

FTIR Spectroscopic and Reaction Kinetics Study of the Interaction of CF₃CFCl₂ with γ -Al₂O₃

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The interaction of CF₃CFCl₂ with γ -Al₂O₃ has been investigated by a combination of reaction kinetics experiments and FTIR spectroscopic studies. The reaction of fresh γ -Al₂O₃ with CF₃CFCl₂ at 573 K resulted in the fluorination of the γ -Al₂O₃ surface. The reaction also resulted in dehydroxylation of the γ -Al₂O₃ and an increase in both the number and strength of Lewis acid sites on the surface. The fluorinated γ -Al₂O₃ was catalytically active for the disproportionation of CF₃CFCl₂ to CF₃CCl₃ and CF₃CF₂Cl at 353 K. Adsorption of CF₃CFCl₂ on γ -Al₂O₃ at temperatures between 298 and 523 K resulted in the formation of surface trifluoroacetate species, which were stable up to 573 K. These species are likely to be the intermediates for the complete oxidation of CF₃CFCl₂ to CO and CO₂. The transformation of γ -Al₂O₃ as a result of the CF₃-CFCl₂ adsorption and reaction is discussed.

Introduction

Metal oxides and metal halides are an important class of materials to convert halogenated molecules. These materials catalyze the oxidative destruction of halocarbons.^{1,2} When a noble metal is supported on aluminum oxides and aluminum fluoride, the hydrodechlorination of chlorofluorocarbons (CFCs) to hydrofluorocarbons (HFCs) readily proceeds at temperatures above 450 K.^{3–5} For these reactions, catalyst activity and selectivity are influenced by the type and stability of the support material.^{5,6} Furthermore, previous investigations have shown that metal oxides and fluorides catalyze disproportionation/isomerization reactions of chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs).^{7–10} However, a molecular-level description of halocarbon conversions on oxides is still lacking.

In the present work, we have conducted FTIR spectroscopic studies of CF₃CFCl₂ adsorption along with reaction kinetics and characterization experiments to understand the mechanism γ -Al₂O₃ fluorination by the CFC. We report that γ -Al₂O₃ is converted during reaction with CF₃CFCl₂ into a partially fluorinated material that retains a surface area above 200 m²/g. This is in contrast to previous reports that concluded that the complete fluorination of γ -Al₂O₃ to low surface area AlF₃ occurs as a result of reaction with CFCs.^{11,12} Furthermore, surface species information is provided along with a mechanistic description of reaction pathways for the disproportionation of CF₃CFCl₂ catalyzed by fluorinated γ -Al₂O₃ at 353 K.

Experimental Section

1. Materials. The materials used for this study were γ -Al₂O₃ (Vista B), AlF₃ (Strem Chemicals, purity > 99%), CF₃CFCl₂ (Dupont, > 99.5%), and CF₃COCl (Aldrich, > 98%). Independent GC analysis of the CF₃CFCl₂ showed that CF₂Cl₂ (<0.1%) was the only detectable impurity. Helium (Praxair, > 99.999%), 10% O₂/He (Liquid Carbonic, > 99.95%), and CO (Praxair, > 99.99%) were used without further purification.

2. Characterization. The sample surface area was determined by N₂ physisorption according to the BET method using a

volumetric sorption analyzer (Micromeritics ASAP 2010). X-ray diffraction (XRD) patterns of the samples were obtained with a Philips XPERT diffractometer using a standard Cu K α radiation source. Energy-dispersive X-ray analysis (EDX) on powdered samples was performed using a EDAX detector equipped with Super-Ultrathin (SUTH) window and attached to a Philips XL 30 scanning electron microscope (SEM).

3. Infrared Spectroscopy. A Mattson Research Series II FTIR spectrometer equipped with a MCT detector was used in the transmission mode for infrared measurements. Spectra were collected in the 400–4000 cm^{–1} range. Approximately 400 scans with a nominal resolution of 4 cm^{–1} were collected and averaged to produce a spectrum with high signal-to-noise ratio. The evacuated cell (10^{–6} Torr) was used as the background for all measurements.

All adsorption experiments were conducted in a vacuum system with a base pressure of 10^{–6} Torr. A stainless steel dosing chamber equipped with two leak valves was used to admit gas into the IR cell. The chamber was also equipped with two pressure manometers (MKS instruments) with a pressure range of 10^{–7}–0.1 Torr and 0.01–1000 Torr, respectively. The placement of the pressure manometers allowed for direct measurement of the gas pressure in the IR cell.

The infrared cell consisted of a quartz tube equipped with Teflon stopcocks for the gas inlet, outlet ports, and a vacuum port. Potassium bromide windows were attached to the lower portion of the cell, which was in the path of the IR beam. The upper portion was equipped with a furnace for the in situ pretreatment of the catalyst. The catalyst wafer was held within a quartz sample holder inside the quartz tube and could be raised into the heated zone of the cell by means of a magnetic bar. The heated zone temperature was measured with a thermocouple in contact with the outside wall of the cell at a distance of approximately 11 mm from the wafer and controlled using a temperature controller (Omega, model CN2011). Independent measurements indicated that the temperature difference between the center of the cell and the external thermocouple was within ± 5 K.

A self-supporting γ -Al₂O₃ wafer was prepared from a powdered sample (<60 mesh) that was pressed in a hydraulic

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press at 830 atm for 3 min. The pressure was gradually relieved in 1 min. In situ pretreatment of the sample was performed by treating the wafer in a 10% O₂/He flow (25 mL/min) and heating from 298 to 773 K at 8 K/min and holding the sample at 773 K for 60 min. Then, the sample was evacuated at 773 K for 60 min and cooled to 298 K under vacuum. The sample thus obtained is referred to as “fresh” γ -Al₂O₃ in the remainder of this paper. A “used” γ -Al₂O₃ sample was obtained from fresh γ -Al₂O₃ by the following in situ treatment. The fresh γ -Al₂O₃ wafer was treated with 10 Torr of CF₃CFCl₂ at 573 K overnight followed by evacuation of the adsorbed species at 673 K and subsequent treatment of the sample in 10% O₂/He as described above.

