

FTIR and Reaction Kinetics Studies of the Hydrodehalogenation of CF₂Br₂, CH₂Br₂, and CD₂Br₂ over a Pd/ γ -Al₂O₃ Catalyst

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A combination of FTIR and chemical reaction kinetics studies was employed to investigate the hydrodehalogenation of CF₂Br₂, CH₂Br₂, and CD₂Br₂ catalyzed by Pd/ γ -Al₂O₃. The products of the CF₂Br₂+H₂ reaction (CF₂H₂, CF₃H, C₁–C₃ hydrocarbons) are typical for a reaction mechanism with the participation of :CF₂ and :CH₂ carbenes as the reaction intermediates. It was not possible to detect :CF₂ carbenes by FTIR during the adsorption studies. It is proposed that the carbenes are unstable on the Pd surface in the absence of H₂ and readily decompose to form carbonaceous deposits and adsorbed halogen atoms. Thus, room-temperature hydrogenation of the surface species formed during adsorption of CF₂Br₂ on Pd/ γ -Al₂O₃ at room temperature yields only CH₄, HBr, and HF. The :CD₂ and :CH₂ carbenes formed from dissociation of CD₂Br₂ and CH₂Br₂ adsorbed on the Pd surface are stable at room temperature, as indicated by the formation of CD₂H₂ upon hydrogenation of adsorbed species by H₂ and D₂, respectively.

Introduction

Dehalogenation has developed into an important branch of environmental catalysis. Although the macroscopic performance of many catalytic systems has been documented, fundamental research is still needed to develop a molecular level description of the elementary reaction steps. Of particular importance are the factors that affect the activation and cleavage of the C–X bond and the hydrogenation of the surface alkyl fragments and halogen atoms. Both the cleavage of the first C–X bond^{1–3} and the hydrogenation of surface chlorine⁴ have been proposed to be the rate-determining step of the reaction.

Supported noble metals are used as catalysts for halocarbon conversion reactions.^{5–8} The rate of C–Cl bond cleavage and the rate of hydrogenation of surface chlorine are sufficiently fast for commercial applications and the deactivation can be controlled.^{6,9–14} Supported palladium catalysts are selective for the complete hydrodechlorination of CFCs to yield hydrofluorocarbons.^{6,9–14} Under steady-state reaction conditions, the CF₂Cl₂ is converted into CF₂H₂ over alumina-supported Pd with the selectivity higher than 60%.¹⁵ On the basis of the analysis of the product distribution of CF₂Cl₂ hydrodechlorination, it was concluded that the reaction pathway includes the participation of difluorocarbenes.^{6,11,12,16}

With CFCs containing two carbon atoms, several surface species have been identified spectroscopically. The adsorption of CF₃CFCl₂ on the surface of a Pd/ γ -Al₂O₃ catalyst at room temperature results in the formation of adsorbed CF₃CF= carbene and CF₃C≡ trifluoroethylidyne species that were identified by their IR spectra.¹⁷ These surface species are hydrogenated to CF₃CFH₂ and CF₃CH₃, the products of the CF₃-CFCl₂+H₂ reaction, upon exposure to H₂ at room temperature. However, there is no direct spectroscopic evidence that :CF₂

carbenes form as intermediates during the hydrodechlorination of CF₂Cl₂. In the presence of hydrogen, supported Pd catalyzes the conversion of CF₂Cl₂ into methane and a mixture of saturated and unsaturated hydrocarbons C₁–C₄. This indicates that C–F bond dissociation also takes place on the Pd surface and suggests that, similar to the Fischer–Tropsch reaction,^{18–20} the :CH₂ carbenes may be a reaction intermediate for the reaction of hydrocarbon formation from CF₂Cl₂ and CH₂X₂.¹²

Thus, it was our objective to probe by spectroscopy and kinetics the surface species that are formed from C₁ halocarbon conversion reactions catalyzed by supported noble metals. The spectroscopic investigations were linked to kinetics investigations through the use of the same catalyst, Pd/ γ -Al₂O₃, and the catalyst pretreatment conditions. The bromofluorocarbon molecule (CF₂Br₂) was used instead of CF₂Cl₂, as the C–Br bonds are weaker than the C–Cl bonds and would facilitate the formation of the :CF₂ carbenes during adsorption. When interpreting the results from this investigation, it was assumed that the mechanisms of CF₂Br₂ debromination and CF₂Cl₂ dechlorination catalyzed by Pd are the same and the effect of the coadsorbed surface halide on the bonding and reactions of the surface species is small.²¹ Another aspect of the research centered on the dissociation of CH₂Br₂ and CD₂Br₂ on the surface of alumina-supported Pd to form adsorbed :CH₂ and :CD₂ carbene species, and the reactivity of these species toward coadsorbed H atoms was also investigated.

