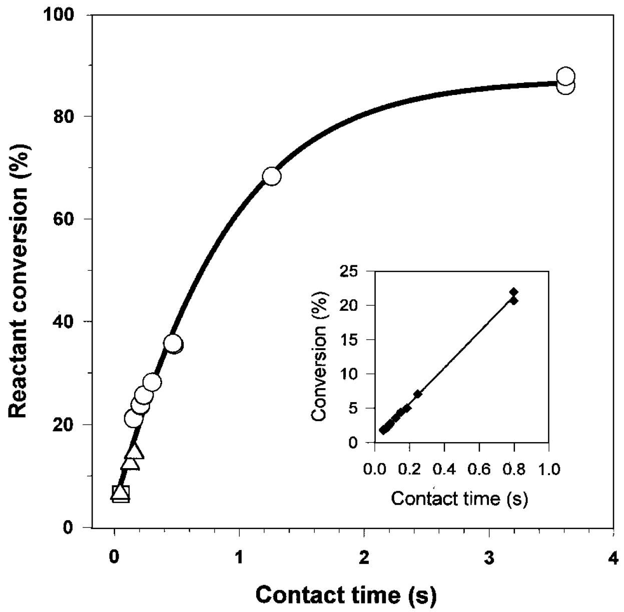

FIG. 2. The effect of contact time on reactant conversion in hydrodechlorination of CF_3CFCl_2 over 2 wt% Pd/γ-Al_2O_3 reduced at 300°C (reaction conditions: 140°C, H_2/CF_3CFCl_2 ratio = 20). Open symbols (circles, squares, and triangles) represent data collected in different runs. Insert: analogous data for the catalyst reduced at 525°C (filled diamonds) for the reaction temperature 121°C (linear fit with correlation coefficient $r^2 = 0.999$).

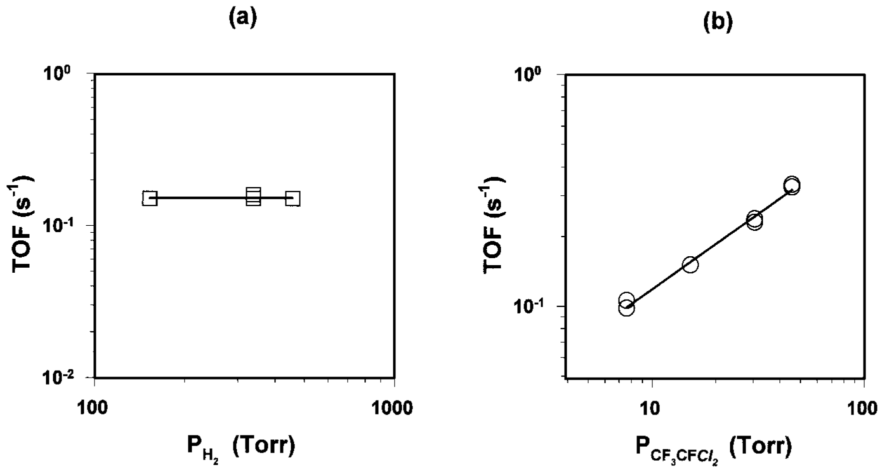

FIG. 3. The effect of partial pressures of reactants on turnover frequency (TOF) in hydrodechlorination of CF_3CFCl_2 over 2 wt% Pd/Al_2O_3 reduced at 450°C: (a) hydrogen dependence, (b) CF_3CFCl_2 dependence. Reaction temperature 140°C.

slopes were 0.65 ± 0.02 for 1,1,1,2-tetrafluoroethane, 0.58 ± 0.03 for 1,1,1-trifluoroethane, and 0.67 ± 0.03 for 1-chloro-1,2,2,2-tetrafluoroethane. The effect of partial pressures of H_2 and CF_3CFCl_2 on the product selectivity is shown in Figs. 5a and 5b. There was essentially no change in the product distribution in either case.

