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Nuclear Magnetic Resonance Investigation of Fluorinated Oxide Catalysts

II. Fluorinated Alumina and Aluminosilicates

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Pulsed nuclear magnetic resonance (NMR) techniques have been used as direct spectroscopic probes of the local chemical environments of the hydroxyl groups and fluorine atoms of fluorinated aluminas and aluminosilicates. Analysis of the fluorine spectra of fluorinated alumina indicates that fluoride ions bond to the aluminum atoms of the oxide. Fluorination of aluminosilicates containing 11 wt% alumina results in fluoride ions bound only to silicon atoms. Fluorination of aluminosilicates containing 48 wt% alumina results in the formation of both SiF and AlF bonds. Data obtained from Carr–Purcell–Meiboom–Gill experiments show that the hydroxyl groups and fluorine atoms are isolated from like nuclei for aluminosilicates having fluorine concentrations up to 5 wt%.

INTRODUCTION

In an earlier paper (*1*), fluorinated silicas were investigated using hydrogen and fluorine nuclear magnetic resonance (NMR) spectroscopy. Although silica serves as a useful model for an initial study of fluorinated catalytic oxides, fluorinated aluminas and aluminosilicates are more important industrial catalysts. Their catalytic activity has been investigated extensively (*2, 3*). Patents describing the activation of inorganic oxides using fluoride reagents have been issued as recently as 1984 (*4*). Fluorination of alumina and aluminosilicates influences the activity of these oxide catalysts for polymerization (*5–7*), dehydration (*4*), isomerization (*5, 8–11*), and cracking (*12–17*) reactions. A maximum in catalytic activity is usually observed for catalysts with fluorine concentrations between 1 and 10 wt%. Fluorination can cause changes in the selectivity of the catalysts for a given product (*5, 14, 17, 19*). Fluorinated aluminas have been used as catalyst supports for $MoO_3 \cdot NiO$ (*18*) and Re (*19*). A significant reduction in coke formation during cracking reactions has been reported also (*14, 17*).

The acid sites of fluorinated oxide catalysts have been studied extensively (*5, 12, 13, 20–24*). The results from these investigations have been complex and are very dependent on sample preparation. In addition, the data describe the interactions between adsorbed molecules and surface sites and do not describe the surface sites directly.

Infrared spectroscopy has been the most widely used spectroscopic technique for studying these catalysts (*6, 22, 25–28*). However, SiF, SiOF, AlF, and AlOF vibrations have not been identified in the infrared spectra which have been reported since their bands are superimposed on the lattice vibrations of the unmodified oxides. In addition, the identification of surface sites from infrared data often is based on the spectra of adsorbed molecules, and not upon direct observation of the surface sites

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themselves. X-ray photoelectron spectroscopy (XPS) has been used to investigate fluorine on the surface of fluorinated aluminas (*25, 29, 30*). By combining the results from XPS and X-ray diffraction studies, the presence of aluminum trifluoride, aluminum hydroxyfluorides, and isolated surface fluorine atoms have been reported, depending upon the particular sample preparation.

Hydrogen and fluorine NMR spectroscopies probe specifically the environments of the hydrogen and fluorine atoms on the oxide. O'Reilly (*31*) used fluorine NMR to study fluorinated alumina with fluorine concentrations ranging from 0.3 to 12.5 wt%. He concluded that a bulk aluminum fluoride phase forms at fluorine concentrations greater than 5 wt%. Golovanova and coworkers (*32*) obtained hydrogen and fluorine wide line NMR spectra of fluorinated aluminas. Spectra obtained at 80 K and at 300 K showed that the linewidth of the fluorine atoms did not increase as the temperature was lowered, which suggests that the fluorine atoms are immobile. Hydrogen was present even on aluminas containing 11 wt% fluorine.

Techniques and equipment developed for high resolution NMR in solids have extended the capacity of NMR techniques to provide chemical information on catalyst systems. In this investigation, the ability of Fourier transform NMR spectroscopic techniques to probe directly the chemical environment of the hydroxyl groups and fluorine atoms on fluorinated alumina and aluminosilicates was demonstrated.

EXPERIMENTAL DETAILS

Sample Preparation

The alumina samples were prepared from a commercial alumina catalyst, Alcoa F-20. The reported surface area was 210 m^2/g. The alumina was calcined at 773 K under flowing oxygen for 3 h. Fluorinated alumina was prepared by impregnation using an aqueous 5.4 m*M* ammonium fluoride solution. After soaking the catalyst in this solution for 3 h, the excess solution was evaporated without boiling. Two samples were prepared from this material, one calcined at 573 K and the other at 873 K. All other aspects of the sample preparation were identical. An unmodified alumina was prepared by placing it in water containing no fluoride ion and calcining at 773 K.

