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Transient kinetics investigations of reaction intermediates involved in CF_2Cl_2 hydrodechlorination

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Abstract

The reaction intermediates formed during hydrodechlorination of CF_2Cl_2 catalyzed by Pd supported on AlF_3 have been investigated using steady state and transient kinetics experiments. The formation of the coupling product C_2H_6 and its dependence on H_2 partial pressure have been used to investigate the pathways by which possible surface carbene species react. Reactions of surface species formed during the CF_2Cl_2 hydrodechlorination with scavenging agent C_2H_4 yielded addition products typical of metal-carbenes. Information from these experiments suggests that for carbene and fluorocarbene species formed on the surface of a Pd/AlF_3 catalyst the rates of hydrogenation vs. coupling reactions are different.

Keywords: Dechlorination; CF_2Cl_2; CFC; Palladium; Carbene; Hydrodechlorination

1. Introduction

The widespread interest in converting halogenated compounds into environmentally benign materials has motivated many recent investigations [1–6]. Of particular importance is the conversion of chlorofluorocarbons (CFCs) to hydrofluorocarbons (HFCs). HFCs are now utilized as refrigerants, heat transfer media, aerosol propellants, solvents, etc. [7–9]. The hydrodechlorination reaction is catalyzed by noble metals [10]; for CFC hydrodechlorination, Pd-supported on high surface area materials has shown excellent activity and selectivity.

Efforts to understand the hydrodechlorination reaction mechanism have focused on chemical reaction kinetics [4–6,11,12]. Based on the product distribution analysis for the hydrodechlorination of CF_2Cl_2 [5] and CF_3CFCl_2 [6], surface fluorocarbenes are speculated to be the reaction intermediates. This suggestion is centered on the observation of high selectivity towards the product in which both chlorine atoms are replaced by hydrogen atoms. However, direct evidence for the metal-carbene species is lacking. Moreover, there is little fundamental understanding of the stability and reactivity of metal-carbenes in heterogeneous catalytic systems.

The reactivity of carbenes and fluorocarbenes has been extensively studied for homogeneous gas phase reactions. Carbenes readily undergo coupling reactions and addition to saturated or unsaturated molecules. Reactions of carbenes with olefins typically yield products formed through the addition of the carbene to the olefin double bond [13]. The specificity

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of these addition reactions has been used to identify different types of carbenes and to compare their chemical reactivity [14]. Many of the same reactions take place in the homogenous liquid phase media. Reactions using organometallic catalysts have been central in the formation of polymers and olefins via metal-carbene intermediates [15].

In contrast to the body of homogeneous work, relatively few studies of carbene chemistry have been carried out with heterogeneous catalytic systems. "Reactive scavenging" has been used to investigate the surface intermediates formed over heterogeneous catalysts [16]. This technique involves the chemical reaction of a scavenging agent (olefin) with an adsorbed surface intermediate leading to the formation of specific addition products. For example, using ethylene and cyclohexene as scavenging agents of surface species formed during Fischer–Tropsch synthesis catalyzed by supported Ru, Ekerdt and Bell [17] observed the formation of propene, methyl and ethyl cyclohexene, respectively. From the analysis of the product mixtures they suggested that CH_2 surface species scavenged by the olefins were likely to be the building blocks for the chain propagation involved in the Fischer–Tropsch reactions. Wang and Ekerdt [18] further extended this technique to investigate the surface species formed over Fe/SiO_2 catalysts using pyridine and cyclohexene as scavengers. Also, addition reactions of C_2H_4 with surface carbene species formed on supported Mo catalysts during olefin metathesis have been investigated by Shelimov et al. [19] using a combination of UV–vis diffuse reflectance spectroscopy and mass spectrometry. They suggested that the formation of propene by the reaction of C_2H_4 with the adsorbed surface species was evidence for the presence of $Mo{=}CH_2$ carbene.

The present study was undertaken to investigate the role of carbenes as reaction intermediates in CF_2Cl_2 hydrodechlorination. Information about the reactivity of surface intermediates with ethylene has been obtained from this investigation. Most importantly, these transient kinetics trapping experiments have provided insight into the stability and reactivity of the surface carbenes and fluorocarbenes at temperatures and pressures used for catalytic CFC hydrodechlorination.