Varying the extent of reactant conversion had a minimal effect on the product selectivity (Fig. 6), even at very low conversions (Fig. 6b). Over the entire conversion range (2–95%) the selectivity toward the desired product (1,1,1,2-tetrafluoroethane) decreased by only 3%. It is important to point out that the reactions were conducted with a high H_2/CFC feed ratio (20/1). At low ratios where the deactivation is more extensive, changes occur in product selectivity with increasing conversion and time-on-stream.

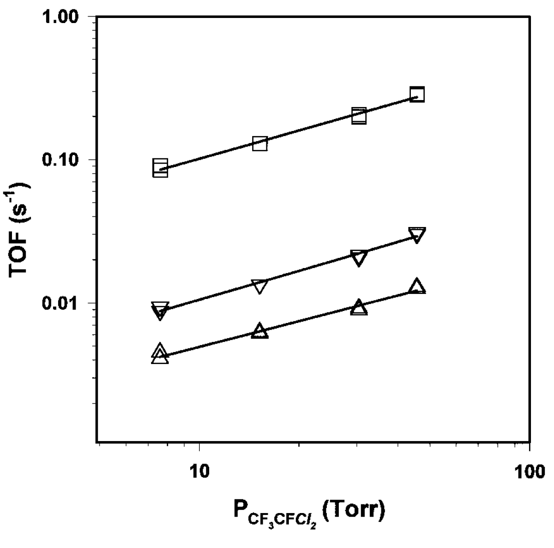

FIG. 4. The effect of partial pressure of CF_3CFCl_2 on turnover frequency (TOF) in the formation of individual products: 1,1,1,2-tetrafluoroethane (squares), 1-chloro-1,2,2,2-tetrafluoroethane (reversed triangles), 1,1,1-trifluoroethane (upright triangles) in hydrodechlorination of CF_3CFCl_2 over 2 wt% Pd/Al_2O_3 reduced at 450°C. Reaction temperature 140°C.

The effect of reduction temperature (300, 450, and 600°C) on turnover frequencies and product selectivities is presented in Table 2. The selectivity appears to be independent of *reduction* temperature, but is weakly influenced by *reaction* temperature. In all cases, increasing the reaction temperature increased the selectivity toward 1,1,1-trifluoroethane and decreased the selectivity toward the desired product (CF_3CFH_2). Increasing the pretreatment temperature resulted in an increase in the overall TOF (Table 2).

Figures 7a–7c present Arrhenius-type plots for the hydrodechlorination of CF_3CFCl_2. The reaction temperature was varied between 140 and 200°C. These plots were obtained using catalysts which had been prereduced at 300, 450, and 600°C. The absence of discontinuities in these relationships suggests that no change in the mechanism occurred over this temperature range. The apparent activation energy associated with the formation of each product ranged from 50 to 68 kJ/mol (Table 3). The highest energies were associated with the formation of CF_3CH_3 which involved the removal of all three halogens from the α-carbon. The lowest energies were associated with the formation of the desired product. Reducing the catalyst at higher temperatures resulted in a small but consistent increase in the apparent activation energies (Table 3). This trend was observed for the formation of the three major products and, thus, also for the conversion of reactant.

In contrast to the kinetics results obtained for the CFC reaction, the TOF for ethane hydrogenolysis catalyzed by Pd/Al_2O_3 was independent of prereduction temperature in the range 300–600°C and did not follow any trend for

