

# A Nuclear Magnetic Resonance Investigation of Fluorinated Oxide Catalysts

## I. Fluorinated Silica

J. R. SCHLUP<sup>1</sup> AND R. W. VAUGHAN<sup>†</sup>

*Division of Chemistry and Chemical Engineering, California Institute of Technology,  
Pasadena, California 91125*

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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 silica. Hydroxyl groups and fluorine atom concentrations were obtained from NMR data. The line shapes of the hydroxyl group spectra are narrow (<3 kHz) and asymmetric. The fluorine spectra can be described by isolated SiF groups. The anisotropy of the fluorine chemical shift powder pattern is 96 ppm. The hydroxyl groups do not exist as closely spaced pairs. The same is true of the fluorine atoms. Fluctuations occur in the local magnetic fields of the nuclei. The changes that occur in the line shapes of the hydroxyl group and fluorine spectra when observed at various temperatures depend upon the concentration of the surface species and upon the calcining temperature.

### INTRODUCTION

The halogenation of oxides such as silica, alumina, and aluminosilicates results in materials with catalytic properties differing from those of the untreated oxides (1). For example, the cumene cracking rate of fluorinated silica is reported to be higher than that of unmodified silica (2, 3) and its cumene cracking activity approaches that of an aluminosilicate. The changes which occur upon fluorination of such oxides can be studied by spectroscopic techniques. The effects of fluorination on the hydroxyl groups of silica have been reported based upon infrared spectroscopic data (2, 4-6). In work by Golovanova and co-workers (6), broadline <sup>1</sup>H NMR spectra of the hydroxyl groups of fluorinated silica were studied to understand the local environment of the hydroxyl proton. In the present study, we report proton and fluorine

Fourier transform and line narrowing NMR data for several fluorinated silicas which describe changes in these materials resulting from the sample preparation.

### EXPERIMENTAL DETAILS

*Sample preparation.* The samples were prepared from Grace/Davison Grade 62 silica gel. The initial surface area was reported to be 340 m<sup>2</sup>/g. The silica gel was cleaned by calcining under flowing oxygen at 773 K for 3 h. The cleaned silica was immersed in aqueous ammonium fluoride solutions (5 and 18 mM) for 4 h. The excess ammonium fluoride solution then was removed by evaporation. The dried modified silica was subdivided and each portion was calcined under flowing oxygen for 3 h at the desired temperature.

A heavily modified silica was prepared by immersing cleaned silica in a 2.8 M aqueous ammonium fluoride solution for 70 h. After removal of the excess ammonium fluoride solution, the modified silica was calcined at 773 K under flowing oxygen for 3 h.

<sup>1</sup> Present address: Department of Chemical Engineering, Kansas State University, Manhattan, Kansas 66506.

<sup>†</sup> Deceased.

## NMR MEASUREMENTS

A Fourier transform NMR spectrometer similar to those used in this investigation has been described elsewhere (7). Two spectrometers operating at different field strengths were used in this investigation. The hydrogen data were obtained at field strengths of 1.32 and 2.34  $T$  (which correspond to resonance frequencies of 56.4 and 100 MHz, respectively). The fluorine data were obtained at field strengths of 1.41 and 2.25  $T$  (which correspond to resonance frequencies of 56.5 and 90.1 MHz, respectively). The low signal-to-noise ratio of these samples required accumulation of the signal from as many as 4096 experiments to obtain the data reported herein. Variable temperature spectra were obtained by passing cooled nitrogen gas over the sample.

Since  $T_1 \gg T_2$  for these materials, the room temperature spin-lattice relaxation times ( $T_1$ ) were measured using the  $90^\circ-\tau-90^\circ$  sequence. The hydrogen  $T_1$  varied from 6 to 17 s. The fluorine  $T_1$  varied from 10 to 40 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  $90^\circ$  pulse. The total magnetization is directly proportional to the number of resonant nuclei present (8). Relative standard deviations of 10% were obtained routinely. Corrections for differences in the bulk magnetic susceptibility of the silica samples and the reference were found to be negligible in this investigation.

The nature of the chemical bonding of hydrogen and fluorine to silica was investigated using the center of mass of the Fourier transform of the free induction decay and the fluorine chemical shift anisotropy. The local arrangements of the atoms and the possibility of molecular motion were investigated by using the  $90^\circ-\tau-180^\circ$  (spin echo) and the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences (9). During the spin echo experiment, the

echo is formed from contributions from the heteronuclear dipolar interactions and from the chemical shift interaction. Molecular motion (or other phenomena which can cause fluctuations in interactions with the same symmetry as the spin operator  $I_z$ ) can cause differences in the relaxation times observed from the spin echo and the CPMG experiments.

## RESULTS AND DISCUSSION

*Quantitative Analysis*

The nitrogen BET surface areas, the hydrogen atom concentrations, and the fluorine atom concentrations of the silicas obtained using NMR techniques are shown in Table 1. Hydrogen was present in all samples treated with aqueous 5 and 18 mM  $F^-$  solutions and calcined at temperatures as high as 873 K. The hydrogen concentration of the unmodified silica and the fluorine modified silicas calcined at 573 and 673 K are the same. Calcining the catalysts at 773 K reduces the hydrogen concentration. The hydrogen concentrations of modified silicas prepared using 5 and 18 mM  $F^-$  solutions and calcined at 873 K are the same, 1.2 per 100  $A^2$ . The unmodified silica and the modified silica prepared using a 5 mM  $F^-$  solution and calcined at 773 K have hydrogen atom surface concentrations of 2.4 and 1.8 hydrogen atoms per 100  $A^2$ , respectively. These values are consistent with those reported by Davydov *et al.* (10), Freude *et al.* (11), Hall *et al.* (12), Oehme (13), and Schreiber and Vaughan (14).

