Non-Aqueous Fluorolytic Sol-Gel Synthesis

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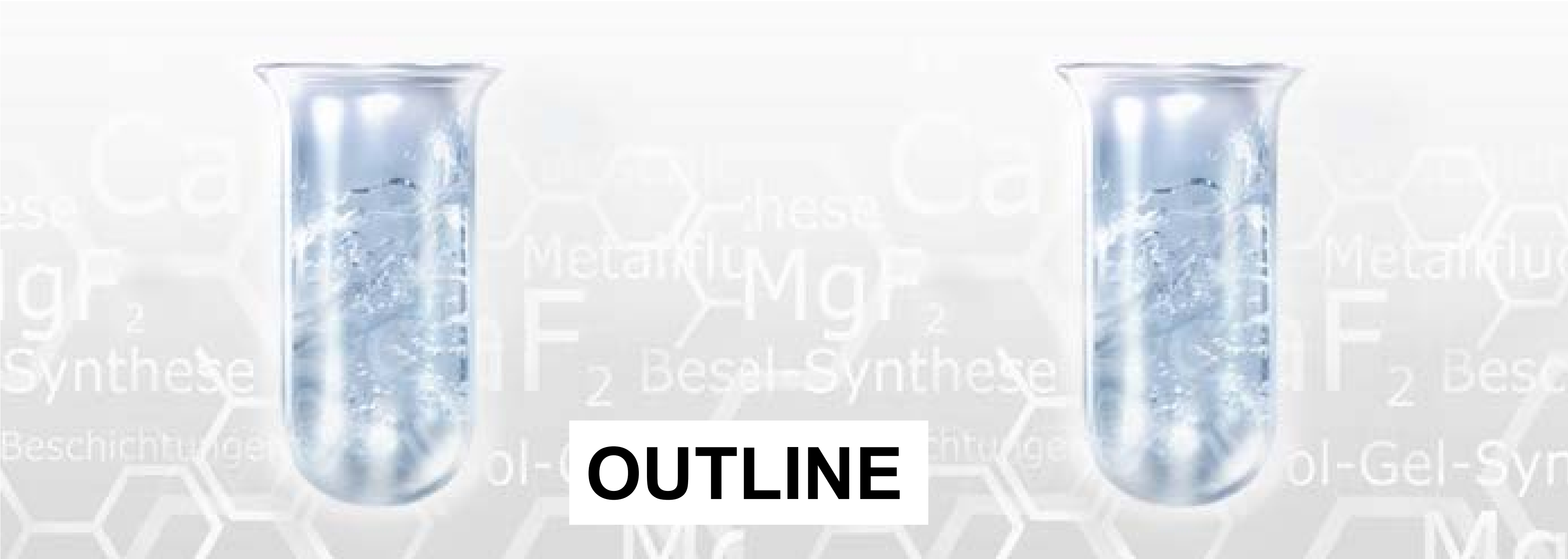
Humboldt-Universität zu Berlin

FHI Berlin, 25th November 2016



OUTLINE

1. The *fluorolytic* sol-gel-synthesis of metal fluorides
    - the principle of the *fluorolytic* Sol-Gel-synthesis
2. Mechanism/reaction path
    - chemical aspects – AlF_3
    - synthesis parameter
3. Applications of nanoscaled metal fluorides
4. Summary

Why metal fluorides?

- Electrochemical energy storage (Li batteries)
- Solid Lewis-acids (catalysis, adsorption)
- Melting point depressiva (welding, ceramics, …)
- Transmission in UV and IR (optics, laser)
- Low refractive index (optics, photovoltaic, glasses)
- Hydrophobicity (coating, sealing,…)
- Anti-fungicidal properties (surface protection)
- Corrosion protection against fluorine-containing gases

