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Structure Insensitivity and Effect of Sulfur in the Reaction of Hydrodechlorination of 1,1-Dichlorotetrafluoroethane (CF_3–$CFCl_2$) over Pd Catalysts

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The kinetics of the hydrodechlorination of 1,1-dichlorotetrafluoroethane (CFC 114a) was studied on Pd(111), Pd(100), and a Pd foil at atmospheric pressure. The three products formed were CF_3–CFH_2 (HFC 134a), CF_3–CFClH (HCFC 124), and CF_3–CH_3 (HFC 143a) with selectivities independent of conversion. The single crystals and foil (model catalysts) were studied in an apparatus that permitted the direct transfer of samples between a high pressure cell (1 atm) and an ultrahigh vacuum chamber. The reaction rates were measured in the temperature range of 350 to 470 K. The reaction is not sensitive to the structure of the catalyst, as indicated by the similar turnover rates for all catalysts tested. The reaction is inverse first order in the reaction product HCl on all samples. Sulfur adsorbed on the Pd surface depressed the rates of formation of 134a more strongly than the rates of 124 and 143a.

1. INTRODUCTION

Hydrodechlorination is a gentle chemical reaction that removes the chlorine from a carbon-chlorine group and replaces it with a hydrogen. The process is catalyzed by several transition metals, and palladium is one of the best catalysts among them. This reaction plays a key role in the removal of chlorine from chlorofluorocarbons (CFCs) to produce hydrofluorocarbons (HFCs) with similar physical properties that are more environmentally benign (1). 1,1-dichlorotetrafluoroethane, CF_3–$CFCl_2$ (also called CFC 114a) is one of the most important molecules in this family of compounds. In this paper, we report its hydrodechlorination to CF_3–CFH_2 (also called HFC-134a) over palladium catalysts. Its utility derives from the use of HFC-134a as a substitute for the refrigerant CF_2Cl_2.

We explored the kinetics and mechanism of this reaction in studies using small area ($\sim$1 cm^2) palladium foils and single crystals (of (111) and (100) orientation) at low conversion (<1%). Atmospheric pressures were utilized, and the temperature range was 350 to 470 K. We found the turnover rates to be the same within error for all of the different types of palladium catalysts, indicating that the reaction is insensitive to the catalyst surface structure.

2. EXPERIMENTAL METHODS

The experiments on the foil and single crystals were carried out in a high pressure (1 atm) batch reactor attached to an ultrahigh vacuum (UHV) chamber with a base pressure of 8×10^{-10} Torr (1 Torr = 133 Pa). The chamber was equipped with low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and a mass spectrometer for temperature programmed desorption (TPD) of CO. The sample was 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 foil was attached to a sample cart containing two pins for resistive heating and two pins (chromel and alumel) for thermocouple temperature readings so the sample could be heated and the temperature measured both in the UHV chamber and in the reactor. The foil was spotwelded directly to the pins, and for the single crystal samples, stainless steel tabs were used to spotweld the side of the crystal to the pins. The type K thermocouple was spotwelded to the center of the rear of the foil and to the side of the single crystals. After reaction, due to desorption of reaction gases, the pressure could not be maintained below 10^{-7} Torr even though a 60 liter s^{-1} turbomolecular pump was connected to the transfer line. After the sample was transferred, the pressure in the main chamber returned to the base pressure in a few minutes.

The batch reactor had a volume of about 700 cm^3. The reactants were circulated with a metal bellows pump (Parker-Model MB 21) with a flow rate of about 1 liter min^{-1}. This

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flow rate permitted a small conversion per pass. Heat and mass transfer limitations are of no concern in this type of experiment since all the active surface area is exposed.

