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Hydrodechlorination of 1,1-Dichlorotetrafluoroethane and Dichlorodifluoromethane Catalyzed by Pd on Fluorinated Aluminas: The Role of Support Material

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The gas phase hydrodechlorination of CF_3CFCl_2 to CF_3CFH_2 and CF_2Cl_2 to CF_2H_2 catalyzed by Pd supported on Al_2O_3, a series of fluorinated Al_2O_3, and AlF_3 was investigated. A combination of reaction kinetics investigations and characterization by *in situ* FTIR spectroscopy has been performed. It has been found that for reactions involving CF_3CFCl_2, all catalysts exhibit a rapid and significant decrease in activity; however, little change in activity with time on stream occurs with CF_2Cl_2. FTIR investigations suggest the occurrence of direct reaction between the CFC and the support material, which results in the consumption of hydroxyl groups during the early stages of reaction. The effect of fluorination of support on catalytic behavior of Pd is discussed.

INTRODUCTION

It is well established that many transition metals exhibit catalytic activity for the hydrogenolysis of C–Cl bonds (1–3). Noble metals are particularly attractive because of their high activities. The hydrogenolysis of carbon–chlorine bonds in chlorofluorocarbons is carried out primarily using a palladium catalyst because the selectivity toward the fully dechlorinated hydrofluorocarbon is high (4, 5). However, previous work has shown that the catalytic behavior of Pd depends not only on the metal, but also on the type of support (4, 6–8). For example, in the hydrodechlorination of CF_2Cl_2 selectivities toward CF_2H_2 in excess of 80% were obtained using a Pd supported on AlF_3 or Al_2O_3 at conversions below 10%, whereas Pd supported on ZrO_2 exhibits a much lower selectivity (∼31%) at the same conversion (4, 9).

Catalytic activity is also influenced by the type of support material. A fivefold difference in steady-state activity ($307\ h^{-1}$ vs $61\ h^{-1}$) was reported for Pd supported on AlF_3 in comparison to Al_2O_3 (4); the metal dispersion was approximately the same. Catalyst stability is also affected by the type of support materials used for such dechlorination reactions. Palladium supported on AlF_3 did not deactivate during CF_2Cl_2 hydrodechlorination, while Pd supported on Al_2O_3 suffered a 20–50% loss in activity during the same 10 h time period (9).

Clearly, understanding the molecular phenomena related to interactions of the reactant molecule with the support material is critical to improving performance. The work described here considers the role of the support in the hydrodechlorination reaction. A combination of reaction studies and FTIR investigations have been conducted to elucidate the extent to which the support participates in the CF_3CFCl_2 and CF_2Cl_2 hydrodechlorination reactions. Comparisons of alumina, fluorinated aluminas, and aluminum fluoride as supports have been conducted.

EXPERIMENTAL

Catalyst Preparation

The initial step in preparing the catalysts involved the synthesis of a series of fluorided aluminas (2, 5, 10, and 30% F by weight). This was accomplished by adding 20 g γ-Al_2O_3 (Vista B) to a precalculated amount of 30% HF solution (Mallinckrodt AR) diluted in 800 cm^3 of distilled H_2O. The slurry was mixed at room temperature for 4 h and left overnight. The solid was removed by filtration and the liquid was analyzed for F content using a fluorine selective electrode. No fluorine was detected in excess of the detection limit ($<10^{-5}$ M), indicating that HF reacted stoichiometrically with the oxide. Afterward, the fluorided supports were dried in air at 393 K. Then they were calcined in 10% O_2/He (30 ml/min) while the temperature was increased at 1 K/min from room temperature to 773 K, and then held at this temperature for 3 h. Subsequently, the material was cooled to room temperature and impregnated with Pd as described below. It is worth noting that despite the difference in density of alumina and aluminum fluoride, no significant change in alumina volume was observed during fluorination. This is consistent with the previous research (10), and it was rationalized therein in terms of fluoride ions occupying interparticle spaces in the expanding AlF_3 lattice, resulting in the reducing of pore volume and surface area.

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Catalysts containing 1 wt% Pd were prepared by impregnating the fluorinated Al_2O_3 samples, γ-Al_2O_3 (Vista-B), and $AlF_3 \cdot xH_2O$ (Aldrich) with a Pd(II)–acetylacetonate (>99%, Strem Chemicals) solution. For each sample, 0.3 g of Pd(II)–acetylacetonate was dissolved in 250 ml toluene (>99.99%, J.T. Baker) and the resulting solution was added to 10 g of desired support. The slurry was stirred at room temperature for 1 h in a rotary evaporator and then the solvent was removed at ~338 K under continuous evacuation (125 Torr) in approximately 4 h. The resulting material was dried overnight in air at 383 K. Finally, the sample was transferred to a 18 mm i.d. Pyrex tube, heated to 773 K (1 K/min) in 10% O_2/He flow (30 ml/min), and held under these conditions for 8 h.