Synthesis of nano-metal fluorides – *state of the art so far*

1. Synthesis of nano-metal oxides (via sol-gel)

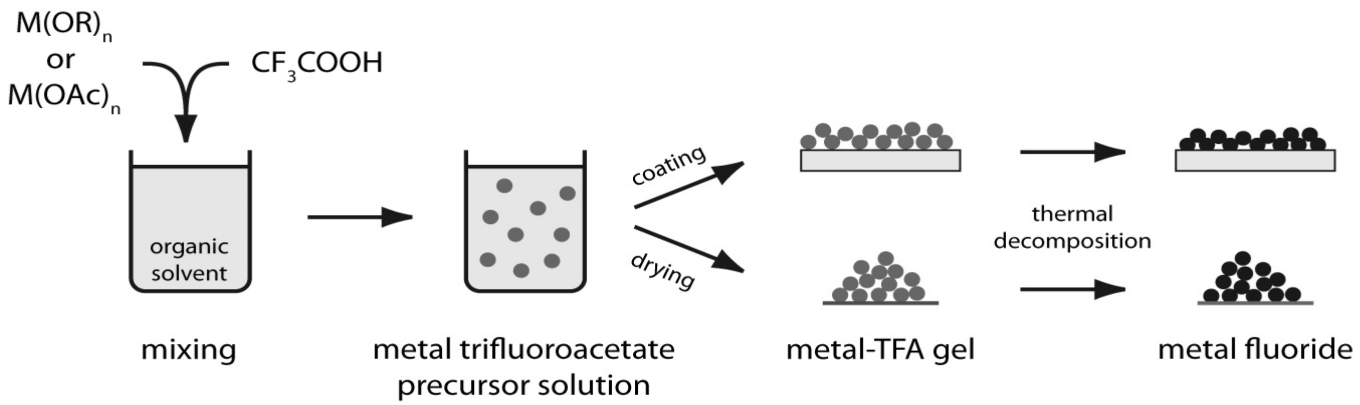
☛ followed by fluorination

$$M(OR)_x \longrightarrow \text{nano-}MO_{2/x} \xrightarrow{T} MF_x$$

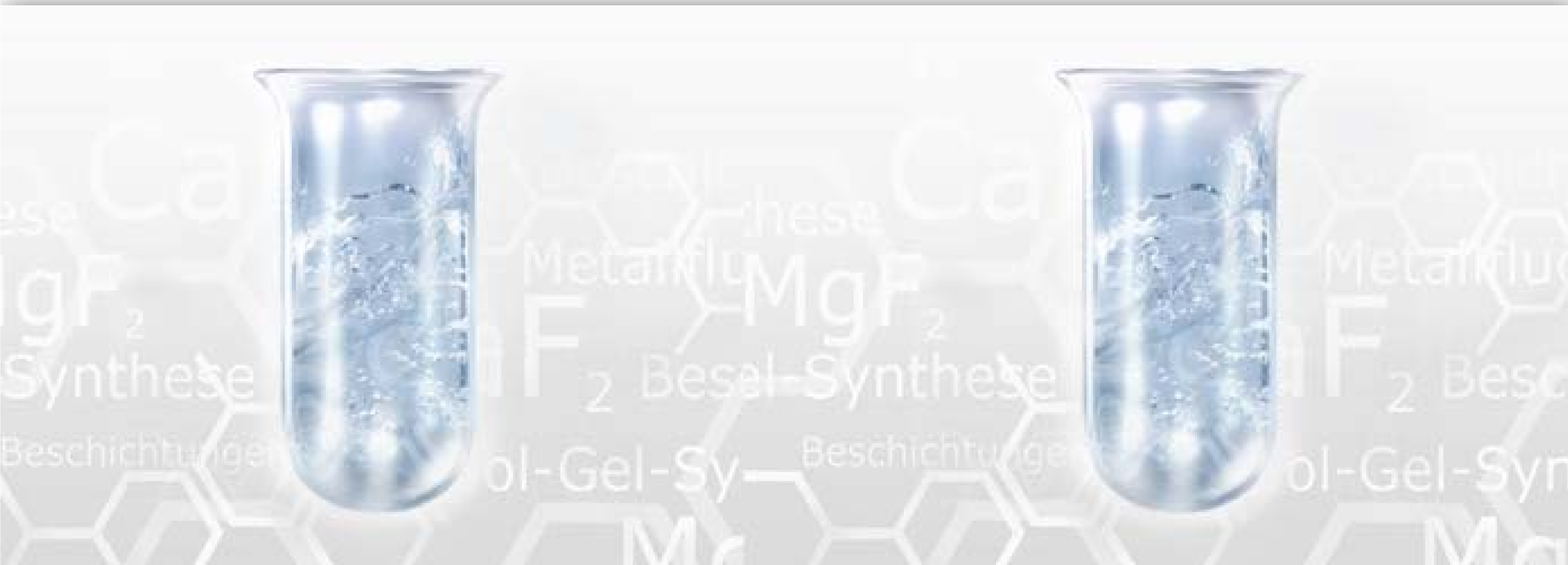
2. Synthesis of metal trifluoroacetates (TFA sol gel route)

☛ followed by thermal decomposition

$$M(OR)_x/MOAc + CF_3COOH \longrightarrow M(TFA)_x \xrightarrow{T} MF_x$$



Fujihara in P. Yang (Edt.), The Chemistry of Nanostructured Materials, World Scientific Publ., Singapore 2003