2. Experimental

2.1. Catalyst preparation

Two catalysts were used in this investigation: a 1 wt% Pd/AlF_3 and a 10 wt% Pd/AlF_3. Different preparation procedures were used to obtain the same metal dispersion while varying the metal loading and AlF_3 was chosen as the support because it is more stable than traditional supports in halogen environment. AlF_3 is known to catalyze the disproportionation of halocarbons – an entirely different class of reactions compared to the hydrogenation reactions under study. The presence of the Pd metal adds the hydrogenation ability to the catalyst. Reactions conducted using only the support material (AlF_3) under the standard hydrodechlorination reaction conditions (200°C, $H_2/CF_2Cl_2=3$, GHSV=10 000 h^{-1}) resulted in the formation of CF_3Cl, $CFCl_3$ and CCl_4 – all of which are present in trace quantities when using the supported Pd. For the 10 wt% Pd/AlF_3, a $Pd(NO_3)_2$ solution was prepared by dissolving 1.35 g of Pd $(NO_3)_2{\cdot}H_2O$ (Strem Chemicals, >99.9%) in 25 ml 10% HNO_3, prepared from concentrated HNO_3 (69–70%, J. T Baker); the solution was added to 5 g AlF_3 powder (Strem Chemicals, >99%). The resulting slurry was mixed (~75 rpm) at 303 K for 1 h in a rotary evaporator before the water was removed by heating from 303 to 353 K along with continuous evacuation (125 Torr) over a 4 h time period. The impregnated sample was further dried overnight at 383 K in air. The sample was then placed in a Pyrex tube (18 mm i.d.), heated to 773 K (1 K/min) in a 10% O_2/He flow (25 ml/min), and held at these conditions for 3 h. The resulting material was stored in a closed vessel. For the preparation of the 1 wt% Pd/AlF_3, a Pd(II) acetylacetonate solution was prepared by dissolving 0.292 g of $Pd(acac)_2$ (Strem Chemicals, >99%) in 250 ml toluene (J.T Baker, >99.9%). This solution was then used to impregnate 10 g of AlF_3 powder (Strem Chemicals, >99%). The resulting slurry was dried, pretreated in 10% O_2, and stored as described above.

2.2. Catalyst characterization

The metal dispersion for both, 1 wt% Pd/AlF_3 and 10 wt% Pd/AlF_3, was determined by H_2 chemisorption at room temperature using the double isotherm method [20]. The catalyst sample (0.5 g) was placed into a quartz U-tube reactor (16 mm i.d., catalyst bed height ~6 mm), heated to 773 K (4 K/min), and calcined in 10% O_2/He flow (20 ml/min) for 30 min. The sample was then evacuated at 773 K to less than 10^{-5} Torr for 15 min and cooled to room temperature under the same vacuum. The catalyst was finally reduced in H_2 flow (30 ml/min) at 573 K (8 K/min) for 1 h, evacuated at 573 K for 1 h and cooled to room temperature under vacuum ($<10^{-5}$ Torr). The metal dispersion for both catalysts was 6%. This corresponded to a Pd particle size of 15 nm using the method suggested by Benson et al. [20]. Nitrogen adsorption isotherms (at 87 K) were used to measure the support surface area. The surface areas of both the 1 wt% Pd/AlF_3 and the 10 wt% Pd/AlF_3 samples were 33 m^2/g, as calculated by the BET method.

2.3. Materials

The CFC used in this study was CF_2Cl_2 (PCR, >99%). In-house gas chromatograph analysis was used to confirm the purity. The analysis revealed that CHF_2Cl was the only detectable impurity (<1.0%) in CF_2Cl_2. Under typical reaction conditions of 473 K and H_2/CFC ratio of 3, the reactivity of CHF_2Cl was found to be less than one-tenth of that of CF_2Cl_2 [21]. Ethylene (>99.5%), O_2 (>99.5%), H_2, He and N_2 (each >99.999%) were obtained from liquid carbonic. In-house analysis revealed that CH_4 (<0.1%) was the only impurity in ethylene. All gases were used without further purification.

2.4. Catalytic experiments

The hydrodechlorination of CF_2Cl_2 was carried out at atmospheric pressure in a stainless-steel flow reaction system consisting of a quartz microreactor (10 mm i.d.) equipped with a quartz frit to support the catalyst. The reactor zone containing the catalyst was heated by an electric furnace and the catalyst temperature was measured and controlled with an accuracy of ±1 K using a temperature controller (Omega model CN2011). Reactants were metered using mass flow controllers (Brooks Instruments model 5850E) and mixed prior to entering the reactor. The reactor effluent was analyzed by on-line GC and, when necessary, GC/MS to identify the reaction products. The GC (HP 5890 series II) was equipped with a 10 ft 60/80 Carbopack B/5% Fluorocol packed column (Supelco) and a flame ionization detector (FID) capable of detecting concentrations >1 ppm for all CFCs, chlorocarbons and hydrocarbons involved in this study. The on-line HP GC/MS system consisted of a HP 5890 series II plus GC (also equipped with a Fluorocol column) connected to a HP 5972 Mass Selective Detector. Independent experiments were performed to determine possible mass transport limitations at the conditions of the CFC hydrodechlorination reaction ($H_2/CF_2Cl_2=3$, 473 K). The CFC conversion was varied by changing space velocity and the slope of the plot of conversion vs. space velocity was found to be -1. This shows the absence of inter-particle diffusion limitations. A carbon mass balance was conducted for each experiment and the amount consumed in comparison to the amount generated agreed within ±5%. HCl and HF were detected by GC/MS but not quantified.