Experimental Section

A 5% Pd/ γ -Al₂O₃ catalyst was prepared by impregnation of powered γ -Al₂O₃ (Vista-B, 300 m²/g, average pore diameter, 55 Å) with an aqueous solution of Pd(NH₄)Cl₂·H₂O (Alfa, 99.9% purity). The material was dried in air at ambient temperature for 10 h and then at 373 K for 20 h. The catalyst sample was treated with flowing O₂ (60 mL min^{–1}) while heated from ambient temperature to 773 K at the rate of 4 K min^{–1} and held at 773 K for 1 h. Then, it was cooled to ambient temperature in flowing O₂ and purged with He (60 mL min^{–1}) for 15 min. The He flow was switched to H₂ (90 mL min^{–1}).

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The catalyst was heated to 573 K at the rate of 4 K min⁻¹, held at 573 K for 1 h followed by purging with He (60 mL min⁻¹) at the same temperature for 15 min, and cooled to room temperature. Subsequently, the fraction of Pd atoms exposed was determined by O₂-H₂ titration.²² Approximately 44% of the Pd atoms were exposed, which corresponds to an average particle size of 2.0 nm.²³

The infrared spectra were recorded with a Research Series II FTIR spectrometer (Mattson, Inc) equipped with a liquid N₂ cooled MCT detector. The IR cell was similar to that described elsewhere.²⁴ The cell volume was 200 cm³ and the light path length was 15 cm. The cell was equipped with glass stopcocks connected to gas inlet/outlet ports. The spectra of adsorbed CF₂Br₂, CH₂Br₂, CD₂Br₂, and CO were measured with a resolution of 4 cm⁻¹ and 400 scans were accumulated per spectrum. The spectra of gaseous products of the CF₂Br₂, CH₂Br₂, and CD₂Br₂ reaction with H₂ were measured with a resolution of 2 cm⁻¹ and 128 scans were accumulated per spectrum.

The self-supporting catalyst wafers (10–30 mg/cm² thick) were prepared from the powdered catalyst by pressing at 830 atm for 3 min. After a wafer was placed in the in situ IR cell, it was pretreated by heating from room temperature to 773 K at 4 K min⁻¹ in a 10% O₂/He mixture (UHP, Liquid Carbonic) flowing at 60 mL min⁻¹. It was held at 773 K for 1 h before cooling to room temperature in the flowing 10% O₂/He mixture. The cell was evacuated for 0.5 h to a pressure of 10⁻⁵ Torr to remove all traces of O₂. Then, the sample was heated in flowing H₂ (UHP, Penn Oxygen) (80 mL min⁻¹) or D₂ (Cambridge Isotope Laboratories, 99.6%) (80 mL min⁻¹) to 573 K at 5 K min⁻¹ and held at this temperature for 1 h before evacuating at 573 K to a pressure of 10⁻⁵ Torr.

The adsorption of the probe molecules was performed after the H₂ treatment. From 5 to 10 Torr of CF₂Br₂ (Aldrich, 97%), CH₂Br₂ (Aldrich, 99%), CD₂Br₂ (Aldrich, 99.6 at. % D), or CO (Air Product, 99.995%) was admitted to the evacuated cell at room temperature for 0.5–3 h, during which spectra were collected, before evacuation for 20 min. The hydrogenation kinetics of the surface species that formed during exposure of the catalyst wafer to CF₂Br₂, CH₂Br₂, or CD₂Br₂ were measured using a reduced fresh²⁵ catalyst wafer. The wafer was exposed to 10 Torr of the corresponding halocarbon at 473 K for 1 h. Then, the wafer was rereduced at 573 K for 1 h, cooled to room temperature, and exposed to 5 Torr of the halocarbon for 0.5 h before evacuation for 20 min. Then, 10 Torr H₂ was admitted to the cell at room temperature, and the vibrational spectra of the gas-phase products were monitored by FTIR as a function of time.

The kinetics of the CF₂Br₂+H₂, CH₂Br₂+H₂, and CD₂Br₂+H₂ reactions were investigated using the wafers that had previously been used in the experiments to hydrogenate surface species from halocarbon adsorption at room temperature. After the hydrogenation experiment, the catalyst wafer was rereduced at 573 K for 1 h and evacuated at the reduction temperature to a pressure of 10⁻⁵ Torr. Then, the wafer was cooled to the reaction temperature of 473 K, and 8 Torr of halocarbon and 40 Torr of H₂ were admitted into the cell. The concentrations of gaseous products from the reaction of CF₂Br₂, CH₂Br₂, and CD₂Br₂ with H₂ were measured in terms of intensities of the signature vibrations for the gaseous compounds:^{26–28} 1140 cm⁻¹ (CF₂Br₂), 1208 cm⁻¹ (CF₃Br), 1090 cm⁻¹ (CF₂H₂), 1152 cm⁻¹ (CF₃H), 1190 cm⁻¹ (CH₂Br₂), 1234 cm⁻¹ (CD₂H₂), 2259 cm⁻¹ (CD₄), 3017 cm⁻¹ (CH₄), 2970 cm⁻¹ (C₂H_{2x+2}). A band at 1030 cm⁻¹, which is characteristic of SiF₄,²⁸ was detected in the experiments

with CF₂Br₂. The SiF₄ forms from the interaction of HF(DF), a product of the CF₂Br₂+H₂(D₂) reaction, with quartz walls of the IR cell.

