## Characterization of fluorine-containing catalysts by <sup>19</sup>F solid-state NMR

**Spectroscopic background:** <sup>19</sup>F nuclei have a spin of I = 1/2 and, therefore, no quadrupole moment. The <sup>19</sup>F isotope has a natural abundance of 100 % and a sensitivity of 0.83 in comparison with <sup>1</sup>H nuclei (1.0), making this isotope a very suitable candidate for NMR studies of solids. For basic principles of solid-state NMR, see lectures "Solid-State NMR Spectroscopy" for Bachelor students or PhD seminars, accessible via the link "Lectures for Students".

One of the reasons for the presence of fluorine in zeolites is the use of fluorinecontaining structure-directing agents (SDA). Furthermore, diluted HF in the aqueous synthesis mixture is utilized as mineralizing agent for the synthesis of zeolites with few framework defects. Fluoride ions mobilize silicon species by dissolving the silica source during the hydrothermal synthesis [1-6]. In as-synthesized zeolites, fluoride ions balance the positive charges of the SDA cations. In the <sup>19</sup>F MAS NMR spectra of **as-synthesized high-silica zeolites Beta**, **SSZ-23**, **ITQ-3**, **ITQ-4**, **ZSM-12**, **and Silicalite-1**, prepared in the presence of fluoride ions as mineralizing agents, signals occur at  $\delta_{19F} = -80$  to -55 ppm, with CFCl<sub>3</sub> as <sup>19</sup>F chemical shift reference ( $\delta_{19F} = 0$  ppm) [2]. Fluoride ions in small structural units, such as [4<sup>6</sup>] cages, cause <sup>19</sup>F MAS NMR signals at  $\delta_{19F} = -39$  to -36 ppm [3]. For detailed <sup>19</sup>F chemical shift values of fluoride ions in various as-synthesized zeolites with different structure types and prepared with different SDAs, see Refs. [2] and [3].

**Upon calcination**, fluoride ions undergo strong interactions with the zeolite framework. In high-silica zeolites, typically, **Si–F bonds at pentacoordinated silicon species (SiO**<sub>4/2</sub>**F)** are formed [2]. The corresponding silicon species cause <sup>29</sup>Si MAS NMR signals at  $\delta_{29Si}$  = -150 to -140 ppm [2].

As an example for <sup>19</sup>F MAS NMR signals of Si–F bonds at pentacoordinated silicon (SiO<sub>4/2</sub>F), Fig. 1, top, shows the spectrum of a siliceous MFI-type zeolite, which was synthesized with tripropylammonium fluoride (Pr<sub>3</sub>NHF) as SDA, recorded after calcination [1]. The well-resolved <sup>19</sup>F MAS NMR signals at  $\delta_{19F}$  = -156 ppm and -151 ppm with spinning sidebands (assigned by asterisks) were ascribed to Si–F species [1]. In the <sup>19</sup>F MAS NMR spectrum of the calcined gallosilicate in Fig. 1, bottom, signals occur at  $\delta_{19F}$  = -140 ppm and  $\delta_{19F}$  = -163 to -155 ppm, caused by T<sup>III</sup>–F (T<sup>III</sup>: Ga) and Si–F species, respectively. This assignment was supported by <sup>19</sup>F





MAS NMR investigations of (NH<sub>4</sub>)<sub>3</sub>AIF<sub>6</sub>, Na<sub>3</sub>AIF<sub>6</sub>, and (NH<sub>4</sub>)<sub>2</sub>Ga(OH)<sub>2</sub>F<sub>3</sub>, yielding signals at  $\delta_{19F} = -140.4$  ppm, -135.0 ppm, and -137.9 ppm (T<sup>III</sup>–F with T<sup>III</sup>: AI or Ga), respectively [1]. Furthermore, <sup>19</sup>F MAS NMR studies of surface fluorinated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> gave signals at  $\delta_{19F} = -154$  ppm, -143 ppm, and -130 ppm, which were explained by fluorine at octahedrally coordinated aluminum in Al(O<sub>5</sub>F), Al(O<sub>4</sub>F<sub>2</sub>), and Al(O<sub>3</sub>F<sub>3</sub>) species, respectively [7]. For <sup>19</sup>F NMR parameters of fluorine atoms in AlPO<sub>4</sub> and SAPO materials, see Refs. [1] and [8].