Fluorinated silicas prepared using a 5 mM  $F^-$  solution and calcined at temperatures as high as 773 K have constant fluorine atom concentrations. The fluorine atom concentration is reduced by 40% upon calcining at 873 K. The fluorine concentration of samples calcined at 573 K depended upon the ammonium fluoride concentration used in sample preparation. However, the hydrogen and fluorine concentrations of modified silicas calcined at 873 K and pre-

TABLE 1  
Hydrogen and Fluoride Concentrations

Fluoride treatment	Calcining temperature (K)	BET surface area (m <sup>2</sup> /g)	Surface concentrations (10 <sup>18</sup> /m <sup>2</sup> )		Weight percentage fluorine (%)
			Hydrogen	Fluorine	
None	773	250 ± 10	2.4 ± 0.3	—	—
5 mM	573	255	2.8	2.1 ± 0.3	1.7 ± 0.2
	673	238	2.7	2.4	1.8
	773	256	1.8	2.4	2.0
	873	223	1.2	1.5	1.1
18 mM	573	232	2.1	6.9	5.1
	873	207	1.3	1.4	0.9

pared using both 5 and 18 mM F<sup>-</sup> solutions are the same within experimental error.

The modified silica prepared using a 2.8 M aqueous solution of ammonium fluoride is very different from silicas prepared using an 18 mM F<sup>-</sup> solution. Treatment with aqueous fluoride solutions having fluoride concentrations less than 20 mM result in a modified silica with the same surface area as an unmodified silica, whereas the use of a 2.8 M aqueous fluoride solution reduced the surface area of the modified silica by 50%. A volatile product was formed at calcining temperatures of 573 K or higher, which condensed as a white solid on the quartz tubing at the cool end of the tube furnace. Preliminary investigation showed that the sublimate volatilized at 473 and 523 K. The material evolved at 473 K has a mass spectrum characteristic of SiH<sub>4</sub> and SiF<sub>4</sub>. The material evolved at 523 K is more complex. Species characteristic of SiH<sub>4</sub>, SiF<sub>4</sub>, SiF<sub>2</sub>O, disiloxane, metasilicic acid, and siloxane have been identified.

#### Room Temperature Free Induction Decays (FID)

The hydrogen spectrum for unmodified silica is shown in Fig. 1. The hydrogen spectra of the fluorine modified silicas are shown in Fig. 2. The centers of mass and

the full widths at half heights of the room temperature spectra are given in Table 2. The center of mass ( $\sigma_{Av}$ ) is calculated using the following convention:

$$\sigma_{Av} = (\nu_{ref} - \nu_{cm})/\nu_{ref} \times 10^6 \quad (1)$$

$\nu_{ref}$  = resonance frequency of the chemical shift reference.

$\nu_{cm}$  = frequency of the center of mass of the spectrum.

The hydrogen spectrum of an unmodified silica has a full width at half intensity of 1.8 kHz at 2.34 T and that line width has only a small dependence upon the strength of the external magnetic field. Therefore, the major contribution to the linewidth is the homonuclear dipolar interaction. The centers of mass of the hydrogen spectra of the fluorine modified silicas range from 5 to -8 ppm relative to tetramethylsilane (TMS). The field dependence of the center of mass of the sample treated with a 5 mM fluoride solution and calcined at 873 K is not significant. The NMR signal for the sample was quite weak due to the hydroxyl group concentration and the sample size. The signal-to-noise level of that data is lower than obtained for the other samples. This results in an error in the center of mass larger than that given on the table.

The field strength, calcining temperature,

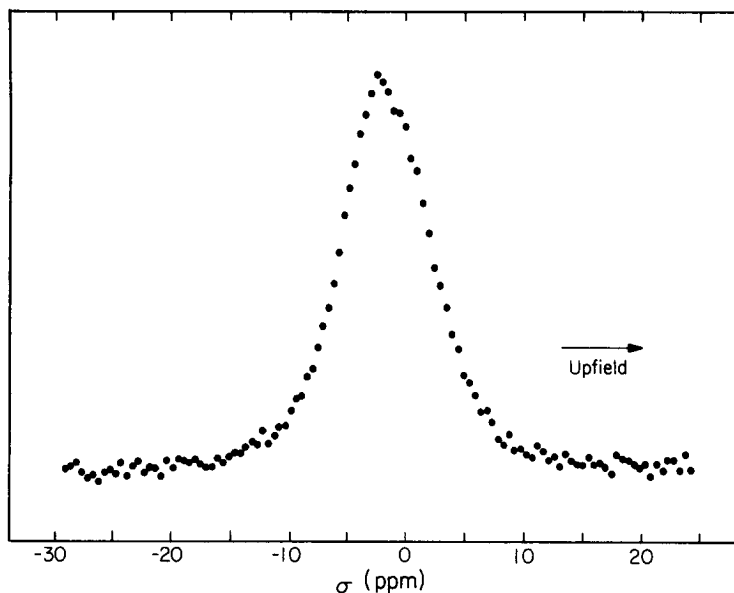


FIG. 1. Room temperature hydrogen FID spectrum of unmodified silica calcined at 773 K. The spectrum was obtained at 2.34 T. Values of the chemical shift are reported relative to tetramethylsilane.

and fluoride treatment have significant effects on the linewidths observed for the hydrogen spectra of fluorinated oxides. In all cases the data are in agreement with linewidths reported for the hydrogen NMR spectrum of unmodified silica (11, 13–15).