The fluorinated aluminosilicates were prepared by the same procedure used for the fluorinated aluminas. The unmodified aluminosilicates were prepared by Chevron Research Company. They were xerogel aluminosilicate catalysts coprecipitated with ammonia from sodium silicate and hydroxy aluminum chloride–acetic acid solutions. One aluminosilicate contained 48 wt% alumina and the other contained 11 wt% alumina. Two fluorinated oxides were prepared from each aluminosilicate. The more heavily fluorinated samples were prepared by placing the aluminosilicates in an aqueous ammonium fluoride solution that was 5.5 wt% fluoride for 70 h. These samples were calcined at 773 K. The lightly fluorinated samples were prepared using an aqueous 5.4 m*M* ammonium fluoride solution and were calcined at 873 K.

All of the unmodified and fluorinated samples were calcined in flowing oxygen for 3 h. Each sample was placed in a quartz tube and sealed following evacuation to a pressure of 1.33 Pa.

NMR Techniques and Apparatus

The room-temperature spin-lattice relaxation times (T_1's) were measured using the 90°-τ-90° sequence since $T_1 \gg T_2$ for these materials. Hydrogen T_1's varied from 5 to 33 s while fluorine T_1's varied from 3 to 23 s.

Quantitative determinations of the hydrogen and fluorine atom concentrations were obtained by measuring the initial magnitude of the free induction decay (FID) observed after a 90° pulse. The total magnetization is directly proportional to the number of resonant nuclei present (33). Probable errors of 10% or less were ob-

tained routinely. Corrections for differences in the bulk magnetic susceptibility between the alumina and aluminosilicate samples and the reference samples were found to be negligible in this investigation.

The nature of the chemical bonding of hydrogen and fluorine to alumina and aluminosilicates was characterized using the center of mass or isotropic chemical shift of the Fourier transform of the free induction decay and the fluorine chemical shift anisotropy. The centers of mass and second moments of the spectra were calculated numerically from the digitized data. The chemical shift (σ) is calculated using the convention below.

$$\sigma = \frac{(\nu_{ref} - \nu_{ob})}{\nu_{ref}} \times 10^6 \qquad (1)$$

ν_{ref} = resonance frequency of the chemical shift reference

ν_{ob} = observed resonance frequency.

The centers of mass and chemical shift parameters for the spectra reported here are not corrected for the effects of the bulk magnetic susceptibility because estimates of these corrections were smaller than the error in the measurement of the chemical shifts. The spectra of the unmodified and fluorinated aluminas were obtained at temperatures as low as 110 K to provide motional information concerning the hydroxyl groups and fluorine atoms.

Only room-temperature NMR relaxation data[3] were obtained. The local arrangements of the atoms and the possibility of molecular motion were investigated using the 90°-τ-180° (spin echo) and the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequences. During the spin echo experiment, the echo is formed from contributions due to the heteronuclear dipolar interactions and due to the chemical shift interaction. Molecular motion (or other phenomena which cause fluctuations in those interactions having the same symmetry as the spin operator I_z) can cause differences between the relaxation times observed from the spin echo and the CPMG experiments.

The Fourier transform NMR spectrometers used in this investigation were the same as those used in the previous study of fluorinated silica (*1*). The spectrometers had field strengths of 1.3 and 2.4 T. The sample probes and the low-temperature equipment were the same as described in the study of fluorinated silica (*1*). The low signal-to-noise ratio of these samples required accumulating the signal from as many as 4096 experiments in order to obtain the data reported.

RESULTS

1. Fluorinated Aluminas

Quantitative analysis. The hydrogen and fluorine atom concentrations of the unmodified and fluorinated aluminas are given in Table 1. The unmodified alumina has a surface hydrogen concentration of 14 hydrogen atoms per square nanometer. The sum of the hydrogen and fluorine concentrations for the sample calcined at 573 K is equal to the hydrogen concentration of unmodified alumina. The hydrogen and fluorine concentration of fluorinated alumina calcined at 873 K are equal. Volatile products were not apparent during calcination of the samples.

Room-temperature free induction decay (FID) data. The hydrogen spectra of alumina and fluorinated alumina are broad with second moments ranging from 0.8 to 2.5 G^2 (see Table 2). The hydrogen spectra of these materials are shown in Fig. 1. When the field strength is increased from 1.31 to 2.34 T, the linewidth of the sample calcined at 873 K remains constant. The second moment of the hydrogen spectrum of fluorinated alumina calcined at 573 K is reduced by a factor of 2 when the sample is calcined at 873 K. The center of mass and the lineshape of the spectra are the same regardless of the calcining temperature.

[3] The following conventions for the relaxation times will be used throughout this discussion: T_2^*, obtained from free induction decay; T_2, obtained from 90°-τ-180° experiment; T_2^+, obtained from CPMG experiment.

