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Sol-Gel Synthesis of Nano-Scaled Metal Fluorides – Mechanism and Properties

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1.1 Introduction

Sols are dispersions of nanoscopic solid particles in, for example, liquids – i.e., colloidal solutions. The particles can agglomerate forming a three-dimensional network in the presence of large amounts of the liquid thus forming a gel. Inorganic sols are prepared via the sol-gel process, the investigation of which started in the nineteenth century. This process received great impetus from the investigations of Stöber et al. [1], who studied the use of pH adjustment on the size of silica particles prepared via sol-gel hydrolysis of tetra-alkoxysilanes.

1.1.1 Sol-Gel Syntheses of Oxides – An Intensively Studied and Widely Used Process

Hydrolysis of alkoxy silanes and later on of metal alkoxides in organic solutions has become an intensively studied and widely used process [2]. The most common products are almost homodispersed nanosized silica or metal oxide particles for, e.g., ceramics or...
glasses, or the aqueous sols are used to prepare different coatings for, e.g., optical purposes. Optical applications depend on differences in the respective indices of refraction of the coated material and the applied layer. The latter has to be of very uniform and thoroughly adjusted thickness.

The sol-gel hydrolysis of alkoxy silanes, the most intensively explored one, basically proceeds in two steps. The first step is the hydrolytic replacement of alkoxy groups, OR, by hydroxyl groups, OH, shown schematically in Equation (1.1) for the first alkoxy group:

$$\text{Si} (\text{OR})_4 + \text{H}_2\text{O} \rightarrow (\text{RO})_3\text{SiOH} + \text{ROH} \quad (1.1)$$

Because of their relatively high hydrolytic stability, hydrolysis of alkoxy silanes (1.1) has to be catalysed by Brønsted acids or bases.

In the second step, the primary hydrolysis products undergo condensation reactions under elimination of water (Equation (1.2)) or alcohol (Equation (1.3)).

$$\text{X}_3\text{Si-OH} + \text{HO-SiX}_3 \rightarrow \text{X}_3\text{Si-O-SiX}_3 + \text{H}_2\text{O} \quad (\text{X} = \text{OR}, \text{OH}) \quad (1.2)$$

$$\text{X}_3\text{Si-OH} + \text{RO-SiX}_3 \rightarrow \text{X}_3\text{Si-O-SiX}_3 + \text{ROH} \quad (\text{X} = \text{OR}, \text{OH}) \quad (1.3)$$

As a result tiny particles with a very open structure are formed. The overall process can be controlled by adjusting the reaction conditions. The colloidal solution of these particles, the sol, can be used as such for, e.g., coating or it can be worked up to yield, eventually, nanoscopic oxide particles. However, metal oxide sols obtained in this way always contain a sometimes remarkable organic part. Its separation demands calcination temperatures of at least 623 K in order to convert the ‘precursors’ into pure metal oxide materials.

Substituting a certain part of the alkoxydic groups by nonhydrolysable ones, such as alkyl groups in the case of alkoxy silanes or phosphonic acid in the case of metal alkoxides, organically modified oxides, i.e. inorganic-organic hybrid materials, have been prepared.

### 1.1.2 Sol-Gel Syntheses of Metal Fluorides – Overview of Methods

Selected metal fluorides can, in application-relevant fields, outperform metal oxides and silica. Thus, for instance, magnesium fluoride and aluminium fluoride and, in particular, alkali hexafluoroaluminates have both a lower index of refraction and a much broader spectral range of transparency even than silica, making them very interesting for optical layers.

Consequently, several approaches for the preparation of nanoscopic metal fluorides and metal fluoride thin layers have been developed and proposed. Besides physical methods such as milling, laser dispersion or molecular-beam epitaxy, different chemical methods exist. Basically, three approaches can be distinguished:

(i) **Postfluorination of a metal oxide preformed via sol-gel route** [3].

This route is shown schematically in Scheme 1.1. The disadvantages of this route are, to name two, incomplete fluorination of the bulk metal oxides and decrease of surface area in course of the fluorination.
(ii) Preparation of a precursor containing a metal compound with organically bound fluorine such as trifluoroacetate, which is calcined to decompose the fluoroorganic component under formation of metal fluoride [5].

This route, shown in Scheme 1.2, also starts from metal alkoxides, which are reacted in solution with, e.g., trifluoroacetic acid to form metal trifluoroacetate sol. This can be

\[
\begin{align*}
\text{M(OR)}_x + x\text{H}_2\text{O} & \rightarrow \text{MO}_{x/2} \text{ (sol)} + x\text{ROH} \\
\text{hydrolysis} & \quad \text{coating} \\
\text{MO}_{x/2} \text{(gel) bulk} & \quad \text{MO}_{x/2} \text{(gel) film} \\
\text{fluorination} & \quad \text{fluorination} \\
\text{calcination} & \quad \text{calcination} \\
\text{MF}_x \text{ or MO}_{x/2}/\text{MF}_x \text{ glass} & \quad \text{MF}_x \text{ or MO}_{x/2}/\text{MF}_x \text{ film}
\end{align*}
\]

Scheme 1.1 Metal fluoride preparation via post fluorination of sol-gel prepared metal oxides (Reproduced from [4] by permission of Elsevier Publishers)

\[
\begin{align*}
\text{M(OR)}_x \text{ and/or MOAc + CF}_3\text{COOH + H}_2\text{O + org. solvent} & \rightarrow \\
\text{drying} & \quad \text{coating} \\
\text{metal trifluoroacetate (TFA) precursor solution} & \\
\text{metal-TFA(gel) bulk} & \quad \text{metal-TFA(gel) film} \\
\text{heating} & \quad \text{heating} \\
\text{metal fluoride powder} & \quad \text{metal fluoride film} \\
\text{heating at higher temperature} & \\
\text{MO}_{x/2}/\text{MF}_x \text{ powder} & \quad \text{MO}_{x/2}/\text{MF}_x \text{ film}
\end{align*}
\]

Scheme 1.2 Metal fluoride preparation via metal fluoroacetate sol-gel formation and following thermal decomposition. (Reproduced from [4] by permission of Elsevier Publishers)
used for coating experiments. The decisive final step is the thermal decomposition of the fluoro-organic constituent, because of which thermolabile materials cannot be coated. Another disadvantage is the probability that oxidic components can be formed as admixtures or oxofluorides.

(iii) Fluorolytic sol-gel process as counterpart to the hydrolytic one.

The fluorolytic sol-gel route follows rather strictly the ‘classical’ hydrolytic one by reacting metal alkoxides in anhydrous solution with hydrogen fluoride instead of the hydrogen oxide of the ‘classical’ process. Consequently, it results eventually in metal fluorides instead of metal oxides.

The fluorolytic sol-gel process, its execution, mechanism, scope as well as properties and possible fields of application of its products are the subjects of this chapter.

1.2 Fluorolytic Sol-Gel Synthesis

Metal alkoxides can be regarded as metal salts of alcohols, where the latter are very weak Brønstedt acids. Acids that are stronger than the respective alcohol can therefore replace alkoxy groups attached to the metal ion under liberation of the alcohol and formation of the metal fluoride according to Equation (1.4).

\[
M(OR)_n + x HF \rightarrow M(OR)_{n-x}F_x + x ROH \quad (M = \text{metal ion})
\]

In fact, starting with aluminium isopropoxide [6], a broad range of metal alkoxides have been subjected to a sol-gel-like liquid-phase fluorination with hydrogen fluoride in organic solution [4, 7]. Although Equation (1.4) closely resembled Equation (1.1) there is an important difference in that condensation reactions like those of Equations (1.2) and (1.3) are not possible in the fluorolysis system. On the other hand, the fluorolysis reactions typically result in the formation of a sol-gel. The formation of a gel was already mentioned in the first paper on metal alkoxide fluorolysis, reporting the reaction of aluminium isopropoxide in alcoholic solution with an ethereal solution of hydrogen fluoride [6]. The gel formation is obviously due to an important consequence of the replacement of alkoxy groups by fluoride, i.e., the Lewis acidity of the metal ion increases leading to a strengthening of the interaction between (liberated) alcohol molecules and metal ions. As a result alcohol molecules that can occupy ligand positions might establish a loose net between (partly) fluorinated metal ions resulting eventually in metal fluoride sol or even gels. Surprisingly, attempts to isolate pure AlF\(_3\) by drying and calcining the gel were not successful; the product obtained had an understoichiometric amount of fluorine even when the primary reaction has been carried out with an overstoichiometric amount of HF [8]. An additional fluorination of the dried gel under gentle conditions (see below) has proved to be a suitable way to remove the attached organic components resulting in X-ray amorphous, highly Lewis acidic aluminium fluoride with unusual large specific surface area, named HS-AlF\(_3\) [9].
1.2.1 Mechanism and Properties

To gain insight into the fluorolytic sol-gel process, elucidating the mechanism and optimizing both the experimental procedure and the properties of the products, the influence of all adjustable synthesis parameters was tested as well as the process. In particular, the products were analysed by a broad range of analytical, experimental and theoretical methods. Most of these investigations focussed on the synthesis and properties of HS-AlF$_3$, followed by HS-MgF$_2$. The results and consequences of these investigations are presented and discussed below as well as in subsequent chapters.