The differential flow kinetics of the CF₂Br₂+H₂ reaction was conducted at atmospheric pressure in a stainless steel flow reaction system consisting of a down-flow quartz microreactor (10 mm i.d.) equipped with a quartz frit to support the catalyst. An electric furnace heated the reactor zone containing the catalyst. The catalyst bed temperature was measured and controlled with an accuracy of ±1 K (Omega model CN2011). The gaseous reactants and pretreatment gases (He, H₂, Praxair, 99.999%) were metered using mass flow controllers (Brooks, model 5850E) and mixed prior to entering the reactor. The CF₂Br₂ was metered into the system by flowing He through a saturator containing the liquid. A constant concentration in the stream was ensured by holding the saturator at a fixed temperature of 273 K using a recirculating cooling system. The reaction temperature was 473 ± 1 K, and the catalyst was maintained at that temperature using an electric furnace and a temperature controller (Omega model CN2011).

Prior to reaction, the catalyst was treated with a mixture of H₂ (20 mL min⁻¹) and He (30 mL min⁻¹) as it was heated from room temperature to 573 K at the rate of 5 K min⁻¹ and then held at 573 K for 2 h. The catalyst was cooled in flowing He (30 mL min⁻¹) to the reaction temperature, and the reactant mixture was introduced. The total flow rate of the reaction mixture was 56 mL min⁻¹ and consisted of 41 300 ppm CF₂Br₂, 206 400 ppm H₂, and the balance He. The catalyst weight was ~0.03 g. The selectivities (*S_i*) toward detectable carbon-containing products were calculated as follows:

$$S_i = \frac{n_i C_i}{\sum_i n_i C_i} \quad (1)$$

where *n_i* and *C_i* are the number of carbon atoms in a molecule and the mole concentration of the product *i* in the effluent gas, respectively. The formation of HF and HBr was detected by GC-MS but not quantified.

Results

The prolonged contact of the reduced fresh 5% Pd/γ-Al₂O₃ catalyst with CF₂Br₂ or CH₂Br₂ resulted in the formation of small quantities of gaseous CF₃Br and CH₄, respectively (not shown). When the catalyst was exposed to CH₂Br₂, CH₄ evolved independent of whether H₂ or D₂ was used for the catalyst reduction (not shown). The FTIR spectra measured at room temperature did not contain any bands associated with C–F or C–H bond vibrations of chemisorbed species formed on the catalyst surface after contact with either CF₂Br₂ or CH₂Br₂ at room temperature.

When the reduced fresh catalyst was exposed to 10 Torr of CF₂Br₂ for 1.5 h and then evacuated at room temperature, the IR bands at 1230, 1460, 1650, 1865, 2105, and 2155 cm⁻¹ appeared (Figure 1a). The bands at 1230 and 1650 cm⁻¹ correspond to the asymmetric C–O bond stretching vibration and the C=O bond vibration of a bidentate carbonate I (Figure 2), respectively. The band at 1460 cm⁻¹ has been attributed to asymmetric C–O bond stretching vibration of carbonate ion CO₃²⁻ (Structure III in Figure 2). The symmetric C–O bond vibration of the carbonate ion is IR inactive.²⁹ The 1865, 2105, and 2155 cm⁻¹ bands are ascribed to CO molecules adsorbed on palladium. The bands at 1860 and 2105 cm⁻¹ correspond to

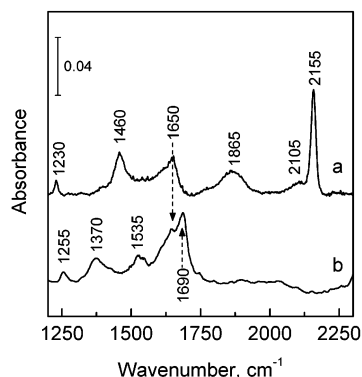


Figure 1. FTIR spectra of the reduced 5% Pd/ γ -Al₂O₃ wafer after the exposure to 10 Torr of CF₂Br₂ (a) or CH₂Br₂ (b) for 1.5 h at room temperature followed by evacuation for 1 h.

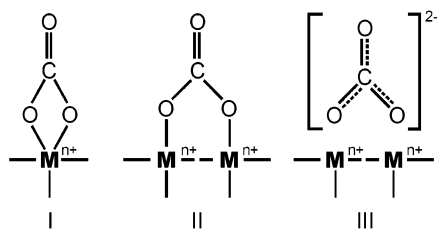


Figure 2. The structures of surface bidentate carbonates.

CO adsorbed on metallic Pd in bridging and linear forms, respectively, while the 2155 cm⁻¹ band is characteristic of complexes of CO with Pd²⁺ cations.³⁰

Several FTIR bands appeared in the 1200–2300 cm⁻¹ range when the reduced fresh catalyst was exposed to CH₂Br₂ (Figure 1b). The bands at 1255 and 1690 cm⁻¹ correspond to the asymmetric C–O bond stretching vibration and the C=O bond vibration in the carbonate I (Figure 2).^{31,32} The two bands at 1370 and 1535 cm⁻¹ are attributed to vibrations of the carbonate II (Figure 2).^{31,32} The bands characteristic of CO adsorbed on Pd are absent in the spectrum of the catalyst exposed to CH₂Br₂.