Catalyst Characterization

Metal dispersions were determined by hydrogen chemisorption at room temperature using the double isotherm method (11). The catalyst sample (500 mg) was placed into a quartz U-tube reactor (i.d. = 16 mm; height of the catalyst bed ~6 mm), heated to 773 K (4 K/min), and calcined in a 10% O_2/He flow (20 ml/min) for 30 min. The sample was evacuated at 773 K to less than 10^{-5} Torr for 15 min and cooled to room temperature under the same vacuum. The sample was exposed to H_2 (30 ml/min) at room temperature. While maintaining the flow of H_2, the temperature was increased at 8 K/min to 573 K and held at this temperature for 1 h. The sample was then evacuated at 573 K for 1 h and cooled to room temperature at $<10^{-5}$ Torr. The mean particle size of Pd was calculated using the empirical equation developed by Benson *et al.*, $d = 0.9/D$, where D is the dispersion of palladium and d is given in nanometers (11). Catalyst surface areas were determined by the BET method using adsorption isotherms of nitrogen at 78 K. Pretreatment consisted of an overnight evacuation at 373 K, and did not include the oxidation and reduction steps. The physical and chemical properties of the catalysts are summarized in Table 1.

TABLE 1

Characteristics of the Supported 1 wt% Pd Catalysts

Support	Fluorine content (%)	Support surface area (m^2/g)	Pd dispersion (H/Pd)	Mean particle size of Pd (nm)[a]
Al_2O_3	0	245	0.12	7.5
2%F–Al_2O_3	2	207	0.14	6.4
5%F–Al_2O_3	5	195	0.12	7.5
10%F–Al_2O_3	10	183	0.06	15.0
30%F–Al_2O_3	30	47	0.07	12.9
AlF_3	n.a.	33	0.06	15.0

[a] $d = 0.9/D$ (11), where D is Pd dispersion.

Catalytic Experiments

The hydrodechlorination of CF_3CFCl_2 (courtesy of DuPont, >99%) was conducted in an atmospheric flow-through microreactor containing a quartz U-tube reactor (i.d. = 10 mm; height of the catalyst bed ~3 mm). The reaction products were analyzed by gas chromatography using a 5% Fluorocol 143 HMW/60/80 Carbopack B column (3 m, from Supelco) maintained at a constant temperature of 353 K. When necessary, products were identified by a GC/MS equipped with the same column as the GC.

To remove water and contaminants that may have accumulated during storage of the catalysts, prior to reaction the catalyst sample (50 mg) was heated from room temperature to 773 K at 4 K/min in 10% O_2/He flow (20 ml/min) and held at 773 K for 30 min. The sample was cooled to room temperature and then purged with 30 ml/min N_2 (UHP, 99.999%, Liquid Carbonic) for 10 min. Then it was treated in H_2 (30 ml/min) as the temperature was increased at 8 K/min to 573 K and held at this temperature for 1 h. The catalyst was subsequently purged with flowing N_2 (30 ml/min) at 573 K for 10 min before the system was cooled to the reaction temperature (473 K). The reaction was started by switching the gas flow from N_2 to the premixed reactant mixture consisting of 6 ml/min H_2, 2 ml/min CF_3CFCl_2, and 92 ml/min He (UHP, 99.999%, Liquid Carbonic) as balance (total flow rate = 100 ml/min; H_2/CF_3CFCl_2 molar ratio = 3.0). This resulted in a space velocity of 100,000 h^{-1}.

For the reaction studies involving difluorodichloromethane (CF_2Cl_2, courtesy of DuPont, >99%), a lower space velocity (10,000 h^{-1}) was used in order to maintain a conversion level comparable to the CF_3CFCl_2 reactions. A total flow rate of 30–50 ml/min was used for the CF_2Cl_2 reaction studies. Thus an increased quantity of catalyst compared to that of CF_3CFCl_2 dechlorination reactions was charged into the reactor to provide the necessary space velocity. All other parameters were the same as for the CF_3CFCl_2 investigations.

Rates per gram of catalyst were calculated by applying the differential reactor approximation in the form

$$\text{Rate (mmol/g s)} = F \cdot y/W,$$

where F is the total molar flow rate, y is the mole fraction of reactant converted, and W is the catalyst weight. Turnover frequencies (TOF) were then calculated using the expression

$$\text{TOF } (\text{s}^{-1}) = R \cdot \text{MW}_{\text{Pd}}/M \cdot d,$$

where R is the rate per gram of catalyst, MW_{Pd} is the molecular weight of Pd, M is the metal loading percent, and d is the particle dispersion expressed as a percentage.

In all experiments the conversion of reactants was maintained below 15%. It was demonstrated in a earlier work (12) that there is a linear relationship between conversion

TABLE 2

Initial and Steady-State Selectivities of the Supported 1 wt% Pd Catalysts Studied in the Reactions of CF_3CFCl_2 Dechlorination

	Selectivity[a]						Conversion (%)	
	CF_3CFH_2		CF_3CH_3		CF_3CFHCl			
Support	1 h	15 h	1 h	15 h	1 h	15 h	1 h	15 h
Al_2O_3	45	76	43	18	3	6	12.0	6.0
2%F–Al_2O_3	47	77	40	18	4	5	7.0	4.5
5%F–Al_2O_3	52	73	38	19	4	7	5.0	3.5
10%F–Al_2O_3	80	71	15	21	3	8	7.0	4.5
30%F–Al_2O_3	86	69	7	24	6	6	30.5	4.5
AlF_3	76	53	16	37	8	9	27.0	3.0

[a] The remaining products were CH_4, C_2H_6, and C_2H_4.

and space velocity for CF_3CFCl_2 dechlorination over Pd/Al_2O_3 at conversions between 0 and 20%, suggesting the absence of transport limitation. For several catalysts, however, the conversion during first few hours on stream was around 30% (Table 2), decreasing eventually due to deactivation. Of course, the error bar for TOFs is larger for higher conversions.