The Pd polycrystalline foil used in this study was 0.1 mm thick, had a total surface area of about 0.5 cm^2 and a purity of 99.99% (Johnson Matthey). The single crystals were about 1-mm thick, 0.5 to 0.8 cm^2, and were cut from bulk material (single crystal rods, Goodfellow) with 0.5° precision and polished with standard techniques. Due to the sample cart design, only one side of the sample could be cleaned by Ar sputtering. The sample was cleaned by cycles of Ar sputtering at 1000 K and 5×10^{-5} Torr, and annealing at 1000 K until no foreign peaks were found by Auger electron spectroscopy (AES). On the single crystals, the LEED pattern was also examined before reaction to verify the single crystal structure. After each reaction, Ar sputtering for 15 min followed by annealing at 1000 K was sufficient, as shown by AES, to clean the surface.

The temperature-programmed desorption of CO was used to characterize the Pd foil before and after reaction. Carbon monoxide was dosed on the surface in various amounts up to saturation. The sample was then heated linearly at a rate of 55 K s^{-1} while the temperature and mass 28 signal were recorded with the help of a computer.

After the sample was transferred into the reactor, it was heated to 373 K and then H_2 was introduced, followed by CFC 114a and Ar (make-up gas) to achieve 770 Torr total pressure. The sample was heated to 373 K before the introduction of reactants because previous experience (2) demonstrated that a combination of high hydrogen pressures (e.g., 500 Torr) and low temperatures (RT) would warp the Pd foil, probably due to the formation of palladium hydride.

The chlorofluorocarbon (CFC 114a) was obtained from DuPont Co. with only one impurity detected, possibly CF_3–CH_2Cl. This impurity did not change its concentration during the experiments. The CFC was degassed by freeze-pump-thaw cycles and then stored in a glass vial filled with a previously reduced 0.5% Pd on carbon supported catalyst. This was done to scavenge any sulfur-containing compounds from the reactant feed. Hydrogen (Matheson, Prepurified) was passed through a liquid nitrogen cold trap to remove any condensable impurities. The Ar (Liquid Carbonic, 99.995%) was used without further purification. The reaction rates were measured in the temperature range of 350 to 470 K, pressure range of 23 to 670 Torr in H_2, 21 to 511 Torr in CF_3–$CFCl_2$ and balance Ar at a total pressure of 770 Torr. The reaction products were analyzed with a gas chromatograph (Hewlett-Packard 5790A) with a flame ionization detector. The products were separated in a 5% Krytox™ 143AC, 60/80 Carbopack B HT $20' \times 1/8''$ column (Supelco). The first analysis was made after 3 min of reaction and subsequent analyses were carried out at intervals of 18 min.

Blank experiments were carried out to certify that the background catalytic activity was not significant. Those experiments were run on a stainless steel foil with a feed of 150 Torr of CFC 114a and 630 Torr of H_2. At 423 K, where most of the experiments were run, background reactions could not be detected, to a level at least 1000 times lower than the level obtained with a Pd foil.

3. RESULTS

3.1. Measurement of Rates

We reported before that on the Pd foil the rates of formation of HFC 143a, HFC 134a, and HCFC 124 are inhibited by the reaction product HCl (2). For all the catalysts used in this study, the reaction order in HCl was also -1 as calculated from the accumulation plots of the batch reactor runs (details below). The immediate consequence of this inhibition is that the turnover rate will be a strong function of conversion (Fig. 1.A). An explanation for the procedure used to calculate the turnover rate follows. For a batch reactor operating at the low conversion levels of this study (<1%) the rate of reaction should have been constant with time (pseudo-zero order reaction) and straight lines should have been obtained in Fig. 1.A. However, because the reaction is inverse first order in the product HCl the rate will be $r = -A/\chi$, where χ is the conversion and A depends on the concentration of the reactants and is essentially constant (low conversion). Using the rate above, the equation for the batch reactor will then be

$$d\chi/dt = B/\chi, \qquad [1]$$

where t is time and B is a constant. Integrating this equation will produce $\chi^2 = 2Bt$. This integrated equation has a linear dependence between the square of conversion (or the number of turnovers) and time (Fig. 1.B). The slope of the line (2 B) can then be used in Eq. [1] to calculate the rate at any conversion.