Before admitting the CFC, a spectrum of the pretreated wafer was recorded at room temperature and 10⁻⁶ Torr pressure. Then for a typical adsorption experiment, 1–5 Torr of CF₃CFCl₂ or CF₃COCF₃ was introduced in the cell at room temperature. The spectra of the strongly bound adsorbed species were obtained by heating the wafer to the desired temperature (298–523 K) in the presence of the gas phase followed by evacuation of the cell to < 10⁻⁶ Torr at 298 K to remove the gas phase and the weakly bound species. The wafer was then lowered into the beam and the spectrum recorded at 298 K. The stability of the adsorbed species formed by adsorption of CF₃CFCl₂ was investigated by monitoring the decay in the intensity of the bands associated with the adsorbed species while heating the wafer at 523–673 K under continuous evacuation after the adsorption step described above.

Carbon monoxide adsorption was carried out by introducing 10 Torr of CO at 298 K into the cell containing the γ -Al₂O₃ wafer. Prior to CO adsorption, the γ -Al₂O₃ was exposed to CF₃CFCl₂ at different temperatures for 15 min (as described above) followed by evacuation of the CFC gas phase (<10⁻⁶ Torr) at 298 K.

The formation of gas-phase reaction products, due to the interaction of CF₃CFCl₂ or CF₃COCF₃ with γ -Al₂O₃, was monitored by recording the gas-phase spectra as follows. The reactant (1–5 Torr) was introduced into the IR cell containing the pretreated sample at 298 K and the spectrum of the gas-phase was recorded after 10 min. The temperature of the sample was then increased stepwise from 298 to 593 K. The spectrum of the gas phase in the cell was recorded at each temperature after holding the wafer at that temperature for 10 min.

4. Kinetics Experiments. The CF₃CFCl₂ reaction was conducted at atmospheric pressure in a stainless steel flow reaction system described elsewhere.¹³ Prior to reaction, the sample was treated in flowing 10% O₂/He (25 mL/min) while heating from 298 to 773 K at the rate of 8 K/min and held at 773 K for 60 min. This was followed by purging the sample in He for 60 min at 773 K. The sample was then cooled in flowing He to the reaction temperature (573 K). For a standard reaction, 0.1–0.2 g of sample was used and the total flow of the reactant mixture was 30 mL/min, consisting of CF₃CFCl₂ (2 mL/min) and He as the balance.

Results

1. Kinetics of CF₃CFCl₂ Reaction over γ -Al₂O₃ and AlF₃.

Figure 1 shows the change in reaction rate (expressed per unit surface area of the fresh catalyst) with time on stream (TOS) for the conversion of CF₃CFCl₂ over γ -Al₂O₃ and AlF₃ at 573 K. The activity of the fresh γ -Al₂O₃ changed dramatically during the first 10 h of TOS. Specifically, the initial activity (0.0022 $\mu\text{mol m}^{-2} \text{s}^{-1}$) decreased by 75% during the first hour and reached a minimum between 1 and 3 h TOS. The rate then

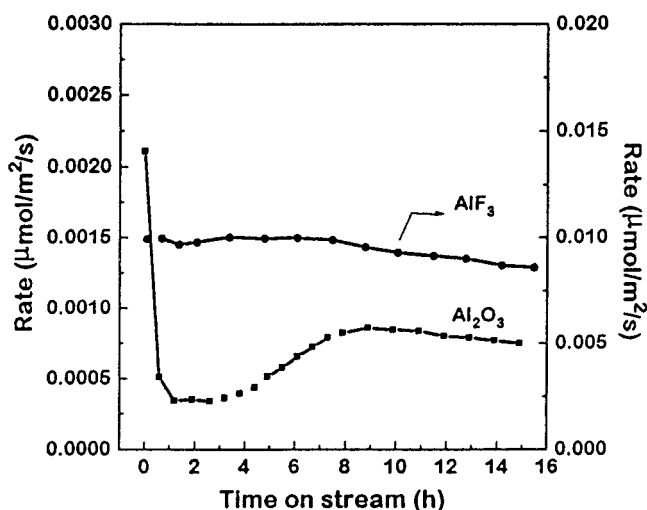


Figure 1. Rate of conversion of CF₃CFCl₂ to halogenated products with TOS at 573 K over γ -Al₂O₃ (■) and AlF₃ (●).

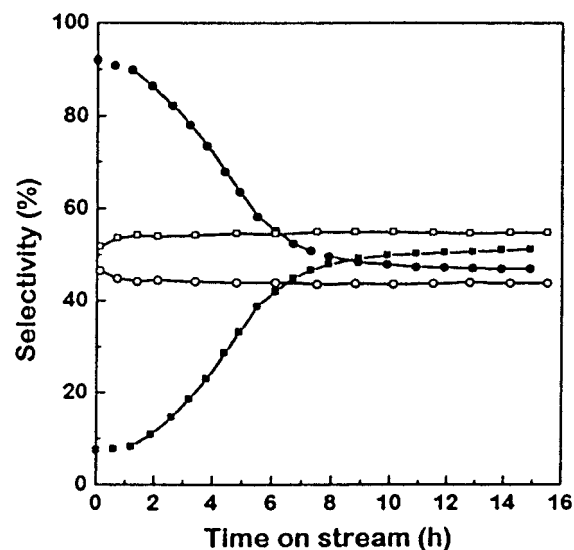


Figure 2. Selectivity toward CF₃CCl₃ (circles) and CF₃CF₂Cl (squares) with TOS at 573 K over γ -Al₂O₃ (filled symbols) and AlF₃ (open symbols).

increased monotonically reaching a maximum value of 0.0009 $\mu\text{mol m}^{-2} \text{s}^{-1}$ after 9 h. During the next 5 h of TOS, the activity change was less than 5%. The activity loss exhibited by fresh AlF₃ was <5% during the first 10 h of TOS. Compared to the activity of the γ -Al₂O₃ after 10 h TOS, AlF₃ was a factor of 10 more active.

Figure 2 shows the change in the product selectivity with TOS of the CF₃CFCl₂ reaction on γ -Al₂O₃ and AlF₃ at 573 K. With γ -Al₂O₃, the two major reaction products were CF₃CCl₃ and CF₃CF₂Cl accounting for >95% of all halogen-containing products. Trifluoromethane and CF₂Cl–CFCl₂ (together <5%) were the only other halogen-containing products observed. The formation of CO and CO₂ during the reaction was also detected using the GC-MS, but they were not quantified.

At early TOS, CF₃CCl₃ was the major product formed on γ -Al₂O₃ (selectivity > 90%). With increasing TOS, the selectivity toward CF₃CCl₃ monotonically decreased while that of CF₃CF₂Cl monotonically increased. After approximately 9 h TOS, the selectivity ratio of the two major products reached a constant value of 1:1, and remained unchanged thereafter. In the course of reaction, the total concentration of the other products changed insignificantly.