Infrared Studies

Investigations were conducted using a Mattson Research Series II FTIR spectrometer equipped with a MCT detector with a resolution of 4 cm^{-1}. A self-supporting pellet of 5–10 mg/cm^2 “thickness” was pressed from the catalyst sample and placed into a quartz IR cell (volume = 140 cm^3). The pellet temperature was measured at the outer wall of the quartz cell, approximately 6 mm from pellet surface. The catalyst pretreatment consisted of heating to 773 K (4 K/min) in 10% O_2/He flow (25 ml/min) and immediately cooling to room temperature. Oxygen traces were removed by evacuating the cell for ∼15 min ($<10^{-5}$ Torr) before exposing the catalyst to pure H_2. The reduction was then performed as described earlier. The reduction step was followed by evacuation ($<10^{-5}$ Torr) at 573 K for 1 h in order to remove chemisorbed H_2 from the sample.

For experiments involving CO as a probe molecule, after the previously described pretreatment the pellet was exposed to 10 Torr of CO (99.99%, Liquid Carbonic) at room temperature for 5 min. The gas phase and weakly adsorbed CO were removed by evacuation for 10 min ($<10^{-5}$ Torr). Spectra of the catalyst pellet were taken before and after CO chemisorption. Thus, the intensity of the bands associated with the chemisorbed CO was determined by subtracting the spectrum of the pellet prior to exposure to CO from that acquired after removing the gaseous and weakly interacting CO.

FTIR was used to monitor changes in the catalyst surface under *in situ* reaction conditions. The reaction was conducted by introducing 10 Torr CF_3CFCl_2 and 10 Torr H_2 into the cell while the catalyst pellet temperature was maintained at 473 K. The reaction was run for the desired length of time. To regenerate the catalyst the cell was evacuated to a pressure of $<10^{-5}$ Torr at 473 K for 10 min and the pellet was heated to 673 K (8 K/min) while maintaining the same vacuum. Then, the used catalyst pellet was reduced in H_2 (30 ml/min) at 573 K following the same procedure as for the fresh catalyst. The irreversible changes in the support and the metal after reaction were probed by CO chemisorption by monitoring changes in intensity and position of the characteristic CO vibrations.

RESULTS

Table 1 summarizes the characterization of the six catalysts used for this investigation. While it must be pointed out that these results are dependent upon the preparation procedure, there were two trends that were apparent from these analyses. First, as fluorine content increased during the conversion of alumina (245 m^2/g) to aluminum fluoride (33 m^2/g), the surface area decreased by approximately an order of magnitude. Second, there were two distinct dispersion regimes. For catalysts containing up to 5% fluorine the Pd dispersion was 12–14%, whereas for the high fluorine content catalysts the dispersion was only 6–7%. This resulted in corresponding regimes of Pd particle size (6.4–7.5 nm for low F, and 12.9–15 nm for high F content catalysts).

With respect to the reaction kinetics the hydrodechlorination of 1,1-dichlorotetrafluoroethane (CF_3CFCl_2) catalyzed by Pd supported on γ-Al_2O_3 containing 0 to 5% fluorine exhibited an initial deactivation period followed by a gradual approach to steady state (Fig. 1). Catalyst deactivation was most rapid during the first 5 h on stream, during which up to 30–40% of the initial activity was lost. The rapid

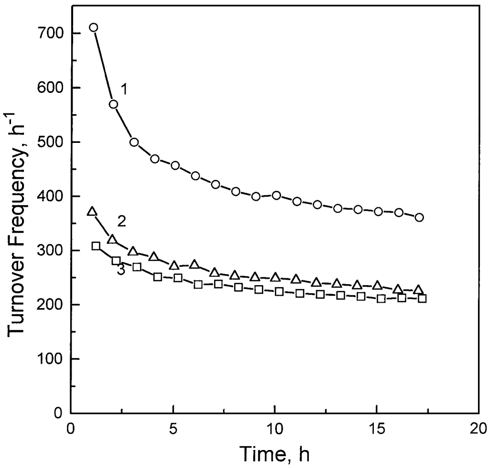


FIG. 1. Activity vs time on stream in dechlorination of CF_3CFCl_2 over 1 wt% Pd supported on Al_2O_3 (1), 2%F–Al_2O_3 (2), and 5%F–Al_2O_3 (3) at 473 K.

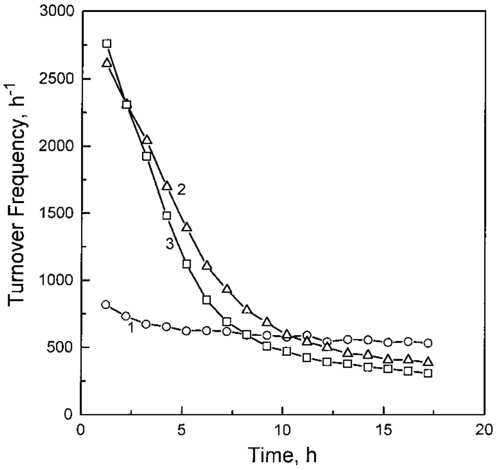


FIG. 2. Activity vs time on stream in dechlorination of CF_3CFCl_2 over 1 wt% Pd supported on 10%F–Al_2O_3 (1), 30%F–Al_2O_3 (2), and AlF_3 (3) at 473 K.

deactivation was followed by a slower rate of deactivation, approximately 1% per h for the duration of the experiment. On a "per exposed metal atom" basis (Fig. 1), the initial activity of the alumina-supported catalyst was nearly double that of the 2 and 5% fluorine samples (720 h^{-1} vs ~360 h^{-1}). At the end of each 20 h experiment, the activity of the alumina-supported catalyst was still higher than that of the other two catalysts.