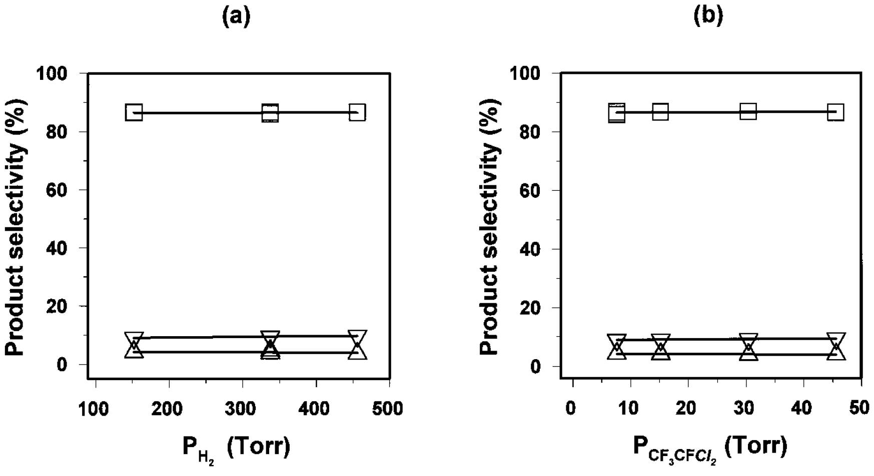

FIG. 5. The effect of partial pressures of (a) H_2 and (b) CF_3CFCl_2 on product selectivity in hydrodechlorination of CF_3CFCl_2 on 2 wt% Pd/Al_2O_3 reduced at 450°C (reaction temperature 140°C). Squares, formation of 1,1,1,2-tetrafluoroethane; reversed triangles, 1-chloro-1,2,2,2-tetrafluoroethane; and upright triangles, 1,1,1-trifluoroethane.

the apparent activation energies (Table 4). These reactions were conducted at a significantly higher temperature due to the higher activation energy associated with ethane hydrogenolysis.

DISCUSSION

Given the nature of the results obtained in this investigation, it is possible to make a number of suggestions regarding the mechanism of 1,1-dichlorotetrafluoroethane hydrodechlorination. It is also possible to gain insight into the nature of the active catalyst. Accordingly this discussion section has been divided to consider the mechanism and catalyst separately.

Reaction Mechanism

Our understanding of the reaction mechanism comes from an examination of the reaction kinetics. Under the conditions of this investigation the catalyst yielded a steady state TOF in the range 0.03–3.6 s^{-1} (Table 2). Steady state was established after a short period of deactivation during which the catalyst lost approximately 20% of its initial activity (Fig. 1). This extent of deactivation is at the low end of the range (20–50%) reported by Coq *et al.* for hydrodechlorination of dichlorodifluoromethane using a Pd/Al_2O_3 catalyst (11). Greater deactivation has been observed at lower H_2/CFC ratios. Presumably, excess H_2 is needed to minimize the coverage of strongly adsorbed species which block active sites.

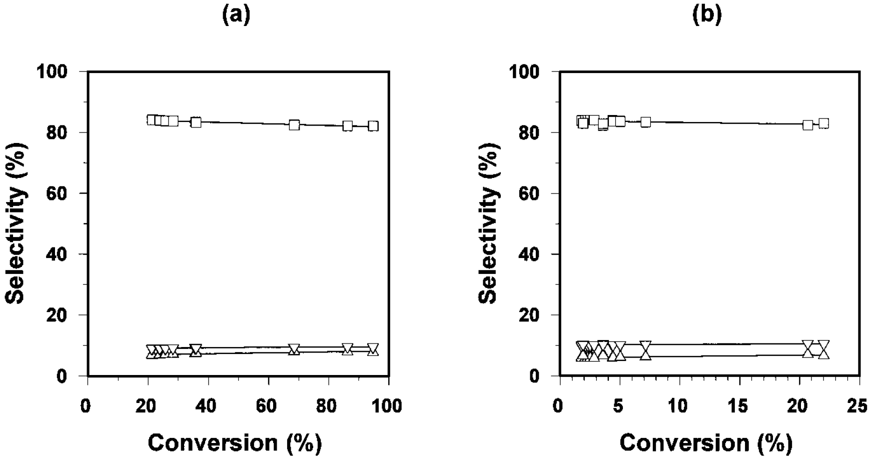

FIG. 6. The effect of reactant conversion of product selectivity in hydrodechlorination of CF_3CFCl_2 over 2 wt% Pd/Al_2O_3: (a) for higher conversions (20–95%) on the catalyst reduced at 300°C, reaction temperature 140°C, (b) for low conversions (1–22%) on the catalyst reduced at 525°C, reaction temperature 121°C. Squares, formation of 1,1,1,2-tetrafluoroethane; reversed triangles, 1-chloro-1,2,2,2-tetrafluoroethane; and upright triangles, 1,1,1-trifluoroethane.