TABLE 1: Fundamental Gas-Phase Stretching Vibrations of CF₃CFCl₂, CF₃CCl₃, and CF₃CF₂Cl

CF ₃ CFCl ₂			CF ₃ CF ₂ Cl			CF ₃ CCl ₃		
mode	this work	ref 37	mode	this work	ref 37	mode	this work	ref 37
sym CF ₃	1295	1295	sym CF ₃	1349	1351	sym CF ₃	1249	1255
asym CF ₃	1232	1232	asym CF ₃	1240	1241	asym CF ₃	1223	1227
C–F	1109	1110	sym CF ₂	1183	1185	C–C	907	909
C–C	942	943	asym CF ₂	1129	1133	asym C–Cl	858	859
asym C–Cl	896	897	C–C	982	982	sym C–Cl	713	714
sym C–Cl	736	735	C–Cl	762	762			

With AlF₃, the selectivity ratio of CF₃CCl₃ to CF₃CF₂Cl was ~1:1 at early TOS and remained constant throughout the course of the reaction. The results presented in Figure 2 demonstrate that the product selectivity of CF₃CFCl₂ conversion over fresh γ -Al₂O₃ differed markedly from that over AlF₃.

2. FTIR Study of CF₃CFCl₂ Conversion under Static Conditions. The identification of gas-phase products formed by the interaction of CF₃CFCl₂ with a fresh or used γ -Al₂O₃ wafer at elevated temperatures was based on the analysis of gas-phase IR spectra of individual CFCs. The position of the absorption bands and their assignments are presented in Table 1.

After contact of CF₃CFCl₂ with fresh γ -Al₂O₃ at temperatures lower than 473 K, the gas-phase spectra were the same as the spectrum of gaseous CF₃CFCl₂ (Figure 3A). At higher contact temperatures, the band intensities characteristic of CF₃CFCl₂ decreased while new absorption bands with maxima at 855 and 1220 cm⁻¹ appeared. After contact of CF₃CFCl₂ with fresh γ -Al₂O₃ at 593 K, the spectrum of gas-phase species consisted of a superimposition of the spectra of gaseous CF₃CF₂Cl and CF₃CCl₃ with comparable intensities (Figure 3B). Contact of CF₃CFCl₂ with γ -Al₂O₃ at 593 K for longer times resulted in the gradual development of IR bands characteristic of gas-phase CO, CO₂, and HCl (not shown).

Conversion of CF₃CFCl₂ over used γ -Al₂O₃ occurred at significantly lower temperatures than that over fresh γ -Al₂O₃. Figure 4 shows the gas phase spectrum after contact of CF₃CFCl₂ for 10 min with a used γ -Al₂O₃ wafer at 353 K. (As in the previous case, the initial IR cell CF₃CFCl₂ pressure was 3 Torr and the wafer temperature was 298 K). The bands corresponding to gaseous CF₃CFCl₂ were of very low intensity. Further, the spectrum is well approximated by the superimposition of the spectra of gaseous CF₃CF₂Cl and CF₃CCl₃ with the concentration ratio close to 1:1 (Figure 4b).

3. Surface Characterization of Fresh and Used Aluminas.

Table 2 shows the change in the surface area of the γ -Al₂O₃ and AlF₃ samples as a result of the CF₃CFCl₂ reaction at 573 K. Exposure of fresh γ -Al₂O₃ to a He flow (30 mL/min) at 573 K for 15 h did not change the BET surface area (297 m²/g). In contrast, the fresh γ -Al₂O₃ BET surface area decreased by ca. 20%, to 241 m²/g, after 6 h of reaction with CF₃CFCl₂. The reaction with CF₃CFCl₂ for longer times (up to 15 h) did not further decrease the surface area significantly. The surface area of the AlF₃ (47 m²/g) did not change during the reaction with CF₃CFCl₂ for 15 h.

X-ray diffraction (XRD) patterns of fresh and used γ -Al₂O₃ (CF₃CFCl₂ reaction at 573 K for 15 h) were similar and possessed only characteristic lines of the γ -Al₂O₃ phase. Similarly, fresh and used AlF₃ (also after CF₃CFCl₂ reaction at 573 K for 15 h) had the same XRD patterns, characteristic of AlF₃. In addition to Al and O peaks detected in fresh γ -Al₂O₃, energy-dispersive X-ray spectroscopy (EDX) of used γ -Al₂O₃ revealed the presence of fluorine, but no chlorine.

Figure 5a shows the OH-group spectrum of a fresh γ -Al₂O₃ sample preheated in a 10% O₂/He flow at 773 K. It consists of

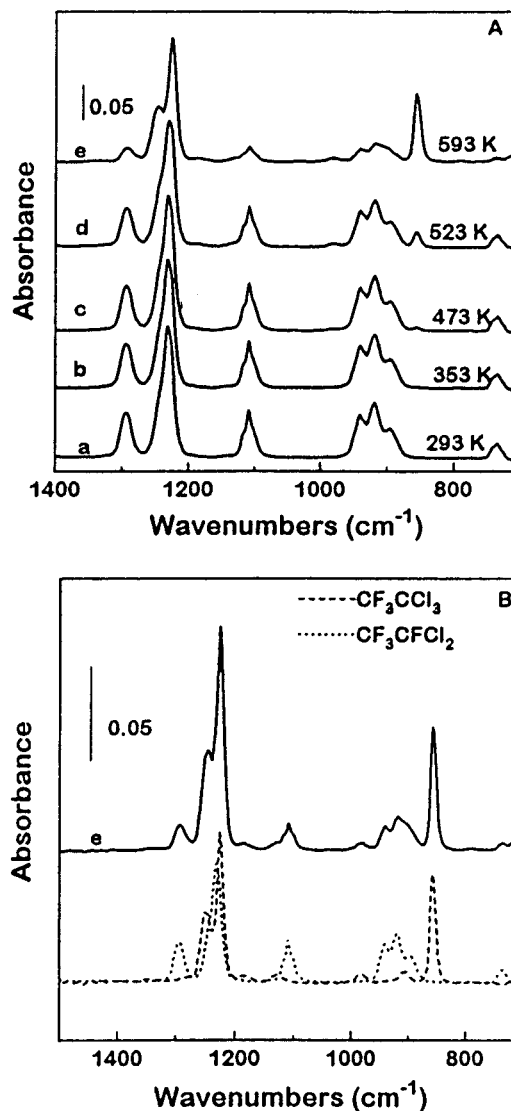


Figure 3. Infrared spectra of gas phase after the exposure of the wafer of fresh γ -Al₂O₃ to 3 Torr of CF₃CFCl₂ at different temperatures (A) and deconvolution of the spectrum (e) into CF₃CFCl₂ and CF₃CCl₃ constituents (B).