The qualitative time-on-stream behavior for catalysts with high fluorine contents (10% F–Al_2O_3, 30% F–Al_2O_3, AlF_3) was similar to that of the samples containing up to 5% F, namely an initial deactivation period followed by a slow approach to steady state (Fig. 2). However, a number of features were markedly different. The magnitude of deactivation was higher for the 30% F and AlF_3 catalysts, each losing ~80% of its initial activity. These catalysts were also initially more active (more than three times higher than with alumina). Even though the activity decreased markedly, the long-term activity of the high fluorine content catalysts was still ~40% higher than that obtained with the 2–5% F containing samples. It is worth noting that the higher fluorine content catalysts have similar, but lower, Pd dispersion compared to low fluorine containing samples (Table 1). As was shown previously, an increase in particle size of alumina-supported Pd from 11 to 53 nm results in an increase in the hydrodechlorination TOF of CF_3CFCl_2 from 2.3 to 5.0 s^{-1} (12). A similar result, a twofold increase in TOF when metal particle size in Pd/Al_2O_3 catalysts was increased from 1.5 to 8 nm, was observed for of CF_2Cl_2 dechlorination (9). However, there is a relatively small change in TOF when Pd dispersion decreased from 12–14% to 6–7% (Figs. 1 and 2). Such a small change does not allow us to address this issue in the discussion below.

Surprisingly different behavior was observed when CF_2Cl_2 was the reactant, as shown in Fig. 3 for 1% Pd supported on Al_2O_3, 30% F–Al_2O_3, and AlF_3. More stable activity as a function of time on stream was observed when CF_2Cl_2 was the reactant in comparison to CF_3CFCl_2 (Figs. 1 and 2). The catalyst deactivated less than ~30% during the first several hours on stream with CF_2Cl_2, (independent of the support used) compared to ~50% deactivation when using CF_3CFCl_2. It was also evident that under similar conditions, the one carbon CFC (CF_2Cl_2) had an initial activity of 30 to 80 times less than that of its two carbon analog (CF_3CFCl_2). As mentioned in the Experimental section, the space velocity was a factor of 10 lower for the CF_2Cl_2 reaction, and thus the contact time was a factor of 10 greater. Considering the results on a TOF basis, the alumina-supported catalyst had lower activity than the 30% F or AlF_3. This trend was the same for both reactants.

Selectivity was also a function of time on stream. Table 2 summarizes the initial versus steady state selectivity

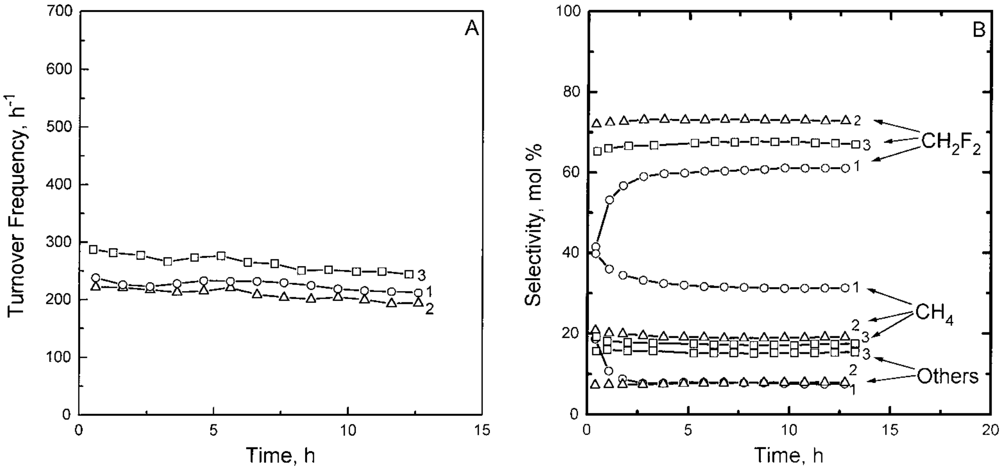


FIG. 3. Activity (A) and selectivity (B) vs time on stream in dechlorination of CF_2Cl_2 over 1% Pd supported on Al_2O_3 (1), 30%F–Al_2O_3 (2), and AlF_3 (3) at 473 K.

behavior for the hydrodechlorination of CF_3CFCl_2. Three major products were formed—CF_3CFH_2, CF_3CH_3, and CF_3CFHCl—comprising >90% of the products. The remaining products were methane, ethane, and ethylene. For the low F content materials (Al_2O_3, Al_2O_3–F(2%), and Al_2O_3–F(5%)) the selectivity to CF_3CFH_2 increased from ~45 to ~75% in 15 h time on stream. In the same time period the selectivity to CF_3CH_3 decreased from ~40 to ~20%. Surprisingly, the selectivity to CF_3CFHCl remained nearly constant at ~5%.