Several adsorption complexes of adsorbed CO formed with the catalyst that had been rereduced after preexposure to CH₂Br₂ and CF₂Br₂ and then exposed to CO. The spectra for both samples contained the bands at 1860, 1915, and 2155 cm⁻¹ (Figure 3, Spectra 1). The 1860 and 1915 cm⁻¹ bands have been assigned to CO molecules adsorbed on metallic Pd in triple- and double-coordinated modes.³³ The band at 2155 cm⁻¹ corresponds to a complex of CO with Pd²⁺ cations.³⁰ There is, however, a little difference between Spectrum 1 shown in Figure 3A and 3B. The bands of multi-coordinated modes of CO adsorbed on Pd are less intense and more clearly resolved for the catalyst preexposed to CH₂Br₂ (Figure 3A). The better resolution of the triple- and double-coordinated CO bands for this sample seems to be a result of a larger fraction of double-coordinated complexes (band at 1915 cm⁻¹) than for the sample preexposed to CF₂Br₂ (Figure 3B).

When CF₂Br₂ or CH₂Br₂ was adsorbed on the catalysts with preadsorbed CO, the band at 1915 cm⁻¹ either disappeared or red-shifted, leaving only a single symmetric band with a maximum at 1875 cm⁻¹ in the region of CO adsorbed on metallic Pd (Figure 3, spectra 2A and 2B). The integral intensity of the spectrum of CO adsorbed on metallic Pd in multi-coordinated modes noticeably decreased after the CF₂Br₂ adsorption (Figure 3B). However, it increased after CH₂Br₂ adsorption (Figure 3A). The adsorption of halocarbons on the sample with preadsorbed CO also resulted in the disappearance of the IR band for the CO adsorbed on Pd⁰ in the linear mode

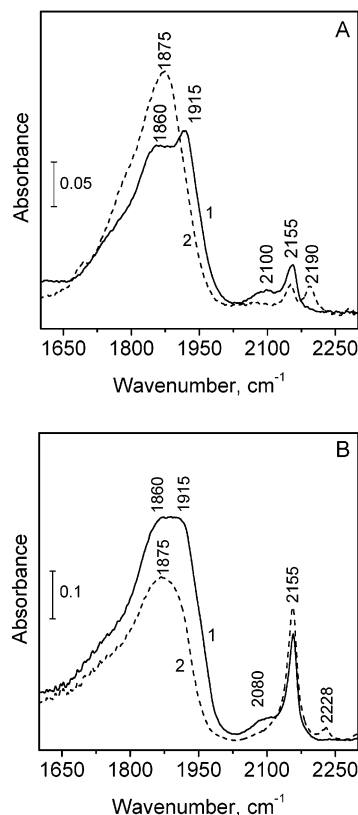


Figure 3. FTIR spectra of CO adsorbed on a reduced 5% Pd/ γ -Al₂O₃ sample preexposed to 10 Torr of CH₂Br₂ (A) and CF₂Br₂ (B) at ambient temperature for 3 h followed by repeated reduction with 100 Torr H₂ under static conditions; 1, spectra of CO resulting from the exposure of the catalyst wafer to 10 Torr CO for 20 min at room temperature followed by evacuation for 0.5 h; 2, spectra 1 after exposure of the catalyst wafer to 5 Torr of CF₂Br₂ (A) or CH₂Br₂ (B) and subsequent equilibration between surface and gas phase.

(2080–2100 cm⁻¹) and the appearance of bands at 2190 cm⁻¹ (Figure 3A) and 2228 cm⁻¹ (Figure 3B) which are characteristic of CO adsorbed on coordinatively unsaturated Al³⁺ cations in octahedral and tetrahedral coordinations, respectively.^{34,35}

After heating the catalyst in CF₂Br₂ or CH₂Br₂ at 473 K and then reducing in H₂ at 573 K, the reactivity of the catalyst surface decreased. This is evident by the lack of IR bands in the region of carbonate species vibrations (1200–1700 cm⁻¹) after subsequent adsorption of CF₂Br₂ or CH₂Br₂ at ambient temperature. The bands characteristic of gas-phase CF₃Br and CH₄ formed from adsorption of CF₂Br₂ or CH₂Br₂ were also absent. However, when the same catalyst wafer was exposed to H₂ (10 Torr) at room temperature after prolonged evacuation at room temperature, methane evolved into gas phase. Substituting D₂ for H₂ resulted in the formation of CD₄ and CH₂D₂. Gas-phase CH₂D₂ also formed when CD₂Br₂, instead of CH₂Br₂, was adsorbed and then the catalyst was exposed to H₂ at room temperature.

