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FTIR study of a perfluoroacyl fluoride chemisorption onto alumina

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Abstract

The chemisorption of a perfluoroacyl fluoride onto an alumina surface calcined at 523 K has been investigated via transmission infrared spectroscopy. It was found that a hydrogen bond is formed between an isolated surface hydroxyl group and the carbonyl oxygen atom of $CF_3OCF(CF_3)COF$. The CF bond of the COF functional group was not broken in the chemisorption process, indicating that the nucleophilic attack of a surface hydroxyl group at the carbonyl carbon atom did not occur. The Al^{3+} Lewis acid sites were not involved in the chemisorption process and the isolated hydroxyl groups on the alumina surface were consumed. No perfluorocarboxylate surface species was detected in the desorption study. No AlF_3 formation was observed when the alumina surface was heated to 400 °C with excess $CF_3OCF(CF_3)COF$.

Introduction

Most of the perfluoropolyalkylether (PFPAE) degradation research conducted to date has been performed in the liquid phase. Typically, a reaction vessel containing PFPAE lubricant, in the presence or absence of metal, is heated to a certain temperature. The resulting gaseous products and the remaining degraded liquid are then analyzed by MS, IR or NMR techniques. For example, Zehe and Faut [1] have reported the complete degradation of Fomblin Z at 185 °C in the presence of Fe_2O_3. They propose that the degradation mechanism of Fomblin Z can be viewed as a two-stage process. The first stage is a slow process in which Fe_2O_3 interacts with the reactive gaseous decomposition products from Fomblin Z to produce FeF_3. The second stage is the rapid catalytic degradation of the PFPAE by the Lewis acid sites of the newly-formed FeF_3.

Kasai *et al.* [2], using mainly the NMR spectroscopic technique, studied the thermal degradation of Fomblin Z, Fomblin Y, Krytox and Demnum in the presence of alumina. Fomblin Z was found to degrade at 200 °C. Krytox and Demnum are stable because of the lack of a difluoroacetal unit ($-O-CF_2-O-$) in their molecular structures. They proposed a similar mechanism to that reported by Zehe and Faut [1], viz. Al_2O_3 is converted to AlF_3 during a long induction period, and the resulting AlF_3 is responsible for the rapid, complete decomposition of Fomblin Z.

The present work was designed to study the interaction of Al_2O_3 with models of the degradation products of PFPAE lubricants in an effort to verify the mechanism reported by Zehe and Faut [1], and by Kasai *et al.* [2]. One of the major PFPAE degradation products resulting from interaction with a metal surface is a perfluoroacyl fluoride, R_fCOF, where R_f is C_nF_{2n+1}. In this study, perfluoro-2-methoxypropanoyl fluoride, $CF_3OCF(CF_3)COF$, was chosen to react with an alumina surface. It is clear that the fluorine atom of the $-COF$ functional group is more active than the rest of the fluorine atoms in the molecule. Particular attention was given to the role played by this C–F bond in the course of the study. This report will focus on the interaction between alumina and R_fCOF [$R_f = CF_3OCF(CF_3)$], not only at room temperature but also at high temperature.

Experimental

An impregnation method [3] was used to prepare the alumina surface. A suspension consisting of 1.4 g of Al_2O_3 (Degussa, Al_2O_3-C, 100 m^2 g^{-1}), 10 ml of H_2O and 140 ml of acetone was sprayed with an airbrush onto a KBr disk (32 mm diameter) maintained at 350 K to flash-evaporate the solvents. The KBr disk was then mounted in the IR cell described previously [4].

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A dosing tube was pointed toward the center of the sample disk at an oblique angle, thus allowing the dosing gas to interact with the Al_2O_3 surface directly and evenly. Before dosing with any adsorbates, the Al_2O_3 surface was calcined at 523 K under vacuum for 36 h.