Prior to reaction, the catalyst was treated in flowing O_2 (10 ml/min) while being heated from 303 to 773 K at the rate of 4 K/min and held at 773 K for 5 min. The catalyst was then cooled in flowing He (or N_2) to 303 K. Next, the gas stream was switched to a mixture of H_2 (20 ml/min) and He (or N_2) (30 ml/min) and the catalyst was heated from 303 to 573 K at a rate of 4.5 K/min. This step was followed by purging the catalyst in He (or N_2) (30 ml/min) at 573 K for 30 min, after which the catalyst was cooled in He (or N_2) to reaction temperature.

For a standard hydrodechlorination reaction, 0.1 g of the 1 wt% Pd/AlF_3 catalyst was used and the total flow of the reactant mixture was 30 ml/min consisting of CF_2Cl_2 (2 ml/min), H_2 (6 ml/min) and He (or N_2) as the balance. The reaction was carried out at 473 K until steady state was achieved (~ 1 h) and then the temperature or H_2/CF_2Cl_2 partial pressure was varied such that the effect of each parameter on the reaction could be studied independently. For experiments in which H_2 partial pressure was varied, both the catalyst weight and the total flowrate were adjusted, keeping a constant space velocity (10 000 h^{-1}).

Stopped-flow transient kinetic experiments were conducted using ethylene as a scavenging agent. A standard CFC hydrodechlorination reaction (as described above) was carried out until steady state was attained. Then the reactant stream was replaced with a flowing mixture of ethylene (0.5 ml/min) and He (22 ml/min) while maintaining the reaction temperature constant. Analysis by GC/MS was used to identify the products formed due to addition of the surface species to the ethylene. Typically 14 aliquots of the product stream were acquired over a 30 min time period using a 16-loop sample valve (Valco). Subsequently, these samples were analyzed quantitatively using the GC. For the transient kinetics experiments in which it was desired to increase the surface concentration of reaction intermediates available for reaction with ethylene, the CFC flow was switched on during ethylene+He flow. The product stream of this CFC+ethylene+He flow over the catalyst was also sampled using the 16-loop valve as described above. Initially, these experiments were carried out using both the 1 wt% and the 10 wt% Pd/AlF_3 catalysts. However, the extremely low concentration of trapping product (<25 ppm) necessitated the use of the catalyst with higher Pd loading in order to obtain good quantitative analysis.

3. Results

The hydrodechlorination of CF_2Cl_2 is readily catalyzed by 1 wt% Pd/AlF_3 at a reaction temperature of 473 K and H_2/CF_2Cl_2 ratio of 3. At a space velocity of 10 000 h^{-1} the conversion of CF_2Cl_2 was below 10% for all experiments. As shown in Fig. 1, the turnover frequency (TOF) or rate per exposed Pd atom, for the CF_2Cl_2 hydrodechlorination reaction was initially 0.082 s^{-1} and it decreased by ~7% during the first hour of time on stream. During the next 11 h on stream the TOF decreased at a rate of approximately 1% h^{-1}. The catalyst performance after 1 h time on stream was defined as steady-state behavior. A similar performance was observed for the 10 wt% Pd/AlF_3 catalyst.

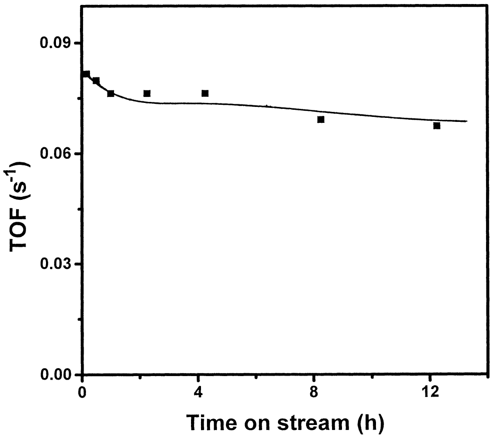


Fig. 1. Catalyst activity as a function of time on stream for the hydrodechlorination of CF_2Cl_2 over 1 wt% Pd/AlF_3. Reaction conditions: 473 K and $H_2:CF_2Cl_2=3$.