TABLE 1

Hydrogen and Fluorine Concentrations

Oxide	Fluoride treatment	Calcining temperature (K)	Specific surface area (m^2/g)	Surface hydrogen concentration ($10^{18}/m^2$)	Fluorine concentration surface	
					$10^{18}/m^2$	wt%[a]
Alumina	None	773	156	14 ± 2.0	—	—
	5.4 m*M*	573	207	6.7 ± 0.2	7.0 ± 1	4.6
		873	173	4.4 ± 0.6	4.4 ± 0.2	2.4
Aluminosilicate (11 wt% alumina)	5.4 m*M*	873	379	1.1 ± 0.1	0.9 ± 0.2	1.1
	5.5 wt%	773	156	0.9 ± 0.1	16.0 ± 2	8.0

[a] Relative error of 10%.

These data imply that the dominant contributions to the linewidths are effects due to dipolar interactions.

The centers of mass and second moments for the fluorine spectra are given in Table 2. The fluorine spectra are shown in Fig. 2. The lineshapes of the room-temperature spectra are neither Lorentzian nor Gaussian. The fluorine spectra are much broader than the hydroxyl group spectra. The second moments of the fluorine spectra for these two fluorinated aluminas are the same regardless of the calcining temperature. Since the hydrogen and fluorine concentrations decrease as the calcining temperature increases, the second moments of the fluorine spectra are dominated both by the chemical shift anisotropy and by the aluminum–fluorine dipolar interaction.

The fluorine isotropic chemical shift observed for fluorinated alumina is typical of aluminum–fluorine bonds. The observed centers of mass are too far upfield to be explained by an oxyfluoride species (—OF) since $-454 \text{ ppm} < \sigma_{OF} < -210 \text{ ppm}$. Chemical shift data available for fluoride ion

TABLE 2

Centers of Mass and Second Moments of the Hydrogen and Fluorine Free Induction Decay Spectra

Oxide	Fluoride treatment	Calcining temperature (K)	External field (T)	Hydrogen data		Fluorine data	
				Center of mass[a] (ppm)	Second moment[b] (G^2)	Center of mass[c] (ppm)	Second moment[d] (G^2)
Alumina	None	773	1.32	4.0 ± 3	0.82	—	—
			2.34	−1.0	1.1	—	—
	5.4 m*M*	573	2.34	−4.0	2.5	—	—
			2.25	—	—	1.03 ± 5	5.6
		873	1.32	12.0	1.5	—	—
			1.41	—	—	11.4	6.0
			2.25	—	—	13.0	4.9
			2.34	−3.0	1.3	—	—
Aluminosilicate (11 wt% alumina)	5.4 m*M*	873	2.25	—	—	−8.0	0.54
			2.34	−1.8 ± 0.3	0.044	—	—
	5.5 wt%	773	1.41	—	—	−3.0	0.54
			2.25	—	—	−11.0	1.0
$AlF_3 \cdot xH_2O$	—	—	2.25	—	—	−7.0	29.0

[a] Relative to tetramethylsilane.
[b] Relative error of 15%.
[c] Relative to hexafluorobenzene.
[d] Relative error of 20%.

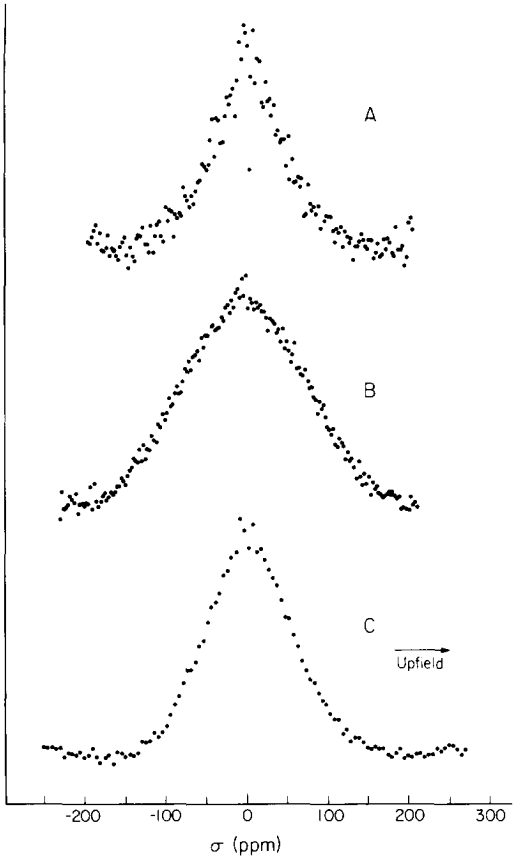

FIG. 1. Room-temperature hydrogen spectra of (A) unmodified alumina calcined at 773 K, of (B) fluorinated alumina calcined at 573 K, and of (C) fluorinated alumina calcined at 873 K. The spectra were obtained at 2.3 T. Values of the chemical shift are reported relative to tetramethylsilane.