1.2.1.1 Approach to Mechanism and Resulting Properties

The fluorolytic sol-gel synthesis of metal fluorides is summarized in Scheme 1.3.

The synthesis was investigated in detail, aiming its optimization for HS-AlF$_3$ [8] and also for HS-MgF$_2$ [10, 11]. In short, the metal alkoxide, the structure of which can be very complex [12], is dissolved in an alcohol or another suitable organic solvent (step 1 in Scheme 1.3), so that in the case of aluminium isopropoxide the tetrameric structure is predominantly preserved. A solution of hydrogen fluoride in, e.g., ether or alcohol is added in approximately stoichiometric amounts to the alkoxide solution. Ratios of HF:Al from 2 to 4 are well tolerated, resulting in a clear, translucent sol (step 2 in Scheme 1.3), which more-or-less rapidly becomes a gel, depending on concentration and type of solvent (step 3 in Scheme 1.3). Varying the type of alkoxide, from methoxide to ethoxide, isopropoxide to butoxide, did not markedly affect the outcome of the fluorolytic reaction. The only meaningful criteria for estimation of these and other synthesis parameters were thus the surface area and especially Lewis acidity of the final HS-AlF$_3$. 

Scheme 1.3  Fluorolytic sol-gel synthesis of high surface area metal fluorides (for explanations of the numbers 1 to 5 see text)
There is yet another route to the synthesis of metal fluoride sol-gel, exemplified for aluminium and magnesium, namely the direct reaction of the metal with an alcoholic HF solution [13]. Upon drying the sol-gel under mild conditions, at about 343 K under vacuum or freeze drying, or under microwave irradiation, a solid, X-ray amorphous dry gel is formed (step 4 in Scheme 1.3), which contains, in case of the Al-F-system, large amounts of organic material, indicated by a carbon content of about 20 %-30 %. An empirical formula based on elemental analysis for a dry gel prepared from Al(OiPr)3 in ‘PrOH is AlF2.7(OCH(CH3)2)0.3\cdot0.7-0.8(CH3)2CHOH. With metal ions of lower Lewis acidity, decisive lower carbon contents were found, e.g. 3 %-7 % C in the Mg-F-system. Obviously, part of the alcohol, which is the predominant constituent of the wet gel, is very tightly attached to the highly Lewis acidic Al3+ ion, as can also be seen from its thermo-analysis (Figure 1.1).

The weakly endothermic mass loss of about 24 % up to 473 K can clearly be attributed to the release of solvating ‘PrOH and the more pronounced smaller one around 495 K to the split off of alkoxide groups. Evaluating thermal analysis data of many different experiments, it became obvious that the mass loss proceeds stepwise. The alcohol content of the steps corresponds to the respective compositions of about AlF3:1ROH after heating at 343 K under vacuum, about AlF3:0.45ROH after heating at 573 K in N2, and about AlF3:0.1ROH after continued heating up to about 600 K [13]. The exothermal peak in Figure 1.1 at 836 K is due to crystallization, i.e. of α-AlF3 formation. In order to obtain a still X-ray amorphous aluminium fluoride, the dry gel with its understoichiometric fluorine content has to be freed from its organic constituents under fluorinating conditions. This can be accomplished in a gas-solid reaction at elevated temperatures up to 573 K with vaporized fluorocarbon compounds such as CHClF2 diluted with an inert gas. An aluminium fluoride is obtained, named HS-AlF3, which is still amorphous, has a specific surface area of about 200 m2/g and shows extremely high Lewis acidity (see below). An unwanted consequence of the extreme Lewis acidity is the readily occurring coke formation preventing the use of fluorochloroethane compounds as fluorinating agents. The postfluorination step is essential for HS-AlF3 formation, therefore all parameters have been comprehensively tested, such as type and concentration of the fluorinating agent, flow rate, temperature, and also ageing of the Al-F-sol. Even under optimum conditions with CHClF2 or CH2F2 the formation of black spots or sometimes of ‘channels’ could be observed indicating that at these spots the formation of HS-AlF3 had started, which then subsequently catalysed coke formation. Such side reactions are, for obvious reasons, not possible using HF as fluorinating agent. In addition, the stronger fluorinating HF can be used at lower temperatures and should preserve the amorphous state with its high surface area even better. The latter criterion could only be fulfilled using rather diluted HF, obviously to reduce the otherwise high reaction enthalpy. However, ‘HS-AlF3’ prepared with gaseous HF did not show the expected Lewis acidity. It turned out that HF had behaved as base, which became attached to the strongest Lewis acid sites of the solid, thereby blocking them. Only by additional longer flushing with a stream of inert gas or, even better, of CHClF2 vapour at elevated temperatures (up to 573 K) did the material become the expected strong solid Lewis acid, i.e. HS-AlF3. HS-AlF3 could also be prepared with elemental fluorine using a dry Al-F-gel of low carbon content obtained by microwave heating of an Al-F-sol under autologous pressure followed by microwave-assisted drying.
The results of experimental investigation are in accordance with the following tentative mechanism of the sol-gel fluorination. Upon addition of HF to the alkoxide solution a stepwise replacement of –OR by –F starts, whereby the coordinating alcohol as linking group prevents the formation of a three dimensional purely F-linked crystal. The sol-gel state, almost immediately formed, kinetically prevents the stoichiometric fluorination of the aluminium species. Upon removing the alcohol under gentle conditions the gel structure only partly collapses; alcohol molecules of the first ligand sphere remain obviously attached to Al. When these molecules are removed under appropriate mild conditions there is no crystallization taking place but the disordered X-ray amorphous state connected with an unusual high surface area remains and a part of the Al atoms becomes co-ordinately unsaturated consequently exhibiting very high Lewis acidity (see below). For HS-AlF₃ a surface area up to 400 m²/g has been determined by N₂ adsorption/desorption experiments. Typical isotherms are shown in Figure 1.2.

Figure 1.1  TA-MS of AlF₂₇[OCH(CH₃)₂]₀.₇–₀.₈(CH₃)₂CHOH; (a) Thermoanalytical curves in N₂ (19.50 mg); (b) Ion current curves for m/z 41 (C₃H₅⁺), m/z 45 (C₂H₅O⁺), and m/z 87 (C₅H₁₁O⁺), indicating the release of propene, i-propanol, and diisopropyl ether, respectively. (Reprinted with permission from [9] Copyright (2005) RSC.)
The tentative mechanism is given in more detail and supported by the analytical investigations discussed in the following section.

1.2.2 Insight into Mechanism by Analytical Methods

Different spectroscopic, microscopic and diffraction methods like IR and Raman spectroscopy, TEM or XRD were applied to characterize educts, intermediates or products of the sol-gel process. For a detailed insight into the mechanism of the fluorolytic sol-gel process, however, the application of NMR spectroscopy is the method of choice. The NMR experiments, both in liquid and in solid state, allow direct observations of local structures and their changes even if the matrices suffer from a loss of lattice periodicity. For the fluorolytic so-gel process both liquid state NMR experiments were realized for the alkoxide solutions, sols and thin gels as well as solid state MAS NMR experiments for the alkoxide, dried alkoxide fluoride gels and high-surface fluorides including $^1$H, $^{13}$C, $^{27}$Al and $^{19}$F as sensitive spin probes. The same spin probes along with the use of 1D and 2D NMR experiments allow local structures in liquids and solids to be addressed and directly compared, to follow their changes with a progressive degree of fluorination and finally to derive a possible reaction pathway for this process. Due to the good experimental accessibility of the mentioned spin probes, a detailed study was conducted for the reaction steps ending up with HS-AlF$_3$. Results of these studies are presented briefly in the following section.