Several different products were formed during the CF_2Cl_2 hydrodechlorination reaction. The two major reaction products were CH_2F_2 (69±1%) and CH_4 (18±1%). In addition, several monochloro and monofluoro products were formed. These were CH_3Cl (<6%), CHF_2Cl (<3%), CH_3F (<2%), $CHFCl_2$ (<2%), C_2H_6 (<0.5%). Fig. 2(a) shows the selectivity towards the major products as a function of time on stream. The product selectivity pattern did not change with time on stream after the catalyst attained steady state. As shown in Fig. 2(b), at early time on stream (<1 h), the selectivity towards the two major products showed gradual change. Methane selectivity decreased from 25% to 18% while CH_2F_2 selectivity increased from 62% to 68%. However, the selectivity towards all other products changed by <1% during this period.

The partial pressure of H_2 influenced the product distribution. Of particular importance for the current investigation is the selectivity towards C_2H_6, which is shown in Fig. 3(a). Two distinct regimes are apparent with respect to the stoichiometric H_2/CFC ratio required to form the desired product, CH_2F_2-H_2 partial pressures below stoichiometric (<182 Torr, H_2/CFC <2) and H_2 partial pressures greater than stoichiometric (>182 Torr, H_2/CFC >2). At a H_2 partial pressure of 30 Torr, corresponding to a H_2/CF_2Cl_2 ratio of 0.3, the C_2H_6 selectivity was 1.5%. Increasing the H_2/CF_2Cl_2 ratio from 0.3 to 6 resulted in a rapid decrease in the selectivity towards C_2H_6. Indeed, the C_2H_6 selectivity decreased by a factor of 25 as the H_2/CF_2Cl_2 ratio was increased from 0.3 to 6. The selectivity towards CH_4 showed a trend opposite to C_2H_6 selectivity (Fig. 3(b)). As the H_2 partial pressure was decreased from 547 Torr (corresponding to H_2/CFC ratio of 6) to 30 Torr (corresponding to H_2/CFC ratio of 0.3) the CH_4 selectivity decreased from 16.7% to 14.6%. The selectivity towards the other hydrodechlorination products, including CH_2F_2, did not

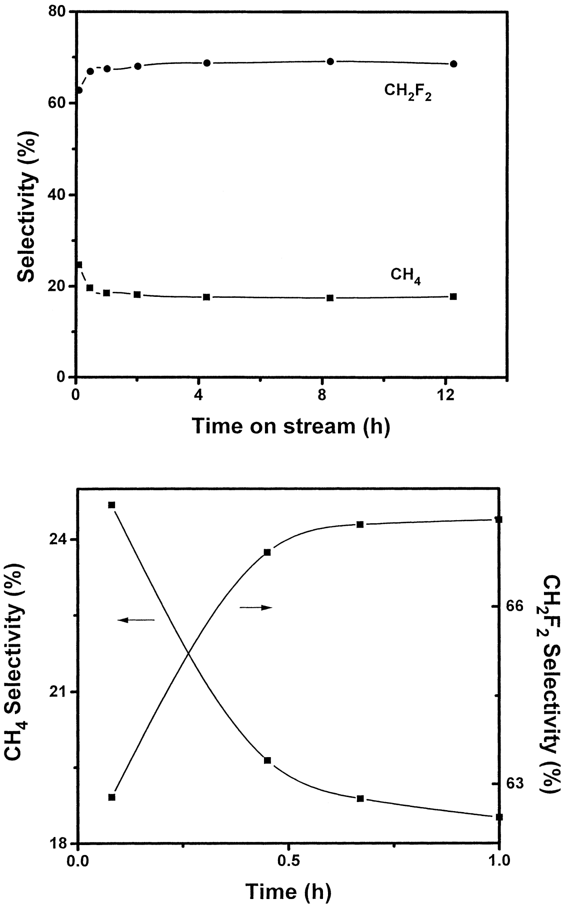


Fig. 2. Selectivities to the formation of the major products CH_2F_2 (●) and CH_4 (■) for the hydrodechlorination of CF_2Cl_2 over 1 wt% Pd/AlF_3 at long time on stream (a) and short time on stream (b). Reaction conditions: 473 K and H_2:CF_2Cl_2=3.