Infrared spectra were recorded using a Perkin–Elmer 1750 FTIR spectrometer over the 4000–400 cm^{-1} range at 4 cm^{-1} resolution. A KBr beamsplitter and a DTGS detector were used. Each spectrum was an average of 100 accumulated scans. Measurements at the 10^{-3} absorbance level were achieved with good signal-to-noise ratios. Most of the spectra reported here are difference spectra which were obtained by subtracting the IR spectra with and without a given amount of adsorbate. The glass cell was securely mounted and remained stationary throughout the course of data acquisition, thus minimizing artifacts in the subtraction technique. Pressure was monitored with Baratron capacitance manometers covering a range of 10^{-3}–10^{3} Torr.

Results and discussion

The infrared spectra of the gaseous and chemisorbed species for $CF_3OCF(CF_3)COF$ are shown in Fig. 1. The 1888 cm^{-1} band ($\nu_{C=O}$ mode) disappeared as the molecules were chemisorbed onto the calcined alumina surface at room temperature. New bands, at 1669 cm^{-1} and 1425 cm^{-1}, are gradually formed with chemisorption time elapse as shown in Fig. 2. The increasing band intensities reveal that the adsorption sites were gradually occupied by the adsorbate molecules. Upon reaching equilibrium, the system was evacuated. The band intensities did not decrease, indicating a strong interaction between the surface sites and the perfluoroacyl fluoride.

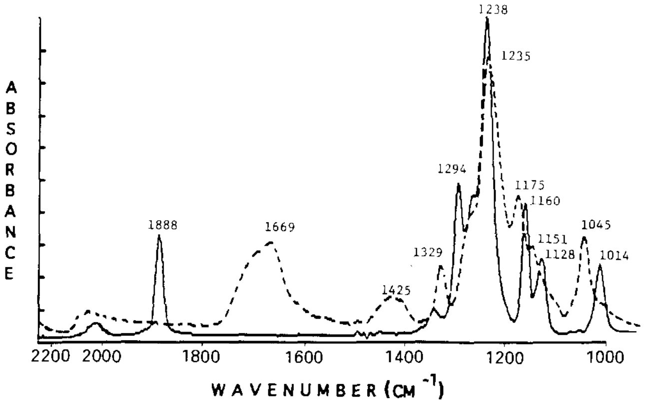


Fig. 1. Infrared spectra of gaseous (solid line, designated as (a)) and chemisorbed (broken line, designated as (b)) species of $CF_3OCF(CF_3)COF$.

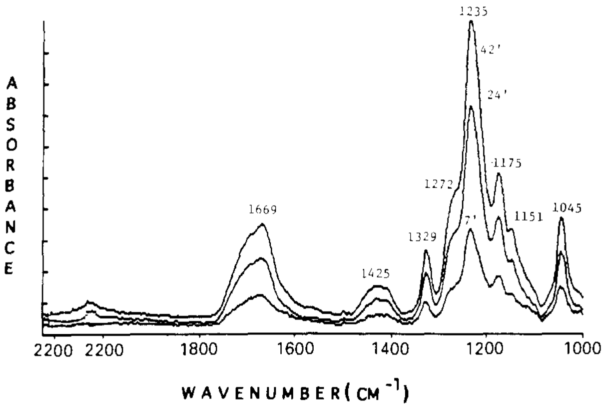


Fig. 2. Infrared spectra arising from the room-temperature chemisorption of $CF_3OCF(CF_3)COF$ at 0.0022 Torr pressure onto an alumina surface calcined at 523 K at the following time intervals: bottom trace, 7 min; middle trace, 24 min; top trace, 42 min.

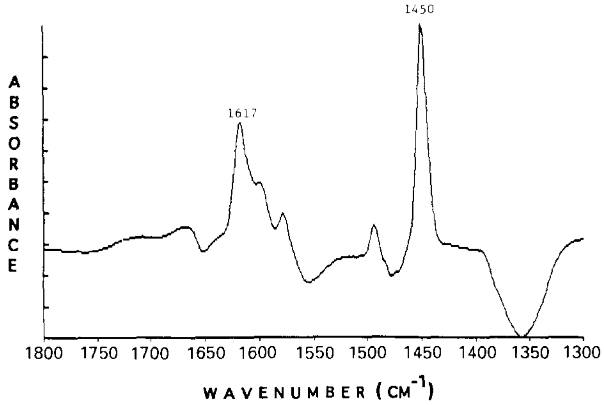


Fig. 3. Infrared spectrum of pyridine chemisorbed onto Al^{3+}, Lewis acid alumina surface sites. The alumina surface was heated to 450 K and then exposed to 10 Torr pressure of pyridine.