The full widths at half height increase with increasing field strength. The field dependence of the hydrogen spectra for modified silicas indicates that the chemical shift interaction makes a significant contribution to the linewidth of the spectra. However,

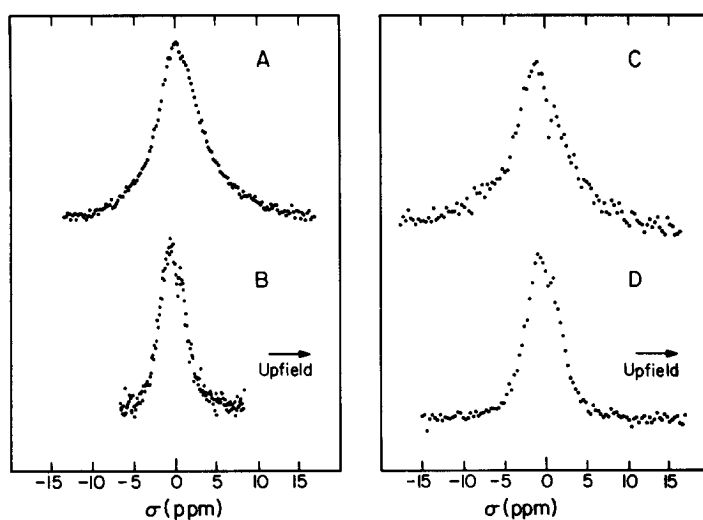


FIG. 2. Room temperature hydrogen FID spectra of fluorinated silicas. The external field strength was 2.34 T. At left are the fluorinated silicas prepared using a 5 mM  $F^-$  solution and calcined at (A) 573 K and (B) 873 K. At right are the fluorinated silicas prepared with an 18 mM  $F^-$  solution and calcined at (C) 573 K and (D) 873 K. Values of the chemical shift are reported relative to tetramethylsilane.

TABLE 2  
Parameters From Room Temperature FID Spectra

Fluoride treatment	Calcining temperature (K)	Hydrogen data			Fluorine data	
		External field (T)	Center of mass <sup>a</sup> (ppm)	Full width at half weight (Hz)	External field (T)	Center of mass <sup>b</sup> (ppm)
None	773	1.32	0.0 ± 1	1500	—	—
		2.34	-3.0	1800	—	—
5 mM	573	1.32	3.0	2150	1.41	-11.0 ± 2
		2.34	5.0	2600	2.25	-12.0
	673	—	—	—	2.25	-11.0
	773	—	—	—	2.25	-10.0
	873	1.32	-8.0	1200	—	—
18 mM	573	1.32	0.0	1400	1.41	-16.0
		2.34	-5.0	2000	2.25	-10.0
	873	1.32	-5.0	1200	1.41	-11.0
		2.34	-2.0	1600	2.25	-8.0
2.8 M	773	—	—	—	2.25	-11.0

<sup>a</sup> Relative to tetramethylsilane.

<sup>b</sup> Relative to hexafluorobenzene.

the line shape cannot be described satisfactorily by chemical shift anisotropy alone. The observed spectra could result from the effects of anisotropic motion or the presence of two or more resonance lines.

The centers of mass of the room temperature fluorine spectra (Table 2) are independent of the fluoride treatment and the calcining temperature. Reported values for the chemical shift of fluorine covalently bound to silicon (relative to hexafluorobenzene) range from 54 ppm for FSiH<sub>3</sub> to -54 ppm for F<sub>3</sub>SiH. Two fluorine chemical shifts reported for fluorinated disiloxanes are 8 ppm for <sup>28</sup>SiF<sub>3</sub>-O-<sup>29</sup>SiF<sub>3</sub> and -25 ppm for HF(CH<sub>3</sub>)Si-O-Si(CH<sub>3</sub>)HF. The chemical shifts reported for fluoride ions range from -154 to -35 ppm with the exceptions of NaF at 62 ppm and CdF<sub>2</sub> at 24.8 ppm. The chemical shifts of oxyfluorides range from -454 to -210 ppm. The chemical shift data show clearly that oxyfluoride species (Si-OF) are not formed on any of the silicas reported herein. The centers of

mass are at slightly higher field than one would expect for a fluoride ion. The observed centers of mass are consistent with the reported values of the chemical shifts for fluorine covalently bound to silicon (16).

Figure 3 shows the fluorine spectra of the fluorinated silicas prepared using a 5 mM F<sup>-</sup> solution. As the calcining temperature is increased, the spectral features sharpen. This would be expected if the broadening is due to dipolar interactions and the internuclear distance increases as the calcining temperature increases. The increasing internuclear distance with increasing calcining temperature is confirmed by the decrease in the fluorine concentration when the samples are calcined at 873 K. The asymmetry observed in the fluorine spectra and the shape of the resonance line can be described by a broadened chemical shift powder pattern. The solid line through the data in Fig. 3C was obtained by fitting such a function to the experimental data. Figure