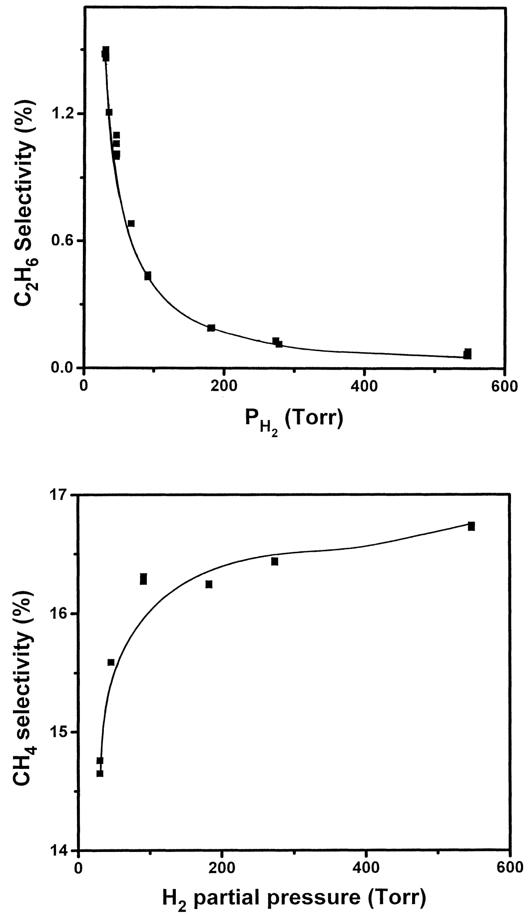


Fig. 3. Selectivity to the formation of C_2H_6 (a) and CH_4 (b) as a function of H_2 partial pressure for the hydrodechlorination of CF_2Cl_2 over 1 wt% Pd/AlF_3. Reaction temperature: 473 K.

change (within experimental error) at different H_2 partial pressures.

Pathways by which a C_2 product could be formed from a C_1 reactant were explored through the transient addition of a surface species "scavenging agent". Olefins are known for their specificity for addition to carbenes [14]. In this study ethylene was used as a scavenging agent. Fig. 4 shows the concentration of propene formed after a hydrodechlorination feed flowing and reacting at steady-state over 10 wt% Pd/AlF_3 was switched to a 2.2% ethylene flow. The reaction conditions were the same as Fig. 1. The steady-state CF_2Cl_2 conversion was ~ 10% and the selectivities towards CH_2F_2 and CH_4 were 70% and 20%, respectively. The scheme for flow changes is shown below:

$t < 0$: $CF_2Cl_2 + H_2 + He$

(steady-state hydrodechlorination reaction)

$t > 0$: $C_2H_4 + He$ (surface scavenging)

Prior to the addition of C_2H_4, no detectable amounts of propene or other C_3 compounds were present in the product stream. However, 1 min after the switch was made, the time at which the first sample was collected, the concentration of propene was 20 ppm. Subsequently, the concentration of propene decayed exponentially to less than 1 ppm over a 30 min time period. Other products detected during the transient experi-

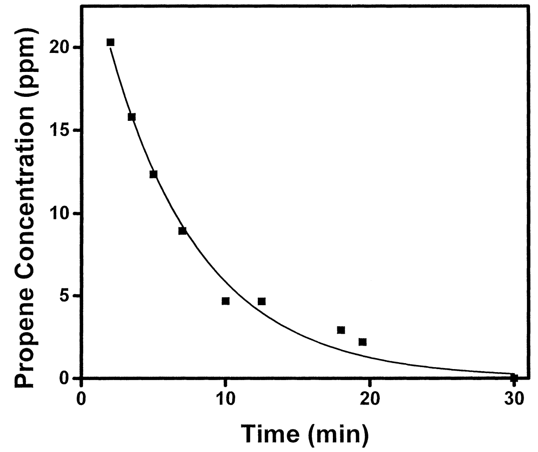


Fig. 4. Concentration of propene with time on stream during the transient kinetics experiment over 10 wt% Pd/AlF$_3$. Reaction conditions: temperature=473 K, flowrates: C_2H_4=0.5 ml/min, He=22 ml/min.