The high F content catalysts exhibited different behavior (Table 2). For the Al_2O_3–F(10%), the selectivity to CF_3CFH_2 decreased from 80 to 71%, while the selectivity to CF_3CH_3 increased from 15 to 21%. There was also a slight increase from 3 to 8% in CF_3CFHCl formation. Similar behavior was observed for the 30% fluorinated sample and the aluminum fluoride; the selectivity to CF_3CFH_2 decreased from 86–69% and 76–53%, respectively. There was also a corresponding increase in the production of CF_3CH_3 (7–24% for the Al_2O_3–F(30%) and 16–37% for the aluminum fluoride). The selectivity to CF_3CFHCl remained constant for each catalyst, at 6 and ~8%, respectively.

Figure 3B shows the selectivity behavior of 1% Pd supported on Al_2O_3, Al_2O_3–F(30%), and AlF_3 catalysts for the CF_2Cl_2 dechlorination reaction as a function of time on stream. The major products of this reaction were CF_2H_2 and CH_4, accounting for >85% of the total products. Other products observed were CF_2HCl, C_2H_6, CH_2FCl, CH_3Cl, CF_3Cl, and CH_3F, none of which comprised more than 3% of the reaction products. Several important observations are made from Fig. 3B. With the alumina support, the selectivity to the desired product (CF_2H_2) increased 20% in the first 5 h time on stream, which corresponded to a decrease in the selectivity to the other products (CH_4, CF_2HCl, C_2H_6, CH_2FCl, CH_3Cl, CF_3Cl, and CH_3F). However, there was no significant change (<2%) in the time-on-stream selectivity with the 30% F–Al_2O_3 and aluminum fluoride. Also, the selectivity toward the desired product was lower for the alumina support (~60%) than for the fluorinated supports (65–73%). A complete summary of the time on stream selectivity for the C_1 and C_2 reactants is given in Tables 2 and 3.

Characterization of each catalyst was done by FTIR. Figure 4 shows the FTIR spectra associated with CO adsorbed on Pd supported on Al_2O_3, 2% F–Al_2O_3, 10% F–Al_2O_3, and AlF_3. The bands at wave numbers between 2200 and 1800 cm^{-1} are characteristic of CO adsorbed on Pd (13), while the bands in the 1200 to 1800 cm^{-1} range have been previously assigned to CO interacting with the Al_2O_3 support (14). The position of each band did not shift as a function of the degree of fluorination. This is a particularly important observation with respect to the vibrations associated with CO adsorbed on the metal (1800–2200 cm^{-1}), as previous investigations have suggested that a shift in the position is indicative of an electronic change of the Pd (15). However, more detailed investigations are needed to answer whether the electron state of Pd depends on the degree of support fluorination, as the position of CO absorption band is determined by both electron state of adsorption center and CO coverage.

TABLE 3

Initial and Steady-State Selectivities of the Supported 1 wt% Pd Catalysts Studied in the Reactions of CF_2Cl_2 Dechlorination

	Selectivity[a]						Conversion (%)	
	CF_2H_2		CH_4		CFHCl			
Support	1 h	15 h	1 h	15 h	1 h	15 h	1 h	15 h
Al_2O_3	53	61	36	31	1	1	6.0	6.0
30% F–Al_2O_3	72	73	20	19	2	2	4.0	3.5
AlF_3	66	67	18	18	2	2	4.5	3.5

[a] Other products observed were CF_2HCl, C_2H_6, CH_2FCl, CH_3Cl, CF_3Cl, and CH_3F, none of which comprised more than 3% of the reaction products.

The intensity of the bands associated with CO adsorbed on the catalyst varied as a function of fluorination. The single peak at ~2100 cm^{-1}, characteristic of CO linearly bonded with Pd, decreased in intensity as a function of fluorine content. The peak and shoulder just below 2000 cm^{-1} have been previously assigned to CO bridge-bonded to two Pd atoms (13). The most dramatic change in intensity, however, was associated with CO adsorption onto the support. Spectrum 1 in Fig. 4 shows the adsorption of CO on Al_2O_3 in the absence of Pd, demonstrating that the peaks below 1800 cm^{-1} are associated with the alumina support; most belong to vibrations of surface carbonates (15). The peaks below 1800 cm^{-1} were most intense for the Pd on Al_2O_3 (spectrum 2). The reason for their increased

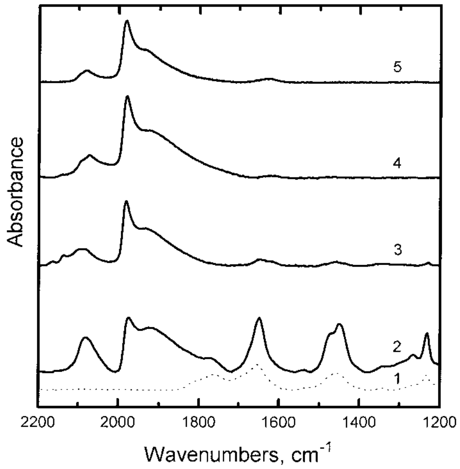


FIG. 4. IR spectra of CO adsorbed on pure alumina (1) and 1% Pd supported on Al_2O_3 (2), 2% F–Al_2O_3 (3), 10% F–Al_2O_3 (4), and AlF_3 (5).