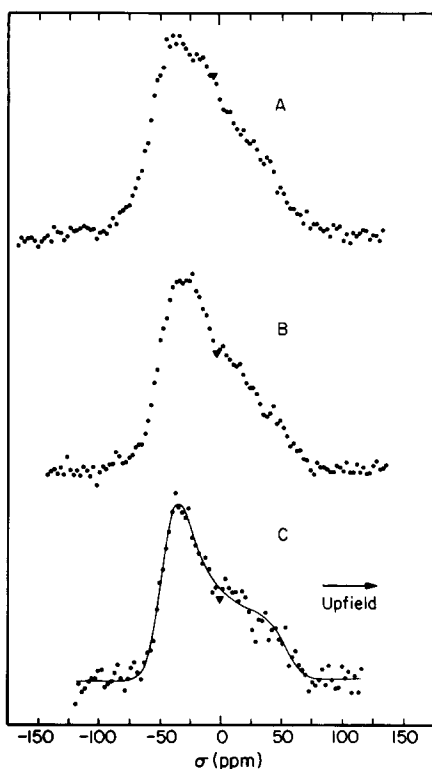


FIG. 3. Room temperature fluorine FID spectra obtained at 2.25  $T$  of fluorinated silicas prepared using a 5  $mM$   $F^-$  solution and calcined at (A) 573 K, (B) 773 K, and (C) 873 K. Values of the chemical shift are reported relative to hexafluorobenzene.

4 compares the fluorine spectra of silicas prepared with an 18  $mM$   $F^-$  solution but calcined at different temperatures. The spectrum of the sample calcined at 573 K not only has broader features, but the line shape varies considerably from the line shape of the sample calcined at 873 K. Figure 5 compares the fluorine spectrum at two different field strengths of the fluorinated silica prepared using an 18  $mM$   $F^-$  solution and calcined at 573 K. The linewidth scales with the field and the structure of the line shape at 1.41  $T$  is quite different from that observed for samples calcined at 873 K.

Table 3 contains the results of fitting the expression for a chemical shift powder pattern convoluted with a Gaussian broadening function to the fluorine FID spectra. The conventions used in defining the principal components,  $\bar{\sigma}$ ,  $\delta$ , and  $\eta$  are given by

$$\sigma_{zz} - \bar{\sigma} \geq \sigma_{xx} - \bar{\sigma} \geq \sigma_{yy} - \bar{\sigma} \quad (2)$$

$$\bar{\sigma} = \left(\frac{1}{3}\right)\text{tr } \underline{\underline{\sigma}} \quad (3)$$

where

$\underline{\underline{\sigma}}$  is the tensor describing the chemical shift anisotropy

$$\delta = \sigma_{zz} - \bar{\sigma}$$

$$\eta = (\sigma_{yy} - \sigma_{xx})/\delta$$

All values are reported in parts per million relative to hexafluorobenzene. Positive values of the chemical shift are upfield from the reference.

Samples treated with aqueous fluoride solutions with fluoride concentrations of 5 and 18  $mM$  and calcined at temperatures of 673 K or higher can be described by chemical shift tensors which have the same principal components. Since  $\eta$  is small ( $<0.1$ ) the spectra can be described by an axially symmetric chemical shift tensor. Using the

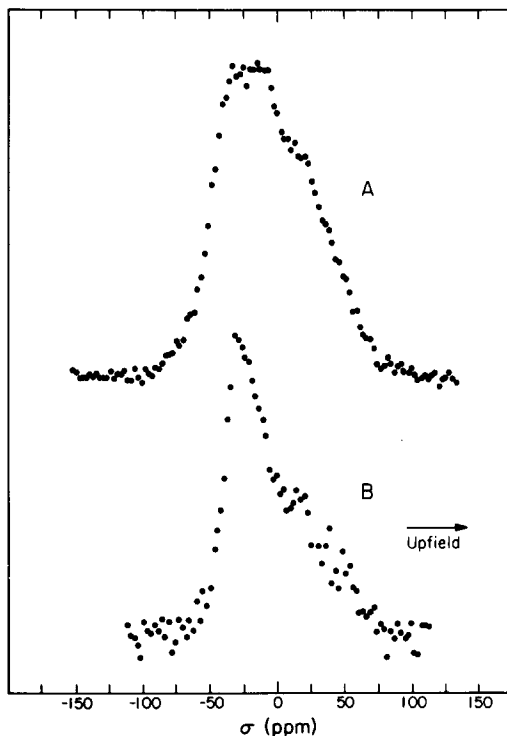


FIG. 4. Room temperature fluorine FID spectra obtained at 2.25  $T$  of fluorinated silicas prepared using an 18  $mM$   $F^-$  solution and calcined at (A) 573 K and (B) 873 K. Values of the chemical shift are reported relative to hexafluorobenzene.

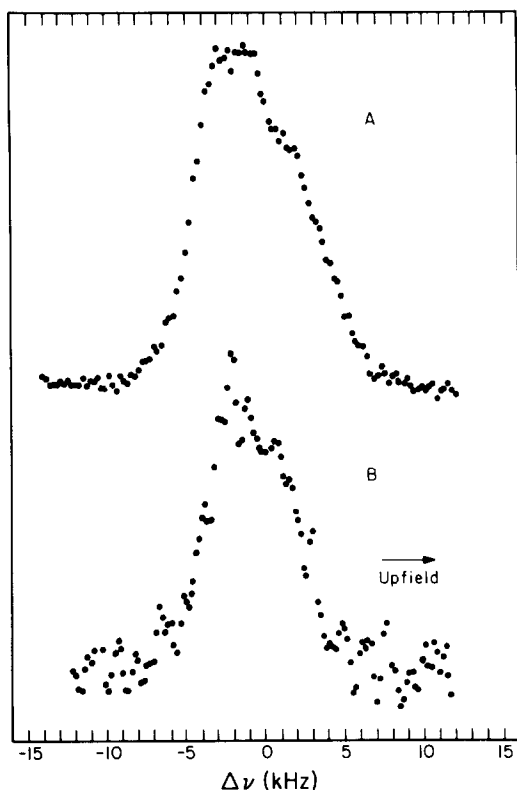


FIG. 5. Room temperature fluorine FID spectra of fluorinated silica prepared using an 18 mM  $F^-$  solution and calcined at 573 K. The external magnetic field strengths used were (A) 2.25 T and (B) 1.41 T.