The measurement of rates on the model catalysts were made difficult by the deposition of sulfur on the sample which caused the catalyst to deactivate. Sulfur was deposited whenever HCl was formed during reaction. It is necessary to know if sulfur deposition affects the measurement of rates. The first step was to find a calibration for the amount of sulfur, determined by the ratio of Pd to sulfur AES peaks. This calibration was possible because sulfur forms ordered structures on Pd single crystal surfaces.

At the end of the reaction (after 2 to 3 h), a ratio of Auger intensities S_{152}/Pd_{330} of about 0.25 was determined for the foil, 0.24 for Pd(111) and 0.20 for Pd(100). Table 1 shows the literature data for the structures of sulfur formed on Pd single crystals (as determined by LEED) and corresponding sulfur coverages (as determined by AES). All measurements reported here are for a reaction temperature of 423 K

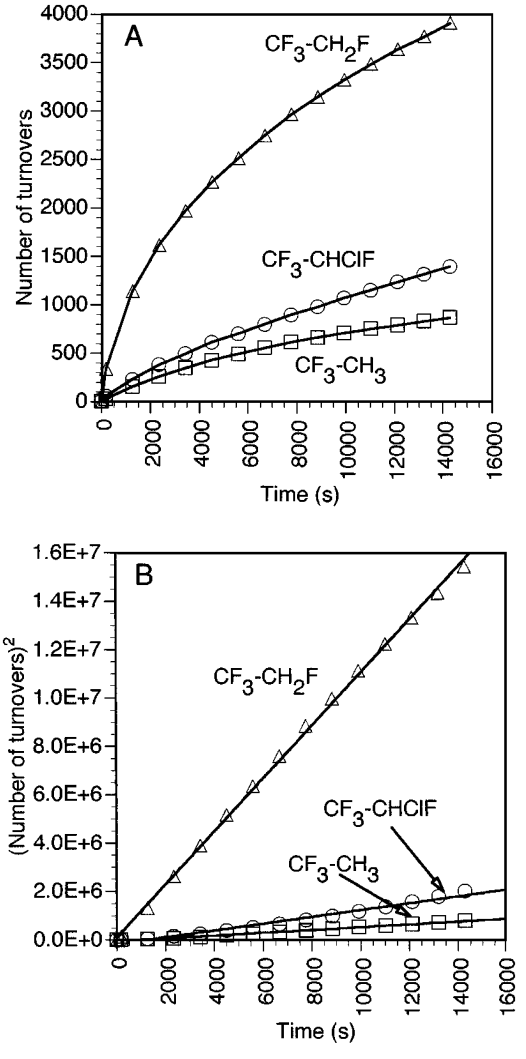

FIG. 1. (A) Accumulation plot (number of turnovers versus time) and (B) integrated equation plotted in linear form (accounting for effect of HCl) for the reaction of CFC 114a (CF_3–$CFCl_2$) (24.9 Torr), H_2 (50.2 Torr), Ar (697.7 Torr) at 423 K on Pd (111). The reaction products were: HFC 134a (CF_3–CFH_2) (△); HCFC 124 (CF_3–CFClH) (○); and HFC 143a (CF_3–CH_3) (□).

and are presumably saturation coverage. No higher coverage was detected by AES at higher reaction temperature, but at low temperature (e.g., at 400 K) the values could be 50 to 80% of the saturation values which also corresponded to a lower deactivation. The single crystals gave LEED patterns which were consistent with the highest-coverage structures of sulfur known on the respective crystal faces, at least 0.4 monolayers in each case. Specifically, the 0.5 monolayer c(2 × 2) structure was formed on Pd(100) (3) and the $(\sqrt{7}\times\sqrt{7})$R19° structure on Pd(111). The $(\sqrt{7}\times\sqrt{7})$R19° S structure on Pd(111) has been studied by several groups using LEED, AES, and STM (4–7). General agreement exists that this structure is formed above 400 K (which is close to our reaction temperature) and that the geometry of this structure is rather complex. Presumably this phase comprises a mixed palladium–sulfur overlayer, where some of the sulfur atoms have been incorporated into the subsurface region. The agreement of the AES values measured here approximates the values in the literature. The higher coverage c(2 × 2) structure exhibits a lower coverage in our AES data. One possible explanation is that the AES spectra of the $(\sqrt{7} \times \sqrt{7})$R19° structure contains additional disordered sulfur which does not appear in the LEED pattern. Bömermann *et al.* (6) detected disordered layers of sulfur on Pd(111) which could account for the higher AES intensities we have observed on this face. AES spectra obtained on both crystal faces were utilized to calibrate the sulfur coverage of the foil. On the foil, we find an AES peak ratio S/Pd equal to 0.25, which corresponds, based on the calibration of the single crystals, to a saturation surface coverage of 0.4–0.5 monolayers.