Figure 1.2 $N_2$ adsorption/desorption isotherms and pore size distribution of HS-AlF$_3$ (Reprinted with permission from [6] Copyright (2003) Wiley-VCH.)
1.2.2.1 Sol-Gel Reaction

1.2.2.1.1 Aluminiumisopropoxide (Al(OiPr)₃) as Solid Precursor Compound

The basis for an understanding of changes during the fluorination process is the knowledge and assignment of molecular structures existing in solid Al(OiPr)₃ and its solution in iPrOH. ²⁷Al MAS NMR measurements of solid Al(OiPr)₃ give unambiguous indications for the existence of two distinguishable aluminium sites in the matrix in agreement with XRD findings [14, 15] (Figure 1.3). A simulation of the spectrum (Figure 1.3) results in typical chemical shift values for AlO₄ (δᵣ = 61.5 ppm) and AlO₆ (δᵣ = 1.7 ppm) units [16, 17]. Both the kind and the intensity ratio of AlO₄:AlO₆ as 3:1 confirm the tetrameric molecular structure (see also Figure 1.5, 1) existing in the tetragonal crystal structure [14, 15].

In addition to ²⁷Al, the respective ¹H-¹³C CP MAS NMR spectrum allows a distinction to be made not only between CHO and CH₃ groups but also between terminal (Al-O) and bridging (Al-O-Al) isopropoxide units. Very narrow line widths in part allow the assignment of 18 distinguishable carbon sites in the NMR spectrum in agreement with the crystal structure (see Figure 1.10 (top)) [14, 15]. According to suggestions made by Abraham [17], terminal (63 ppm) and bridged (66 ppm) CHO – groups are located in the low-field part of the spectrum; terminal CH₃ groups are detected in the range between 28–30 ppm and bridging CH₃ groups dominate the high-field part of the spectrum (see Figure 1.10 (top)), [16]).

1.2.2.1.2 Aluminiumisopropoxide (Al(OiPr)₃) Dissolved in Isopropanol

First ¹H NMR studies on possible structures of Al(OiPr)₃ in different solutions range back to 1963 [18] followed by first ²⁷Al NMR measurements in 1973 [19]. Since that...
time aluminium isopropoxide solutions and possible species therein, using CCl₄, benzene or toluene as solvents, are subjects of current interest applying different NMR techniques [20–22]. Isopropanol is the standard solvent used for the fluorolytic sol-gel synthesis [4, 6–8], so results of a careful reinvestigation of possible isopropanolic solution are presented in summary.

²⁷Al NMR spectra of Al(OiPr)₃ dissolved in isopropanol are shown in Figure 1.4a,b; the spectrum recorded for the same sample dissolved in diethylether is depicted in Figure 1.4c.

![Figure 1.4](image-url) ²⁷Al NMR spectra of different Al(OiPr)₃ – solutions: a and b Al(OiPr)₃ in iPrOH recorded with a 400 MHz – spectrometer (a) and a 600 MHz – spectrometer (b), c Al(OiPr)₃ in diethylether (400 MHz – spectrometer). For all: solid: experimental spectrum, dashed: simulation and dotted: decomposition. (Reprinted with permission from [23] Copyright (2007) American Chemical Society.)

The spectrum obtained for the etheric solution (Figure 1.4c) indicates the existence of only tetrameric aluminium isopropoxide species in solution (AlO₆ (2.5 ppm, 26.7 %), AlO₄ (61.8 ppm, 73.3 %), 1 in Figure 1.5) but the situation in isopropanolic solution is much more complex. Applying two different fields (Figure 1.4a,b), both spectra reveal, beside AlO₆ and AlO₄, the existence of an additional fivefold coordinated aluminium species AlO₅ at 32 ppm. They support therewith the existence of trimeric Al(OiPr)₃ species (3 in Figure 1.5). Calculated intensities of the spectra support the assumption of further species. Cyclic trimeric species (2 in Figure 1.5) with possible distorted AlO₄ polyhedra explain the strong low-field shifted resonance observed at 85 ppm [16, 23].
Moreover, an equilibrium between different trimeric species seems to be feasible, which involves a trimeric species with central sixfold oxygen-coordinated aluminium. The latter may result from the interaction of trimeric species 3 (Figure 1.5) and a solvent molecule as shown in Figure 1.6 [16].

In the appropriate $^1$H and $^{13}$C NMR spectra, no indications are observable that distinguish between tetramers 1 and trimers 2 and 3 (Figure 1.5), respectively. The only possible discrimination between bridging and terminal isopropoxide groups holds for all of the mentioned Al(OiPr)$_3$ species (Figure 1.5) [16]. Summing up these results it can be concluded that the isopropanolic solution of Al(OiPr)$_3$ is dominated by the tetrameric Al(OiPr)$_3$ species 1 (Figure 1.5) accompanied by a smaller amount of trimeric species.

### 1.2.2.2 Structural Changes at the Fluorination Process in Sols and Thin Gels

On the basis of the $^{27}$Al NMR spectra of isopropanolic Al(OiPr)$_3$ solution, structural changes were followed after adding increasing amounts of HF/iPrOH solution to the aluminium isopropoxide solution according to Equation (1.4). In dependence on the molar Al:F ratio the appearance of the reaction mixture ranges from clear sols (4:1) to opaque gels (1:3). Figure 1.7 represents the $^{27}$Al and $^{19}$F NMR spectra obtained with rising content of fluorine (from a to d). It is obvious that in this order the amount of AlO$_6$ species
(narrow line in Figure 1.4a,b; central units of I (Figure 1.5) is decreased. In the same manner a decreasing proportion of the sum over all fourfold Al species is found and, contrary to that, an increasing amount of fivefold coordinated aluminium species AlO$_5$ (signals at about 35 ppm) [23].

Figure 1.7  $^{27}$Al NMR and $^{19}$F NMR spectra of different sols and wet gels ($B_0=9.4$ T). For all: solid line: experimental spectrum, dashed: simulation, dotted: decomposition. From a to d increasing content of fluorine. Molar ratios Al: F: (a) 4 : 1, (b) 2 : 1, (c) 1 : 1, (d) 1 : 2. (Reprinted with permission from [23] Copyright (2007) American Chemical Society.)

All $^{19}$F spectra are characterized by a group of three sharp signals (–161 ppm, –163 ppm, –165 ppm) with different intensities. All these signals are in a typical region for fluorine bounded on aluminium centres in a mixed oxygen-fluorine coordination with different fluorine ratios [13, 24–28]. With higher fluorine content, the intensity of the $^{19}$F NMR spectrum is more and more dominated by a broad peak at about –160 ppm (Figure 1.7, $^{19}$F,d). These line-broadening effects result mainly from $^{19}$F–$^{19}$F homonuclear dipolar couplings ending up in one broad peak in the static $^{19}$F NMR spectrum for the gel with molar ratio Al:F as 1:3. $^1$H and $^{13}$C NMR spectra of sols and gels show two main effects
with increasing fluorine supply: the portion of bridging isopropoxide groups is decreasing while the portion of terminal isopropoxide groups is affected only with higher fluorine supply [16, 23]. Obviously, the fluorination starts by protonation of bridging isopropoxide groups with the consequence of a line broadening of the corresponding signals, while the intensities of signals of terminal groups first remain constant. This first step is also supported by recently accomplished DFT calculations [23, 29]. A subsequent fluorination step may involve an attack of fluorine ions or HF on the central Al atoms of 1 (Figure 1.5) and the substitution of the protonated isopropoxide group by fluorine.

**1.2.2.2.1 Isolated Single Crystals as Intermediates**

Evidence for a stepwise introduction of fluorine into the coordination sphere of Al is also given by the successful isolation of single crystals of partly fluorinated aluminium as well as magnesium alkoxide fluorides, $\text{Al}_3(\text{OiPr})_8\text{F}_x\cdot\text{DMSO}$ (Figure 1.8a) [9], $\text{Al}_3(\text{OiPr})_8\text{F}_x\cdot\text{Py}$ (Figure 1.8b) [30] and $\text{Mg}_6\text{F}_2(\text{OMe})_{10}(\text{MeOH})_{14}$ (Figure 1.11) [31, 32]. In each case the isolation of single crystals works only if the fluorine supply is very low, i.e. $\text{Al:F or Mg:F} > 1$.