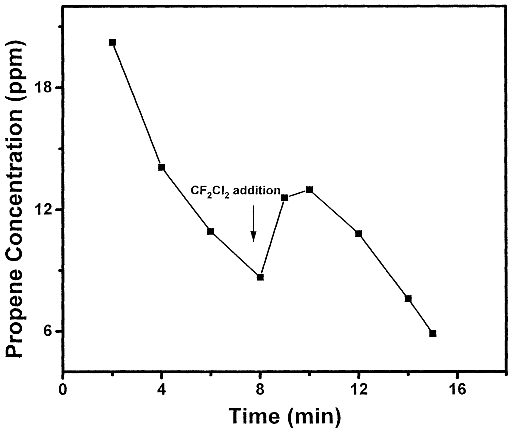


Fig. 5. Concentration of propene with time on stream during the transient kinetics experiment over 10 wt% Pd/AlF$_3$. Reaction conditions: temperature=473 K, flowrates (t<7.5 min): C_2H_4= 0.5 ml/min, He=22 ml/min, (t>7.5 min): C_2H_4=0.5 ml/min, He= 22 ml/min and CF_2Cl_2=2 ml/min.

ment were C_2H_6, CH_2F_2 and CH_4. The concentrations of CH_2F_2 and CH_4 showed a rapid step-decrease from 5430 ppm to <20 ppm and from 1215 ppm to <20 ppm, respectively. This was of course expected because the residual amounts of hydrodechlorination reactants CF_2Cl_2 and H_2 were removed from the system when the inlet stream was switched to C_2H_4. Hydrocarbon/halocarbon products higher than C_3 were not formed during the experiment in concentrations above the detectibility limit of the GC or GC/MS. The formation of all products ceased in approximately 30 min after starting the transient experiment. Blank runs with only ethylene + He were carried out on 10 wt% Pd/AlF$_3$ at 200°C. Ethylene reacted to form C_2H_6 (~97%) and CH_4 (~3%) as the only detectable products. The initial C_2H_4 conversion was ~4.8% and the catalyst deactivated rapidly reaching zero conversion in ~2 h. The formation of the reaction products could have been aided by the fact that prior to the reaction with C_2H_4, the catalyst was treated in flowing H_2 as part of the standard pretreatment.

Verification that the species which were scavenged by olefin were in fact species present on the surface of the catalyst prior to adding C_2H_4 was accomplished by adding more CF_2Cl_2 to the reaction stream. Fig. 5 shows the result of adding CF_2Cl_2 to the flowing ethylene stream. The scheme for flow changes is shown below:

$$t > 0: \quad CF_2Cl_2 + H_2 + He$$
$$\text{(steady-state hydrodechlorination reaction)}$$

$$0 < t < 7.5: \quad C_2H_4 + He \quad \text{(surface scavenging)}$$

$$t > 7.5: \quad CF_2Cl_2 + C_2H_4 + He$$
$$\text{(surface scavenging with CFC addition)}$$

During the first 7.5 min time on stream when only ethylene was entering the reactor, the concentration of propene steadily decreased. This result agrees well with the results shown in Fig. 4 for the same time interval. The continuous addition of CF_2Cl_2 for t>7.5 min of the transient experiment resulted in an immediate increase of the propene concentration to 13 ppm. Further, the propene concentration decayed from this new value to less than 1 ppm in 30 min.

Along with an increase in propene concentration, the concentration of CH_2F_2 in the product stream showed an increase with the addition of CF_2Cl_2. The concentrations of the two major hydrodechlorination products (CH_2F_2 and CH_4) formed during the transient experiment as a result of CF_2Cl_2 addition to the C_2H_4 stream are shown in Fig. 6. At early time on stream (t<7.5 min) during the ethylene scavenging experiment, the concentrations of both CH_2F_2 and CH_4 decreased. On addition of CF_2Cl_2 to the flowing

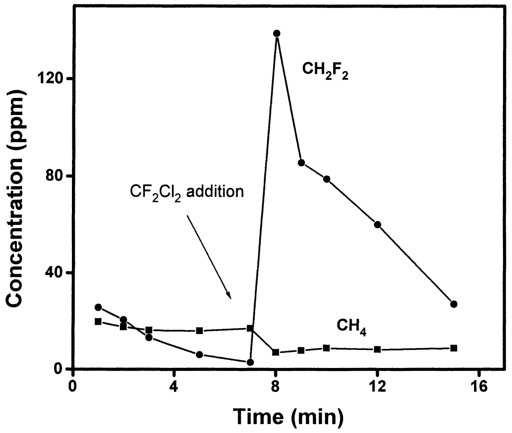


Fig. 6. Concentrations of the hydrodechlorination reaction products CH_2F_2 (●) and CH_4 (■) as a function of time during the transient kinetics experiment over 10 wt% Pd/AlF_3. Reaction conditions same as Fig. 5.