three absorption bands with maxima at 3680, 3723, and 3770 cm⁻¹. These bands have been previously assigned to isolated hydroxyls coordinated to three octahedral Al³⁺ cations, to a tetrahedral and to an octahedral Al³⁺ cation and to a single tetrahedral Al³⁺ cation, respectively.^{14,15}

The changes of the hydroxyl group vibration intensity after γ -Al₂O₃ treatment with CF₃CFCl₂ are most clearly seen in the difference spectrum (Figure 5b), in which the spectrum of the fresh γ -Al₂O₃ was subtracted. The intensity of the hydroxyl vibration bands did not change after room-temperature contact of CF₃CFCl₂ with γ -Al₂O₃ followed by evacuation of physisorbed molecules. However, after a 10 min exposure of CF₃CFCl₂ at 523 K and evacuation of physisorbed molecules at

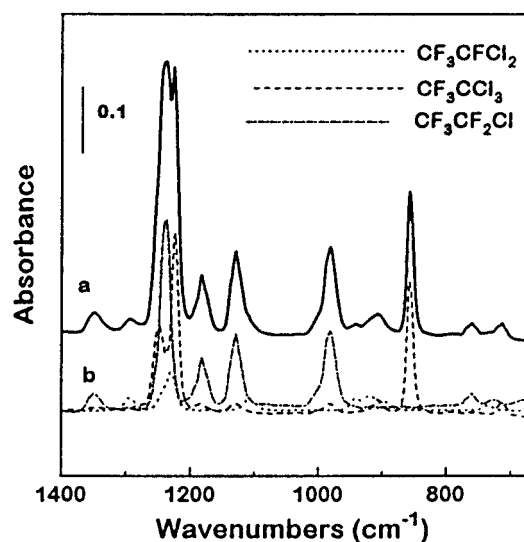


Figure 4. Infrared spectra of gas phase after the exposure of the wafer of used γ - Al_2O_3 to 3 Torr of CF_3CFCl_2 at 353 K (curve a) and the deconvolution of the spectrum into CF_3CFCl_2 , $\text{CF}_3\text{CF}_2\text{Cl}$, and CF_3CCl_3 constituents (curves b).

TABLE 2: BET Surface Area of γ - Al_2O_3 and AlF_3 Samples during the Course of Reaction with CF_3CFCl_2

material	time on stream, h	BET surface area, m^2/g
γ - Al_2O_3	fresh	298
	2.0	260
	6.0	241
	9.5	248
	15.0	235
AlF_3	fresh	47
	15.0	48

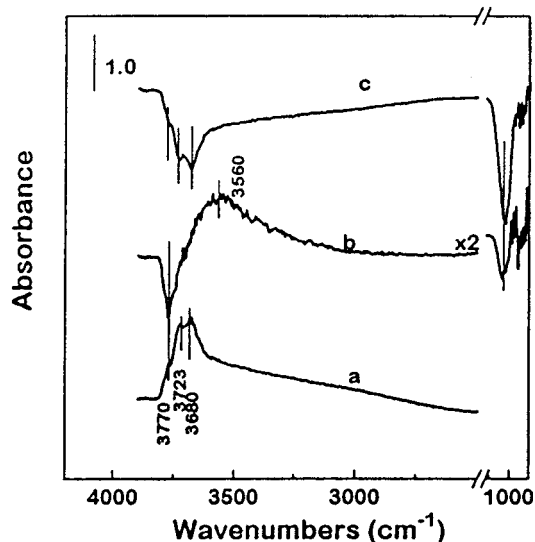


Figure 5. IR spectrum of (a) fresh γ - Al_2O_3 after oxidation at 773 K, (b) γ - Al_2O_3 wafer on exposure to CF_3CFCl_2 at 523 K followed by evacuation of gas phase at 298 K (referenced to the fresh γ - Al_2O_3 , spectrum a) and (c) γ - Al_2O_3 pellet following exposure to CF_3CFCl_2 at 673 K and treatment in 10% O_2/He at 773 K (referenced to the fresh γ - Al_2O_3 , spectrum a).

room temperature, the band at 3770 cm^{-1} disappeared while the bands at 3680 and 3723 cm^{-1} remained. The disappearance of the narrow band at 3770 cm^{-1} was accompanied by the development of a broad band centered at 3560 cm^{-1} , characteristic of hydrogen bonded OH-groups. Some of the chemisorbed species, resulting from CF_3CFCl_2 adsorption at 523 K, are probably localized near the OH-groups coordinated to a

TABLE 3: Summary of Positions and Intensities of the Band of CO Adsorbed at 298 K on γ - Al_2O_3 Exposed to CF_3CFCl_2 in Different Conditions

no.	sample	$\nu_{\text{CO}}, \text{cm}^{-1}$	I_{CO}, au
1	fresh γ - Al_2O_3	2202	0.026
2	sample 1 after chemisorption of CF_3CFCl_2 at 298 K	2203	0.021
3	sample 2 after chemisorption of CF_3CFCl_2 at 473 K	2204	0.015
4	sample 3 following evacuation at 673 K	2207	0.016
5	sample 4 after chemisorption of CF_3CFCl_2 at 523 K	2212	0.014
6	sample 5 following evacuation of at 673 K	2213	0.047
7	sample 6 after chemisorption of CF_3CFCl_2 at 573 K followed by treatment in O_2/He at 773 K	2225	0.052

single tetrahedral Al^{3+} cation and perturb those hydroxyls via hydrogen bonding.

Chemisorption of CF_3CFCl_2 not only perturbed the OH groups but also resulted in a negative band at 1050 cm^{-1} in the difference spectrum (Figure 5b). This band has been previously assigned to an Al–O vibrational mode localized in strained surface groups such as $[\text{Al}^{\delta+}\cdots\text{O}^{\delta-}-\text{Al}]$.¹⁵ Thus, it appears that these groups participate in CF_3CFCl_2 chemisorption. More severe treatment of γ - Al_2O_3 with CF_3CFCl_2 resulted in an almost complete disappearance of surface OH groups and a more pronounced negative peak in the range of 1000 – 1100 cm^{-1} (Figure 5c).