Three distinguishable aluminium sites and one fluorine site are expected for $\text{Al}_3(\text{OiPr})_8\text{F}_x\cdot\text{Py}$ in the $^{27}\text{Al}$ and $^{19}\text{F}$ MAS NMR spectra, which are given in Figure 1.9. Simulation of the $^{27}\text{Al}$ NMR spectrum supports this assumption and the decomposition obtained is given in Figure 1.9. The chemical shift values are close to those of crystalline $\text{Al(OiPr)}_3$ emphasizing their structural similarity. As a consequence of the coordination of fluorine and a solvent molecule the originally higher symmetric $\text{AlO}_6$ unit, now $\text{AlO}_4\text{FPy}$, has considerably larger quadrupolar parameters [30].

The closeness to the $\text{Al(OiPr)}_3$ structure may also be seen by comparing the two $^1\text{H}-^\text{13C}$ CP MAS NMR spectra (Figure 1.10).
Those CHO and CH$_3$ groups located on bridged Al-O-Al positions (s. 1, 3 in Figure 1.5), i.e. at the positions > 65 ppm and < 25 ppm, respectively, are especially strongly affected by the new substituents on the central aluminium site. In contrast, the terminal groups are, as expected, less influenced.

**Figure 1.9** $^{27}$Al and $^{19}$F MAS NMR spectra of Al$_3$(OiPr)$_8$F-Py; ($\nu_{\text{rot}} = 25$ kHz, $B_0 = 9.4$ T) (Reprinted with permission from [30] Copyright (2008) Humboldt University of Berlin.)

**Figure 1.10** $^1$H-$^{13}$C CP MAS spectrum of Al$_3$(OiPr)$_8$F-Py (bottom) in comparison with analogous spectrum of its precursor Al(OiPr)$_3$ (top) ($\nu_{\text{rot}} = 10$kHz, $B_0 = 9.4$ T) (Reprinted with permission from [16] Copyright (2006) Humboldt University, Reprinted with permission from [30] Copyright (2008) Humboldt University of Berlin.)
Likewise, the polymeric nature of magnesium methylate results in the bulky Mg$_6$F$_2$(OMe)$_{10}$(MeOH)$_{14}$ (Figure 1.11), the synthesis of which can easily be reproduced. In this case the structure is also very similar to that of the fluorine-free compound Mg(OCH$_3$)$_2$ [33]. To preserve the cube-like shape, two fluorine ligands have to be introduced. The high symmetry of the crystal, however, results in one narrow $^{19}$F signal at $-174$ ppm, as shown in [32, Figure 5 therein].

![Figure 1.11](image)

**Figure 1.11** Crystal structure of Mg$_6$F$_2$(OMe)$_{10}$(MeOH)$_{14}$ (Reprinted with permission from [31] Copyright (2008) Wiley-VCH.)

1.2.2.3 Changes in Dry Gels with Progressive Fluorination

Isolated single crystals and their structures only give an idea of very early steps of fluorination, producible only with an understoichiometric fluorine supply. Changes in the local aluminium and fluorine coordination in solutions, sols and thin gels are
highlighted above (Figure 1.7). Drying of such thin and thick wet gels with different Al:F molar ratios leads exclusively to X-ray amorphous materials. However, based on the relevant liquid state NMR spectra (Figure 1.7), fundamental modifications can also be expected for the local coordinations in these solids. Together with the data already presented, a consistent mechanism of the fluorination process is then deducible.

Taking all results into account, three stages of the sol-gel fluorination process can be identified, which are shown in the following. The first stage is primarily represented by samples with molar ratios Al to F higher than 1 (meaning low F-contents). Samples with molar ratios 1:1 and 2:3 (stage 2) mark for the solids the changeover to the third stage, the aluminium isopropoxide fluoride xerogels, samples with Al:F ratios lower than 0.5.

$^1$H-$^{13}$C CP MAS, $^{27}$Al and $^{19}$F MAS spectra of dried gels with varying composition, as depicted in Figures 1.12 and 1.13, illustrate these findings. Beside a general shift of the $^{13}$C

![Diagram of Al(OiPr)$_3$ and Al : F ratios](image)

Figure 1.12 $^1$H-$^{13}$C CP MAS NMR spectra (central transitions) of Al(OiPr)$_3$ and aluminium isopropoxide fluoride solids prepared with different molar ratios Al: F as given in the figure ($\nu_{\text{rot}} = 10$ kHz, $B_0 = 9.4$ T) (Reprinted with permission from [34] Copyright (2009) American Chemical Society.)
signals to higher fields (CH$_3$ groups) and lower fields (CHO groups), a considerable broadening effect is observable for all bridging CHO – and CH$_3$ groups, and after that, with a higher proportion of fluorine, also a broadening and finally disappearing of the signals of the terminal groups (Figure 1.12) [34]. The spectral changes (peak maxima, line forms) deducible only from the $^1$H MAS NMR spectra are only minor and the superimposition of the several signals makes it difficult to discuss them separately [34]. $^{27}$Al and $^{19}$F MAS NMR spectra however address local changes in the solids during continued fluorination very clearly.

As mentioned above, the greatest change can be observed by introducing more and more fluorine and passing the molar ratio Al to F equal to one (see also Figure 1.13). Whereas the spectral features of the initial Al(O$i$Pr)$_3$ are still present in the $^{27}$Al MAS NMR spectra of samples with low fluorine content, a rising signal at 38 ppm is detected, which is provoked by a tetrahedrally coordinated aluminium site in the proximity to fluorine as evidenced by $^{19}$F $^{27}$Al CP MAS NMR experiments [34]. Their $^{19}$F MAS NMR spectra (Figure 1.13) are dominated by very sharp signals (FWHM less than 1 kHz), which indicate ordered (‘crystal-like’) local structures. Most of the species in these solids are more-or-less

![Figure 1.13](image-url)  

*Figure 1.13* $^{27}$Al and $^{19}$F MAS NMR spectra of Al(O$i$Pr)$_3$ and aluminium isopropoxide fluoride solids prepared with different molar ratios Al: F as given in the figure ($\nu_{rot} = 25$ kHz, $B_0 = 9.4$ T) (Reprinted with permission from [34] Copyright (2009) American Chemical Society.)
isolated; no proximity of the certain F-sites to each other can be stated from $^{19}$F-$^{19}$F spin exchange experiments [34]. The 3QMAS NMR spectra of samples d and e (Figure 1.13) indicate the existence of a set of different $\text{AlF}_x(\text{OiPr})_{4-x} - \text{AlF}_x(\text{OiPr})_{5-x}$ and $\text{AlF}_x(\text{OiPr})_{6-x}$ species (for the latter $x = 3–5$) [34]. They are also responsible for the remarkable line-broadening effects in the corresponding fluorine spectra. The existence of certain fourfold and fivefold coordinated $\text{AlF}_x(\text{OiPr})_{\text{CN}-x}$ species as intermediate structures in aluminium isopropoxide fluorides was also unambiguously shown utilizing, for the first time, ultra high-field MAS NMR at magnetic fields $B_0$ up to 21.1 T [35].

Moving to the third stage, a more and more stable network is formed with Al:F ratios equal to 1:2 and 1:3. The amount and spread of fourfold and fivefold coordinated Al-species decreases, ending up with sixfold $\text{AlF}_x(\text{OiPr})_{6-x}$ species ($x = 4$ and 5) as deduced from the chemical shift correlation graphs [26–28, 36, 37].

The comparison of the development of the intensities of single species with rising fluorination degree with the general development of the certain contributions of the appropriate $^{19}$F MAS NMR spectra allows a simple correlation of Al and corresponding F-species. Besides, a variety of possibly terminal fluorine-sites are evident for the highly disordered and amorphous aluminium isopropoxide fluorides in the up-field part of the spectra [35].

1.2.2.4 Structure of Wet and Dry Aluminium Alkoxide Fluoride Gels

An attribution of local structures in wet gelatinous and air-sensitive fluoride gels implies many difficulties, which made the development and testing of inserts for MAS experiments necessary. Alternatively, low-temperature MAS NMR experiments at temperatures below the melting point of the solvent used allow the gel to be filled directly into the rotor [38]. $^{27}$Al and $^{19}$F MAS NMR spectra of a wet gel recorded at a spinning speed of 10 kHz both in a quartz insert and at low temperature are shown in Figure 1.14 together with the corresponding static spectra.