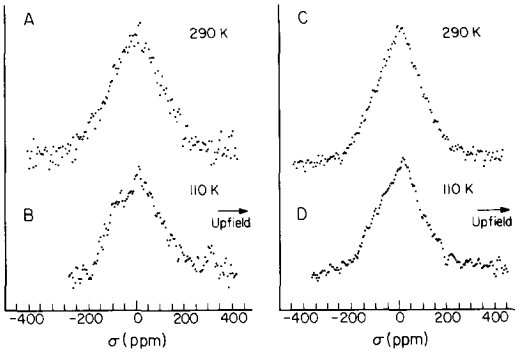

FIG. 2. Fluorine spectra of fluorinated aluminas obtained at 2.3 T. At left are the spectra of samples calcined at 573 K and observed at (A) 290 K and at (B) 110 K. At right are the spectra of samples calcined at 873 K and observed at (C) 290 K and at (D) 110 K. Values of the chemical shift are reported relative to hexafluorobenzene.

show that -154 ppm $< \sigma_{F^-} < 90$ ppm. Previously reported chemical shift data for aluminum–fluorine species are listed in Table 3. From the data available it is not possible to determine if the Al—F bond is ionic or covalent.

Relaxation data. The decay constants obtained during hydrogen 90°-τ-180° (spin echo) and Carr–Purcell–Meiboom–Gill experiments are given in Table 4 for unmodified and fluorinated aluminas. The hydrogen CPMG relaxation time, T_2^+, is 20 times longer than the spin echo relaxation time, T_2, for the unmodified alumina. The large value of T_2^+ means that the hydrogen–hydrogen homonuclear dipolar interactions are negligible. The difference between T_2

TABLE 3

Previously Reported Fluorine Isotropic Chemical Shift Data for Al—F Species

Species	Isotropic chemical shift[a] (ppm)	Reference
$[AlF]^{2+}$	145	*34*
$[AlF_2]^+$	144	*34*
AlF_3	98	*35*
$AlF_2(OH)$	217	*35*
$AlF(OH)_2$	240	*35*
$FAl(C_2H_5)_2$	128	*34*

[a] Relative to hexafluorobenzene.

TABLE 4

Hydrogen and Fluorine Relaxation Times

Oxide	Fluoride treatment	Calcining temperature (K)	Hydrogen		Fluorine, T_2^+[b] (ms)
			T_2[a] (ms)	T_2^+[b] (ms)	
Alumina	None	773	0.17	3.8	—
	5.4 m*M*	573	0.076	0.57	1.1
			—	3.3	4.5
		873	0.20	1.7	0.41
			—	—	5.3

[a] Relative error of 20%.
[b] Relative error of 15%.

and T_2^+ means that either the hydroxyl groups are mobile on the surface or the interactions between neighboring hydroxyl groups and fluorine atoms are time dependent. The relaxation time for the CPMG experiment was independent of the pulse spacing for $2\tau \leq 100$ μs.

The hydrogen CPMG data for the modified alumina samples were modeled by assuming two Lorentzian decay envelops with relaxation times of 0.57 and 3.3 ms. The CPMG data show that two dipolar environments exist for hydrogen on fluorinated alumina calcined at 573 K. The statistical theory developed by Anderson (*36*) to describe the absorption curve for a magnetically dilute material broadened by dipolar effects has been used to compare the average internuclear distances of two homonuclear diplor environments observed in CPMG data (*1*). For fluorinated alumina calcined at 573 K, the initial slope represents hydroxyl groups which are 1.8 times closer to one another than those contributing to the latter part of the CPMG decay. The second component of the decay has the same relaxation time as the hydroxyl groups of the unmodified alumina.

The decay envelop of the fluorine spin echo experiment cannot be described by a simple Lorentzian or Gaussian lineshape. The fluorine CPMG data can be described by two Lorentzian lineshapes. The fluorine CPMG data show that fluorine atoms on fluorinated alumina exist with two average fluorine internuclear distances, one being 1.6 times greater than the other when the sample is calcined at 573 K. At 873 K, the internuclear distances between fluorine atoms represented by the initial portion of the CPMG data has decreased. The internuclear distances between the more isolated fluorine atoms did not change significantly.

Hydroxyl groups were retained upon calcining at 873 K. However, the hydroxyl groups which were more isolated from neighboring hydroxyl groups were removed by calcining at this temperature. Both fluorine homonuclear dipolar environments were retained upon calcining at 873 K.

Low-temperature spectra. The centers of mass and second moments of the hydrogen spectra for the unmodified and fluorinated aluminas are given in Table 5. The hydrogen spectra broaden as the samples are cooled, but the low-temperature hydrogen spectra of these aluminas suggest that the hydroxyl groups are still mobile at 110 K.