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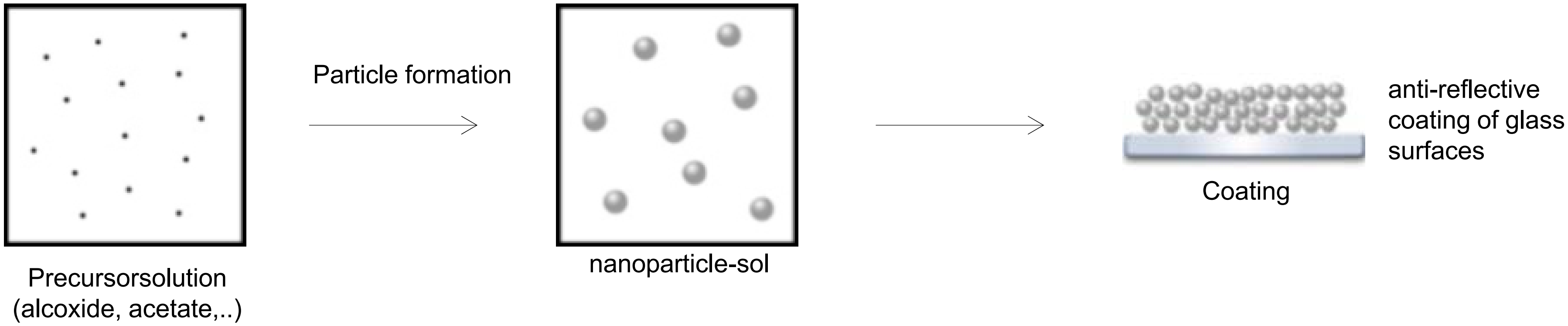