A broad signal around 0 ppm was obtained for the $^{27}$Al static NMR spectrum (Figure 1.14a), completely covering the region for $\text{AlO}_4, \text{AlO}_5, \text{AlO}_6, \text{AlO}_x F_y$ or $\text{AlF}_6$ species. The very broad static $^{19}$F signal is superimposed by narrow lines at $-150 \text{ ppm}$ and $-171 \text{ ppm}$. The latter can be assigned to ‘free’ and mobile F- ions. Rotation at $10 \text{ kHz}$ discloses a substantial line narrowing with a $^{27}$Al line at $-16 \text{ ppm}$ with a shoulder and an asymmetric decay in the high-field part. The $^{19}$F MAS NMR spectra of the wet gel observed using the quartz insert and applying low temperature are also comparable (Figure 1.14). A broad main signal is visible at $-163 \text{ ppm}$ together with spinning side bands superimposed by narrow peaks as contributions from the solvent.

Comparing the MAS spectra of wet and dry gels, it becomes obvious that most of the structural features are already preformed in the jelly-like gel and in principle conserved and strengthened in the dry gel. This holds for all studied nuclei ($^{19}$F, $^1$H, $^{13}$C, $^{27}$Al [38]). For $^{27}$Al this comparison is given in Figure 1.15 [38]. The shoulder and the position of the $^{27}$Al central lines as well as the wide spread of spinning side bands are characteristic features for both wet and dry gels. Sixfold coordinated Al-species ($\text{AlF}_x\text{O}_{6-x}$) are the dominating units in their structure. Second-order quadrupolar broadening is the main line-width factor of the Al signals. Four different structural units could be assigned by additional MQMAS experiments (Figure 1.16, [40]).
The reconstruction of the $^{27}$Al MAS NMR spectrum of the xerogel was possible with the four sites (A-D, Figure 1.16) obtained by analysis of the 3QMAS spectrum. [40]. These sites are attributed to AlF$_{0-2}$O$_{6-4}$ units (A), AlF$_{4-5}$O$_{2-1}$ units (38 %, B and C) and AlF$_{5}$O$_{1}$ units (53 % D) in the network [27, 40].

The existence of already immobilized –OiPr-groups, incorporated into or associated on the network, can be unambiguously proven for the wet gel by $^{13}$C CP MAS experiments [38]. In addition, the more rigid structure of the dry gel allows distinctions to be made between matrix groups and associated immobilized iPrOH molecules [38, 41]. The main structural features of the dried gel are already built up in the jelly-like gel and change only little in aging and drying processes.

1.2.2.5 Network Formation with Increasing Fluorine Content

Bearing in mind all NMR spectra recorded for sols, thin wet gels and dried gels (Figures 1.7, 1.12–1.16) in comparison with those of solid and liquid educts, the following mechanism can be derived for the fluoro lytic sol-gel reaction. In the first step of the synthesis route of HS-AlF$_{3}$, which is usually applied, the tetrameric structure of Al(OiPr)$_{3}$
as dominating species (Figure 1.5, 1) represents the starting point for the further reaction pathway and finally for the formation of the gel network. The fluorination begins with a protonation of bridging isopropoxide groups, which makes a subsequent attack of fluorine ions or HF to central Al atoms easy. As result, a substitution of protonated isopropoxide groups by fluorine occurs.

At early fluorination states (state 1, Scheme 1.4) unconverted Al(OiPr)_3-molecules exist in the sols and gels to some degree – either in its tetrameric or in its linear trimeric form. In the following the latter may be partly fluorinated and, if stabilizing donors (D) are

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**Figure 1.15** $^{27}$Al MAS NMR spectra of the wet and dried gel (xerogel) with focus on the central region (400 MHz spectrometer; na: number of accumulations): (a) comparison of $^{27}$Al MAS NMR spectra of the frozen wet gel with (solid line, 160 K) and without (dotted line, 155 K) $^{19}$F (cw) decoupling at cryo-temperatures, for both: $\nu_{\text{rot}} = 10$ kHz, na: 1000; (b) possible different contributions to the spectrum of the xerogel including the $n = 0$ spinning sideband of the satellite transition: (---). (s. also Neuville, Massiot [39]); experimental spectrum (——); simulated spectrum (-----) and decomposition (-----) (see also Table 2 in [38]). (Reprinted with permission from [38] Copyright (2007) Elsevier Ltd.)
accessible, even crystals of Al$_3$(O^iPr)$_8$F•D can be isolated (Scheme 1.4, 3). Nevertheless, for aluminium isopropoxide fluorides resulting from sols without donor molecules the formation of ordered similar species Al$_3$(O^iPr)$_8$F•PrOH is presumable as evidenced, for example, by the corresponding sharp signals centred at –160 ppm and –171 ppm ($^{19}$F).

The early formation of tetrahedrally coordinated species AlF$_4$ can be demonstrated for solids prepared with low fluorine supply. This species does not seem to exist in the corresponding sols. Instead, it is plausible that these species are stabilized as solvated species AlF$_x$(HO^iPr)$_{6-x}$/C$_0^x$ species ($x$ = 4) in the sols. Drying results in a partial loss of the solvent molecules and the formation of ‘incorporated’ AlF$_4$-species. Additionally, further linking processes of the AlF$_x$(HO^iPr)$_2$/C$_0^x$ species lead to the formation of bigger units (beginning of a gelous network), which, as a consequence, are predominantly built of AlF$_x$(H)O^iPr)$_6$/C$_0^x$-octahedra ($x$ = 3 to 5).

The rise of the F-content (molar ratio Al: F < 1) leads to an irregularly strongly distorted and disordered solid. The corresponding sol consists of a loose network, imaginable in solution as presented earlier in [23]. Vacuum drying leads to cleavage of PrOH molecules coordinating to Al-species existing in these sols and gels, forming a variety of fourfold, fivefold and sixfold coordinated Al-species like AlF$_x$(H)O^iPr)$_{4-x}$, AlF$_x$((H)O^iPr)$_{5-x}$ and AlF$_x$((H)O^iPr)$_{6-x}$ as identified by 3QMAS and ultra high-field MAS NMR measurements [34, 35]. The units are sterically separated; as in the $^{19}$F-$^{19}$F EXSY NMR experiments, nearly no spin exchange could be observed ([34], state 2, s. Scheme 1.5).

Finally this gelous network is strengthened and stabilized by cross-linking with higher fluorine supply. Vacuum drying leads then to xerogels that consist predominantly of sixfold coordinated AlF$_x$((H)O^iPr)$_{6-x}$ species ($x$: 3–5) [38, 40]. Coordinating solvent molecules are stabilized by the formation of H-bridges. The local structures of the xerogel are preformed in the wet gel. Nevertheless, ordered local structures are also observable for the xerogels.

The derived mechanism is schematically depicted in Schemes 1.4 and 1.5.

Figure 1.16  3QMAS spectrum of the aluminium alkoxide fluoride gel (Al:F = 1:3) acquired at 14.1 T (Reprinted with permission from [40] Copyright (2009) American Chemical Society.)
Scheme 1.4 Derived mechanism for the beginning sol-gel fluorination process with low fluorine supply (O*: iPrOH; O: -O-iPr). (Reproduced from [34] by permission of the American Chemical Society.)

Scheme 1.5 Derived mechanism for a progressive fluorination degree (reproduced from [34] by permission of the American Chemical Society)
1.2.2.6 Structural Characterization of Sol-Gel Derived High-surface Fluorides

1.2.2.6.1 Vibrational Spectroscopy of HS-AlF$_3$

The IR transmission spectra of HS-AlF$_3$ were recorded and compared with those of aluminium isopropylate and of dry aluminium fluoride gel – i.e. the Al moieties involved in HS-AlF$_3$ synthesis (Figure 1.17) [8], as well as of crystalline AlF$_3$ phases (Figures 1.18 and 1.19) [42]. In Figure 1.17 the CH$_3$ and CH as well OH absorption bands of isopropoxide and/or isopropanol can be seen at wave numbers higher than 2800 cm$^{-1}$ in the spectra of aluminium isopropylate and of dry aluminium fluoride gel, whereas the broad band in the HS-AlF$_3$ spectrum can be attributed (i) to water adsorbed in course of sample preparation due to the high Lewis acidity, and (ii) to water residues present in the bulk as a consequence of the formation of diisopropylether at postfluorination. At low wave numbers there are the absorption bands of Al-O and Al-F valence vibrations (360–700 cm$^{-1}$) and of C-C frame vibrations of the organic constituents. These spectra show the disappearance of organic components converting the dry gel, the ‘precursor’, into HS-AlF$_3$.