The kinetics of CH₄ and CH₂D₂ formation in the IR cell during the reaction of H₂ with a catalyst wafer that was preexposed to CF₂Br₂ or CD₂Br₂ are shown in Figure 4. The rate of CH₄ formation from the catalyst preexposed to CF₂Br₂ was much larger than that of CH₂D₂ formation after preexposing to CD₂Br₂. However, the maximum concentration of CH₂D₂ was about an order of magnitude higher than that of CH₄ (not shown).

In the presence of hydrogen, CF₂Br₂ was converted at 473 K over a rereduced Pd/ γ -Al₂O₃ catalyst into CF₃H, CF₂H₂, CH₄, HBr, and HF,³⁶ which were identified using IR spectra reported

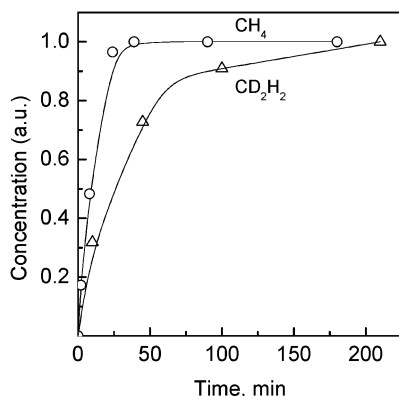


Figure 4. Kinetics of the CH_4 and CD_2H_2 formation at room temperature, respectively, from chemisorbed CF_2Br_2 and CD_2Br_2 . The H_2 pressure in the IR cell was 10 Torr.

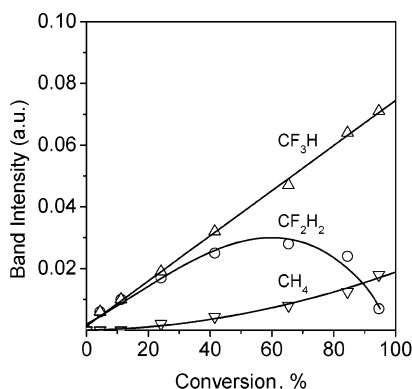


Figure 5. The dependence of the product concentration on CF_2Br_2 conversion in the presence of hydrogen at 473 K. The initial concentrations of CF_2Br_2 and H_2 were 8 and 40 Torr, respectively.

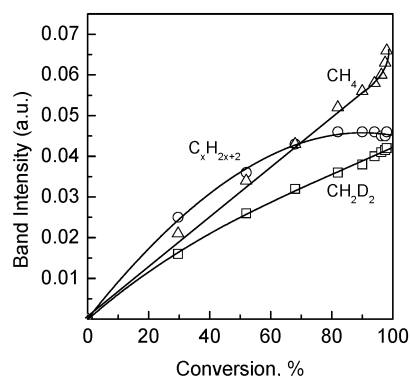


Figure 6. The dependence of the product concentration on CD_2Br_2 conversion in the presence of hydrogen at 473 K. The initial concentrations of CD_2Br_2 and H_2 were 8 and 40 Torr, respectively.

in the literature.^{26–28} Figure 5 shows the relation between CF_2Br_2 conversion and the band intensities characteristic of CF_3H (1152 cm^{-1}), CF_2H_2 (1090 cm^{-1}), and CH_4 (3017 cm^{-1}). In the conversion range of 0–95%, there was a linear increase in CF_3H concentration with increasing CF_2Br_2 conversion. The concentration of CF_2H_2 reached a maximum value when the CF_2Br_2 conversion was 60%. At higher conversions, the CF_2H_2 concentration decreased and the concentration of CH_4 and SiF_4 increased (not shown).

The reaction of CD_2Br_2 and H_2 at 473 K yielded CD_2H_2 , CH_4 , heavier hydrocarbons, and HBr (Figure 6). When the CD_2Br_2 conversion was less than 90%, there was almost a linear relationship between the CD_2Br_2 conversion and the band intensities of CD_2H_2 and CH_4 . The concentration of C_2+

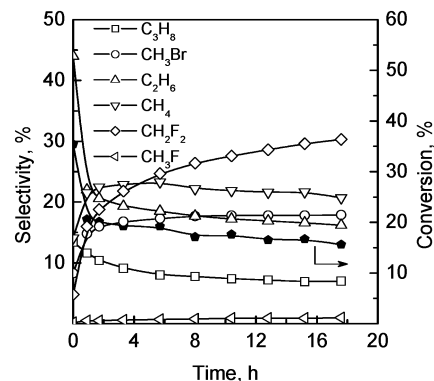


Figure 7. Time on stream performance of the $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ in the $\text{CF}_2\text{Br}_2 + \text{H}_2$ reaction at 473 K in a continuous flow reactor at 473 K.

hydrocarbons increased until the CD_2Br_2 conversion reached 80% and remained essentially constant thereafter.

The selectivity of the $\text{CF}_2\text{Br}_2 + \text{H}_2$ reaction catalyzed by the $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ varied with time on stream (TOS), as measured in a continuous flow reactor. Initially, the catalyst was selective toward C_2 – C_3 hydrocarbons ($\sim 60\%$) and was unselective toward CF_2H_2 ($\sim 5\%$) (Figure 7). With increasing TOS, the selectivity toward C_2H_6 and C_3H_8 decreased, whereas the selectivity toward CF_2H_2 and CH_4 increased. After approximately 3 h on stream, CF_2H_2 and CH_4 were the major products. The selectivity toward CH_3Br was relatively high ($\sim 18\%$), and there was no CF_3H formed during the $\text{CF}_2\text{Br}_2 + \text{H}_2$ reaction.