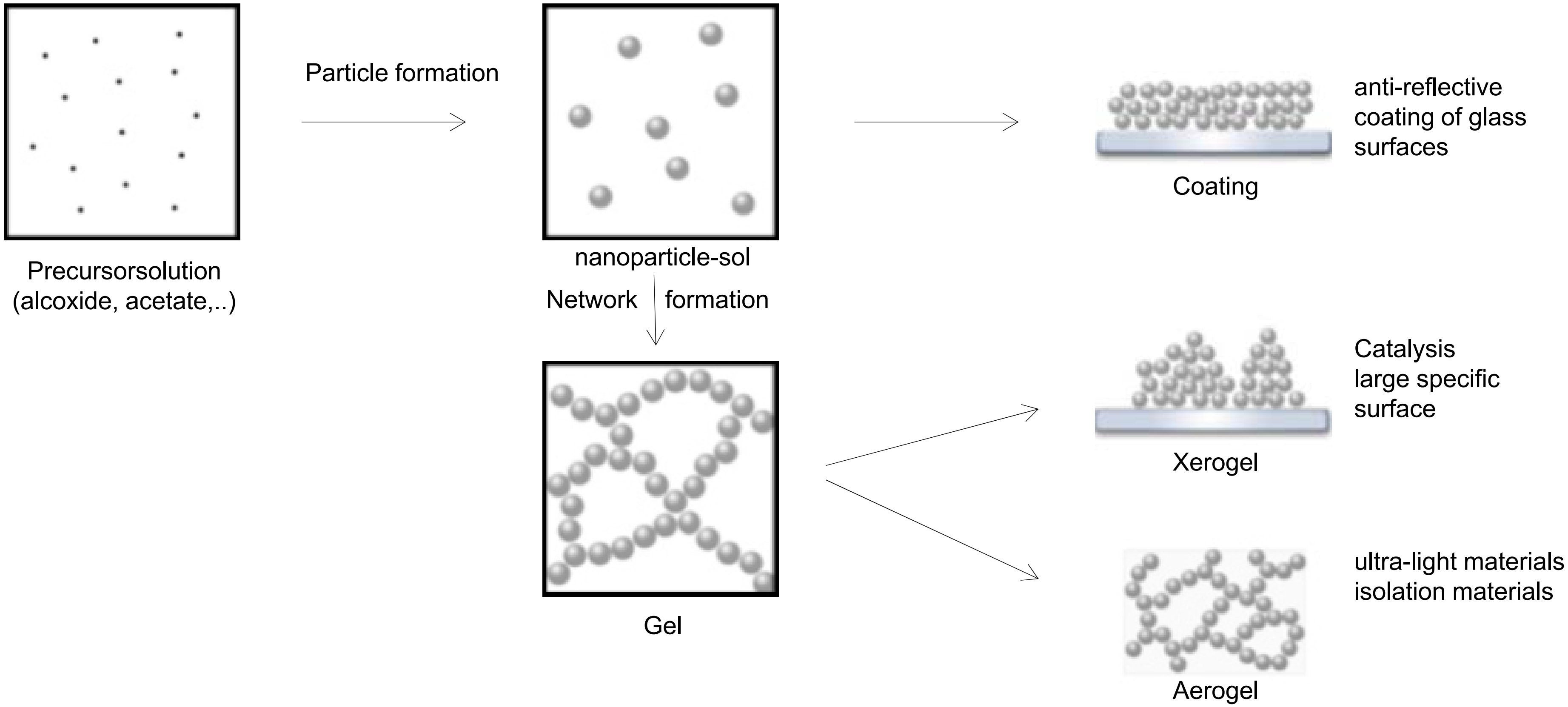
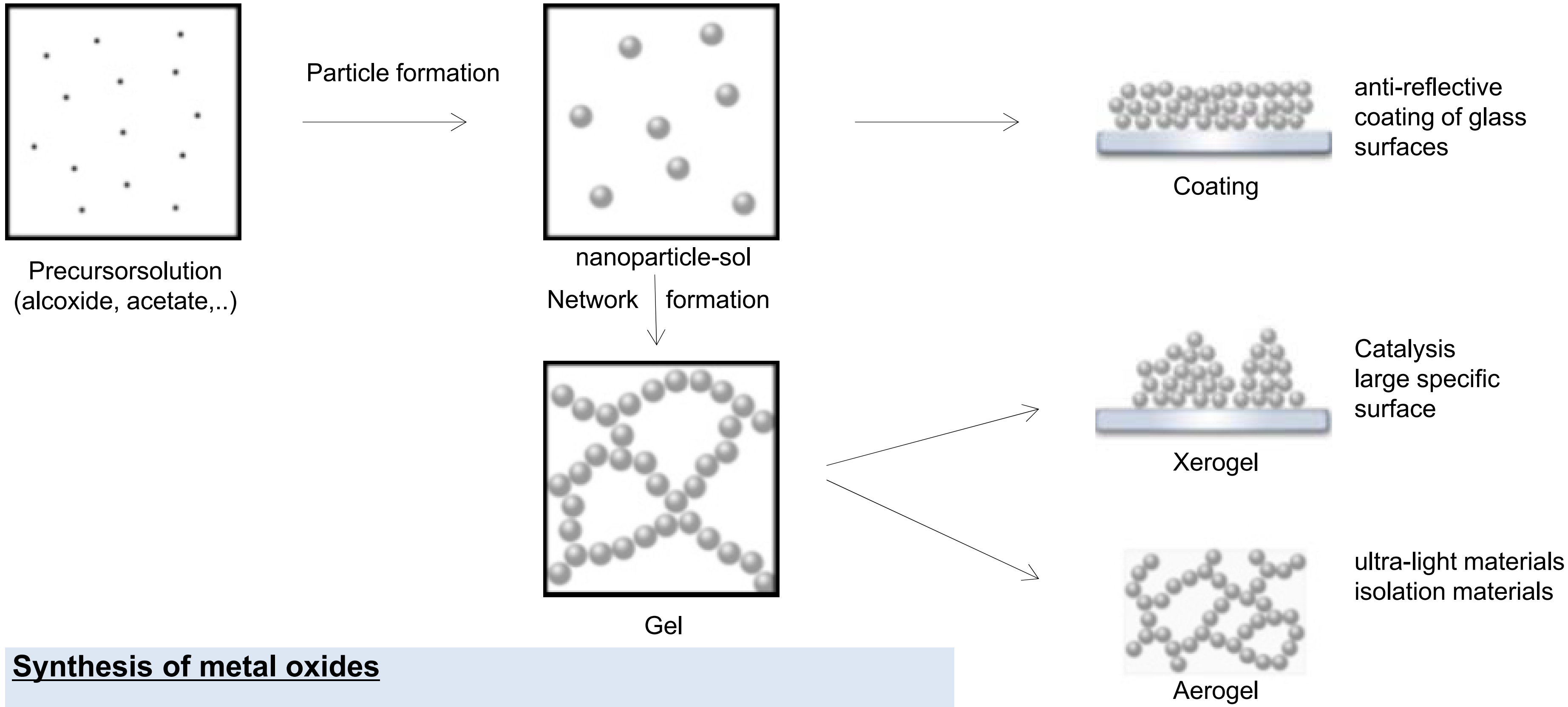
Sol-Gel Synthesis