Lewis acidity, an important characteristic of γ - Al_2O_3 , is usually associated with coordinatively unsaturated Al^{3+} cations formed during high-temperature γ - Al_2O_3 surface dehydroxylation. The FTIR spectra of CO adsorbed on fresh γ - Al_2O_3 and γ - Al_2O_3 pretreated with CF_3CFCl_2 under different conditions, consisted of a single band corresponding to C=O bond stretching vibrations of molecules adsorbed on coordinatively unsaturated Al^{3+} cations. Table 3 shows the main characteristics of these spectra, such as band position and intensity.

Room-temperature CF_3CFCl_2 adsorption on fresh γ - Al_2O_3 did not affect the 2202 cm^{-1} CO absorption band. Preadsorption of CF_3CFCl_2 at 473 K followed by CO adsorption also did not influence the position of the CO band but decreased its intensity slightly. However, adsorption of CO after evacuation at 673 K following CF_3CFCl_2 adsorption at 298 and 523 K resulted in a blue shift of the band maximum of 3 and 5 cm^{-1} , respectively. Further, the band intensity increased by a factor of ~ 3 .

Treatment of a sample with CF_3CFCl_2 preadsorbed at 573 K in flowing 10% O_2/He mixture at 773 K did not change the band intensity of the adsorbed CO but increased its maximum frequency from 2202 to 2225 cm^{-1} . This shift is attributed to the increase of electron pair donation from the coordinated CO molecule 5σ orbital to the empty Al^{3+} cation $3p$ orbital. Therefore, it reflects an increase of electron-accepting properties of Al^{3+} cations or their Lewis acidity. It should be noted that CF_3CFCl_2 chemisorption had little influence on the adsorbed CO band intensities. This suggests that chemisorbed species formed upon CF_3CFCl_2 adsorption did not block the γ - Al_2O_3 surface Lewis acidic sites.

4. FTIR study of CF_3CFCl_2 Adsorption on γ - Al_2O_3 . Figure 6 shows the FTIR spectra of chemisorbed species formed on the surface of fresh and used γ - Al_2O_3 , due to CF_3CFCl_2 adsorption at 473 K. The fresh γ - Al_2O_3 surface species spectrum (bottom spectrum) consisted of six absorption bands with maxima at 1666, 1500, 1425, 1243, 1215, and 1189 cm^{-1} . The IR spectrum of chemisorbed species formed upon adsorption of CF_3CFCl_2 under the same conditions on used γ - Al_2O_3 (top

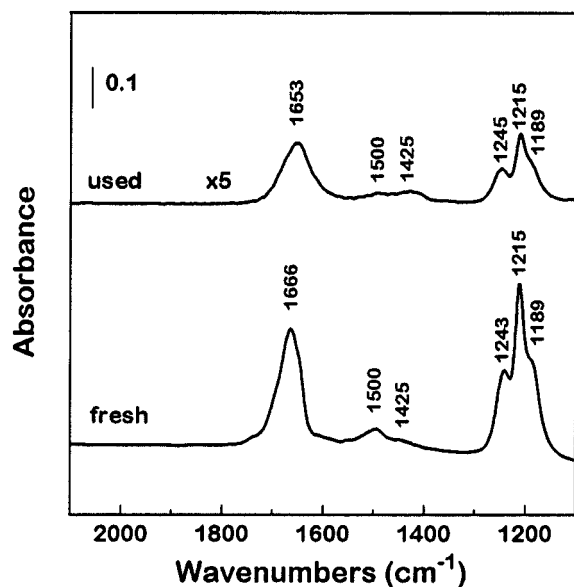


Figure 6. Infrared spectra of chemisorbed species formed after adsorption of 3 Torr of CF_3CFCl_2 at 473 K followed by evacuation of the gas phase at 298 K, on the surface of fresh $\gamma\text{-Al}_2\text{O}_3$ (bottom curve) and used $\gamma\text{-Al}_2\text{O}_3$ (top curve).

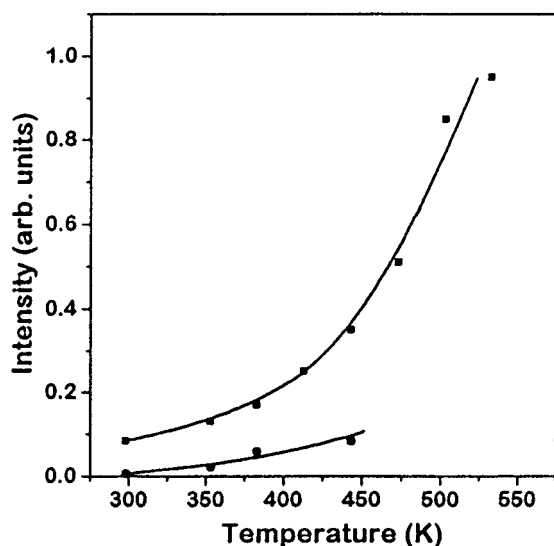


Figure 7. Change in intensity of the IR band at 1215 cm^{-1} of surface species formed on chemisorption of CF_3CFCl_2 on fresh (■) and used (●) $\gamma\text{-Al}_2\text{O}_3$ as a function of adsorption temperature.

spectrum) also consisted of six absorption bands (1653 , 1500 , 1425 , 1245 , 1215 , and 1189 cm^{-1}). However, the band intensities associated with the used $\gamma\text{-Al}_2\text{O}_3$ was lower compared to the band intensities associated with the fresh $\gamma\text{-Al}_2\text{O}_3$. The primary differences between spectra of chemisorbed species on fresh and used aluminas was the shift of the band at 1666 to 1553 cm^{-1} with the broadening of the latter. On both fresh and used $\gamma\text{-Al}_2\text{O}_3$, the intensity of the absorption bands gradually decreased in a vacuum at 553 K while the ratio between the intensities of all the bands remained constant. This indicates that the bands belong to one type of surface species. A GC-MS analysis of the gases that evolved during heating in a vacuum at 573 K of $\gamma\text{-Al}_2\text{O}_3$ (with CF_3CFCl_2 preadsorbed at 473 K) established that the only products resulting from decomposition of chemisorbed surface species were CO and CO_2 .