For clarifying the silicon species, which are directly neighboured to fluorine atoms, <sup>19</sup>F to <sup>29</sup>Si cross-polarization NMR experiments (<sup>29</sup>Si{<sup>19</sup>F} CPMAS NMR) were utilized. By this way, the pentacoordinated silicon species, SiO<sub>4/2</sub>F, occurring in the <sup>29</sup>Si CPMAS NMR spectra of high-silica zeolites at  $\delta_{29Si}$  = -150 to -140 ppm were identified [2]. Similarly, <sup>27</sup>Al{<sup>19</sup>F} CPMAS NMR pulse sequences in 2D heteronuclear correlation (HETCOR) NMR experiments were utilized for the identification of the aluminum species, which are directly neighboured to fluorine atoms in surface fluorinated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (**Fig. 2**, Fig. 7 in Ref. [7]).

The sample used for recording the 2D <sup>27</sup>Al{<sup>19</sup>F} HETCOR NMR spectrum in **Fig. 2** was a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 0.8 wt.% fluorine atoms, introduced by pore-volume impregnation with an aqueous solution of NH<sub>4</sub>HF<sub>2</sub> (Prolabo) and subsequent calcination at *T* = 773 K ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/0.8 wt.% F) [7]. For the <sup>19</sup>F spins, the 2D HETCOR NMR spectrum consists of one correlation peak at  $\delta_{19F} = 9$  ppm, referenced to C<sub>6</sub>F<sub>6</sub>, which

corresponds to a signals at  $\delta_{19F} = -154$  ppm, referenced to CFCI<sub>3</sub>. For the <sup>27</sup>Al spins, the correlation peak occurs at  $\delta_{27AI} \cong 0$  ppm, which hints at the formation of Al–F species at octahedrally coordinated aluminum atoms in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [7].



See **Table 1** for an overview on the <sup>19</sup>F chemical shift values of the above-mentioned and some additional materials, referenced to CFCl<sub>3</sub> ( $\delta_{19F} = 0$  ppm).

Materials	$\delta_{\! 19 {\sf F}}$ / ppm	Refs.
Si-F bonds (SiO <sub>4/2</sub> F) in calcined zeolite MFI	-156, -151	[1]
AI <sup>VI</sup> (O <sub>5</sub> F) in fluorinated γ-Al <sub>2</sub> O <sub>3</sub>	-154	[7]
AI <sup>VI</sup> (O <sub>4</sub> F <sub>2</sub> ) in fluorinated $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	-143	[7]
Ga-F bonds in calcined MFI-type gallosilicate	-140	[1]
(NH <sub>4</sub> ) <sub>3</sub> AIF <sub>6</sub>	-140	[1]
<b>AI-F bonds</b> in calcined AIPO <sub>4</sub> with AFI, AEL, CHA, FAU structures	-139 to -136	[1]
(NH <sub>4</sub> ) <sub>2</sub> Ga(OH) <sub>2</sub> F <sub>3</sub>	-138	[1]
Na <sub>3</sub> AIF <sub>6</sub>	-135	[1]
AI <sup>VI</sup> (O <sub>3</sub> F <sub>3</sub> ) in fluorinated $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	-130	[7]
<b>AI-F bonds</b> in AIPO <sub>4</sub> and SAPO with SFO structure (EMM-8)	-119 to -103	[8]
https://michael-hunger.de	•	

fluorine atoms related to structure defects in as- synthesized ZSM-5	-80 to -79	[1], [12], [13]
<b>fluorine atoms in SDAs</b> of as-synthesized zeolites MFI $([4^15^26^2] \text{ cages})$ , MTT, TON	-74 to -64	[1], 12], [13]
fluorine atoms in SDAs of as-synthesized zeolites Beta, SSZ-23, ITQ-3, ITQ-4, ZSM-12, Silicalite-1	-80 to -55	[2]
<b>fluoride ions in small [4<sup>6</sup>] cages</b> of zeolites Beta, ITQ- 7, ITQ-10, ITG-14, AST	-39 to -36	[3]