Sol-Gel Synthesis



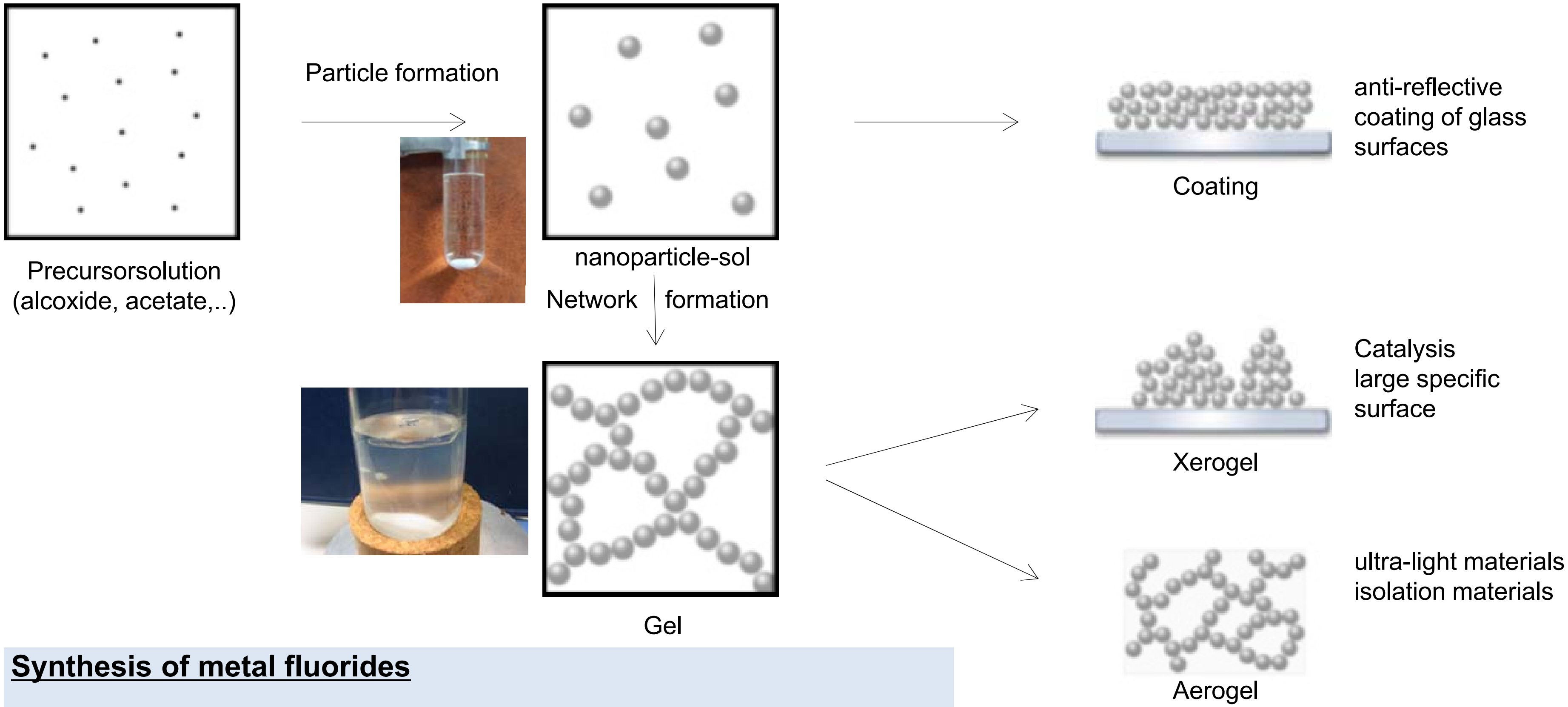
Sol-Gel Synthesis



<u>Synthesis of metal oxides</u>

M-OR	+	H_2O	$\longrightarrow$	M-OH	+	ROH	*Hydrolysis*
M-OH	+	HO-M	$\longrightarrow$	M-O-M	+	H_2O	
M-OR	+	HO-M	$\longrightarrow$	M-O-M	+	ROH	*Condensation*

Fluorolytic Sol-Gel Synthesis



Synthesis of metal fluorides

M-OR	+	HF	⟶	M-F	+ ROH	*Fluorolysis*
2n M-F			⟶	$(\text{-M-F-M-F})_n$		*Bridging*

AlF_3, MgF_2, CaF_2, Na_3AlF_6
- high BET surface areas
- moderate to strong Lewis-acidity
- high transparency

Angew. Chem. 2003, 115, 4383-4386 / Review: Dalton Trans. 2008, 1117-1127
Review: *Dalton Trans.*, **2015**, *44*, 19411-19431