The concentration of chemisorbed species formed on the surface of fresh and used aluminas was dependent on the CF_3CFCl_2 adsorption temperature (Figure 7). Increasing the adsorp-

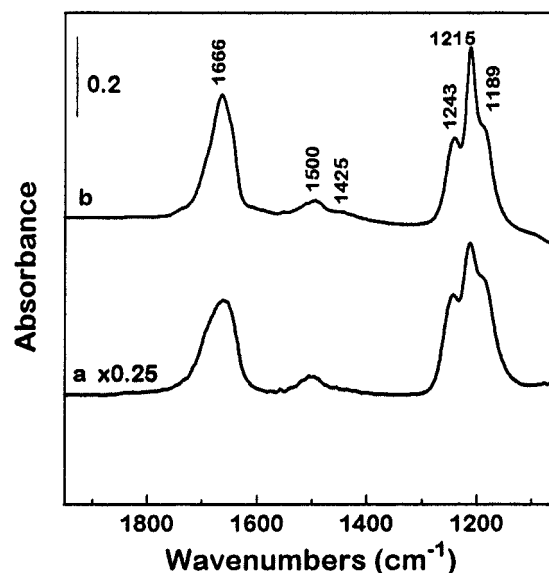


Figure 8. IR spectra of chemisorbed species (a) after adsorption of 2.2 Torr of CF_3COCl at 373 K and (b) after adsorption of 3 Torr of CF_3CFCl_2 at 473 K on fresh $\gamma\text{-Al}_2\text{O}_3$ followed by evacuation of the gas phase at 298 K in each case.

tion temperature to 543 K resulted in a gradual increase in the concentration of chemisorbed species on the surfaces of both fresh and used $\gamma\text{-Al}_2\text{O}_3$. However, at the same CF_3CFCl_2 adsorption temperature, the concentration of chemisorbed species on the used $\gamma\text{-Al}_2\text{O}_3$ was much lower than on the fresh $\gamma\text{-Al}_2\text{O}_3$. The increased surface species concentration with increasing adsorption temperature indicated that the chemisorption of CF_3CFCl_2 is activated for both fresh and used $\gamma\text{-Al}_2\text{O}_3$.

A spectrum of chemisorbed species similar to that of CF_3CFCl_2 adsorption on fresh $\gamma\text{-Al}_2\text{O}_3$ was obtained by adsorption of CF_3COCl molecules on $\gamma\text{-Al}_2\text{O}_3$. Figure 8 shows the spectra of chemisorbed species on fresh $\gamma\text{-Al}_2\text{O}_3$ after CF_3COCl adsorption at 373 K (spectrum a) and after CF_3CFCl_2 adsorption at 473 K (spectrum b). With the exception of the low intensity band at 1425 cm^{-1} (for the adsorbed CF_3CFCl_2), both spectra consisted of bands with the same maximum positions but with significantly different intensities. The intensity of IR bands due to the surface species resulting from CF_3COCl chemisorption were ~ 4 times more intense than those resulting from CF_3CFCl_2 adsorption, despite the lower adsorption temperature of CF_3COCl .

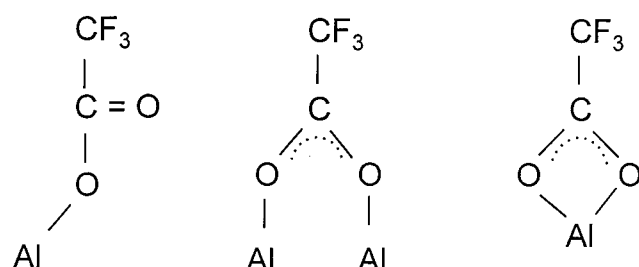
Discussion

The literature provides several examples demonstrating that halocarbons halogenate $\gamma\text{-Al}_2\text{O}_3$ at elevated temperatures,^{11,12} and the present research shows that CF_3CFCl_2 is no exception. However, transformation of the oxide creates new sites, both active and selective for disproportionation of CF_3CFCl_2 . The results of this investigation provide the framework for understanding the nature of the active site for CF_3CFCl_2 disproportionation and the crucial mechanistic aspects of the reaction.

1. The Nature of Surface Species Formed upon CF_3CFCl_2 Chemisorption on $\gamma\text{-Al}_2\text{O}_3$. The similarity of the FTIR spectra of chemisorbed species formed during adsorption of either CF_3CFCl_2 or CF_3COCl (Figure 8) provides insight into the nature of those species. One could expect that during CF_3COCl chemisorption on $\gamma\text{-Al}_2\text{O}_3$, the surface species formed are similar to those produced from acetic acid decomposition on metal oxides. It is known that adsorption of acetic acid on TiO_2 ¹⁶ or MgO ¹⁷⁻¹⁹ results in the formation of surface acetate species

TABLE 4: Fundamental Stretching Vibrations of Gaseous Trifluoroacetyl Chloride, Solid Aluminum Trifluoroacetate, and Surface Trifluoroacetate Species

vibration	this work				ref 23	ref 31	ref 29	ref 38
	CF ₃ CFCl ₂ adsorption on fresh γ -Al ₂ O ₃	CF ₃ CFCl ₂ adsorption on used γ -Al ₂ O ₃	CF ₃ COCl adsorption on fresh γ -Al ₂ O ₃	gaseous CF ₃ COCl	(CF ₃ CO ₂) ₃ Al (solid)	CF ₃ CF=CF ₂ adsorption on TiO ₂	CF ₃ COCF ₃ adsorption on TiO ₂	(C ₂ F ₅) ₂ O adsorption on Al ₂ O ₃
ν_{asym} O—C—O	1666	1653	1666	1810	1670	1734	1580	1700
ν_{sym} O—C—O	1500	1425	1501		1485	1470	1480	1491
ν_{sym} CF ₃	1243	1245	1245	1274	1205	1258		1248
ν_{asym} CF ₃	1215	1215	1215	1239	1160	1204 ^a		
ν_{asym} CF ₃	1189	1189	1189	1202	1050	1124		
bonding	bridging	unidentate	bridging	n/a	unidentate	unidentate	bidentate	

^a Assigned to δ_{CO} bending vibration.**Figure 9.** Possible structures of surface trifluoroacetate species.