TABLE 2

Hydrodechlorination of CF_3CFCl_2 over 2 wt% Pd/γ-Al_2O_3 Reduced at Different Temperatures: Steady State Values of Turnover Frequencies and Selectivities

Reduction temperature (°C)	Reaction temperature (°C)	TOF (s^{-1})	Selectivity, %			
			CF_3CFH_2	CF_3CH_3	CF_3CFHCl	HC[a]
300	101	0.027	86.1	5.2	8.6	—
	138	0.107	83.5	6.4	10.0	0.1
	201	0.83	77.3	11.3	11.1	0.3
450	101	0.039	85.4	4.6	9.0	—
	140	0.257	84.3	5.5	10.2	0.1
	198	1.79	80.7	8.3	10.4	0.5
600	101	0.063	82.4	4.5	13.1	—
	140	0.532	82.7	5.1	12.1	0.1
	201	3.607	75.8	10.3	13.0	0.9

[a] Selectivity toward dehalogenated hydrocarbons (see text).

TABLE 3

Hydrodechlorination of CF_3CFCl_2 over 2 wt% Pd/γ-Al_2O_3 Reduced at Different Temperatures: Apparent Activation Energies in the Overall Conversion and for the Formation of Individual Products

Reduction temperature (°C)	CF_3CFCl_2 (E_{app}, kJ/mol)	CF_3CFH_2 (E_{app}, kJ/mol)	CF_3CFH_3 (E_{app}, kJ/mol)	CF_3CFHCl (E_{app}, kJ/mol)
300	51.8 ± 1.5	50.4 ± 1.6	63.3 ± 1.3	54.5 ± 1.3
450	58.0 ± 0.8	57.1 ± 0.9	67.7 ± 1.0	59.6 ± 0.6
600	61.0 ± 1.2	60.6 ± 1.3	68.4 ± 0.8	59.7 ± 0.6

The selectivity toward the desired product, 1,1,1,2-tetrafluoroethane, is always greater than 80% under the range of conditions spanned in this investigation. The other major products are 1-chloro-1,2,2,2-tetrafluoroethane and 1,1,1-trifluoroethane. The selectivity is independent of the partial pressure of CFC and the conversion. It is only weakly dependent on the reaction temperature in the range 100–200°C. Selectivity toward CF_3CFH_2 tends to decrease slightly with increasing reaction temperature and is compensated by an increase of CF_3CH_3 formation. Correspondingly, the apparent activation energy for the formation of CF_3CH_3 is higher than for the other two reactions (by ~10 kJ/mol, Table 3), in good agreement with the apparent activation energies reported by Coq *et al.* (11) for the hydrodechlorination of CF_2Cl_2 over supported Pd catalysts. This observation can be rationalized in terms of a relative difficulty in breaking the C–F bond compared to the strength of the C–Cl bond (108 kcal/mol for FCH_3 vs 81 kcal/mol for $ClCH_3$ (14).

It should be mentioned that during the reaction of 1,1-dichlorotetrafluoroethane, the three fluorine atoms on the