TABLE 5

Parameters from Low-Temperature Spectra of Fluorinated Alumina

Fluoride treatment	Calcining temperature (K)	Observation temperature (K)	Hydrogen data		Fluorine data	
			Center of mass[a] (ppm)	Second moment[b] (G^2)	Center of mass[c] (ppm)	Second moment[d] (G^2)
None	773	290	-1.0 ± 2	1.1	—	—
		110	−9.8	2.0	—	—
5.4 m*M*	573	290	−4.5	2.5	1.0 ± 5	5.6
		110	2.4	4.2	20.0	6.8
	873	290	−2.9	1.3	13.0	4.9
		140	—	—	10.0	5.0
		115	−6.4	2.2	—	—
		110	—	—	20.0	6.3

[a] Relative to tetramethylsilane.
[b] Relative error of 15%.
[c] Relative to hexafluorobenzene.

The centers of mass and the second moments of the low-temperature fluorine spectra are given in Table 5 as well. The low-temperature fluorine spectra of the fluorinated aluminas are shown in Fig. 2. Although the room-temperature fluorine spectra are symmetric, an asymmetry appears downfield from the centers of mass for spectra obtained at 110 K. The same asymmetry is observed for fluorinated aluminas calcined at both 573 and 873 K.

2. Aluminosilicate (11 wt% Alumina)

The hydrogen and fluorine concentrations of these samples are given in Table 1. The hydrogen and fluorine atom concentrations of these samples agree closely with the values obtained for fluorinated silica prepared in a similar manner. Hydrogen is still present even when the fluorine concentration is 7.9 wt%.

A 68% reduction in the specific surface area occurred when the aluminosilicate was treated with an aqueous ammonium fluoride solution that is 5.5 wt% fluoride. A volatile material was produced upon calcination. Neutron activation analysis of the volatile product showed that it is 52 wt% fluorine, 19 wt% silicon, and 290 ppm aluminum. These data could be explained by a mixture of fluorinated silanes, siloxanes, and silicic acids, as was observed in the mass spectrum of the volatile products of a similarly prepared fluorinated silica (*1*).

The spectral parameters for the room-temperature hydrogen spectrum of the lightly modified sample are given in Table 2. The hydrogen spectrum is shown in Fig. 3. The lineshape is symmetric. The center of mass and second moment agree well with those measured for a fluorinated silica prepared in a similar manner (*1*). Similar linewidths have been reported for an unmodified aluminosilicate that was 12.5 wt% alumina (*31, 37*).

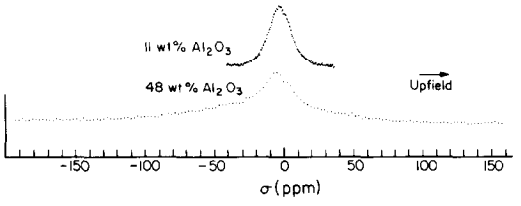

FIG. 3. Room-temperature hydrogen spectra of fluorinated aluminosilicates obtained at 2.3 T. The aluminosilicaters contain (A) 11 wt% alumina and (B) 48 wt% alumina. Values of the chemical shift are reported relative to tetramethylsilane.

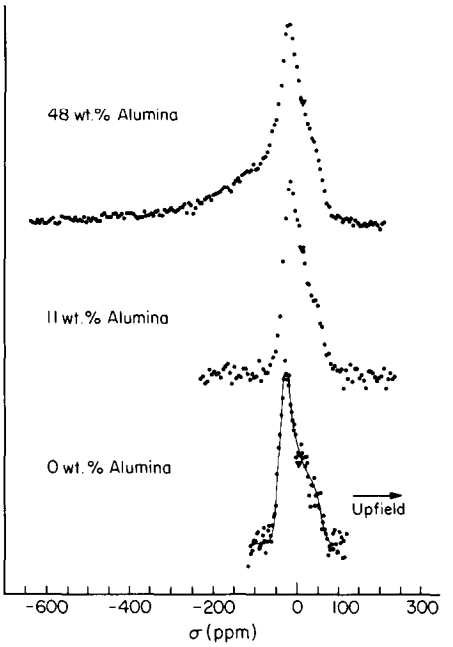

FIG. 4. Room-temperature fluorine spectra of fluorinated aluminosilicates containing varying amounts of alumina. The oxides contain (A) 48 wt% alumina, (B) 11 wt% alumina, and (C) 0 wt% alumina. Values of the chemical shift are reported relative to hexafluorobenzene.

The fluorine spectrum is shown in Fig. 4. The center of mass and second moment are given in Table 2. The lineshape can be described by the following parameters for an axially symmetric chemical shift tensor.

$$\sigma_{\parallel} = 48 \text{ ppm} \qquad \bar{\sigma} = \tfrac{1}{3} \text{tr}\, \bar{\sigma} = -10 \text{ ppm}$$

$$\sigma_{\perp} = -39 \text{ ppm} \qquad \Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} = 87 \text{ ppm}$$

$$\delta = \sigma_{\parallel} - \bar{\sigma} = 58 \text{ ppm}$$

All values are in parts per million relative to hexafluorobenzene.