## Table 1

For enhancing the Broensted acidity and catalytic activity of zeolites and mesoporous materials, these silicate and aluminosilicates were treated with NH<sub>4</sub>F [9, 10]. Mesoporous [AI]MCM-41 material with a  $n_{Si}/n_{AI}$  ratio of 15 was treated with different amounts of an aqueous solution of 0.1 M ammonium fluoride at room temperature and subsequently calcined at T = 723 K. The obtained catalysts were labelled as [AI]MCM-41/*n*, where *n* is the number of fluorine atoms in mmol/g. Fig. 3 shows the <sup>19</sup>F MAS NMR spectra of the rehydrated [AI]MCM-41/*n* materials with up



to three signals at  $\delta_{19F} = -156$  ppm, -155 ppm, and -153 ppm [10]. The signals occurring at  $\delta_{19F} = -156$  ppm and -155 ppm in the spectrum of [AI]MCM-41/*n* can be assigned to fluorine atoms in Si–F species [1, 2]. Starting with the sample [AI]MCM-41/1.05, an additional broad signal appears at  $\delta_{19F} = -153$  ppm. This signal is due to <sup>VI</sup>AI(O<sub>5</sub>F) species [7]. Hence, <sup>19</sup>F MAS NMR spectroscopy of [AI]MCM-41 materials, treated with NH<sub>4</sub>F, indicates an incorporation of fluorine atoms into at least two different local structures: The formation of Si–F species and the other consists of <sup>VI</sup>AI(O<sub>5</sub>F) species (see **Fig. 4**) [10].



Fig. 4

To clarify, whether the NH<sub>4</sub>F treatment of [AI]MCM-41 material is accompanied by an improvement of the catalytic activity, the conversion of 2-propanol was investigated. In comparison with the parent [AI]MCM-41/0 material, a **significant increase of the 2-propanol conversion** was observed on the [AI]MCM-41 material, treated with 0.44 mmol NH<sub>4</sub>F per gram ([AI]MCM-41/0.44) [10]. In [AI]MCM-41/0.44, exclusively S–F species and no AI–F species were formed. Adsorption of ammonia and subsequent <sup>1</sup>H MAS NMR spectroscopy (see Section "method 19") demonstrated that this catalyst has the largest number of Broensted acid sites of the [AI]MCM-41/*n* materials under study [10].

*Catalyst preparation:* Most of the sample materials studied by <sup>19</sup>F MAS NMR spectroscopy are used in the hydrated state.

<sup>19</sup>*F* MAS NMR studies: The <sup>19</sup>F MAS NMR spectra in Fig. 3 were recorded at a Bruker MSL 300 spectrometer, at a <sup>19</sup>F resonance frequency  $\nu_0$  = 282.2 MHz, with a https://michael-hunger.de

7 mm Bruker MAS NMR probe, and a sample spinning rate of  $v_{rot} = 3.5$  kHz. The <sup>19</sup>F chemical shifts of the spectra in Figs. 1 and 3 are referenced to CFCl<sub>3</sub> ( $\delta_{19F} = 0$  ppm). In literature, sometimes other reference materials are used, such as C<sub>6</sub>H<sub>6</sub> [7]. Ref. [11] gives a survey on the relative shift values of different <sup>19</sup>F NMR reference materials and hint at required corrections of the <sup>19</sup>F chemical shift values published in earlier studies. The experimental details of the solid-state NMR spectra in **Figs. 1** and **2** are given in Refs. [1] and [7], respectively.