and hydroxyl groups. In both cases, the IR spectrum of the chemisorbed species contained two absorption bands in the 1300–1600 cm^{-1} region. These bands are assigned to the symmetric and asymmetric C—O bond stretching vibrations of the O—C—O fragment of surface metal acetates based on a comparison to the IR spectra of different solid metal acetates which consist of two absorption bands in the 1350–1600 cm^{-1} range attributed to the C—O stretching vibrations of O—C—O fragments.^{20,21} For metal trifluoroacetates, those two C—O bond stretching vibrations are shifted to higher frequencies (1400–1750 cm^{-1}).^{22–24} For all acetates, including trifluoroacetates, the asymmetric C—O bond stretching vibration frequency is higher than the symmetric frequency. The chemisorbed CF₃CFCl₂ high-frequency IR bands (centered at 1666 and 1500 cm^{-1} for fresh γ -Al₂O₃ and 1653 and 1425 cm^{-1} for used γ -Al₂O₃) are therefore assigned to the asymmetric and symmetric C—O bond stretching vibrations of the O—C—O fragment of surface aluminum acetates.²⁵ The 1243–1245 cm^{-1} band is ascribed to the symmetric stretching vibration of the CF₃ group, while the bands at 1215 and 1189 cm^{-1} are assigned to the nondegenerate asymmetric vibrations of CF₃. Such an assignment of low-frequency bands is quite reasonable. Indeed, in different CF₃ compounds in which the CF₃ group is attached to a carbon atom (e.g., acetates), the symmetric C—F bond stretching vibration frequency is higher than that of asymmetric vibration.²³ Further, for gaseous trifluoroacetyl chloride (CF₃COCl), with a geometric structure analogous to monodentate acetate, the asymmetric C—F bond stretching vibration is nondegenerate due to distortion of the CF₃ group symmetry from C_{3v} (see Table 4).

Figure 9 shows the possible structures of the acetate species that may form on metal oxide surfaces. Analysis of the frequency difference between asymmetric and symmetric C—O bond stretching vibrations of O—C—O fragment ($\Delta\nu_{\text{as-s}}$) has been used to determine the structure of acetates.^{20,25} In general, a frequency difference of less than 100 cm^{-1} is characteristic of a bidentate acetate coordinated to a single metal cation. For unidentate acetate, the frequency difference is usually greater

than 200 cm^{-1} , while a $\Delta\nu_{\text{as-s}}$ between 100 and 200 cm^{-1} indicates a bridging structure.^{26,27} The analysis of the frequency difference between asymmetric and symmetric C—O bond stretching vibrations of the O—C—O fragment was also used to determine the structure of the adsorbed acetate and fluoroacetate species. The following examples illustrate these assignments. First, the surface species formed upon adsorption of ethanol on γ -Al₂O₃ was assigned to a bidentate acetate based on the value of $\Delta\nu_{\text{as-s}} = 106 \text{ cm}^{-1}$.²⁸ Second, for the adsorption of hexafluoroacetone on TiO₂, an assignment of bidentate trifluoroacetate species was made based on $\Delta\nu_{\text{as-s}} \approx 100 \text{ cm}^{-1}$.²⁹ Third, for the adsorption of hexafluoroacetone on γ -Al₂O₃, a $\Delta\nu_{\text{as-s}} = 193 \text{ cm}^{-1}$ led to an assignment of bridge-bonded formate.³⁰ Finally, a $\Delta\nu_{\text{as-s}} = 264 \text{ cm}^{-1}$ for the adsorption of CF₃CF=CF₂ on TiO₂ resulted in the assignment of a unidentate trifluoroacetate.³¹

In the present investigation, the frequency difference between the asymmetric and symmetric C—O bond stretching vibrations of the acetate species O—C—O fragment, formed upon CF₃CFCl₂ chemisorption on fresh and used γ -Al₂O₃, is 166 and 228 cm^{-1} , respectively. The frequency difference for acetate species on the surface of the used γ -Al₂O₃ ($\Delta\nu_{\text{as-s}}$) is higher than 200 cm^{-1} , allowing one to conclude that the surface acetate has a unidentate structure. The lower frequency difference between asymmetric and symmetric C—O bond stretching vibrations of O—C—O fragments of surface acetates for the fresh γ -Al₂O₃ suggests a bridging structure.

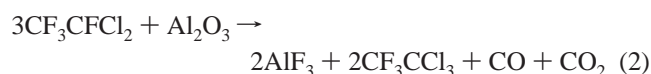
It is known that hydrogen bonding of acetates with the surface OH groups of γ -Al₂O₃ can decrease the difference in frequency between asymmetric and symmetric stretching vibrations of O—C—O fragments in surface acetates. For example, small values of $\Delta\nu_{\text{as-s}} = 120$ –130 cm^{-1} for unidentate acetates formed on MgO upon adsorption of acetic acid were explained by hydrogen bonding between neighboring surface acetates.¹⁷ However, the possibility of hydrogen bonding of OH-groups of γ -Al₂O₃ with surface acetates appears unlikely, because the OH-groups are the most reactive and sterically accessible groups on the surface of γ -Al₂O₃. Thus, the OH-groups are consumed immediately during reaction with CF₃CFCl₂ to form HCl and, probably, a CF₃CFCl—O—Al= species that transforms into the acetate. The HCl either desorbs into the gas phase or interacts with Al—O—Al fragments on the surface to form adjacent =Al—Cl and HO—Al= groups. The latter case is confirmed by the development in the IR spectrum of a broad absorption band at 3560 cm^{-1} , characteristic of hydrogen bonded OH groups (Figure 5b).

Table 4 shows the characteristic IR absorption bands and possible band assignments for the surface trifluoroacetate species, formed upon adsorption of various fluorine compounds onto oxides.

2. Pathways to γ -Al₂O₃ Fluorination. The fluorination of γ -Al₂O₃ by CF₃CFCl₂ involves its chemisorption to form a surface aluminum trifluoroacetate by abstraction of F and Cl atoms from the -CFCl₂ group. Then, the surface Cl atoms are substituted for fluorine by an exchange reaction with CF₃CFCl₂ to form the chlorine-enriched product CF₃CCl₃:

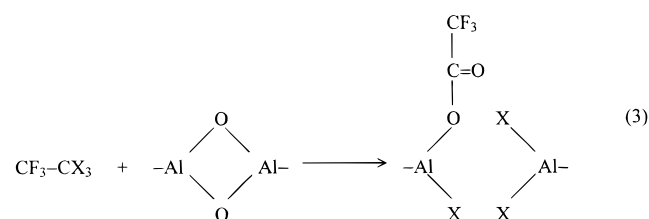


The final fluorination step is the decomposition of the trifluoroacetate species forming only CO and CO₂. The following general scheme represents the overall fluorination process:



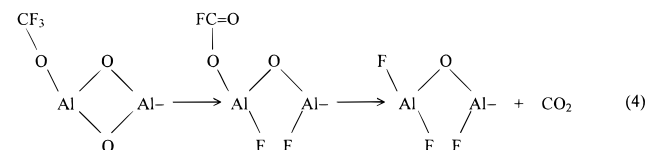
A strong decrease in OH group concentration was observed in the regenerated sample after treatment with CF₃CFCl₂ at high temperature (Figure 5c). This observation, combined with the appearance of gaseous HCl during prolonged heating of fresh γ -Al₂O₃ in CF₃CFCl₂ at 573 K indicates that partial removal of Cl from the surface proceeds through HCl elimination from interacting adjacent Al-Cl and Al-OH groups.