The fluorine spectrum of the aluminosili-

cate fluorinated using a 5.5 wt% F^- solution can be described by an axially symmetric chemical shift tensor also. The observed chemical shift parameters relative to hexafluorobenzene are given below.

$$\sigma_{\parallel} = 49 \text{ ppm} \qquad \bar{\sigma} = -14 \text{ ppm}$$
$$\sigma_{\perp} = -46 \text{ ppm} \qquad \Delta\sigma = 95 \text{ ppm}$$
$$\delta = 63 \text{ ppm}$$

The chemical shift data observed for these fluorinated aluminosilicates are the same as that for similarly prepared fluorinated silicas (*1*). The chemical bonding of the fluorine is characteristic of fluorine covalently bonded to silicon. Also, the chemical bonding of the fluorine atoms to the aluminosilicate did not change with a more severe fluoride treatment.

The relaxation time for the fluorine Carr–Purcell–Gill experiment (T_2^+) of the aluminosilicate treated with the 5.4 wt% F^- solution is 10 ms. The fluorine homonuclear dipolar interaction would have a full width at half height of 32 Hz and would make a negligible contribution to the total linewidth of the fluorine spectra. Fluctuations are occurring in the local fields of the fluorine nuclei since the fluorine T_2^+ is an order of magnitude longer than the fluorine T_2 measured for this sample.

3. Aluminosilicate (48 wt% Alumina)

The Fourier transform of the spin echo envelopes for hydrogen and fluorine give a two-component lineshape. The hydrogen and fluorine spectra of the aluminosilicate treated with the 5.4 m*M* F^- solution are shown in Figs. 3 and 4, respectively. From Fig. 4 it is clear that the narrow component of the fluorine spectrum is identical to the fluorine spectra of the fluorinated silica (*1*) and the fluorinated 11 wt% alumina aluminosilicate prepared in the same manner. The same is true for the hydrogen spectrum. Therefore, the narrow components of these spectra are contributions from isolated fluorine atoms and hydroxyl groups bonded to silicon atoms; i.e., SiF and SiOH. Figure 5 compares the fluorine spectra of this fluorinated aluminosilicate with those of fluorinated alumina and aluminum trifluoride ($AlF_3 \cdot xH_2O$). The broad component of the fluorine spectrum corresponds to fluorine bonded to aluminum atoms (AlF groups). Similarly, the broad component of the hydrogen spectrum is explained by hydroxyl groups bonded to the aluminum atoms (see Figs. 1 and 3).

The aluminosilicate treated with a 5.4 m*M* F^- solution has average surface concentrations of 2.5 F/nm^2 and 1.6 OH/nm^2. The SiF concentration can be obtained by extrapolating the behavior of the FID at long times to the origin using a procedure

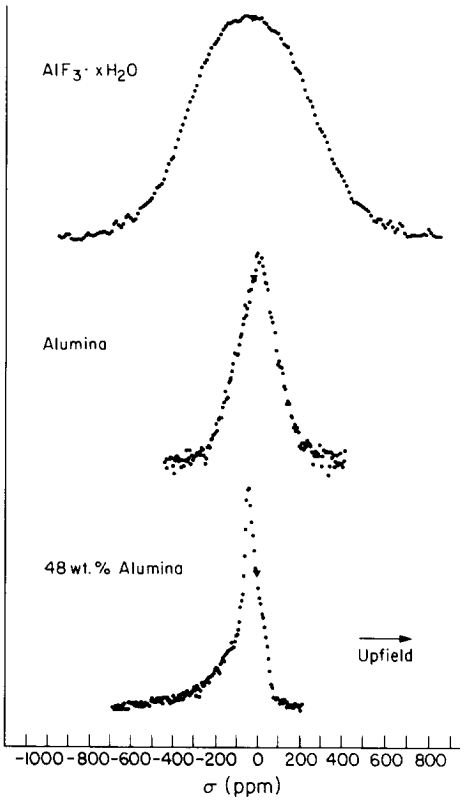

FIG. 5. Room-temperature fluorine spectra of (A) aluminum trifluoride, of (B) fluorinated alumina calcined at 873 K, and of (C) a fluorinated aluminosilicate containing 48 wt% alumina calcined at 873 K. The external field strength was 2.3 T and the values of the chemical shift are reported relative to hexafluorobenzene.

described by Schreiber and Vaughan (*37*). The difference between this intercept and the total amplitude is a measure of the AlF concentration. The intercept for the total amplitude was obtained by subtracting the extrapolation of the long-time behavior of the FID from the observed amplitudes in the short-time region and extrapolating this difference to zero time. A similar procedure was followed to determine the hydroxyl group concentrations.