data for lightly modified silica prepared using a 5 mM  $F^-$  solution calcined at 873 K, the following parameters were obtained.

$$\sigma_{\perp} = \sigma_{xx} = \sigma_{yy} = -44 \text{ ppm}$$

$$\sigma_{\parallel} = \sigma_{zz} = 52 \text{ ppm}$$

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} = 96 \text{ ppm} \quad (4)$$

The fluorine spectrum obtained at 1.41 T for the sample prepared using an 18 mM  $F^-$  solution and calcined at 873 K can be described by the same chemical shift parameters. Therefore, the line shape is dominated by the chemical shift anisotropy.

The parameters of the axially symmetric chemical shift tensors obtained from fits of the fluorine spectra for both samples calcined at 873 K are identical within experimental error. Therefore, the bonding of the fluorine to the silica is the same for both samples.

#### Relaxation Time Measurements

The hydrogen relaxation times<sup>2</sup> measured at room temperature are reported in Table 4. The hydrogen spin echo and CPMG results for the fluorinated silicas are shown in Figs. 7 and 8, respectively.

Figure 6 shows the hydrogen CPMG and spin echo results for the unmodified silica calcined at 773 K. The CPMG data exhibit a two-component decay, the decay constants of which differ from the measured  $T_2$ . The

<sup>2</sup> The following conventions for the relaxation times will be used throughout this discussion:  $T_2^*$ , obtained from free induction decay;  $T_2$ , obtained from  $90^\circ$ - $\tau$ - $180^\circ$  experiment;  $T_2^+$ , obtained from CPMG experiment.

TABLE 3

Principal Components of  $^{19}F$  Chemical Shift Tensors for Fluorinated Silica

Fluoride treatment	Calcining temperature (K)	$\sigma_{xx}$ (ppm)	$\sigma_{yy}$ (ppm)	$\sigma_{zz}$ (ppm)	$\sigma$ (ppm)	$\delta$ (ppm)	$\eta$
5 mM	573	$-46.0 \pm 3$	$-34.0 \pm 3$	$49.0 \pm 3$	$-10.0 \pm 2$	60.0	0.21
	673	-41.0	-35.0	47.0	-10.0	57.0	0.10
	773	-38.0	-35.0	50.0	-7.0	58.0	0.05
	873	-43.0	-38.0	53.0	-10.0	63.0	0.08
18 mM	573	—	—	—	—	—	—
	873	-38.0	-35.0	53.0	-6.0	60.0	0.05
2.8 M	773	-54.0	-31.0	52.0	-11.0	63.0	0.63

Note. Principal components and isotropic shifts are reported relative to hexafluorobenzene.

TABLE 4  
Relaxation Times

Fluoride treatment	Calcining temperature (K)	Hydrogen data (ms)		Fluorine data (ms)	
		$T_2^a$	$T_2^{+b}$	$T_2^c$	$T_2^{+c}$
None	773	0.33	0.63	—	—
			14.0	—	—
5 mM	573	0.21	17.0	—	12.0
	873	0.66	1.5	—	1.6
18 mM	873		18.0	—	—
		0.48	10.0	0.26	8.3
		0.74	19.0	0.80	8.2

<sup>a</sup> Relative error of  $\pm 20\%$ .

<sup>b</sup> Relative error of  $\pm 10\%$ .

<sup>c</sup> Relative error of  $\pm 15\%$ .

relaxation time obtained from the CPMG experiment,  $T_2^+$ , has an initial value that is twice as large as  $T_2$ . The CPMG data are

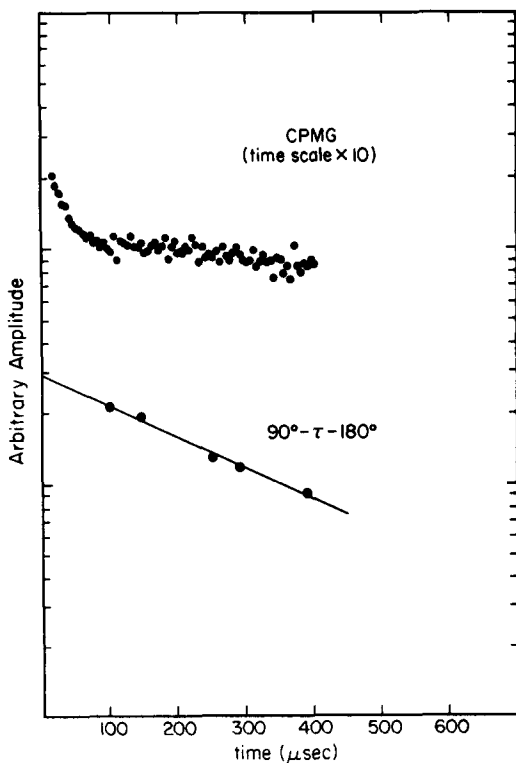


FIG. 6. Comparison of the hydrogen Carr-Purcell-Meiboom-Gill (CPMG) and  $90^\circ\text{-}\tau\text{-}180^\circ$  decays of unmodified silica calcined at 773 K. Note the difference in the times scales between the two decays.