It is well known that a calcined alumina surface contains coordinatively unsaturated Al^{3+} Lewis acid sites and isolated hydroxyl groups as well as associated hydroxyl groups [5]. Usually, the former two sites participate in the chemisorption process. In order to differentiate between these two sites, a calcined alumina surface was heated to 450 K and then exposed to 10 Torr pressure of pyridine, a compound whose interaction with the Al_2O_3 surface has been well studied [5, 6]. The cell was then evacuated and the surface cooled to room temperature to obtain IR spectra. As expected, the Lewis acid sites, Al^{3+}, interacted with pyridine molecules, and a pair of bands appeared at 1617 cm^{-1} and 1450 cm^{-1} in the spectrum as shown in Fig. 3. In effect, the pyridine had blocked the Lewis acid sites of the alumina surface.

Approximately 2×10^{-3} Torr of $CF_3OCF(CF_3)COF$ was administered to the Al^{3+}-blocked surface and a spectrum obtained. A difference spectrum was then produced by subtracting the pyridine-only spectrum from the $CF_3OCF(CF_3)COF$ + pyridine spectrum. This cancelled out the pyridine bands leaving only the $CF_3OCF(CF_3)COF$ bands as shown in Fig. 4. As can be seen, Fig. 4 and Fig. 2 are essentially the same, with minor band shifts which are probably caused by the intermolecular repulsion between the two chemisorbed species, $CF_3OCF(CF_3)COF$ and pyridine. This clearly indicates that the Lewis acid sites, Al^{3+}, blocked by pyridine were not involved in the chemisorption process.

Figure 5 shows the hydroxyl stretching region of the IR spectrum following chemisorption of the acyl fluoride onto an alumina surface. The disappearance of the isolated hydroxyl groups (3743 cm^{-1}, 3685 cm^{-1}) and the enhancement of the associated surface hydroxyl group (approx. 3470 cm^{-1}) may be clearly observed. This shows that isolated, rather than associated, surface hydroxyl groups were involved in the chemisorption process. Thus, a hydrogen bond is proposed as being formed between the isolated surface hydroxyl group and the carbonyl oxygen atom of the $CF_3OCF(CF_3)COF$ molecule as shown in Scheme 1.

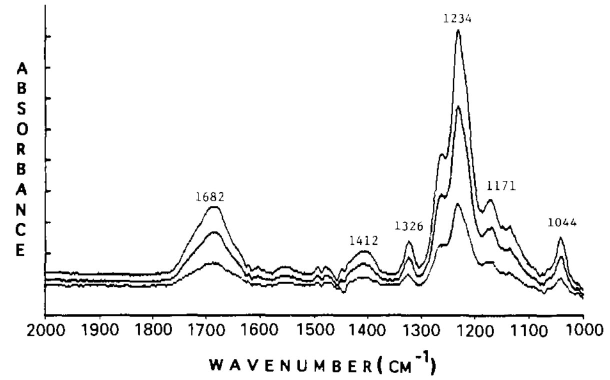


Fig. 4. Infrared spectra arising from the room-temperature chemisorption of $CF_3OCF(CF_3)COF$ at 0.0021 Torr pressure onto a pyridine-adsorbed alumina surface at the following time intervals: bottom trace, 7 min; middle trace, 19 min; top trace, 29 min.