The sulfur contamination did not come from impurities in the H_2 or CFC 114a, as the amount of sulfur after heating the sample in pure H_2 or pure CFC 114a at reaction temperature was close to background level. The amount of sulfur on the sample correlated with the amount of HCl (amount of conversion) produced in the reaction. We believe that the source of sulfur is the following: H_2/HCl mixtures are good hydrodesulfurization agents (8) and any residual sulfur compound can be transformed into the corresponding chloride and H_2S. This last compound will eventually contaminate the catalyst. The most significant breakthrough in controlling the sulfur poisoning was to remove the rough vacuum oil pump, which was used to pump down the reaction manifold to 10^{-1} Torr before the turbopump could be used. The use of the rough pump constantly added sulfur compounds to the reactor by backstreaming. The replacement of the rough pump with a sorption pump decreased the amount of contamination to a level where initial rates could be measured without the interference of sulfur. To prove this point, the amount of sulfur as a function of reaction time was studied in a series of experiments at 423 K, 260 Torr of CFC 114a and 510 Torr H_2 on the Pd foil (Fig. 2). As explained above, when the square of concentration is plotted as a function of time (Fig. 2.B), the dependence on HCl is removed and the new plot should be linear with time. Any curvature in the graph will be due to sulfur poisoning. It is concluded then that at the particular conditions used, sulfur starts to affect the rates significantly after about

TABLE 1

Ordered Sulfur Structures on Pd Single Crystals

Surface	Sulfur structure	Nominal coverage	S_{152}/Pd_{330} eV	References
Pd(100)	c(2 × 2)	0.50	0.195 ± 0.016	(3)
Pd(111)	$(\sqrt{7} \times \sqrt{7})$R19°	0.43	0.239 ± 0.021	(4–7)