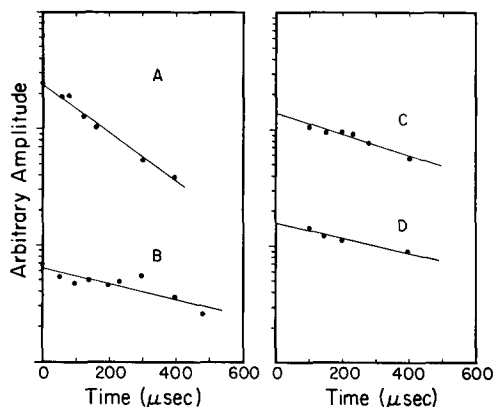


FIG. 7. Comparison of the hydrogen  $T_2$  decays as a function of sample preparation for the fluorinated silicas. At left are the decays of fluorinated silicas prepared using a 5 mM  $F^-$  solution and calcined at (A) 573 K and (B) 873 K. At right are the decays of the fluorinated silicas prepared using an 18 mM  $F^-$  solution and calcined at (C) 573 K and (D) 873 K.

independent of the pulse spacing for  $2\tau \leq 100 \mu\text{s}$ . The spin echo and CPMG data for fluorine modified silicas are similar to those obtained for the unmodified silica.  $T_2$  increases as the calcining temperature increases for both fluorine modifications. There is a significant difference between  $T_2$  and  $T_2^+$  for all samples, which would result if fluctuations occur in the local fields experienced by the nuclei.

The long decay constants observed during the CPMG experiment are characteristic of well-isolated nuclei. The measured values of  $T_2^+$  for samples calcined at 873 K are in close agreement with one another. Using a statistical approach developed by Anderson (17), the expression for the half width at half height of an absorption curve broadened by dipolar effects for a magnetically dilute material is

$$\delta = (2\pi^2/3\sqrt{3})\gamma^2\hbar n \quad (5)$$

where  $n$  is the density of spins.

If two samples, which are identical in all ways except the spin density, are compared and if the dipoles are assumed to be distributed uniformly throughout the samples, then the relationship between the ratio of the half widths at half height of the absorp-



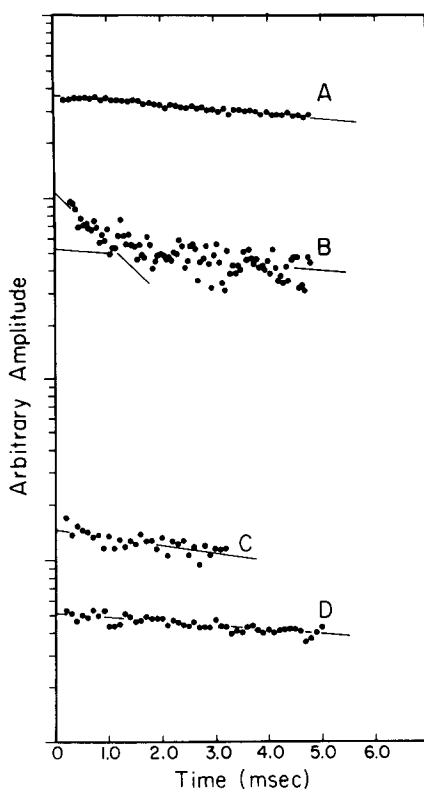


FIG. 8. Comparison of the hydrogen CPMG ( $T_2^+$ ) decays as a function of sample preparation. The top two decays are of fluorinated silicas prepared using a 5 mM  $F^-$  solution and calcined at (A) 573 K and (B) 873 K. The bottom two decays are fluorinated silicas prepared using an 18 mM  $F^-$  solution and calcined at (C) 573 K and (D) 873 K.

tion curves of the two samples and the ratio of the internuclear distances between dipoles ( $r_{ij}$ ) is

$$\delta_1/\delta_2 \propto r_{ij,2}^3/r_{ij,1}^3 \quad (6)$$

The hydrogen CPMG data of the fluorinated silica prepared using a 5 mM  $F^-$  solution and calcined at 873 K can be described by two exponential decays. If  $2\delta_{II}$  is the contribution to the full width at half height due to homonuclear dipolar interactions, then  $2\delta_{II} = 1/\pi T_2^+$ . Using  $T_2^+ = 18$  ms, then  $2\delta_{II} = 17.6$  Hz = 4.2 mG. When  $T_2^+ = 1.5$  ms, then  $2\delta_{II} = 212$  Hz = 50 mG. Since the parameters in Eq. (6) are identical for both parts of the decay, except for the density of spins, then

$$\delta_2/\delta_1 = 17.6/212 = 0.083 = r_{ij,1}^3/r_{ij,2}^3$$

or  $r_{ij,2} = 2.3 r_{ij,1}$ . Therefore, the second part of the CPMG decay represents hydroxyl groups with twice the internuclear separation of those contributing to the first part of the decay.

The full widths at half intensity of hydrogen on fluoride-modified silicas measured at 99.7 MHz ranged from 1200 to 2600 Hz. If  $T_2^+ = 1.5$  ms, then the homonuclear dipolar effects contribute significantly to the linewidth. When  $T_2^+$  is greater than 10 ms, homonuclear dipolar effects have a negligible contribution to the linewidth.