## **References:**

- L. Delmotte, M. Soulard, F. Guth, A. Seive, A. Lopez, J.L. Guth, <sup>19</sup>F MAS n.m.r, studies of crystalline microporous solids synthesized in the fluoride medium, Zeolites 10 (1990) 778-783, DOI: 10.1016/0144-2449(90)90061-U.
- [2] H. Koller, A. Wölker, L.A. Villaescusa, M.J. Diaz-Cabanas, S. Valencia, M. A. Camblor, *Five-coordinate silicon in high-silica zeolites*, J. Am. Chem. Soc. 121 (1999) 3368-3376, DOI: 10.1021/ja9840549.
- M.A. Camblor, P.A. Barrett, M.-J. Díaz-Cabañas, L.A. Villaescusa, M. Puche, T. Boix, E. Pérez, H. Koller, *High silica zeolites with three-dimensional* systems of large pore channels, Microporous Mesoporous Mater. 48 (2001) 11-22, DOI: 10.1016/S1387-1811(01)00325-0.
- K.P. Nartowski, D. Malhotra, L.E. Hawarden, J. Sibik, D. Iuga, J.A. Zeitler, L. Fabian, Y.Z. Khimyak, <sup>19</sup>F NMR spectroscopy as a highly sensitive method for the direct monitoring of confined crystallization within nanoporous materials, Angew. Chem. Int. Ed. 55 (2016) 8904-8908, DOI: 10.1002/anie.201602936.
- [5] J. Martinez-Ortigosa, R. Millán, J. Simancas, J.A. Vidal-Moya, C. Martineau-Corcos, F. Rey, T. Blasco, New insights into fluoride's role in MFI zeolites: Unveiling the link between location and synthesis conditions, Inorg. Chem. (2025), DOI: 10.1039/d4qi03001j.
- [6] K. Zhang, M. Cai, M. Wang, P. Yang, K. Zhu, Z. Wang, J. Gong, H. Ying, Exploring the effect of nanopore microstructures on crystallization and the evolution of molecular assembly structure by <sup>19</sup>F solid state nuclear magnetic resonance spectroscopy, Anal. Chem. (2025), DOI: 10.1021/acs.analchem. 4c06353.
- [7] L. Fischer, A,V. Harle, S. Kasztelan, J.B. d'Espinose de la Caillerie, Identification of fluorine sites at the surface of fluorinated gamma-alumina by two-dimensional MAS NMR, Solid State Nucl. Magn. Reson. 16 (2000) 85-91, DOI: 10.1016/S0926-2040(00)00058-8.

- [8] M. Afeworki, G. Cao, D.L. Dorset, K.G. Strohmaier, G.J. Kennedy, *Multinuclear and multidimensional solid-state NMR characterization of EMM-8*, Microporous Mesoporous Mater. 103 (2007) 216-224, DOI: 10.1016/j.micromeso. 2007.01.048.
- T. Horvath, M. Seiler, M. Hunger, A comparative study of methyl-tert-butyl ether synthesis on zeolites HY, HBeta, HBeta/F and HZSM-5 by in situ MAS NMR spectroscopy under flow conditions and on-line gas chromatography, Appl. Catal. A: General 193 (2000) 227-236, DOI: 10.1016/S0926-860X(99)00432-9.
- M. Xu, W. Wang, M. Seiler, A. Buchholz, M. Hunger, *Improved Broensted acidity of mesoporous [AI]MCM-41 material treated with ammonium fluoride*, J. Phys. Chem. B 106 (2002) 3202-3208, DOI: 10.1021/jp014222a.
- [11] C.P. Rosenau, B.J. Jelier, A.D. Gossert, A. Togni, *Exposing the origins of irreproducibility in fluorine NMR spectroscopy*, Angew. Chem. Int. Ed. 57 (2018) 9528-9533, DOI: 10.1002/anie.201802620.
- E. Dib, T. Mineva, P. Gaveau, E. Veron, V. Sarou-Kanian, F. Fayon, B.
  Alonso, *Probing Disorder in AI-ZSM-5 Zeolites by* <sup>14</sup>N NMR Spectroscopy,
  J. Phys. Chem. C 121 (2017) 15831-15841, DOI: 10.1021/acs.jpcc.7b04861.
- [13] J. Martinez-Ortigosa, J. Simancas, J.A. Vidal-Moya, P. Gaveau, F. Rey, B. Alonso, T. Blasco, Host-guest and guest-guest interactions of P- and N-containing structure directing agents entrapped inside MFI-type zeolite by multinuclear NMR spectroscopy, J. Phys. Chem. C 123 (2019) 22324-22334, DOI: 10.1021/acs.jpcc.9b05689.