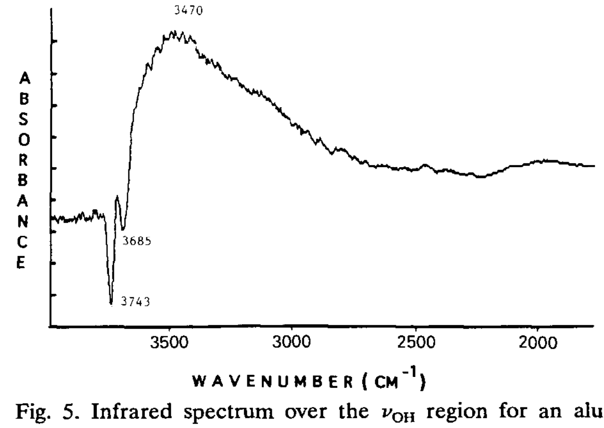
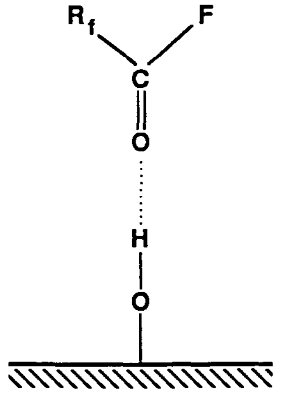
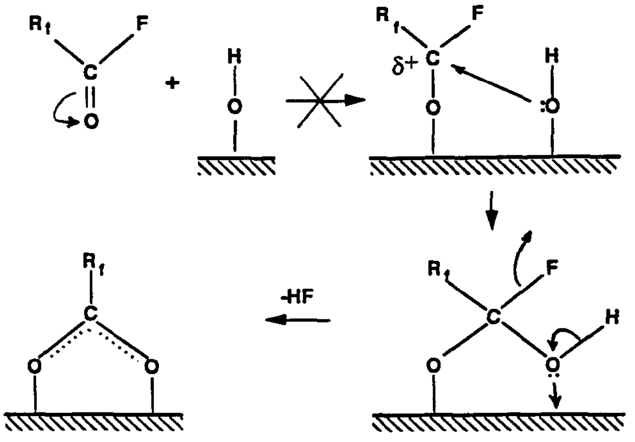


Fig. 5. Infrared spectrum over the ν_{OH} region for an alumina surface on which $CF_3OCF(CF_3)COF$ had been chemisorbed.



Scheme 1.



Scheme 2.

The relatively low energy 1014 cm^{-1} band shown as spectrum (a) in Fig. 1 merits further discussion. Electron diffraction studies have shown that the acyl C—F bond length is about 0.015 Å longer than the other C—F bonds in CF_3COF [7]. Berney has assigned the lowest frequency in the C—F stretching region to the $\nu_{C-F(acyl)}$ fundamental in CF_3COF [8]. Similar results would be expected for $CF_3OCF(CF_3)COF$. Consequently, the 1014 cm^{-1} band has been assigned to the $\nu_{C-F(acyl)}$ mode. Upon chemisorption, this band shifted to 1045 cm^{-1}. The presence of this band indicates that the acyl C—F bond was strengthened and not broken during the formation of the surface species. This shows that nucleophilic attack of surface hydroxyl groups at the electrophilic carbon atom of the carbonyl group (as shown in Scheme 2) did not occur.

In studies of the chemisorption of formaldehyde on tin oxide [9] and alumina [10], it was reported that a doublet appeared at approx. 1580 cm^{-1} and approx. 1380 cm^{-1}. These bands were assigned to the asymmetric and symmetric carboxylate stretching vibrations, respectively. It is tempting to make the same assignments in this study, i.e. to assign the 1669 cm^{-1} and the 1425 cm^{-1} bands to the asymmetric and symmetric carboxylate stretching vibrations, respectively. However, because the acyl C−F bond was not broken, Scheme 2 (which is common to ketones and aldehydes) will not apply to the chemisorbed species of perfluoroacyl fluorides. Consequently, the 1669 cm^{-1} and 1425 cm^{-1} bands may be assigned to the $\nu_{C=O}$ and δ_{O--H} vibrations of the newly formed hydrogen bond, C=O−−H. In studies of CF_3COCl, CF_3COF and CF_3CF_2COF, similar patterns of chemisorption were observed [11].