![Figure 1.17 IR spectra of Al(OiPr)$_3$, the AlF$_{2.3}$OiPr$_{0.7}$.xiPrOH gel, and HS-AlF$_3$ (Reprinted with permission from [8] Copyright (2007) Springer Science + Business Media.]

The amorphous, highly disordered state of HS-AlF$_3$ follows convincingly from a comparison of its IR spectra with those of $\alpha$-AlF$_3$ shown in Figure 1.18. Since crystalline $\alpha$-AlF$_3$ also gives a well resolved Raman spectrum (Figure 1.19) all the distorted X-ray amorphous phases of HS-AlF$_3$ do not yield any useful information.

The very broad peaks in the IR-spectrum of HS-AlF$_3$ are obviously the consequence of its amorphous state and can be interpreted as superposition of many unresolved peaks, also covering the range of vibration bands of the $\alpha$- and $\beta$-AlF$_3$ phases.

1.2.2.6.2 X-ray Diffraction and TEM Investigations of HS-AlF$_3$

In contrast to vibrational spectroscopy, the X-ray diffraction patterns of HS-AlF$_3$ and of its precursor, the AlF$_{2.3}$OiPr$_{0.7}$.xiPrOH dry gel, show no peak and therefore only indicate the
X-ray amorphous state of these samples. Only after heating above the crystallization temperature of about 836 K do peaks corresponding to $\alpha$-AlF$_3$ become apparent (Figure 1.20).

In the TEM micrograph (Figure 1.21) both the agglomeration of nano-particles to micro-particles as well as the partial crystalinity of the nano-particles can be seen.

### 1.2.2.6.3 Solid State NMR of HS-AlF$_3$

Subsequent drying of the xerogel in vacuum results in a noticeable loss of –OiPr-groups and associated iPrOH molecules, which can easily be followed by $^1$H-$^{13}$C CP MAS

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**Figure 1.18** IR-transmission spectra of $\alpha$-AlF$_3$, $\beta$-AlF$_3$, and HS-AlF$_3$ (Reprinted with permission from [42] Copyright (2007) American Chemical Society.)

**Figure 1.19** Raman spectrum of $\alpha$-AlF$_3$ (rhombohedral phase) (Reprinted with permission from [42] Copyright (2007) American Chemical Society.)
experiments [44]. Both \(^{19}\text{F}\) and \(^{27}\text{Al}\) MAS NMR spectra exhibit after removal of the organic components the typical shape as recorded for HS-AlF\(_3\). The maximum broad \(^{19}\text{F}\) MAS NMR signal lies typically at –165 ppm [41]. The effect of such a drying process is shown exemplarily for \(^{27}\text{Al}\) in Figure 1.22. The spectrum on the bottom (Figure 1.22) is almost identical with the central line usually measured for HS-AlF\(_3\). In contrast to the xerogel (AlF\(_{2.3}\)OiPr\(_{0.7}\)-xiPrOH) the \(^{27}\text{Al}\) MAS NMR signal line widths do not narrow

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**Figure 1.20** X-ray powder diffractograms of (a) AlF\(_{2.3}\)OiPr\(_{0.7}\)-xiPrOH dry gel, (b) AlF\(_{2.3}\)OiPr\(_{0.7}\)-xiPrOH dry gel heated to 623K, (c) HS-AlF\(_3\), and (d) AlF\(_{2.3}\)OiPr\(_{0.7}\)-xiPrOH dry gel heated to 973 K (Reprinted with permission from [8] Copyright (2007) Springer Science + Business Media.)

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**Figure 1.21** TEM micrograph of HS-AlF\(_3\) (Reprinted with permission from [6] Copyright (2003) Wiley-VCH.)
much upon increase of the applied magnetic field. Therefore the comparison of MQMAS experiments at different magnetic field strength is most important for an assignment of various species. Although the data analysis is very difficult, the presence of various signals was revealed [40].

A 3QMAS spectrum of HS-AlF$_3$ is given in Figure 1.23.

![3QMAS NMR spectrum of HS-AlF$_3$](image)

**Figure 1.22** $^{27}$Al MAS NMR spectra (central lines) of a AlF$_{2.3}$OiPr$_{0.7}$-xiPrOH gel thermally dried in a vacuum at different temperatures ($\nu_{rot} = 25$ kHz, $B_0 = 9.4$ T) (Reprinted with permission from [44] Copyright (2009) Humboldt University of Berlin.)

![MQMAS spectrum of HS-AlF$_3$](image)

**Figure 1.23** 3QMAS NMR spectrum of HS-AlF$_3$ acquired at 19.9 T (Reprinted with permission from [40] Copyright (2009) American Chemical Society.)
The line shape analysis of the $^{27}$Al MAS NMR spectrum of HS-AlF$_3$ required more than the two Al-sites extracted from the 3QMAS spectrum (Figure 1.23). A successful fit was only possible by implementation of two further Al-sites. For all of them the simulation required the Czjzek-model, i.e. distributions of quadrupolar parameters were used [40]. Now 65% of the integral intensity of the Al signal belongs to AlF$_{5-6}$O$_{1-0}$ and AlF$_6$ units, respectively. Residues of AlF$_{4-5}$O$_{2-1}$ units (25%) and AlF$_{0-2}$O$_{6-4}$ units (11%) are still present [40].

1.2.3 Exploring Properties

The most remarkable property of HS-AlF$_3$ is its outstanding Lewis acidity [6, 8, 9, 45], which is far higher than that of AlCl$_3$, as will be shown later. It is interesting to note that on a theoretical basis for an isolated ‘AlF$_3$-molecule’ already a Lewis acidity was predicted ranking among the highest ones at all [46]. In the following a variety of investigations showing the very high Lewis acidity of HS-AlF$_3$ will be presented and discussed.

1.2.3.1 Adsorption of Probe Molecules

The strength and/or nature and/or amount of acid sites accessible at the surface of a solid can principally be determined measuring the interaction with a basic probe molecule. The higher the acidity of the solid the lower can be the basicity of the probe and vice versa. For investigations of HS-AlF$_3$, pyridine and its derivatives, ammonia and carbon monoxide, were employed. Their interactions with the solid have been analysed studying in case of ammonia desorption with increasing temperature, Temperature Programmed Desorption TPD, and in case of the other probes via IR spectroscopy.

$\text{NH}_3$-TPD: HS-AlF$_3$ was saturated with gaseous NH$_3$ followed by flushing with N$_2$. Upon gradually heating the sample up to 773 K, i.e. below the crystallization temperature, the adsorbed NH$_3$ is gradually released as shown in Figure 1.24. Compared to the well-known solid Lewis acid $\beta$-AlF$_3$ the desorption from HS-AlF$_3$ occurs up to much higher temperatures corresponding to a much higher Lewis acidity, and the total amount of NH$_3$ is also much higher, indicating a higher number of acidic sites per gram.

Pyridine adsorption: The chemical nature of the acid sites can be seen from photoacoustic infrared spectra (PAS) of adsorbed pyridine (Figure 1.25). Frequencies and intensities of the IR bands show for HS-AlF$_3$ (almost) only Lewis acid sites, whereas a HS-AlF$_3$ sample showed after treatment with HF predominantly Brønsted acid sites (Figure 1.25b).