The magnitude of the fluorine-fluorine dipolar interaction was determined from CPMG experiments.  $T_2$  was measured on two samples and the results compared their  $T_2^+$  to check for the possibility of fluorine diffusion. The  $^{19}F$  CPMG experiments showed that  $T_2^+ > 1.5$  ms for all samples (see Table 4). Therefore, the fluorine atoms are widely separated from one another and the fluorine homonuclear dipolar interaction makes a negligible contribution to the linewidth of the fluorine spectra. The decay constant,  $T_2^+$ , for fluoride treatment using an 18 mM  $F^-$  solution is 8.3 ms regardless of the calcining temperature. A comparison of the  $T_2$  and  $T_2^+$  data for samples treated with an 18 mM  $F^-$  solution show that fluorine atoms experience fluctuations of some kind in their local magnetic fields.

There are several possible causes for this fluctuation. 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 (18, 19). 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 magnetization during spin echo experiments. This could cause the fluorine relaxation times ( $T_2$  and  $T_2^+$ ) to 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.

#### Low Temperature Free Induction Decays

Free induction decays were obtained at several temperatures. Three types of behavior may be expected as the temperature is lowered. Any motional averaging causing narrowing of the line will slow or cease as the sample temperature is lowered, resulting in an increase in the linewidth. Slowing of anisotropic motion may cause changes in the line shape since the motional averaging of the chemical environment that the nuclei experiences will change. If the atoms are exchanging rapidly between two or more sites, lowering the temperature will slow the rate of exchange until the resonances for each individual species are observed rather than the averaged resonance.

Figure 9 shows that the hydrogen spectra for unmodified silica change as a function of temperature. The center of mass begins to move slightly downfield as the temperature is decreased. The values of the center of mass and the full width at half height are found in Table 5. The centers of mass and the full widths at half height of the hydrogen spectra for the fluorine modified silicas are found in Table 5 also. In all cases, with the exception of the moderately fluorinated silica calcined at 573 K, the centers of mass shift downfield as the temperature decreases. The maximum downfield shift is 14 ppm. Line shapes and full widths at half height of samples prepared using an 18 mM  $F^-$  solution show little change as a function of temperature. No broad components appear in the spectra of any sample at any observation temperature. The asymmetries in the hydrogen spectra are retained at all observation temperatures.

The changes observed in the hydrogen

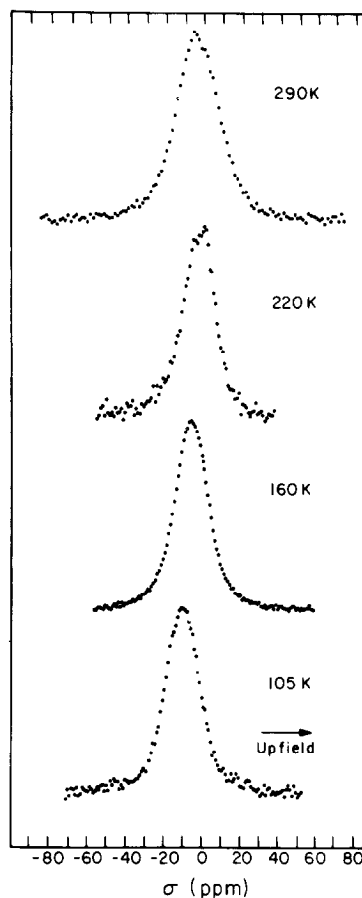


FIG. 9. Hydrogen FID spectra as a function of temperature of an unmodified silica calcined at 773 K. The temperatures at which the data were obtained are given beside each spectrum. Values of the chemical shift are reported relative to tetramethylsilane.

chemical shifts with decreasing temperature are not understood. They could result from changes in the bulk susceptibility of the sample or the external reference as the temperature decreases. The bulk magnetic susceptibility correction to the chemical shift was estimated to be less than 2 ppm at room temperature. The magnitude of this correction is inversely proportional to the temperature. Therefore, a correction as large as 6 ppm might be expected at 110 K.

The fluorine chemical shift parameters of the low temperature spectra of the modified silicas are given in Table 6. The room temperature fluorine NMR spectrum of silica treated with a 5 mM  $F^-$  solution and

TABLE 5  
Low Temperature Hydrogen Data

Fluorine treatment	Calcining temperature (K)	Observation temperature (K)	Center of mass <sup>a</sup> (ppm)	Full width at half height (kHz)
None	773	290	-3.0 ± 1	1.8 + 0.1
		220	-4.0	2.0
		160	-6.0	2.0
		105	-10.0	2.0
5 mM	573	290	5.0	2.8
		165	-5.0	2.8
		140	-8.0	3.0
		110	-9.0	2.8
	873	290	-2.0	1.6
		160	-6.0	1.8
		110	-6.0	2.2
18 mM	573	290	-5.0	2.2
		141	5.0	3.0
		115	-1.0	2.4
	873	290	-2.0	1.6
		160	-4.0	1.4
		145	-7.0	1.8
		110	-10.0	1.4

<sup>a</sup> Relative to tetramethylsilane.

calcined at 573 K differs little from the spectra observed at 115 K. However, the silica treated with an 18 mM F<sup>-</sup> solution and calcined at 573 K shows changes in its line shape upon going from room temperature to 115 K. The fluorine spectra of both samples calcined at 573 K are very similar when observed at 115 K. The fluorine spectra of fluorinated silica prepared using an 18 mM F<sup>-</sup> solution and calcined at 573 K at four observation temperatures are shown in

Fig. 10. There are no large increases in the linewidth of the spectra as the observation temperature is lowered. The room temperature spectrum cannot be described by a chemical shift powder pattern for rigid nuclei. As the temperature is lowered, the spectrum loses intensity near its center of mass. At 110 K the fluorine spectrum can be described by a chemical shift powder pattern which has the principal components  $\sigma_{xx} = -73$  ppm,  $\sigma_{yy} = -49$  ppm, and  $\sigma_{zz} = 39$  ppm, relative to hexafluorobenzene. The low temperature fluorine NMR spectra of the fluorinated silicas calcined at 873 K do not change with temperature.