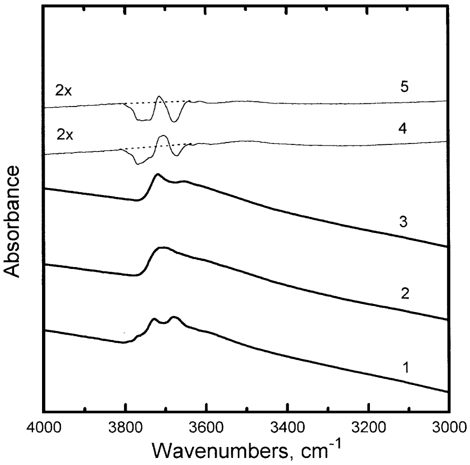


FIG. 5. IR spectra of the surface OH groups of 1% Pd supported on Al_2O_3 (1), 2%F–Al_2O_3 (2), and 10%F–Al_2O_3 (3). Spectra 4 and 5 represent the difference spectra obtained by subtraction of spectrum 1 from spectra 2 and 3, respectively.

intensity compared to pure support is not clear and needs further investigation. However, the intensity of these peaks dramatically decreased for the 2% F–Al_2O_3 catalyst as a result of the decrease in the surface concentration of oxygen resulting from fluorination. At higher fluorine content the peaks were absent (spectra 4–5).

Fluorination also influenced the hydroxyl region of the FTIR spectra. Figure 5 shows the FTIR spectra of the OH region for the Al_2O_3, 2% F–Al_2O_3 and 10% F–Al_2O_3 catalysts. The characteristic peaks associated with hydroxyl groups on the catalyst surface are in the 3000 to 4000 cm^{-1} range (16). Several broad bands between 3680 and 3745 cm^{-1} were present. These bands have previously been assigned to OH groups of varying acidity (16). Subtraction of the Al_2O_3 spectrum from the fluorinated samples (4 and 5) revealed that several vibrations were absent for the fluorinated samples. In addition, the difference spectra showed that the fluorination of the support resulted in the formation of a new peak at 3710 cm^{-1}.

Carbon monoxide adsorption was also used to monitor the changes in the catalyst surface after reaction with CF_3CFCl_2 in the presence and absence of hydrogen. Similar to the effect of prefluorination, the bands in the low-frequency region (1800–1300 cm^{-1}) were absent after *in situ* reaction of CF_3CFCl_2 alone and in the presence of H_2 at 200°C (Fig. 6A). For spectra 2 and 3 the sample pellet was pretreated, as described in the Experimental section, prior to CO adsorption. The Pd was also altered during the hydrodechlorination reaction. There was a decrease in the intensity of the 2080 cm^{-1} peak and a slight increase in the peak at $\sim$1920 cm^{-1}, in both cases in comparison to the fresh sample.

Exposure of the catalyst to CF_3CFCl_2 alone and in the presence of H_2 affected the concentration of the surface hydroxyl groups (Fig. 6B). The difference spectra presented in Fig. 6B show the loss of OH groups during reaction with CF_3CFCl_2 alone and in the presence of H_2. The behavior was similar to the effect of prefluorinating the support.

DISCUSSION

The corrosive and highly reactive nature of the halogenated species which are formed on the surface of the catalyst or as products of the hydrodehalogenation reaction contributes to the highly dynamic behavior observed in these systems. The results of the present investigation provide a framework in which to understand the interaction of these halogenated species with the supported metal

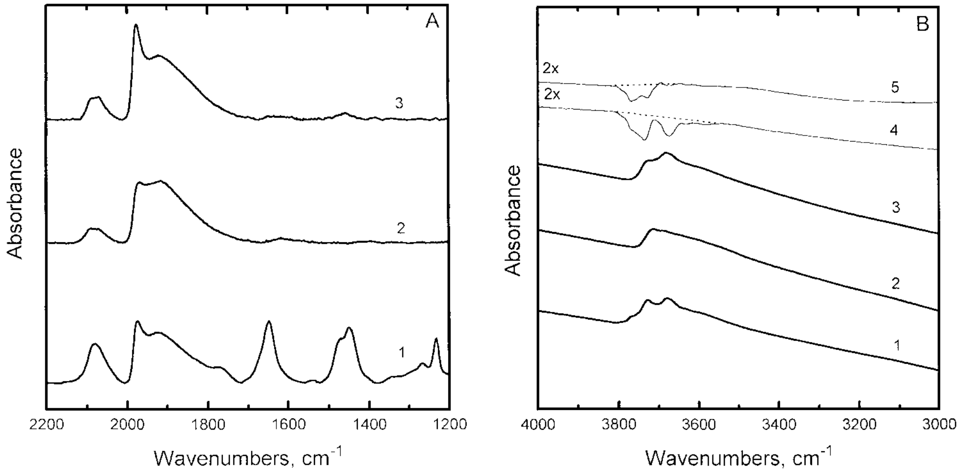


FIG. 6. IR spectra of CO adsorbed on (A) and surface OH groups of (B) fresh 1% Pd/Al_2O_3 catalyst (1), regenerated 1% Pd/Al_2O_3 catalyst following the 90 min exposure to $CF_3CFCl_2 + H_2$ at 473 K, and the fresh 1% Pd/Al_2O_3 catalyst after 90 min exposure to CF_3CFCl_2 at 473 K. Curves 4 and 5 represent the difference spectra obtained by subtraction of spectrum 1 from spectra 2 and 3, respectively.

catalyst. Two primary facets of the chemistry are worth considering: the influence of halogenated species on the supported metal catalysts and the effect of these changes on the overall catalytic performance.