The formation of surface trifluoroacetate species proceeds via abstraction of all halogen atoms X (X = Cl or F) from the -CFCl₂ group of CF₃CFCl₂ and attachment of surface oxygen atom of γ -Al₂O₃ to carbon atom of chemisorbed substance:



The resulting Al-X pairs act as active sites for high-temperature halogen exchange reactions between the γ -Al₂O₃ surface and CF₃CFCl₂ to form the chlorine enriched CF₃CCl₃. In this case, the fluorine atom abstraction from the -CFCl₂ group of CF₃CFCl₂ probably becomes thermodynamically more favorable because of the higher bond energy of Al-F compared to the Al-Cl bond.

Only adsorbates containing two carbons are observed. This suggests that the limiting step of trifluoroacetate decomposition is the carbon-carbon bond cleavage with simultaneous CO molecule abstraction. As a result, trifluoromethoxy groups are formed that rapidly convert into fluoroformates, the decomposition of which leads to CO₂ evolution and further γ -Al₂O₃ fluorination.

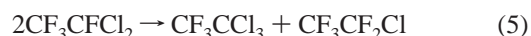


The properties of surface Al³⁺ cation-O²⁻ anion pair sites is markedly different for γ -Al₂O₃ samples treated at 773 K than those treated at lower temperatures.³² According to XPS results for Al and O binding energies of γ -Al₂O₃, new strong acid-base cluster sites (consisting of Al³⁺ and O²⁻ ions) are formed when the sample is dehydroxylated at and above 773 K.³² A characteristic feature in the IR spectrum is an absorption band at ~1050 cm⁻¹ corresponding to an Al-O vibrational mode

localized to strained groups of the Al^{δ+}...O^{δ-}-Al type. Similar sites seems to be responsible for the thermal decomposition of aluminum trifluoroacetates on the surface of γ -Al₂O₃.

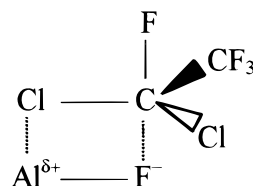
Evidence for the involvement of these "strained" sites in the decomposition of surface acetates comes from the results presented in spectra b and c of Figure 5. This figure shows the disappearance of the IR absorption band in the 1000–1100 cm⁻¹ range in the spectrum of the γ -Al₂O₃ after CF₃CFCl₂ adsorption. The disappearance of a similar band at 1034 cm⁻¹, after adsorption of CCl₄ on a highly dehydroxylated γ -Al₂O₃, was explained by the depletion of Al³⁺-O²⁻ cluster sites due to formation of monodentate carbonate ions.¹⁰

3. Low-Temperature Activity of γ -Al₂O₃ in Halogen Exchange Reaction. According to FTIR spectroscopic studies under static conditions, the halogen exchange reaction



catalyzed by the used γ -Al₂O₃ proceeds rapidly at 353 K, while with the fresh γ -Al₂O₃ the transformation of CF₃CFCl₂ into CF₃CCl₃ was detected only at temperatures higher than 473 K. The low-temperature activity of the used γ -Al₂O₃ for the halogen exchange reaction is connected with the fluorination of γ -Al₂O₃ during pretreatment with CF₃CFCl₂ at elevated temperatures. According to Peri, fluorination of γ -Al₂O₃ leads to a strengthening of the surface Lewis acid sites, coordinatively unsaturated Al³⁺ cations.³³ It was also observed that an increase in the Lewis acidity of oxides results from an interaction with CFCs.^{34,35} Corma et al. concluded that for γ -Al₂O₃ the total number of Lewis sites decreases with increasing fluorine content, but the concentration of strong Lewis acidic sites exhibits a maximum for fluorine concentrations between 2% and 4%.³⁶ Our FTIR spectroscopic study results of CO adsorption on γ -Al₂O₃ samples pretreated with CF₃CFCl₂ also demonstrate the strengthening of Lewis acidic sites (coordinatively unsaturated Al³⁺ cations) upon CF₃CFCl₂ chemisorption, especially after thermal decomposition of chemisorbed species. The IR spectra band intensity of the coordinated CO molecules, after high-temperature vacuum treatment with preadsorbed CF₃CFCl₂ at 523 K, provide a measure of the number of Lewis acidic sites. The observed increase in Lewis acidic sites is attributed to removal of surface chlorine anions by formation of gaseous HCl.

Accordingly, it is suggested that the coordinatively unsaturated Al³⁺ cations surrounded by F⁻ anions on the fluorinated γ -Al₂O₃ surface participate in low-temperature halogen exchange reactions between CF₃CFCl₂ and the halogenated surface. Indeed, Coulson et al.⁷ reported that the formation of the disproportionation products follows a monomolecular scheme involving halogen exchange with the surface Lewis acid sites. Similar to exchange reactions of CCl₄ with prefluorinated chromia,³⁵ a four-center intermediate for chloro-fluoro exchange in CF₃CFCl₂ on fluorinated γ -Al₂O₃ surface is proposed.



Conclusions

The CF₃CFCl₂ reaction over γ -Al₂O₃ leads to a modification of the γ -Al₂O₃ surface due to fluorination. The modified surface possesses sites that readily catalyze the disproportionation of CF₃CFCl₂ at 353 K. FTIR spectroscopic studies show the

formation of unidentate and bridge-bonded trifluoroacetate species as a result of adsorption of CF_3CFCl_2 on the surface of $\gamma\text{-Al}_2\text{O}_3$ at 298–573 K. More importantly, the decomposition of trifluoroacetates results in formation of CO and CO_2 and the fluorination of the $\gamma\text{-Al}_2\text{O}_3$ surface. Such catalytically active fluorinated $\gamma\text{-Al}_2\text{O}_3$ possesses increased Lewis acidity as measured by FTIR spectroscopy using CO adsorption.

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