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    - the principle of the *fluorolytic* Sol-Gel-synthesis
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    - **chemical aspects – AlF_3**
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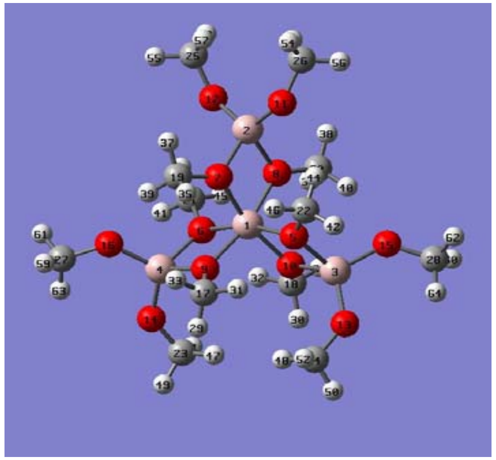
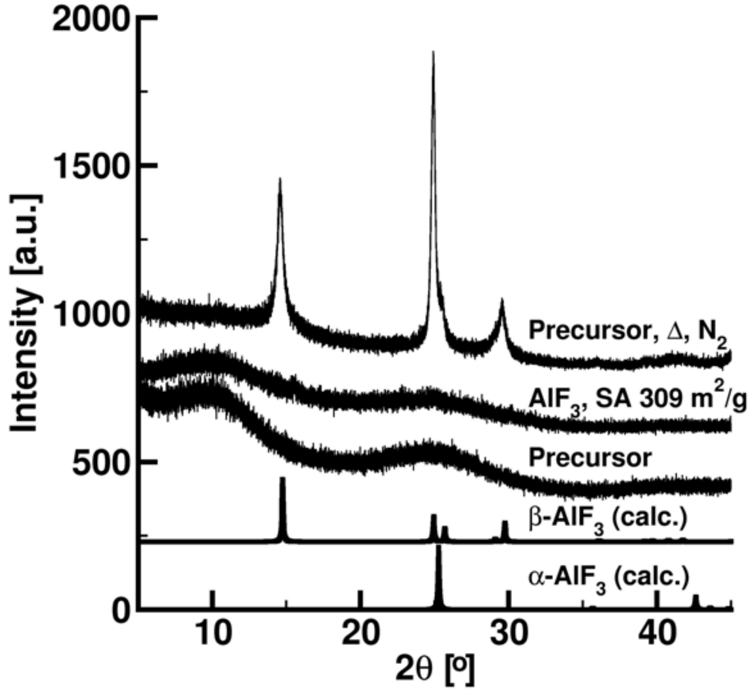
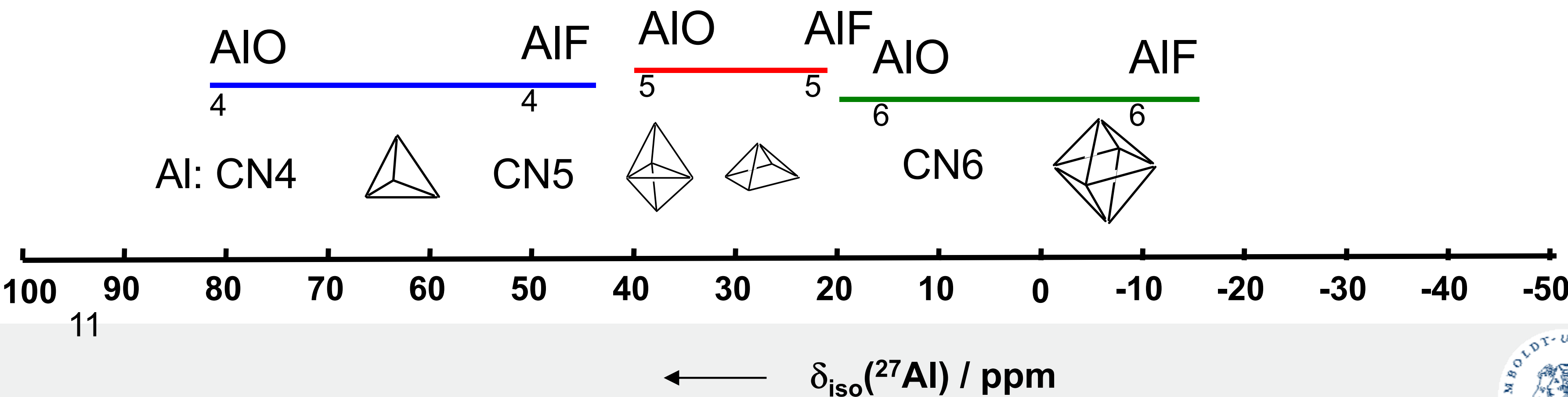
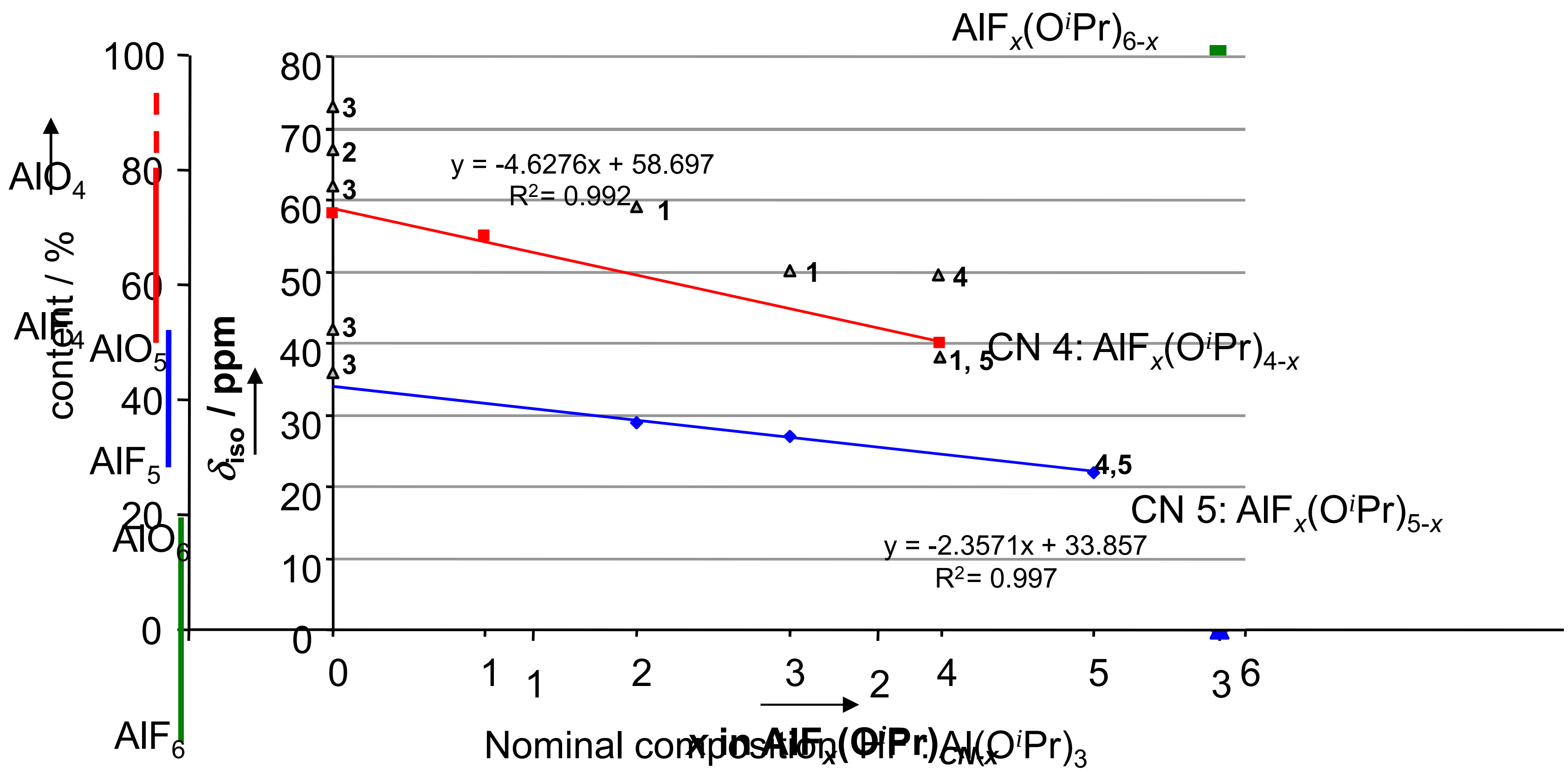
MAS-NMR as a powerful tool to follow the reaction path of the fluorolytic sol-gel reaction