Fluorination Mechanism

It is well established that alumina is fluorinated by a variety of reactants. Typical reactants include gaseous or aqueous HF; ammonium bifluoride in either the gas or the aqueous phase; and fluorocarbons such as HCF_3, CF_4, and C_6H_5F (10, 17). The reactions of alumina with the HF and NH_4HF_2 are generally carried out at temperatures near 600°C (to produce anhydrous AlF_3 in the case of gas phase reactions). The reactivity of organic fluorine containing compounds varies significantly. A temperature range of 400–600°C is usually used for aluminum oxide fluorination with organic fluorocarbons. However, as was shown by IR spectroscopy, CHF_3 interacts with the surface of γ- and η-Al_2O_3, resulting in CO formation even at room temperature and pressures of only several Torr (18). Thus, it appears reasonable to conclude that in the present system the CF_3CFCl_2 reactant modifies the alumina, as supported by the results presented in Fig. 6B. In the presence of hydrogen this process is even accelerated because both HF and HCl formed during dechlorination reaction readily react with alumina. The support of the Pd/Al_2O_3 catalyst under conditions of CF_2Cl_2 hydrodechlorination (200°C) is reported to turn into a mixture of aluminum fluoride and aluminum oxifluoride (4, 9).

The results of support fluorination via exposure to HF bring up several points that are worthy of discussion. When aqueous HF is used, the surface areas of the fluorinated samples are relatively low (Table 1), as much as five times lower than the parent Al_2O_3 in the case of 30% F–Al_2O_3 (the surface area of aluminas fluorinated with CHF_3 decrease by less than a factor of two for samples with a comparable content of fluorine) (10). The reason for this difference becomes evident from consideration of the alumina fluorination conditions. An acid will catalyze the hydration of aluminum oxide, resulting in its partial dissolution followed by reprecipitation. Consequently, this results in a dramatic change of the initial Al_2O_3 structure and a significant decrease in surface area, even if there is a low degree of fluorination. Indeed, aqueous HF-prepared AlF_3 samples do not always exhibit a strong correlation between AlF_3 content and surface area (10). The AlF_3 used in the present investigation had a surface area of 33 m^2/g. This is substantially higher than previously reported for pure rhombohedral AlF_3 (3.3 m^2/g) (10). This suggests that residual Al_2O_3 is present, which leads to the higher surface area (19). It is reasonable to conclude that the aluminum oxide in AlF_3 is formed by the water of crystallization, which is capable of hydrolyzing Al–F bonds during calcination (20).

Support Acidity

An understanding of the factors which affect support acidity is always important because of its impact on side reactions. Several authors (21–26) have concluded that it is possible to create, by fluorination, both strong Brønsted acid sites and strong Lewis acid sites on the surface of γ-alumina. The FTIR results highlight the dynamic behavior of surface hydroxyl groups during fluorination—one group forms while the other is consumed (Figs. 4 and 5). It is generally accepted that, after fluorination, the less acidic hydroxyl groups are removed while hydroxyls of strong acidity are created (25). The possible production of strong Brønsted acid sites is most plausible for the AlF_3 used in this investigation, given the conditions of pretreatment. As mentioned above, calcination of hydrated AlF_3 at temperatures above 300°C favors hydrolysis of Al–F bonds. Under such conditions the resulting concentration of Al_2O_3 is in excess of 8% (20).

The effect of fluorine atoms in the vicinity of a hydroxyl group will increase the acidity of the support. Fluorination of γ-Al_2O_3 usually results in an increase in the total number of acid sites and the acid strengths for both Brønsted and Lewis sites (27). Infrared studies of CO_2 and CO adsorption show that fluoride strengthens certain Lewis acid sites (α-sites) of alumina (17). Due to the inductive effect of fluoride, the partial replacement of O and OH by F results in an increase in the acidity of fluorinated aluminas. However, even pure aluminum fluoride itself, without any trace alumina, can possess strong Lewis acidity (28).

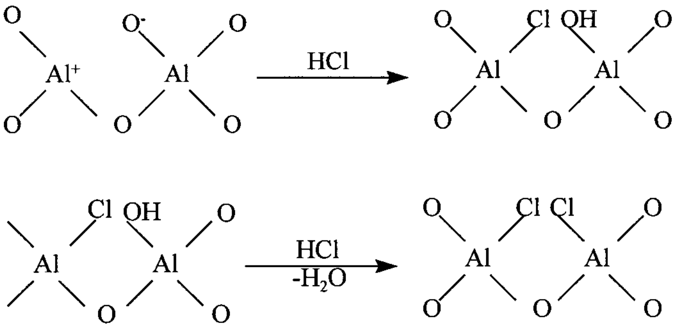
Catalytic Performance

One trend that has been established in the present investigation is that both catalytic activity and selectivity change as the degree of halogenation of the support changes. The activity for all of the catalysts which were tested (1% Pd deposited on Al_2O_3; AlF_3; and aluminas containing 2, 5, 10, and 30 wt% of fluorine) decreased during the first 5–10 h time on stream (Figs. 1 and 2). There are several possible reasons for this deactivation: deposition of carbonaceous species, deposition of halogens, consumption of support oxygen atoms which results in a decreased rate of reaction with the support, and loss in Pd dispersion during runs. The last reason is unlikely, because before catalytic test all catalysts were presintered at 500°C for 8 h in flowing oxygen.

The FTIR data clearly show direct reaction with the support. However, taking into account that fluorocarbons show significant rate of interaction with bulk alumina at temperatures above 400°C and typical reaction temperatures are 100–200°C lower (10), it is reasonable to suggest for the present investigation that dichlorotetrafluoroethane reacts with the alumina surface much faster than with the bulk. Moreover, given that the types of products which are formed during the initial deactivation period are the same as those formed during the steady-state period, it is reasonable to conclude that direct reaction with the support does not strongly contribute to the overall performance of the system.