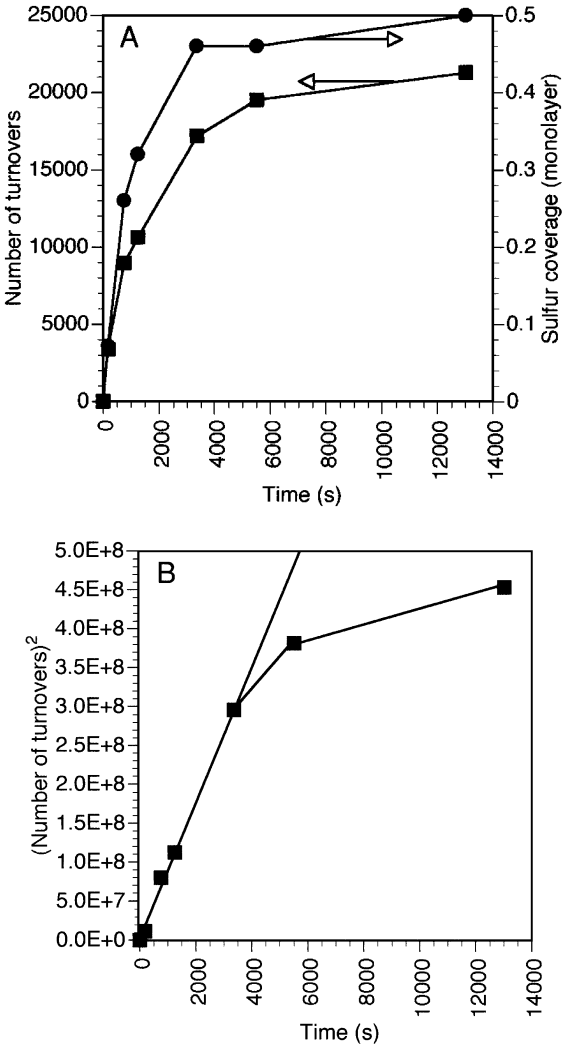

FIG. 2. (A) Amount of HFC 134a (CF_3–CFH_2) (number of turnovers) and amount of sulfur versus time. (B) Integrated equation plotted in linear form (accounting for effect of HCl). Reaction conditions were: CFC 114a (CF_3–$CFCl_2$) (260 Torr); H_2 (510 Torr), 423 K on a Pd foil.

4000 s. The curvature on the linearized graphs depended on the amount of HCl formed; at low temperature (e.g., 350 K) the rate of formation of HCl is slow, as is the rate of S deposition, and no curvature due to sulfur is found. At the highest temperature tried (470 K), the curvature appears after 1000 s. In conclusion, the initial rates could be measured without interference from sulfur.

3.2. Influence of Catalyst Structure on Rates and Selectivity

To study the dependence of turnover rates with the catalyst structure, the turnover rates (based on the total number of Pd surface atoms) on two single crystals and a foil were compared (Table 2). The three catalysts have different structures. The single crystals are the close packed (pseudo-hexagonal) Pd(111) and square Pd(100). The Pd foil is polycrystalline and it is probably composed of (111) planes with defects. The CO TPD from the foil, however, is very similar to the TPD of CO from Pd(111) (9, 10) and thus the defect sites do not produce a different CO desorption peak. Thus, we were not able to quantify the defects on the surface. Table 2 reveals a small variation for the rates. For the product formed with the highest selectivity (HFC 134a) the ratio between the maximum and the minimum rate among the various catalysts is less than three. The widest variation is on the rate of the product formed in the least amount (HFC 143a). The selectivities in Table 2 vary even less than the rates. Note that the comparison of reaction selectivities is simplified in this reaction because the selectivities are independent of conversion. It seems that the reaction is insensitive to the structure of the Pd catalyst.

The foil and single crystals were characterized after reaction. The AES spectra after reaction revealed only sulfur and Pd on the surface. The LEED revealed that the crystallinity of the single crystals was not affected by the reaction and that additional spots, due to a sulfur superstructure, were detected. As discussed before, the Pd(100) formed a c(2 × 2) structure and Pd(111) exhibited a $(\sqrt{7} \times \sqrt{7})$R19° structure.

It is surprising that no chlorine and fluorine are detected on the surface of the catalyst after reaction when we know from the reaction kinetics on the foil (2) that chlorine is the most abundant reaction intermediate. To test why chlorine is not observed after reaction, we first dosed Cl_2 to saturation (60 Langmuir) on the Pd foil through a leak valve and verified that the excitation electron beam used in AES did not desorb it from the foil. Next, we verified that heating the chlorine saturated Pd surface at 373 K in 1.0 Torr of H_2 for 1 min in the high pressure cell was sufficient to remove the chlorine. Thus, when the reactor is pumped down after reaction there is enough hydrogen to react away chlorine adsorbed on the surface. For surface fluorine, there may be a problem in detecting it by AES. It seems that fluorine is easily desorbed by an electron beam, as used for excitation in AES (11).

TABLE 2

Turnover Rate for Model Pd Catalysts

	Turnover rate[a]/s^{-1} (selectivity[b]/%) reaction products		
Catalyst	CF_3–CH_3 (HFC-143a)	CF_3–CFH_2 (HFC-134a)	CF_3–CFClH (HCFC-124)
Pd foil	6.4×10^{-2} (3)	2.1 (85)	3.0×10^{-1} (12)
Pd(100)	8.0×10^{-2} (6)	1.2 (84)	1.4×10^{-1} (10)
Pd(111)	18×10^{-2} (10)	1.3 (74)	2.8×10^{-1} (16)

[a] Rates corrected for 50 Torr CF_3–$CFCl_2$, 100 Torr H_2, 0.1 Torr HCl, 423 K.