#### CONCLUSIONS

Reproducible fluorinated silicas have been prepared using aqueous fluoride solutions with fluoride concentrations up to 20 mM. If aqueous ammonium fluoride solutions with fluoride concentrations of 2.8 M are used, volatile silicon compounds are formed upon calcination. Therefore, the fluoride modification of oxide catalysts containing silicon must be done carefully.

The use of nuclear magnetic resonance spectroscopy has provided directly information concerning the local environment of hydroxyl groups and fluorine atoms on modified silicas. Hydroxyl groups are present after calcining at temperatures up to 873 K unless concentrated aqueous fluo-

TABLE 6  
Low Temperature Fluorine Chemical Shift Parameters

Fluoride treatment	Calcining temperature (K)	Observation temperature (K)	Principal components			$\delta$ (ppm)	$\eta$
			$\sigma_{zz}$ (ppm)	$\sigma_{xx}$ (ppm)	$\sigma_{yy}$ (ppm)		
5 mM	573	290	49.0 ± 5	-46.0 ± 3	-34.0 ± 3	60.0	0.21
		115	50.0	-45.0	-40.0	62.0	0.09
	873	290	53.0	-43.0	-38.0	63.0	0.08
		110	49.0	-50.0	-42.0	64.0	0.14
18 mM	573	110	39.0	-73.0	-49.0	67.0	0.35

Note. All values of the principal components are given in parts per million relative to hexafluorobenzene.

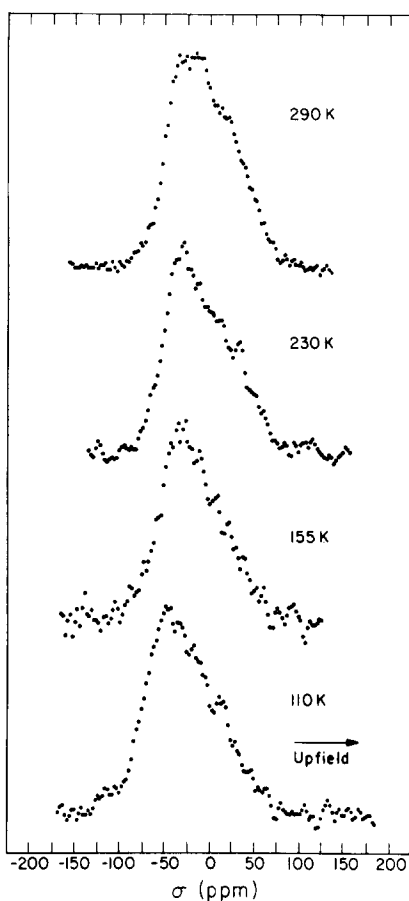


FIG. 10. Fluorine FID spectra as a function of temperature for a fluorinated silica prepared using an 18 mM  $F^-$  solution and calcined at 573 K. The temperatures at which the data were obtained are given beside each spectrum. Values of the chemical shift are reported relative to hexafluorobenzene.

ride solutions are used for sample preparation. The center of mass of the hydrogen spectrum reported herein for unmodified silica is in excellent agreement with the isotropic chemical shift (uncorrected for the bulk magnetic susceptibility) reported for silanol groups by Schreiber and Vaughan (14). The changes in the centers of mass and the linewidths of the hydrogen spectra show the importance of both chemical shift and dipolar interactions.

The fluorine spectra of fluorinated silica is dominated by the chemical shift anisotropy. The spectra are characteristic of isolated fluorine atoms covalently bound to sil-

icon atoms. The nature of the fluorine bonding does not change for calcining temperatures greater than 473 K. Samples calcined at 673 K have uniform fluorine atom and hydroxyl group concentrations if surface degradation has not occurred.

The long CPMG relaxation times,  $T_2^+$ , indicate that the hydroxyl groups do not exist as closely spaced pairs. The fluorine atoms are not bonded to nearest neighbor silicon atoms. The spin echo relaxation times,  $T_2$ , are much shorter than  $T_2^+$  for both the fluorine atoms and the hydroxyl groups in all samples. This relaxation phenomena could result from a number of factors. Fluctuations in the heteronuclear dipolar or the chemical shift interactions would cause significant differences between  $T_2$  and  $T_2^+$ . If molecular motion were sufficiently fast, the linewidths would not be affected at the temperatures studied. Any motion of the fluorine atoms must be anisotropic since a large anisotropy is observed in the room temperature fluorine free induction decays.

The reason for the differences between  $T_2$  and  $T_2^+$  needs to be understood. The differences between  $T_2$  and  $T_2^+$ , the changes in the spectra at different observation temperatures, and the small value of the chemical shift anisotropy of the hydroxyl group spectra show that anisotropic motion is occurring. The rotation of the hydrogen atom of the silanol groups ( $\Rightarrow SiOH$ ) about the Si—O axis is one type of anisotropic motion consistent with the data. A detailed study of the temperature dependence of the relaxation times is needed to identify the type of motion being observed. Spectra must be obtained at temperatures below 100 K if spectra without the effects of anisotropic motion or chemical exchange between different sites are to be observed.

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