Carbon monoxide adsorption: Carbon monoxide behaves towards a strong acid as a weak base the interaction of which can be investigated monitoring the CO stretching region of the IR absorption spectrum of the absorbed CO. The stronger the acid the more is the CO IR frequency blue-shifted. HS-AlF$_3$ shows the strongest blue shift ever reported for a solid acid (for details see Chapter 3) indicating that it is, next to ACF (aluminium chlorofluoride), the strongest solid acid of all [47].
1.2.3.2 Catalytic Test Reactions

Reactions which have to be catalysed by a Lewis acid to proceed can be used as test-reaction for assessment of the acidity of a material under study. Equations (1.5) to (1.8) show four reactions, the use of which has been reported [8, 45]:

$$5 \text{CCl}_2\text{F}_2 \rightarrow \text{CCl}_3\text{F} + 3 \text{CCl}_3\text{F} + \text{CCl}_4$$

(1.5)
The educts of the reactions in Equations (1.5) and (1.6) were used as postfluorination agents in the course of high surface metal fluoride preparation, especially that of HS-AlF₃. As soon as first parts of the dry Al-F-gel are converted into HS-AlF₃, a dismutation reaction according to Equations (1.5) or (1.6) starts, which can be detected by GC. Thus, these fluorinating agents act conveniently as detectors for Lewis acidity. However, the reactions in Equations (1.5) and (1.6) already proceed in the presence of comparable weak Lewis acids; they are therefore no measure of high acidity. The isomerization of CBrF₂CBrFCF₃ (Equation 1.7), on the other hand, proceeds only under the catalytic action of the strongest known Lewis acids, i.e. antimony pentafluoride or aluminium chlorofluoride, and is also catalysed by HS-AlF₃ but not by AlCl₃ [8, 45]. Thus, the isomerization reaction gives convincing evidence for the exceptional high Lewis acidity of HS-AlF₃. As AlCl₃ is widely used in organic synthesis as a Lewis acidic catalyst a further comparison of its Lewis acidity with that of HS-AlF₃ was of interest. Studying the isomerization of CCl₂FCClF₂ (Equation 1.8) as test reaction, AlCl₃, HS-AlF₃, ACF, α-AlF₃ and β-AlF₃ have been compared regarding their respective catalytic activity. It was found that ACF and HS-AlF₃ were catalytically very active, and α-AlF₃ and β-AlF₃ not at all, as expected. Surprisingly, AlCl₃ was also not primarily active but became active only under conditions and after some time as was needed to convert AlCl₃ into ACF. The experimental result was interpreted based on theoretical investigations assuming that under-coordinated Al atoms, which are a result of the high degree of disorder, are responsible for the Lewis acidity of HS-AlF₃ [45].

Radiotracer investigations: Radiotracer experiments, which also gave evidence for the exceptional Lewis acidity of HS-AlF₃, are discussed in Chapter 3.

1.2.4 Possible Fields of Application

1.2.4.1 Range of Metal Fluorides Obtainable via Sol-Gel Fluorination

The fluorolytic sol-gel synthesis of metal fluorides was originally developed and explored for aluminium fluoride, which was a piece of luck since both the stepwise synthesis and the properties of HS-AlF₃ showed the influence of the new synthesis process. Thus, almost immediately after exploration of HS-AlF₃ other binary metal fluorides have been similarly prepared and attempted syntheses of more complex systems started.

Binary metal fluorides: Many binary metal fluorides have been prepared via sol-gel fluorolysis [4, 7]. The applicability of the synthesis process is primarily limited by the ready availability of soluble metal alkoxides. However, the synthesis of metal fluorides, of which the metal ions are very weak Lewis acids, typically does not result in sol formation but finely dispersed solid fluorides, the XRD of which reflect the aimed-for compounds.
Thus, upon fluorolysis of the tert-butoxides of Li, Na, K and Cs in THF solution, only with LiO\textsubscript{t}Bu and NaO\textsubscript{t}Bu did gel formation occur whereas with K- and Cs- alkoxide immediate precipitation was observed. The dried products of all these alkali metal ions reflected the corresponding fluorides in XRD and also gave some indications of the respective hydrogenfluorides due to their higher thermodynamic stability [48]. The most thoroughly investigated example besides HS-AlF\textsubscript{3} is HS-MgF\textsubscript{2} [11]. Other high surface area alkali earth fluorides prepared are HS-CaF\textsubscript{2} and HS-BaF\textsubscript{2} [49].

Mixed metal fluorides: Prompted by a hypothetical model by Tanabe explaining the Lewis acidity of guest-host metal oxide systems [50] and its adaptation for fluoride systems [51], guest-host mixed metal fluoride systems with HS-MgF\textsubscript{2} as host have been prepared (see also Chapter 3). If the radii are comparable, the metal ions guest ions will probably occupy places of Mg\textsuperscript{2+} ions. If the guest ion has a higher positive charge than Mg\textsuperscript{2+}, Lewis acidity should be created in accordance with the model. This way, solid potential metal fluoride catalysts with tunable Lewis acidity are accessible. Thus, with up to 20 mol % of Fe\textsuperscript{3+}, Ga\textsuperscript{3+}, V\textsuperscript{3+}, In\textsuperscript{3+}, and Cr\textsuperscript{3+} as guest components, solid solutions with HS-MgF\textsubscript{2} as host have been prepared [52–54]. The synthesis of such systems basically followed the fluorolytic sol-gel route described above, however, in some experiments compounds other than alkoxides have been employed as guest components to be added to the Mg alkoxide solution. Analyses of these mixed systems by XRD, \textsuperscript{19}F MAS NMR and photoelectron spectroscopy showed no evidence of the guest compounds but gave only of the typical spectral data of MgF\textsubscript{2}, which however, were not identical with those of crystalline MgF\textsubscript{2}.

Obviously the guest metal ions were incorporated into the MgF\textsubscript{2} lattice as expected. ESCA investigations in the Cr\textsuperscript{3+}/MgF\textsubscript{2} system (Figure 1.26) showed, for both Mg 1s and F 1s, binding energies near those of pure MgF\textsubscript{2}, which however, were not identical with those of crystalline MgF\textsubscript{2}. A shift that is only small to lower binding energies gives evidence that the chemical environment of Mg and F in the mixed systems is influenced by Cr\textsuperscript{3+}.

Complex metal fluorides: Complex metal fluorides are especially interesting compounds because of their physical properties, which are suitable for applications such as lasers. Conventional syntheses typically employ thermal methods starting from the respective metal fluorides. Complex metal fluorides can also be conveniently prepared via sol-gel fluorination. The sol-gel syntheses start similar to that of host-guest systems from mixtures of the respective metal alkoxides but in the respective stoichiometric ratio, which are subjected to fluorolysis. Contrary to the host-guest systems, where the host lattice is preserved, complex systems, i.e. fluorometallates, have their specific crystal structure different from those of the respective binary metal fluorides they are composed of. Examples of complex metal fluorides prepared via sol-gel fluorolysis are Li\textsubscript{3}AlF\textsubscript{6}, Na\textsubscript{3}AlF\textsubscript{6}, K\textsubscript{3}AlF\textsubscript{6}, KAlF\textsubscript{4}, CsAlF\textsubscript{4}, LiNa\textsubscript{2}AlF\textsubscript{6} [55] and BaAlF\textsubscript{5}, K\textsubscript{2}MgF\textsubscript{4} and BaMgF\textsubscript{4} [49]. Since Al in AlF\textsubscript{6} units is ideally shielded, such compounds do not show any Lewis acidity and are chemically very stable making them suited especially for nonchemical applications such as protective coating (see below).

1.2.4.2 Application Consequences of the Sol-Gel Synthesis

Specific chemical and physical properties of intermediate states of the sol-gel fluorolysis can be utilized for quite different modifications and applications. Upon reaction of metal
alkoxides with understoichiometric amounts of hydrogen fluoride a defined part of the 
alkoxide groups remain and may be used for chemical modifications of the high surface 
metal fluorides. Such modifications include partial substitution of F by OH, chemical 
immobilization of metal oxide oxidation catalyst onto the metal fluoride and binding 
organic groups to the inorganic metal fluoride. Introduction of highly dispersed noble 
metals on metal fluoride is also possible. The sol state, i.e. the colloidal solution of a metal 
fluoride in a nonaqueous solvent, opens up the possibility of many interesting applications. 
Most important is the ability to prepare different coatings for very different applications. 
Thus, catalytic active metal fluorides can be conveniently deposited on supports, or thin 
metal fluoride layers, can be easily prepared for, e.g., optical or mechanical applications. 

Nano-sized metal fluorides: An optically clear metal fluoride sol contains particles the 
diameter of which is in the range of the wavelength of visible light. Therefore, nano-sized 
metal fluoride particles can be obtained from such sols, which are normally agglomerated, 
after removal of the solvent at moderate temperatures. The size of the individual particles 
has been shown by TEM and was derived from their XRD pattern to be below 5 nm [6, 49]. 
Such tiny particles represent a higher state of energy compared to more bulky material. As 
a consequence these materials can be easily pressed at room temperature to dense glasses. 
Thus, transparent glasses have been obtained from MgF$_2$, CaF$_2$, BaMgF$_4$ [49] and 
Rb$_2$NaAlF$_6$ [56] employing pressures up to 1.1 GPa at room temperature. 

Nano-sized metal fluorides have a promising perspective as inorganic component of 
organic polymers. Due to their small size the particles are invisible even in transparent 
polymers but may, in possibly decisive ways, change physical properties such as dielectric 
constant, index of refraction or mechanical properties. However, preventing agglomera-
tion of these nano particles is a challenging task, but one that is not easy to accomplish and 
that needs to be further developed.