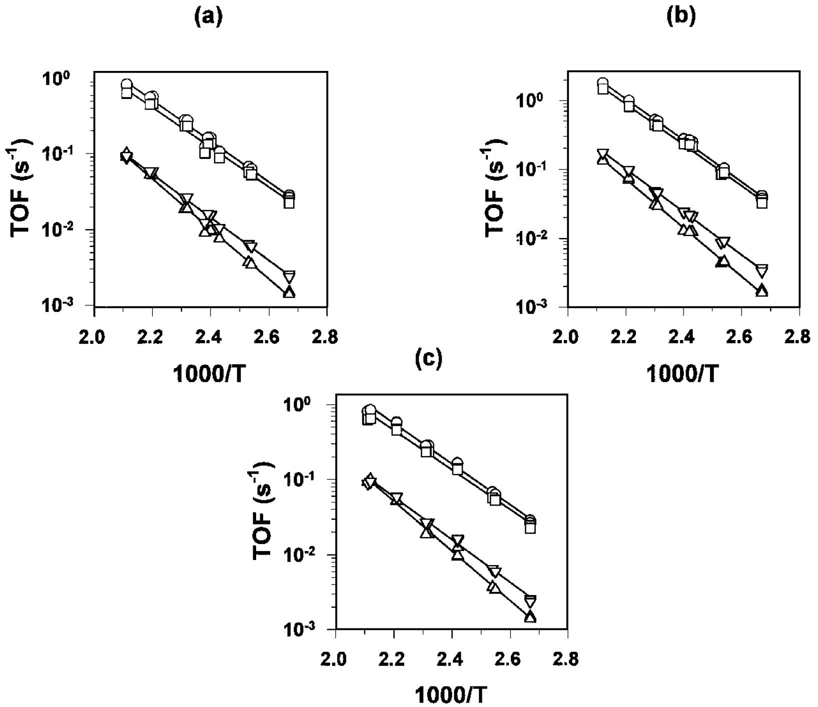

FIG. 7. Arrhenius plots for hydrodechlorination of CF_3CFCl_2 over 2 wt% Pd/Al_2O_3 reduced at 300 (a), 450 (b), and 600°C (c). Circles, overall conversion of CF_3CFCl_2; squares, formation of 1,1,1,2-tetrafluoroethane; reversed triangles, 1-chloro-1,2,2,2-tetrafluoroethane; upright triangles, 1,1,1-trifluoroethane.

TABLE 4

Ethane Hydrogenolysis over 2 wt% Pd/γ-Al_2O_3 Reduced at Different Temperatures: Turnover Frequencies and Activation Energies

Reduction temperature (°C)	Reaction temperature (°C)	TOF (s^{-1})	Activation energy (kJ/mol)
300	279	2.44×10^{-4}	313 ± 9
	290	9.13×10^{-4}	
	300	4.37×10^{-3}	
450	290	1.02×10^{-3}	273 ± 8
	300	3.29×10^{-3}	
	310	9.57×10^{-3}	
	319	2.42×10^{-2}	
600	290	1.32×10^{-3}	308 ± 6
	302	4.84×10^{-3}	
	312	1.70×10^{-2}	
	321	4.25×10^{-2}	

β-carbon are not susceptible to exchange with hydrogen. The relative difficulty in removing these fluorines, compared to the fluorine atom attached to the α-carbon, has been reported by Witt *et al.* (15), who explained this observation in terms of the differences in the dissociation energies for C–F bonds with various substituents on the carbon. For example, D(CH_3CH_2–F) is 105.5 kcal/mol while D(CH_3CF_2–F) is 124.8 kcal/mol (16).

The kinetics data show that the reactions have Arrhenius-type temperature dependence with apparent activation energies varying slightly among the three products ($E_{\mathrm{app}} =$ 50–68 kJ/mol). The Arrhenius-type dependence indicates that one mechanism is active for each product over the temperature range 100–200°C. The fact that the activation energies are similar for all three products suggests a common rate-limiting step.

The kinetics results described above have several implications regarding the nature of the catalytic mechanism. The fact that the reaction rates are independent of H_2 partial pressure suggests that the catalyst surface is saturated with hydrogen and, furthermore, that hydrogen and the CFC reactant do not compete for adsorption sites under these conditions. The high coverage of hydrogen is due to the relatively high partial pressures of H_2 used in this investigation. The dependence of reaction rate on CFC partial pressure (0.67 order in CFC) indicates a surface coverage well below saturation. It is important to note that the possibility of product inhibition has not yet been explored explicitly. Previous work with chlorobenzene has shown that products such as HCl can inhibit the overall reaction rate (17). In our work both HCl and HF are reaction products which could act as either site blocking agents for the adsorption of CFC or as modifiers of catalyst electronic properties. Either of these roles could be the source of the low (less than one) order of the reaction in CFC pressure.