Discussion

Adsorption Studies: Interaction of CF_2Br_2 and CH_2Br_2 (CD_2Br_2) with the Surface of $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ at Room Temperature. The adsorption of CF_2Br_2 at room temperature on a reduced fresh catalyst leads to the formation of bidentate carbonates (bands at 1230 and 1650 cm^{-1}) and carbonate-ions CO_3^{2-} (band at 1460 cm^{-1}) on the alumina surface. There is also CO adsorbed on metallic Pd (bands at 1860 and 2105 cm^{-1}) and on Pd^{2+} cations (band at 2155 cm^{-1}) (Figure 1, spectrum a). The formation of the carbonate species and CO is the result of the direct reaction of the halocarbon with the support. The $\gamma\text{-Al}_2\text{O}_3$ surface is thus halogenated. The fact that this occurs at room temperature is consistent with other investigations with C_1 and C_2 halocarbons. For example, the bands of adsorbed carbonates and those that may belong to CO adsorbed on the coordinatively unsaturated Al^{3+} cations were detected after exposure of metal-free $\gamma\text{-Al}_2\text{O}_3$ to CF_2Cl_2 at temperature as low as 120 K.³⁷ However, neither CO nor CO_2 forms during the reaction of CF_3CFCl_2 with metal-free $\gamma\text{-Al}_2\text{O}_3$ at temperatures below 593 K, but the formation of adsorbed trifluoroacetate species with concomitant halogenation of the alumina surface was observed at temperature as low as 298 K.²⁴

After CF_2Br_2 adsorption, no absorption bands characteristic of chemisorbed species containing C–F bonds were detected. As well, the contact of the catalyst with hydrogen after the preadsorbed CF_2Br_2 was removed by prolonged evacuation at room temperature leads to the CH_4 formation. The strength³⁸ of the C–Br bond is so much less than the C–F bond (68 and 110 kcal mol^{-1} , respectively³⁹) that one would expect that the CF_2Br_2 molecule would readily dissociate to form $:\text{CF}_2$. The absence of CF_2H_2 in hydrogenation products indicates that the $:\text{CF}_2$ carbene is not among chemisorbed species formed from adsorbed CF_2Br_2 . It is possible that the strong interaction of F atoms with the Pd provides a strong driving force for the $:\text{CF}_2$ to undergo subsequent decomposition reactions. Thus, most likely the adsorbed CF_2Br_2 decomposes to form carbon on the

Pd surface that is then hydrogenated at room temperature to form CH₄. The significant decrease in the integral intensity of the band in the range of 1865–1915 cm⁻¹ may indicate oxidation of metallic Pd because of CF₂Br₂ decomposition with the formation of coordinatively unsaturated PdF₂ surface moieties. Similar chemistry was reported for CCl₂F₂ on Fe(110).⁴⁰

The evolution of gas-phase CF₃Br after adsorption of CF₂Br₂ shows that Br exchanges with F in the CF₂Br₂ molecule. The source of fluorine is likely partially fluorinated alumina formed during the decomposition of CF₂Br₂ into carbonates, CO, and carbon. As no oxygen was added to the system, it is clear that oxygen must come from the support to form carbonates and CO.

The carbonates also form on the surface of the reduced fresh catalyst after adsorption of CH₂Br₂ (Figure 1, spectrum b). However, there is no CO adsorbed on Pd (Figure 1, spectrum b). This reflexes different chemistry of the CF₂Br₂ and CH₂Br₂ interaction with the catalyst surface. The CH₄ observed during the adsorption of CH₂Br₂ forms via the disproportionation of CH₂. This chemistry occurs on the Pd surface and results in the deposition of carbonaceous species. The possibility that the CH₄ may form from CH₂ species and adsorbed H atoms leftover from the catalyst reduction step was ruled out by the experiment in which the catalyst was reduced with D₂. No deuterated methanes formed in that case.

Further insight into the interaction of molecular CH₂Br₂ with metallic palladium comes from the spectrum of CO adsorbed on Pd in bridging form (Figure 3A). The fact that the adsorption of CH₂Br₂ on the sample with preadsorbed CO results in the shift of 1915 cm⁻¹ band to 1875 cm⁻¹ suggests that the electronic donor-accepting properties of Pd are modified. This modification is not accompanied by a decrease in the integral intensity of the spectrum of CO adsorbed on palladium. It may mean that CH₂Br₂ does not oxidize the metallic Pd, and the electronic donor-accepting properties of Pd are modified through its interaction with strong Lewis acid sites emerging on the support surface after exposure to CH₂Br₂, as indicated by the band at 2190 cm⁻¹ (Figure 3A).