Oxide fluorides: The amount of alkoxide groups remaining after partial fluorination can be 
tuned over a wide range. These OR groups can subsequently be hydrolysed, i.e. substituted 
by OH, or thermally split off, also resulting in OH and, due to condensation reaction, in the 
formation of oxide groups homogeneously distributed within the fluoride matrix. The metal 
fluorides modified this way exhibit not only Lewis acidity but also some Brønsted acidity or

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**Figure 1.26** Chemical state plots for F 1s and Mg 1s orbitals of chromium(III)-doped MgF$_2$ 
prepared from CrO$_3$ (CrO), CrCl$_3$ (CrCl) or Cr-acetat (CrAc) in different concentrations 
(Reprinted with permission from [54] Copyright (2005) Elsevier Ltd.)

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even basicity. Such bifunctional materials can be valuable solid catalysts (see below). This synthesis principle has been realized for magnesium oxide/hydroxide fluorides within a broad range of compositions [57]. It was found that preparations with low fluorine content, with nominal composition Mg(OH)$_{1.2}$F$_{0.8}$ and Mg(OH)$_{0.8}$F$_{1.2}$, were almost X-ray amorphous even after calcinations at 623 K whereas with higher F content the patterns of MgF$_2$ appeared. In $^{19}$F MAS NMR there was a similar trend to be seen, the low F materials gave broad, complex signals, indicating the presence of many different fluorine species, which became more and more sharp and like those in MgF$_2$ with increasing F content. The higher electronegativity of F compared to OH resulted with increasing F content in a reduced electron density at Mg indicated in increasing Mg 1s binding energy as seen in XPS analysis. Magnesium fluoride-based bifunctional materials have been successfully employed as heterogeneous catalysts for quite different reactions (see below) [57–59].

**Metal oxides linked to metal fluorides:** The performance of a solid catalyst depends to a substantial degree on its surface area, which can often be increased by suitable support, and then also on the chemical and texture properties of the support. Vanadium oxide-based catalysts are very useful in oxidation reactions because of the easy change between different oxidation states. In case of the technically important partial oxidation of organic compounds, a limited oxidation activity of the catalyst is needed to prevent total oxidation to CO/CO$_2$ and H$_2$O. As a consequence the organic educt has to be activated by, e.g., protonation due to Brønsted acidity of a catalyst support. By using a Lewis acidic support a more gentle activation of the educts should be possible resulting in less or no total oxidation. The sol-gel synthesis provides exquisite conditions for a very evenly distributed and highly dispersed VO$_x$ based catalyst deposited on Lewis acidic metal fluoride supports. Employing the principle of under-stoichiometric fluorination there will be OR groups or, after hydrolysis, OH groups available for chemical anchoring of the VO$_x$ species. This way aluminium fluoride-supported VO$_x$ catalysts with outstanding performance have been prepared and thoroughly characterized [60].

**Noble_metals supported by high surface area metal fluorides:** Noble metals especially platinum and palladium are useful catalysts for many reactions such as, e.g., hydrogenations. They are used in a highly dispersed state deposited on suitable supports. For use in hydrodehalogenation reactions the support has to be stable against attack by the hydrogen halogenide formed in course of the reaction. That requirement can be met using metal fluorides as support. MgF$_3$ and AlF$_3$ were often proposed [61]. For the preparation of very tiny noble metal particles supported on a metal fluoride, which has a large surface, the sol-gel fluorination provides excellent conditions. Starting from the metal alkoxide solution or from the already formed metal fluoride sol an organic solution of a suitable noble metal compound, such as the acetyl acetonate, is added and the mixture is worked up as normal for high surface metal fluoride preparation. Only an additional reduction step is necessary to obtain the catalyst. For a Pd$_0$/CaF$_2$ catalyst prepared accordingly the high Pd dispersion is shown in Figure 1.27.

**Organically modified metal fluorides:** Silicon oxide and also metal oxide based inorganic-organic hybrid materials have received broad interest academically and also for technical applications [62]. The development of such hybrids aims to combine useful properties of the inorganic part, mostly the basis of the hybrid, with those of the organic part, whereby the two parts are chemically bound to one another. Basically, two types of synthesis routes
are used. Both can be adapted to metal fluoride systems. One route starts from organically modified molecular alkoxidic precursors, which are subjected to sol-gel hydrolysis; the other starts from preformed nanoscopic or macroscopic particles to which an organic moiety becomes linked. To transpose these synthesis principles to metal fluoride systems, the sol-gel fluorolysis can be conveniently employed attaching either an organic moiety via a HF stable linkage to metal alkoxides, which are consequently subjected to sol-gel fluorolysis. Another route comprises at first formation of colloidal nanoscopic particles by preparing a sol with under-stoichiometric amounts of HF, to which then organic moieties can be linked. First experiments with phenylphosphonate modified aluminium alkoxide have proved successful [30, 63].

**Coatings:** The sol state as primary result of the sol-gel fluorination process is very useful, because it consists of nano-sized, colloidal metal fluoride particles homogeneously dispersed in a nonaqueous liquid. Simply by applying the sol on any solid material wettable by the solvent and subsequent drying a metal fluoride layer is on the surface of the material obtained. Depending on the required properties and intended purposes of the layer and on the texture and geometry of the solid material, different methods can be used for the sol application such as, e.g., soaking, dipping, spin coating etc.

**Catalysis:** For technical reasons it can be necessary to have a catalytically active solid material supported to improve, e.g., its mechanical stability and reduce its flow resistance when used in a flow reactor. The sol-gel fluorination synthesis provides a convenient way for depositing high surface area metal fluorides on supports. For example, HS-AlF₃, which as fine powder makes problems when used as catalyst in flow systems, could be supported by γ-Al₂O₃ whereby its Lewis acidity and consequently its catalytic activity remains almost unchanged [64]. For other catalytic applications, like micro-reactor techniques, deposition of catalytically active thin layers of metal fluorides is also of interest.
Optics: Probably the most important field of application for thin metal fluoride layers is in physics, especially in optics. A reduction of the reflexion of light at the surface of glass, well known for optical devices such as lenses for glasses and cameras, is even more important for solar energy utilization. Antireflective systems are formed of alternating layers of transparent low and high refractive index materials. However, even with a single layer, a very efficient antireflective system is possible in principle. For a wavelength $\gamma$ and an antireflective layer of thickness $\gamma/4$ the reflexions at the air/layer surface and at the layer/glass interface have a phase-shift to each other of $\gamma/2$, that is the precondition for extinction. Total extinction is only possible when the two reflexions are of the same intensity. This can be reached when the index of refraction of the antireflective layer is equal to the geometric mean of air ($n = 1.0$) and glass ($n = 1.5$), i.e. for $n = 1.225$. Typically, the refractive indices of metal oxides are even higher than that of glass, whereas some metal fluorides such as MgF$_2$ ($n_{500} = 1.38$), AlF$_3$ ($n_{500} = 1.35$) and Na$_3$AlF$_6$ ($n_{500} = 1.33$) have distinctly lower indices of refraction, although not as low as 1.225, together with an excellent transparency within a broad range of wavelengths. Consequently, MgF$_2$ thin layers have already found much interest [65]. Methanolic MgF$_2$ sols prepared as described above have been used for spin-coating of planar surfaces [66]. AFM investigations revealed that the layers obtained after drying consist of densely packed particles of 10 to 20 nm diameter as shown in Figure 1.28. The single or multiple MgF$_2$ thin layers showed excellent homogeneity concerning thickness and index of refraction over the experimental range of 5 cm [67].

![Figure 1.28](image-url)  
*AFM image of a 3-fold deposited MgF$_2$ layer on a silicon wafer, after calcinations at 300°C (area 1 x 1 μm$^2$). (Reprinted with permission from [67] Copyright (2008) Wiley-VCH.)*

Protective coating: The facileness of preparing metal fluoride layers from nonaqueous metal fluoride sols also reduces the threshold of their use for protective coating. Homogeneous, mechanically stable metal fluoride layers can protect against UV radiation,
chemical and also mechanical impact, and can form a barrier against microbial attack. A CaF₂ addition to lithium grease has already proved useful in the lab for friction reduction and extreme pressure properties making CaF₂ layers, likewise, interesting.

In conclusion, the new access towards nanoscopic metal fluorides via this recently developed fluorolytic sol-gel synthesis route opens a wide range of applications for metal fluorides due to the distinctive different properties of these nano materials.

References