Desorption studies were also carried out, and the resultant spectra are shown in Fig. 6. All of the bands corresponding to the chemisorbed $CF_3OCF(CF_3)COF$ species lie in the negative direction indicating that the species desorbed from the alumina surface intact. This clearly shows the absence of any surface reaction occurring during the desorption process.

Ketones or aldehydes interact with metal oxides, such as tin oxide [9] or alumina [10], to form carboxylate surface species in desorption studies. However, in the present study, the equivalent perfluorocarboxylate surface species was not detected at desorption temperatures up to 400 °C. The chemisorbed $CF_3OCF(CF_3)COF$ desorbed from the surface intact rather than being degraded. The inherent thermodynamic stability of the C−C, C−O and C−F bonds in perfluoro compounds makes $CF_3OCF(CF_3)COF$ more stable than the analogous hydrocarbon. Hence, the bonds within $CF_3OCF(CF_3)COF$ are stronger than the hydrogen bond formed between surface and adsorbate molecules, as shown in Scheme 1. It is clear from this desorption study that perfluoroacyl fluoride exhibits very different results from those arising from corresponding studies with protonated ketones or aldehydes.

Kasai *et al.* [2] detected the formation of AlF_3 by XPS in the degradation reaction of Fomblin Z with alumina powder. Their experimental temperature was kept at 200 °C and the induction period was *c.* 1 h. In our present study, no formation of AlF_3 (as judged by a comparison of the resultant spectrum with the spectrum of an AlF_3/KBr pellet) was detected even when the alumina surface was heated to 400 °C with $CF_3OCF(CF_3)COF$ in excess. Neither the fluorine atom of the COF functional group, nor any of the other available fluorine atoms, reacted with Al_2O_3 to form detectable amounts of AlF_3 under our experimental conditions. It is possible that some minute quantity of AlF_3 was formed in the desorption process but this was masked by the nonreacted Al_2O_3.

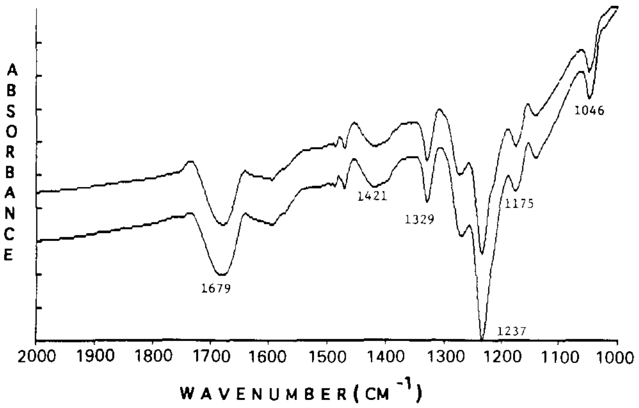


Fig. 6. Desorption spectra of $CF_3OCF(CF_3)COF$ species at different temperatures: top trace, 498 K; bottom trace, 558 K.

It has been reported that $AlCl_3$ was formed in chlorination of alumina by CCl_4 at 300 °C [12]. Thus, there is a precedent for altering the surface acidity by forming $AlCl_3$ from Al_2O_3 by reaction with a halocarbon. In the present study, this conversion did not appear to take place.

Conclusions

(1) No formation of AlF_3 was detected when the alumina was heated to 400 °C in the presence of an excess of $CF_3OCF(CF_3)COF$.

(2) The C=O bond is more active than the acyl C−F in interacting with an alumina surface. The acyl C−F bond was not broken during the chemisorption process. This indicates that nucleophilic attack by the isolated surface hydroxyl group at the carbonyl carbon atom did not occur.

(3) A hydrogen bond was apparently formed between the carbonyl oxygen atom of $CF_3OCF(CF_3)COF$ and the isolated hydroxyl group on the alumina surface. The Lewis acid sites, Al^{3+}, were not involved in the chemisorption process.

(4) No perfluorocarboxylate surface species was formed in the desorption study. Chemisorbed perfluoroacyl fluoride exhibited very different desorption results from its protonated counterparts, where a carboxylate surface species was formed.

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