The CF₂Br₂ interacts with supported metallic Pd as well. This interaction manifests itself by the change in the FTIR spectrum of CO adsorbed on Pd in bridging form after adsorption of CF₂Br₂ on the catalyst (Figure 3B). The significant decrease in the integral intensity of the absorption bands in the range of 1865–1915 cm⁻¹ suggests a partial oxidation of metallic Pd by F atoms originated from the decomposition of CF₂Br₂.

When the alumina surface is halogenated to the extent that there are little to no oxygen atoms on the surface, the adsorbed halocarbon molecules will no longer decompose. With such surfaces, only halogen exchange reactions are possible, and the rate of these reactions is significant only at temperatures greater than 573 K.^{41–45} Hence, it is likely that after adsorption of CF₂Br₂ on the sample pretreated with CF₂Br₂ at 473 K followed by reduction with H₂, active carbon is deposited on the Pd surface. This active carbon is hydrogenated by H₂ or D₂ into CH₄ or CD₄. When CH₂Br₂ is adsorbed on the sample pretreated with CH₂Br₂ at 473 K followed by reduction with H₂, the chemisorbed species are mainly :CH₂ carbenes, which are stable at room temperature. In the presence of H₂ or D₂, the carbenes are hydrogenated into CH₄ or CD₂H₂, respectively. While it is tempting to conclude that the :CH₂ carbenes do not dissociate at room temperature on the Pd surface even in the absence of coadsorbed H atoms, caution must be exercised because the energy of the C–H bond in the :CH₂ carbenes is lower than that of the C–F bonds in the :CF₂ carbenes (101 and 125 kcal

mol⁻¹, respectively^{39,46}). It is quite possible, however, that the lower stability of the :CF₂ species is the result of the strong driving force for the C–F bond dissociation because of the high energy of F atom adsorption on Pd.⁴⁷ The conclusion on different nature of chemisorbed species formed from CF₂Br₂ or CH₂Br₂ is also supported by the vastly different rate of their hydrogenation (Figure 4) and by the evolution of CD₂H₂ during hydrogenation by H₂ of chemisorbed species originated from the adsorbed CD₂Br₂.

For the silica-supported Pd, the :CH₂ carbenes formed by dissociative adsorption of CH₂Cl₂ are stable only in a narrow temperature range (233–243 K).⁴⁸ At temperatures higher than 250 K, the carbenes on Pd/SiO₂ decomposed and CH₄, C₂H₄, HCl, and H₂O form. With Pd/γ-Al₂O₃, the :CH₂ species are stable even at room temperature and consumed only upon exposure to H₂ to form CH₄. Such difference in the stability of the :CH₂ carbenes on the surface of Pd supported on SiO₂ and Al₂O₃ may be caused by different interactions of small Pd particles with different oxide supports.

The reactivity of the surface carbon species formed from CF₂Br₂ and carbene species formed from CD₂H₂ with respect to H₂ is quite different (Figure 4). Gas-phase studies have shown that carbon atoms are not less reactive toward H₂ than :CH₂ carbenes.⁴⁹ By clustering the carbon atoms on the metal surface, the degree of coordinative unsaturation of the atoms is decreased and there is a concomitant loss in reactivity. However, it is reasonable to suggest that a small fraction of the C atoms, likely those located at the corners of the clusters, are still highly coordinatively unsaturated and, hence, highly reactive toward hydrogen. The fact that the amount of CH₄ formed by hydrogenation of the surface species formed from the CF₂Br₂ adsorption is 1 order of magnitude less than the amount of CD₂H₂ formed by hydrogenation of the surface species formed from the CD₂Br₂ adsorption suggests that only a small fraction of the C atoms formed from CF₂Br₂ are sufficiently reactive to be hydrogenated at room temperature.

Reaction Studies: Conversion of CF₂Br₂ over Pd/γ-Al₂O₃ in the Presence of H₂ at 473 K. On the basis of the results of the chemical kinetics experiments, it is reasonable to suggest that two different reaction pathways account for the formation of CF₂H₂ and CF₃H from CF₂Br₂ reaction with H₂ at 473 K (Figure 5). At low conversions, the concentration of both CF₂H₂ and CF₃H increases linearly with increasing CF₂Br₂ conversion and the ratio of the CF₂H₂ and CF₃H concentrations in the limit of zero conversion is a finite quantity. This indicates that both CF₂H₂ and CF₃H are primary reaction products.