Further insight into the mechanism of the reaction is gained by considering the effect of reactant conversion on the individual product selectivities. All three of the major products have a nonzero rate of formation in the limit of zero conversion (Fig. 6), suggesting that they are primary products. Secondary reactions (by readsorption) of CF_3CFHCl to produce CF_3CFH_2 and of CF_3CFH_2 to produce CF_3CH_3 are possible but would be expected to occur at higher temperatures.

In light of the suggestion that under our conditions all three major products are primary, it is remarkable that such a high selectivity toward CF_3CFH_2 is obtained. Similar results were reported by Gervasutti *et al.* (6) when using Pd/C as a catalyst. It is possible that the facile replacement of chlorine by hydrogen occurs via the participation of an adsorbed carbene, CF_3CF:, and that the stability or high surface concentration of this intermediate results in the high selectivity to CF_3CFH_2. A reaction scheme is illustrated in Fig. 8. This reaction network is derived from one proposed by researchers at DuPont (18) but has been simplified by the removal of steps involving readsorption of CF_3CFHCl and CF_3CFH_2 to emphasize that the major products are all primary. A similar reaction network has been suggested for the hydrodechlorination of F_2CCl_2 (11, 19). Moreover, the facile primary formation of carbenes from di-chloro-substituted alkanes on palladium has also been shown for CH_2Cl_2 (20, 21).

The reaction pathway depicted in Fig. 8 illustrates the formation of the major product, CF_3CFH_2, via a carbene intermediate formed by two sequential dechlorination steps. The loss of halogens two at a time is consistent with the results of Coq *et al.* (11) in their study of the dechlorination of chlorofluoromethanes and fluoromethanes. For example, they observed the following reactions: $CF_2Cl_2 \rightarrow CF_2H_2$, $CHF_2Cl \rightarrow CH_3F$, $CF_2H_2 \rightarrow CH_4$. However, in the chlorofluoroethane case, we observe products which results from the elimination of 1 and 3 halogen atoms. In the case of the production of CF_3CH_3, this may also proceed via a carbene intermediate (CF_3CH=). This surface carbene can

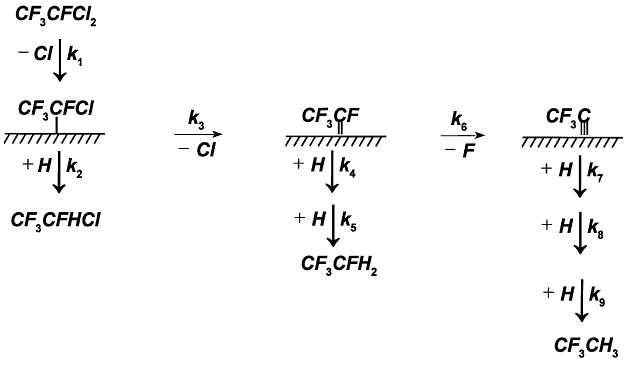

FIG. 8. Proposed reaction mechanism for the hydrodechlorination of CF_3CFCl_2.

be formed from $CF_3CF=$ via either $CF_3C\equiv$ or CF_3CFH- surface species.

While the proposed reaction mechanism is consistent with the observed relationship between product selectivity and conversion, evaluation of the predicted temperature dependence is worthwhile. The simplest analysis is one in which the adsorbed intermediates are all present in steady state and the hydrogen coverage on the catalyst surface is constant with $\theta_H = 1$. The saturation of the hydrogen coverage under our conditions is consistent with the observed independence on the rate on hydrogen pressure. The steady state analysis predicts that the selectivities for the three major products (with respect to the total rate) should be:

$$S_{CF_3CFHCl} = \frac{k_2}{k_2 + k_3}$$

$$S_{CF_3CFH_2} = \frac{k_3k_4}{(k_2 + k_3)(k_4 + k_6)}$$

$$S_{CF_3CH_3} = \frac{k_3k_6}{(k_2 + k_3)(k_4 + k_6)}$$

The complex dependence of the selectivities on the elementary rate constants suggests that they should be a strong function of temperature. The observed weak dependence on temperature could only occur if the activation energies in the rate constants canceled one another. Given that these are rate constants for much different elementary steps this is unlikely unless their barriers are all relatively low. The rate constants which enter into the expressions for the selectivity are for elementary reaction steps involving hydrogenation of chlorofluoroalkyl groups (k_2, k_4), loss of the second chlorine atom (k_3), and loss of the fluorine in the α-position (k_6). Studies by Zaera of the hydrogenation of ethyl groups of the Pt(111) surface indicate that the barrier of hydrogenation is quite low, <6 kcal · mole (22). At first glance it may seem that the barriers to α-dechlorination and α-defluorination ought to be relatively large, at least on the order of that for the first dechlorination reaction having rate constant (k_1). Although there are no direct measurements of rate constants for reactions such as these there is evidence to suggest that their barriers should be substantially less than that of the first dechlorination step. Experimental gas phase and theoretical work by Kumaran *et al.* show that the ClH_2C-Cl bond strength is 85 kcal/mole but once broken leaves a radical with a H_2C-Cl bond strength of 49 kcal/mole, substantially lower (23). Given this result and the proximity of the surface to the carbon–halogen bonds in the adsorbed intermediates $CF_3C(FCl)-Pd$ and $CF_3C(F)=Pd$, perhaps it is not unreasonable that the barriers for the rate constants k_3 and k_6 are substantially lower than that of the initial dechlorination step (k_1). Direct measurements of these rate constants are needed to resolve this issue and provide an explanation of the low temperature dependence of the selectivity.

Catalyst Modification

Our modification of the catalyst has consisted of varying the particle size by increasing the reduction temperature prior to reaction. Prereduction of the catalyst in the temperature range 300–600°C resulted in Pd particle sizes from 11 to 53 nm. As a basis for comparison to hydrodechlorination kinetics, ethane hydrogenolysis rates were measured using these catalysts. Ethane hydrogenolysis is highly structure sensitive for particles in the range of 1–5 nm, but insensitive in the range of Pd particle sizes of our catalysts (24). This is illustrated by the results presented in Table 4. In contrast, the hydrodechlorination reaction appears to depend on a particle size range 11–53 nm, showing an increase in TOF of up to factor of 5 (Table 2). Coq *et al.* reported a similar result for CF_2Cl_2 hydrodechlorination using Pd/Al_2O_3 catalysts with Pd particle sizes of 1.5 and 8 nm (11). In their case the reaction rate increased by a factor of 2.5. One possible explanation for these results is that the hydrodechlorination reactions require relatively large ensembles, the number of which would increase with increasing particle size. The creation of additional reaction sites (greater number of ensembles) with increasing particle size is also consistent with the observation that the TOF increases in spite of a slight increase in the apparent activation energy. As noted in the results section the catalysts are subject to some deactivation even at the high H_2/CFC ratios used in this work. The increased activity of the large particles may be due to the fact that low levels of site blocking will have less influence on the number of ensembles present on large particles than on the small particles. However, the cause of deactivation and its relationship to the particle size effect that we have observed requires further investigation.

CONCLUSIONS

A number of conclusions can be drawn from the results of this investigation. Stable catalytic activity can be obtained for the hydrodechlorination of 1,1-dichlorotetrafluoroethane under reaction conditions of high H_2 partial pressures. The reaction selectivity heavily favors the desired product, CF_3CFH_2, and is weakly dependent on temperature in the range 100–200°C. The kinetics results are consistent with a reaction which occurs via a carbene intermediate. In contrast to ethane hydrogenolysis, the hydrodechlorination reaction rate is increased by increasing the prereduction temperature from 300 to 650°C.

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