The fluorine spin echo behavior shows that the fluorine dipolar environments of fluorinated aluminosilicates prepared using aqueous solutions with fluoride concentrations of 5.4 m*M* and 5.5 wt% are different. The fluorinated aluminosilicate prepared using a 5.5 wt% F^- solution clearly has two fluorine homonuclear dipolar environments. The Fourier transform of the FID ($\tau = 0$) has a two component spectrum. The Fourier transform of the data where $\tau = 40$ μs has only the narrow component of the fluorine spectrum characteristic of SiF groups. The broad-component characteristic of the fluorine atoms bonded to aluminum has the shorter T_2. Therefore, these fluorine atoms are in closer proximity to one another than those bonded to silicon (since $T_2^{(AlF)} < T_2^{(SiF)}$). The large difference in the amplitudes of the two decays at time zero demonstrates that the concentration of the AlF groups is much higher than the SiF group concentration.

The results of the fluorine Carr–Purcell–Meiboom–Gill experiment can be described by two Lorentzian decays. The initial decay constant is the same as T_2 within experimental error. The second decay constant is 14 ms. The ratio between the observed values of T_2^+ shows that the average internuclear distance in the second dipolar environment is 2.4 times longer than in the dipolar environment responsible for the initial decay. The fact that T_2 is approximately equal to the initial T_2^+ indicates that the local fields experienced by the fluorine nuclei are static. The spin echo data were not obtained at sufficiently large pulse separations to observe the long-time behavior of the fluorine homonuclear dipolar interaction.

DISCUSSION

The unmodified alumina sample used in this study had a hydroxyl group concentration of 14/nm^2, which is consistent with the model of monolayer coverage of hydroxyl groups on γ-alumina (*38*) and with other reported data (*8, 39, 40*). The total concentration of fluorine atoms and hydroxyl groups of a modified alumina prepared using an aqueous solution of ammonium fluoride and calcined at 573 K was 14/nm^2 as well. This suggests that the addition of fluoride ions occurred by replacement of hydroxyl groups and the data support the mechanism suggested by Gerberich and coworkers (*8*). Calcination of the modified alumina at 773 K resulted in a decreased concentration of both fluorine atoms and hydroxyl groups.

Modified aluminas having fluorine concentrations similar to those studied herein have been shown to have increased catalytic activity relative to unmodified alumina and AlF_3 (*5, 8, 12*). Although X-ray diffraction and XPS data (*30*) have established that crystallites of aluminum hydroxyfluoride and aluminum trifluoride can form during fluorination of alumina, the chemical shift data reported herein are inconsistent with Al—OF bonds. The spectrum of $AlF_3 \cdot xH_2O$ has a Gaussian lineshape due to extensive fluorine–fluorine dipolar interactions. The lineshapes of the fluorine spectra observed herein are quite distinct from that of $AlF_3 \cdot xH_2O$. The data suggest that the AlF bonds in lightly fluorinated aluminas are similar chemically to those of $AlF_3 \cdot xH_2O$. However, the lineshapes of the fluorine spectra and the fluorine T_2^+ data for the fluorinated aluminas indicate only isolated Al—F species. Therefore, AlF_3 crystallites have not formed. This is consistent with previously reported NMR T_1 data (*31*) and X-ray diffraction data (*30, 41*).

The CPMG (T_2^+) data demonstrate that two fluorine homonuclear dipolar environ-

ments existed on the modified aluminas regardless of the calcining temperature. Calcining at 873 K caused a rearrangement of the fluorine atoms, as evidenced by the reduction in T_2^+ for the initial part of the CPMG decay. The hydrogen CPMG data show that two hydrogen homonuclear dipolar environments existed when the sample was calcined at 573 K, but the hydroxyl environment having the higher surface concentration is removed upon calcining at 873 K.

There are several possible causes for the fluctuations observed in the local magnitic fields of the protons and fluorine atoms. The usual explanation for this behavior is diffusion of the observed species. However, chemical exchange has been reported to affect the results obtained from CPMG experiments (*42, 43*). The values measured for T_2^+ will depend upon the chemical shift between exchange sites, the lifetime between exchanges, and the pulse separation of the CPMG experiment. The CPMG experiment causes contributions to the magnetization from a time-independent hydrogen-fluorine interaction to refocus. However, fluctuations in this interaction from motions of the hydroxyl groups could cause dephasing of the fluorine magnitization during spin echo experiments. The resulting fluorine relaxation times (T_2 and T_2^+) would be dependent on the pulse separation. The rotation of hydroxyl groups or the translational diffusion of hydrogen ions in close proximity to the fluorine atoms could cause such fluctuations.