The CF₂H₂ is likely formed from :CF₂ carbene species. The absence of CH₄ among the reaction products at low CF₂Br₂ conversions suggests that the rate of the surface reaction of :CF₂ carbene hydrogenation to form CF₂H₂ significantly exceeds that of :CF₂ species dissociation to form surface carbon and eventually CH₄. The fact that the concentration of CF₂H₂ increases with increasing CF₂Br₂ conversion only up to 60% and decreases thereafter is consistent with the idea that CH₄ is a secondary product of the CF₂Br₂ conversion. The hypothesis that CF₂H₂ converts into CH₄ at higher conversion was tested in additional experiments on CF₂H₂ conversion in the presence of H₂ at 473 K. Under these conditions, CF₂H₂ selectively converts into CH₄, and HF is detected as SiF₄ because of HF reaction with the quartz walls of the IR cell. In a previous kinetics investigation of the CF₂Cl₂+H₂ reaction, it was also concluded that CH₄ is a secondary product of CF₂Cl₂ hydrodechlorination.¹²

The concentration of CF₃H increases proportionally with CF₂Br₂ conversion from 0 to ~100%. This indicates that CF₃H

does not participate in secondary reactions. The high selectivity toward CF_3H that results from the CF_2Br_2 hydrodehalogenation reaction catalyzed by $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ under static conditions (Figure 5) is difficult to understand. The CF_3H was not among the reaction products when the $\text{CF}_2\text{Br}_2 + \text{H}_2$ reaction was conducted in a continuous flow reactor (Figure 7). In fact, the CF_3H may be a secondary product of the CF_2Br_2 halogen disproportionation reaction catalyzed by the Lewis sites^{24,37,50–52} located at the Pd–alumina interface. The high Lewis acidity of the CF_2Br_2 pretreated alumina is indicated by the IR band at 2228 cm^{-1} of adsorbed CO (Figure 3B). It is possible that the CF_3Br forms by disproportionation of CF_2Br_2 on the Lewis acid site and then diffuses onto the metal sites where the hydrodebromination takes place and CF_3H is formed. As the reactivity of the C_1 fluorohalocarbons increases with a decrease in the number of F atoms in the molecule,^{12,53} the other disproportionation reaction product (CFBr_3) should rapidly convert into surface or bulk carbonates on alumina or into CH_4 on the Pd. The absence of CF_3H among the $\text{CF}_2\text{Br}_2 + \text{H}_2$ reaction products in the continuous flow reactor (Figure 7) indicates that the alumina support does not have strong acid sites under the continuous flow reaction conditions. These sites may be blocked by the C_{2+} hydrocarbon products of the $\text{CF}_2\text{Br}_2 + \text{H}_2$ reaction. A strong inverse correlation between C_{2+} hydrocarbon and CF_3H selectivities for the $\text{CF}_2\text{Cl}_2 + \text{H}_2$ reaction catalyzed by supported Pt bimetallic catalysts was reported earlier.⁵⁴

Reaction Studies: Conversion of CH_2Br_2 and CD_2Br_2 over $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ in the Presence of H_2 at 473 K. In the presence of H_2 at 473 K, the CH_2Br_2 reacts to form CH_4 and heavier hydrocarbons, most likely of the form of $\text{C}_x\text{H}_{2x+2}$. When CD_2Br_2 reacts with H_2 under the same conditions, large amounts of CH_4 and C_{2+} hydrocarbons form in addition to CD_2H_2 (Figure 6). These results are consistent with the idea that $:\text{CD}_2$ carbenes participate in the conversion of CD_2Br_2 . The formation of CH_4 and higher hydrocarbons indicate that $:\text{CD}_2$ carbenes, which form from the dissociative adsorption of CD_2Br_2 at 473 K, undergo H–D exchange followed by either hydrogenation to form CH_4 or oligomerization into C_{2+} hydrocarbons analogous to Fischer–Tropsch synthesis chemistry catalyzed by ruthenium⁵⁵ and iron.⁵⁶

Conclusion

The reaction of CF_2Br_2 , CH_2Br_2 , and CD_2Br_2 hydrodehalogenation catalyzed by a $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ catalyst was investigated by a combination of FTIR and reaction kinetics studies. In a continuous flow reactor, CF_2H_2 , CH_4 , and C_{2-3} hydrocarbons form from the reaction of $\text{CF}_2\text{Br}_2 + \text{H}_2$ at 473 K, whereas CF_3H forms in addition to CF_2H_2 and hydrocarbons in the IR cell under static conditions. The difference in product composition was explained in terms of a different impact of the support to the CF_2Br_2 conversion depending on the reaction conditions.

The adsorption of CF_2Br_2 on the catalyst surface at room temperature results in the complete decomposition of the halocarbon molecules on Pd to form C and halogen atoms thereon. These moieties hydrogenate to CH_4 , HF, and HBr under exposure of the catalyst to H_2 at room temperature. The adsorption of CH_2Br_2 and CD_2Br_2 on a $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ results in the dissociation of both C–Br bonds of the halocarbons on Pd to form surface Br and $:\text{CH}_2$ or $:\text{CD}_2$ species, identified by the products of their reaction with H_2 (HBr, CH_4 , or CD_2H_2) at room temperature.

It was concluded that unlike the $:\text{CH}_2$ carbenes, the $:\text{CF}_2$ species are unstable at room temperature on the Pd surface and tend to decompose in the absence of coadsorbed H atoms. Thus,

the selectivity of the Pd toward CF_2H_2 in the $\text{CF}_2\text{Br}_2 + \text{H}_2$ reaction is determined by the relative rates of two parallel pathways for the intermediate $:\text{CF}_2$ species: dissociation to form surface carbon that is hydrogenated to CH_4 and reaction with coadsorbed H to form CF_2H_2 .

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