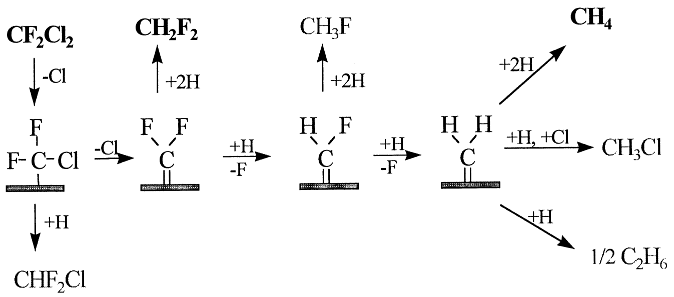
ethylene stream at *t*=7.5 min, the CH_2F_2 concentration increased by an order of magnitude in less than 1 min. Thereafter, the CH_2F_2 concentration showed a decrease with time, similar to the propene decay in Fig. 5. However, there was a small step decrease in the CH_4 concentration at the point of CF_2Cl_2 addition.

4. Discussion

Changes in reaction rate and product selectivities with time on stream can be used to investigate catalyst activity. For the CF_2Cl_2 hydrodechlorination reaction, under typical reaction conditions, the stabilization of catalyst activity is achieved after approximately 1 h of time on stream (Fig. 1). A similar trend is followed by the selectivities towards the two major reaction products, CH_2F_2 and CH_4. Changes in selectivity to these major products were observed only during the first 1 h of time on stream (Fig. 2(b)).

The attainment of steady-state as discussed above by no means suggests that the reaction network is simple. Partially dehalogenated products such as CHF_2Cl-indicating replacement of one chlorine by hydrogen and CH_3F-indicating replacement of 3 halogens by hydrogen were observed at steady-state in the present investigation as well as in previous work [5,22]. Also interesting is the formation of products CH_3Cl and $CHFCl_2$. Both these products suggest a pathway n which defluorination dominates over dechlorination. This is a surprising result considering that C–F bonds (110 kcal/mol) in CF_2Cl_2 are stronger than C–Cl bonds (76 kcal/mol) [23]. Although detailed investigations of the formation of these products during CF_2Cl_2 hydrodechlorination are lacking, it is possible that the coverage of chlorine on the metal is sufficiently high for chlorination of surface fragments to form these products. Ahn et al. [22] have suggested that chlorination of an intermediate CH_3 species leads to the formation of the product CH_3Cl. Similarly, the addition of Cl to a CHFCl surface species would account for the formation of $CHFCl_2$; however, many other pathways are also possible. Possible pathways for formation of reaction products are shown in Scheme 1.

Perhaps the most interesting aspect of the reaction is the formation of the coupled product C_2H_6. The C_2H_6 selectivity observed in the present investigation was less than 2% under all reaction conditions. More importantly, it was a strong function of the H_2 partial pressure (Fig. 3). The rapid increase in C_2H_6 selectivity as the H_2 partial pressure decreases below 182 Torr strongly suggests that coupling may be



Scheme 1. Reaction pathways and intermediates for the hydrodechlorination of CF_2Cl_2 over Pd/AlF_3.

competing with hydrogenation. It is unlikely that the contribution of the ethane hydrogenolysis reaction is important under these conditions as Karpinski et al. [6] have reported ethane hydrogenolysis rates which were more than two orders of magnitude lower than dechlorination rates on supported Pd catalysts. Comparison of Fig. 3(a) and (b) shows that as H_2 partial pressure is decreased the increase in selectivity to C_2H_6 is accompanied by a decrease in selectivity to CH_4. From the above discussion we can speculate that for CF_2Cl_2 hydrodechlorination, the formation of CH_4 and C_2H_6 takes place from the same precursor-CH_2 as shown in Scheme 1. Complete hydrogenation of the CH_2 carbene leads to the formation of CH_4, whereas C_2H_6 formation results from the coupling of CH_2 species on the Pd surface and the subsequent hydrogenation. Further, it seems likely that there is a competition between hydrogenation of CH_2 species leading to CH_4 and their coupling to form C_2H_6.