The inhibiting effect which chlorine has on the hydrodechlorination reactions has been established in a couple of investigations. It was shown for chlorobenzene dechlorination over alumina-supported palladium that the reaction kinetics can be interpreted in terms of a steady state between the chlorination of the metallic surface by chlorobenzene and hydrogen chloride and the reduction of the chlorine-covered metallic surface (29). The reaction order in HCl during CF_3CFCl_2 dechlorination over polycrystalline Pd foil is reported to be negative (30); thus as Cl surface coverage increases, reaction rate decreases. In the present work, the Pd surface is free of chlorine at the start of the reaction. Deactivation of the catalyst occurs as the system approaches a steady-state coverage of chlorine (halogen).

In the context of influencing the coverage of chlorine (or fluorine) on the Pd surface, the support material can be considered a "sink" during the initial transient period. Molecules of HCl or chlorine atoms formed via the dissociation of carbon–chlorine bonds (as well as H atoms formed from dissociation of adsorbed hydrogen) should be sufficiently mobile to "spillover" onto the support. Once associated with the support, they can react with the support according to the scheme as shown below:



The activity results for CF_2Cl_2 are consistent with the idea that chlorine accumulation on the metal surface contributes to the decrease in activity at early time on stream. The CF_2Cl_2 molecule is a factor of 2–5 (depending on the support) less reactive than CF_3CFCl_2 (Fig. 3A). This lower reactivity would result in a lower rate of Cl atoms deposition (if the rate determining step is cleavage of the first C–Cl bond). Nevertheless, "spillover" of halogen from the metal to the support can still occur, resulting in a change of support acidity as described for the CF_3CFCl_2 system.

In light of the role of the support as a sink for halogen during the transient period of the reaction, the impact of increasing the acidity of the support can be more clearly understood. Carbonaceous deposits form more rapidly on the more acidic supports. If AlF_3 and 30%F/Al_2O_3 indeed possess the highest acidity, one can visualize a rapid deposition of coke onto the support. This has the direct consequence of making the oxide site unavailable to react with halogen species spilling over from the metal on which the reaction occurs. Carbonaceous deposits can migrate onto the surface of metal particles, making it inaccessible for reactant adsorption. The relatively low deactivation for the three samples with a low concentration of fluorine fits well with this interpretation in that their lower acidity would result in a slower rate of carbonaceous deposit formation. Hence, more sites would be available for halogen uptake. It is noteworthy that the more carbon atoms in a hydrocarbon molecule, the easier the molecule undergoes coking on acid sites of a catalyst (31). This might be another reason for the lower rate of catalyst deactivation for CF_2Cl_2 dechlorination compared to that of CF_3CFCl_2.

The impact which the change in the catalytic material has on selectivity is most pronounced when the ratio of defluorinated product to dechlorinated product (CF_3CH_3/CF_3CFH_2) is compared. For bulk Pd, the selectivity of CF_3CFCl_2 conversion toward CF_3CFH_2 is 78–82% for the Pd(111) plane (32) and reaches 85% for polycrystalline Pd foil (30). All the catalysts studied have similar, close to bulk Pd, selectivity; however, the catalysts supported on Al_2O_3 or low fluorinated supports (2%F/Al_2O_3, 5%F/Al_2O_3) exhibit this selectivity after 15 h on stream and the catalysts supported on 10%F/Al_2O_3, 30%F/Al_2O_3, and AlF_3 exhibit it after 1 h on stream. Thus, the results can be divided into two categories: selectivity changes associated with low fluorinated supports and selectivity changes associated with highly fluorinated supports.

The selectivity changes with time on stream can be understood in terms of the influence of adsorbed/absorbed fluorine on dehalogenation ability of Pd. Coq *et al.* (9) suggested that fluorine atoms occluded into Pd were responsible for the decreased selectivity toward CH_2F_2 in the reaction of CF_2Cl_2 dechlorination. The same might be true for CF_3CFCl_2 dechlorination, i.e., fluorine incorporated into Pd favors defluorination. In case of low fluorinated supports the availability of oxygen atoms in the vicinity of metal particles creates the driving force for defluorination of the substrate followed by the further fluorination of support. In contrast to the increasing selectivity with time on stream for the low fluorine containing supports, the decrease in selectivity for the highly fluorinated supports suggests the accumulation of halogen (namely fluorine) with time on stream on the metal surface and/or in bulk since Pd itself has some intrinsic defluorination activity. The reactivity of CF_2Cl_2 is much lower compared to that of CF_3CFCl_2, and changes in selectivity with time are less pronounced.

CONCLUSIONS

The catalytic performance of Pd supported on Al_2O_3, AlF_3, and partially fluorinated aluminas was studied for the hydrodechlorination of CF_3CFCl_2 and CF_2Cl_2. For reactions involving CF_3CFCl_2, all catalysts exhibit a rapid and significant decrease in activity; however, little change in activity with time on stream occurs with CF_2Cl_2. The catalyst deactivation during transient period is rationalized in terms of chlorine (fluorine) poisoning and carbonaceous species deposition on the Pd surface. It was also established that the CFC interacts with the support, resulting in halogenation of the surface. Alumina is converted to an aluminum fluoride-type species followed by the consumption of surface hydroxyl groups. The relative rate of support fluorination by the reactant is proportional to the inverse initial F concentration.

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