The lineshapes of the low-temperature fluorine spectra may be caused by several factors. The quadrupolar interaction at the aluminum nucleus could be sufficiently large that the aluminum nucleus is not in a pure Zeeman state. Then the heteronuclear dipolar interactions between the aluminum and fluorine atoms cannot be classified as being either secular or nonsecular (*44*). Another alternative is that the lineshape of the fluorine spectra result from isolated aluminum–fluorine dipole pairs (*45*). Effects due to anisotropic motion may be important as well. Anisotropic motion, such as rotation of hydroxyl groups about the Al—O bond, would provide a consistent explanation for both the relaxation time and line shape data. However, much more data is needed to provide a complete explanation.

The interpretation of the hydrogen and fluorine NMR data of fluorinated aluminosilicates requires an understanding of the atomic organization of the unmodified aluminosilicates. X-Ray diffraction data (*46, 47*) have shown that aluminosilicates containing less than 30 wt% alumina have a silica-like structure with isomorphic substitution of aluminum atoms. For alumina contents between 30 and 50%, an η-alumina phase begins to appear. As the alumina content increases from 50 to 80%, a structure similar to mullite is present. Similar results have been reported based upon X-ray photoelectron data (*48*). Hall and coworkers have reported (*40*) that the results of differential hydrogen analysis of an aluminosilicate containing 12% alumina is unique compared with those of silica, alumina, or a mechanical mixture of silica and alumina. Schreiber and Vaughan (*37*) reported NMR spectroscopic data which showed that AlOH groups were not observed on aluminosilicates with less than 25 wt% alumina.

The hydrogen atom concentration of the fluorinated aluminosilicate containing 11 wt% alumina calcined at 873 K was 4.5×10^{20} per gram. The relationship of the hydrogen atom concentration to the specific surface area is in excellent agreement with that reported by O'Reilly (*31*) for an unmodified aluminosilicate that was 12.5% alumina. This suggests that the hydrogen population has not been disturbed by fluorination using an aqueous 5.4 m*M* fluoride solution. AlOH groups are not present in the spectrum of a fluorinated aluminosilicate containing 11 wt% alumina. AlF groups were not detected in the fluorine spectra of this aluminosilicate as well, even with sample treatment using a 5.5 wt% F^-

solution. The fluoride ion bonds only to silicon atoms. The bond formed is identical to that found in fluorinated silica, even with fluoride concentrations as high as 8 wt%. SiOH, SiF, AlOH, and AlF groups are present on fluorinated aluminosilicates containing 48 wt% alumina. Therefore, an alumina phase was required in the unmodified aluminosilicate if AlOH or AlF groups were to be present on the fluorinated catalyst.

When 48 wt% alumina aluminosilicates are treated with a 5.5 wt% F^- solution, the homonuclear dipolar coupling between the fluorine atoms bonded to aluminum is much greater than that between the SiF groups since T_2^+ (AlF) < T_2^+ (SiF). The large difference in the amplitudes of the two decays at time zero demonstrates that the concentration of the AlF groups is much higher than the SiF group concentration. The T_2 data show that SiF bonds are isolated from the AlF bonds. These data are consistent with the formation of AlF_3 crystallites and isolated SiF groups. This demonstrates preferential adsorption of fluoride ion by the alumina crystallites.

CONCLUSIONS

NMR spectroscopy was used for nondestructive quantitative analysis of hydroxyl group or fluorine atom concentrations while obtaining the NMR spectra of the samples. These techniques have shown that only Al—F and Si—F species are present on fluorine modified aluminas and aluminosilicates containing up to 5 wt% fluorine. Aluminum oxyfluorides were not detected. The Si—OH, Al—OH, Si—F, and Al—F species are isolated from like species for fluorine concentrations less than 5 wt%.

Fluorine is present only as Si—F for 11 wt% alumina aluminosilicates. When the alumina concentration is increased to 48 wt%, both Si—F and Al—F species form. As the fluorine concentration of the 48 wt% alumina aluminosilicate is increased, the fluoride ion is adsorbed preferentially by aluminum atoms. As highly fluorinated aluminosilicates are calcined, volatile silicon-containing species are evolved which contain aluminum only at concentrations of parts per million. Therefore, fluorination of aluminosilicates using concentrated fluoride solutions results in preferential removal of silica from the lattice at high temperature and the silica-to-alumina ratio of these catalysts can change upon calcination.

The use of nuclear magnetic resonance spectroscopy has provided directly information concerning the local environments of hydroxyl groups and fluorine atoms on modified aluminas and aluminosilicates. A multitechnique approach incorporating NMR spectroscopic data with infrared, X-ray diffraction, X-ray photoelectron, adsorption, and catalytic data from samples prepared in a consistent fashion would greatly improve our understanding of the catalytic activity of fluorinated aluminosilicates. In particular, such a study over a wide range of fluorine concentrations and silica-to-alumina ratios is needed.

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