It is important to note that no fluorinated coupling products are observed for different H_2/CFC ratios during the hydrodechlorination of CF_2Cl_2 over the Pd/AlF_3 catalyst. This is surprising because the major product of the hydrodechlorination reaction, CH_2F_2, suggests the presence of CF_2 species on the catalyst surface. A variety of interpretations regarding the molecular level kinetics are possible that could account for the lack of fluorocarbene coupling products. One possible reason is that this process competes unfavorably with CF_2 hydrogenation to form CH_2F_2. Thus the lifetime of the fluorocarbene (CF_2) surface species is short, leading to a lower coupling probability. An interesting point arises when we consider bimetallic catalysts, which are known to form the coupling product. In catalytic investigations of CF_2Cl_2 hydrodechlorination over graphite-supported bimetallic Pd–Fe and Pd–Co catalysts, Coq et al. [24] have reported the formation of the coupling product C_2F_4. The formation of C_2F_4 was a strong function of both the H_2/CFC ratio in the feed and the type of catalyst. Substantial amounts of C_2F_4 were formed at H_2/CFC ratios less than one and, in agreement with the current investigation, catalysts containing only Pd metal were completely unselective towards the formation of C_2F_4. Incorporation of Fe or Co in the catalyst lead to the formation of significant amounts of the fluorinated coupling product. Moreover, the bimetallic catalysts with good selectivity towards C_2F_4 had low selectivities for the hydrogenation product CH_2F_2 relative to supported Pd catalysts. Thus, it is apparent that Pd–Fe and Pd–Co systems which seem to have poor hydrogenation capability for CF_2 species are better coupling catalysts. This suggests that hydrogenation and coupling are competing processes for the surface CF_2 species, in a similar fashion as for the surface CH_2 species.

Insight into the reactivities and lifetimes of the possible CF_2 and CH_2 surface species can be obtained by considering the transient kinetics investigations conducted in this work. The focus of these experiments was to selectively scavenge the surface species with a trapping agent, C_2H_4, under the conditions of the CFC hydrodechlorination reaction. As shown in Fig. 4, typical addition reactions yielded propene as the transient addition product, a product consistent with the addition of a CH_2 surface species to C_2H_4. A calculated estimate of the total coverage of the carbene on the exposed metal surface, assuming 100% efficiency for addition to the C_2H_4, is 3%. In gas phase addition reactions, the CH_2 addition to C_2H_4 is expected to result in the formation of cyclopropane. However, the isomerization of cyclopropane to propene is very likely given that the exothermicity of the addition reaction is $\sim$90 kcal/mol, whereas the activation energy for cyclopropane isomerization is only $\sim$64 kcal/mol [25]. It is likely that a similar rearrangement takes place over heterogeneous surfaces which accounts for the formation of propene rather than cyclopropane.

During the surface scavenging with C_2H_4 no fluorinated addition products were formed. Gas phase experiments have shown that the reactivity of CF_2 for the addition reaction with C_2H_4 is lower than that of CH_2. This trend is related to the electrophilicity of the carbenes. For addition to ethylene (or olefin) the reactivity trend is $CH_2 > CI_2 > CBr_2 > CCl_2 > CF_2$ with the most electrophilic carbene, CH_2, being the most reactive [26]. It is also possible that the carbon atom in a CF_2 species is more electron deficient due to the electronegativity of the fluorine atoms and hence CF_2 species should be more reactive towards the electron-rich C_2H_4 double bond. This apparent contradiction prevents the interpretation of our data on the basis of carbene electrophilicity. A more likely reason for the lack of fluorinated products from scavenging reactions may be the low concentration of fluorocarbene species because of their rapid reaction via the hydrogenation pathway. Analyzing the concentration of the hydrodechlorination products CH_2F_2 and CH_4, which could be assumed to be formed from CF_2 and CH_2 precursors, respectively, suggests that the rate of hydrogenation of CF_2 species is higher than that of the CH_2 species (Fig. 6). This is evident from the instant increase in CH_2F_2 concentration on the addition of CF_2Cl_2, in contrast with the step decrease in CH_4 concentration. It is important, however, to acknowledge that a more realistic comparison involves the hydrogenation of fluorocarbenes and the defluorination and subsequent hydrogenation leading to CH_4 formation. The results from this investigation clearly show that the hydrocarbon species have sufficient concentration and/or lifetime to be scavenged by C_2H_4 or to couple at low H_2 partial pressures. Clearly the cleavage of C–F bonds would be more likely to occur at sites on which the molecule adsorbs more strongly or sites which are intrinsically more active. Thus, it is plausible to speculate that the defluorination reaction pathway may involve different types of sites on the palladium particle such as edges, steps and corners. However, further investigations are necessary to substantiate this speculation.

5. Conclusions

Parallel hydrogenation pathways starting from a common intermediate CF_2 species can explain the formation of the products CH_2F_2 and CH_4 for the hydrodechlorination of CF_2Cl_2 over Pd/AlF_3. The formation of the coupling product C_2H_6 suggests the presence of CH_2 carbene species as a reaction intermediate. Transient kinetics experiments using C_2H_4 as a trapping agent for surface carbenes have provided additional support for the presence of CH_2 species. The absence of either coupling products or trapped products containing F suggests that the rate of hydrogenation of surface CF_2 species is faster than that of surface CH_2 species. Such a reactivity trend is consistent with the observed selectivities for the hydrodechlorination reaction products.

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