[b] Selectivity is constant for conversion lower than 50%. Selectivity = 134a/(143a + 134a + 124).

The activation energies are shown in Table 3 and are around 100 kJ mol^{-1}. There may be a trend of higher activation energies as more halogens are substituted by hydrogen, except for the foil where the activation energy for HFC 143a is lower than for HFC 134a.

3.3. *Effect of Sulfur*

Sulfur was detected by AES at the end of reaction on the Pd foil and single crystals. It was already discussed that the time scale of the sulfur deposition was slow enough to allow for the measurement of initial rates and thus it did not disturb our rate measurements. Sulfur deposition eventually decreased the rates and selectivity. To measure the effect of sulfur, the rates were measured on a sample that had its surface covered with sulfur to saturation. This sample was prepared by carrying out the hydrodechlorination reaction on a clean foil, taking the sample to the UHV chamber for characterization, and not removing the accumulated sulfur before reaction. The final rates on the Pd foil with sulfur for 143a, 134a, and 124 at the standard conditions given in Table 2 (50 Torr CF_3–$CFCl_2$, 100 Torr H_2, 0.1 Torr HCl, 423 K) were respectively 3.7×10^{-2}, 8.0×10^{-2}, and 4.4×10^{-2} s^{-1}. The rates were decreased by a factor of 2 for 143a, 25 for 134a, and 7 for 124. Thus, the selectivity to 134a (the desired product) decreased as sulfur was deposited on the surface. Figure 3 shows the effect of sulfur on the TPD of CO. The addition of sulfur eliminates the higher adsorption energy CO adsorption sites on the foil and decreases the total uptake by a factor of 13. The same decrease in the CO adsorption energy has been observed for sulfur adsorbed on Pd(100) (12). On Pd(111) (13), the sample prepared by adding sulfur to saturation did not adsorb CO at room temperature until it was annealed to create adsorption sites. For the samples that were exposed to sulfur short of sulfur saturation, the CO uptake was proportional to the number of sites that could adsorb acetylene (13). Since the reaction appears to be structure insensitive, the decrease in rate with the addition of sulfur should be directly proportional to the decrease in surface area. The reaction selectivities should not be affected by the addition of sulfur either. The rates and CO uptake decrease by an amount higher than predicted by a blocking mechanism assuming one sulfur atom blocking one Pd atom (about 50% of the surface is covered with sulfur). Changes in the CO uptake, CO desorption temperature, rate, and selectivity suggests that sulfur affects the binding of reaction intermediates on the surface.

We have also found that the deposition of sulfur does not affect the reaction order for HCl, CFC 114a, and H_2 on the Pd foil. The same chemistry is operative when sulfur is deposited.

TABLE 3

Apparent Activation Energy for Model Pd Catalysts

	Apparent activation energy/kJ mol^{-1} reaction products		
Catalyst	CF_3–CH_3 (HFC-143a)	CF_3–CFH_2 (HFC-134a)	CF_3–$CFClH$ (HCFC-124)
Pd foil	95	110	95
Pd(100)	125	85	80
Pd(111)	135	100	85

Note. The error bars were about 10 kJ mol^{-1}.

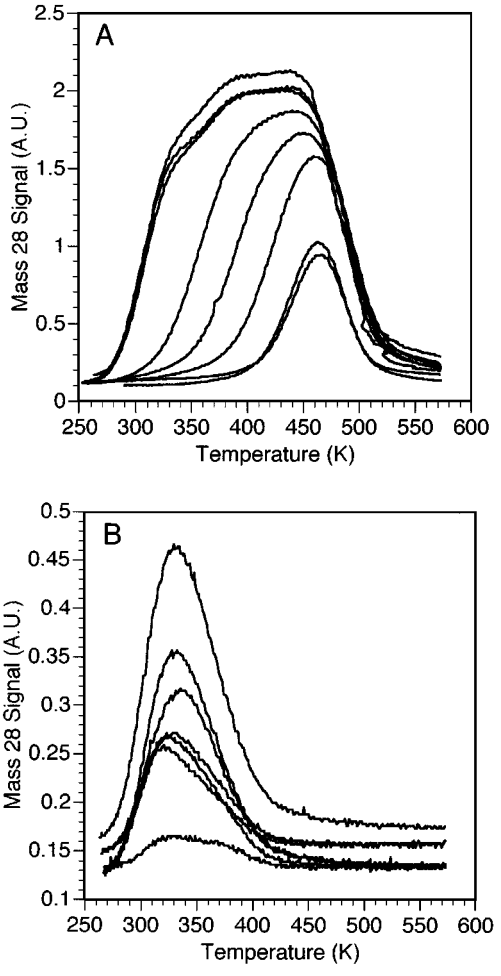

FIG. 3. (A) TPD of CO on Pd foil. CO exposures were 0.1, 0.2, 0.5, 0.8, 1.0, 2.0, 5.0, and 50.0 Langmuir. (B) TPD of CO on Pd foil with 0.5 monolayer of sulfur. CO exposures were 0.1, 0.5, 1.0, 5.0, 10.0, and 50.0 Langmuir. Heating rate 55 K s^{-1}.

4. DISCUSSION

The main result of this paper is the small variation of rates and selectivities as the structure of the catalyst is changed. These results indicate that the reaction is structure insensitive. Fung and Sinfelt (14), based on the small variation of turnover rates (two orders of magnitude) across a period in the periodic table for the hydrodechlorination of methyl

chloride, suggested that hydrodechlorination reactions may be structure insensitive on group VIII metals.

A comparison of our rates with reaction rates reported in the literature was difficult because there are not many studies reported for CFC 114a on Pd. Gervasutti *et al.* (15) also studied hydrodechlorination of CFC 114a, but these authors did not report a turnover rate, making a comparison with our rates very difficult. Karpinski *et al.* (16) studied this reaction on Pd supported on alumina, but their reaction order in HCl appears to be zero, as it is apparent from the contact time versus conversion plot, and not −1 order in HCl as in this case. Thus a comparison cannot be made in this case since the reaction chemistry seems to be very different on alumina-supported samples. Another possibility for comparison is to use the rate data for similar CFCs. However, this is difficult because the rate is highly dependent on the distribution of halogens in the molecule, and there is no correlation available to account for these differences.

Comparison of activation energies is also difficult for the same reasons discussed above for the turnover rates. The only additional comment is that if the inhibition by HCl is not accounted for in the calculation of the rate constant, the resulting Arrhenius plot (usually obtained by varying the temperature and keeping the other variables constant) will produce an "apparent activation energy" that will be two times lower than the one with the HCl effect accounted for. In other words, the rates will appear not to increase as much as expected with the temperature due to the effect of HCl. The activation energies here are higher than the ones observed by Karpinski *et al.* (16) by a factor of almost two but the difference may be again related to the alumina support. It appears that the activation energy increases with the number of halogen atoms that are removed from the reactant (Table 3). The mechanism advanced from the foil data for the two most abundant products (134a and 124) (2) has a common rate-determining step for these two compounds and thus the activation energies should be the same. More experiments are necessary to decide if there is a trend of higher activation energies as more halogen bonds are broken. However, it is reasonable to assume that for 143a the higher activation energy indicates that the reaction mechanism is different than for the other two products in that a higher energy carbon-fluorine bond may be broken in the rate-determining step.

It is surprising that sulfur modifies the reaction selectivity when changes in the catalyst morphology will not affect the rates. The fact that it affects the selectivities of a structure insensitive reaction is an indication that sulfur is changing the binding energies of the reaction intermediates.

5. CONCLUSION

The reaction of hydrodechlorination of 1,1-dichlorotetrafluoroethane is insensitive to the structure of the Pd catalyst. This result implies that the rates of hydrodechlorination will be proportional to the total Pd surface area.

Sulfur decreases the rates of all products, but it decreases the rate of HFC 134a more strongly than the other two products, thus decreasing the reaction selectivity for this most desirable product.

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