Fluorolysis: $AlF_x(OR)_{3-x}$ • ROH ^{27}Al chemical shift

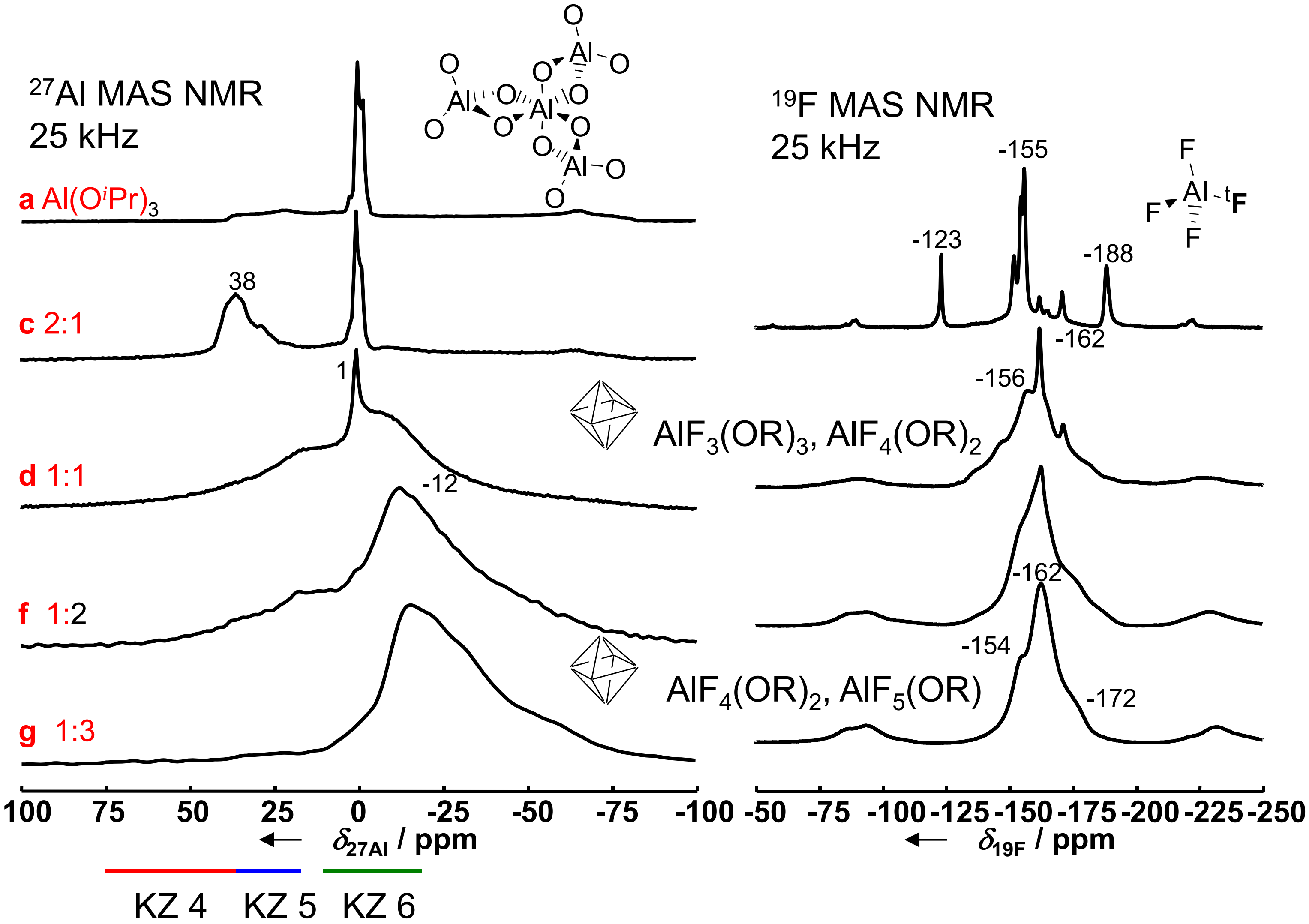


$AlF_x(O^iPr)_{CN-x}$	Al δ_{iso} / ppm	F-species bridging δ_{iso} / ppm	F-species terminal δ_{iso} / ppm
CN: 4, x = 4	38	-156	-188
CN: 5, x = 2-5	29, 27, 22	-149, *-130*, *-137*	*(-172),-182, -189*
CN: 6, x = 3-5	-1 bis -12	-162, *-156*, *-172*	

J. Phys. Chem. C **2009**, *113*, 15576–15585

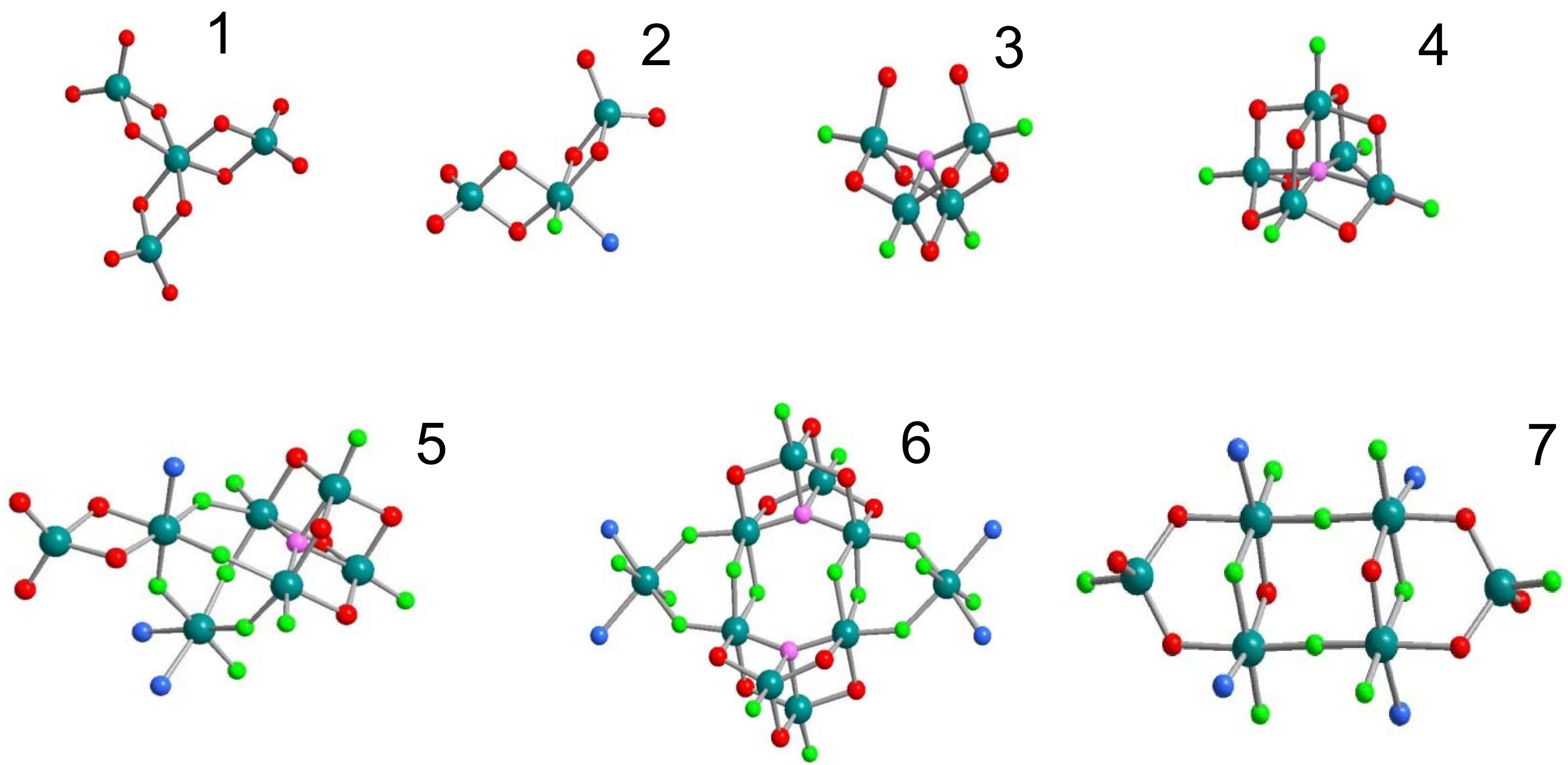
Fluorolysis: $AlF_x(OR)_{3-x} \cdot ROH$

$$Al(OR)_3 + xHF \rightarrow Al(OR)_{3-x}F_x$$



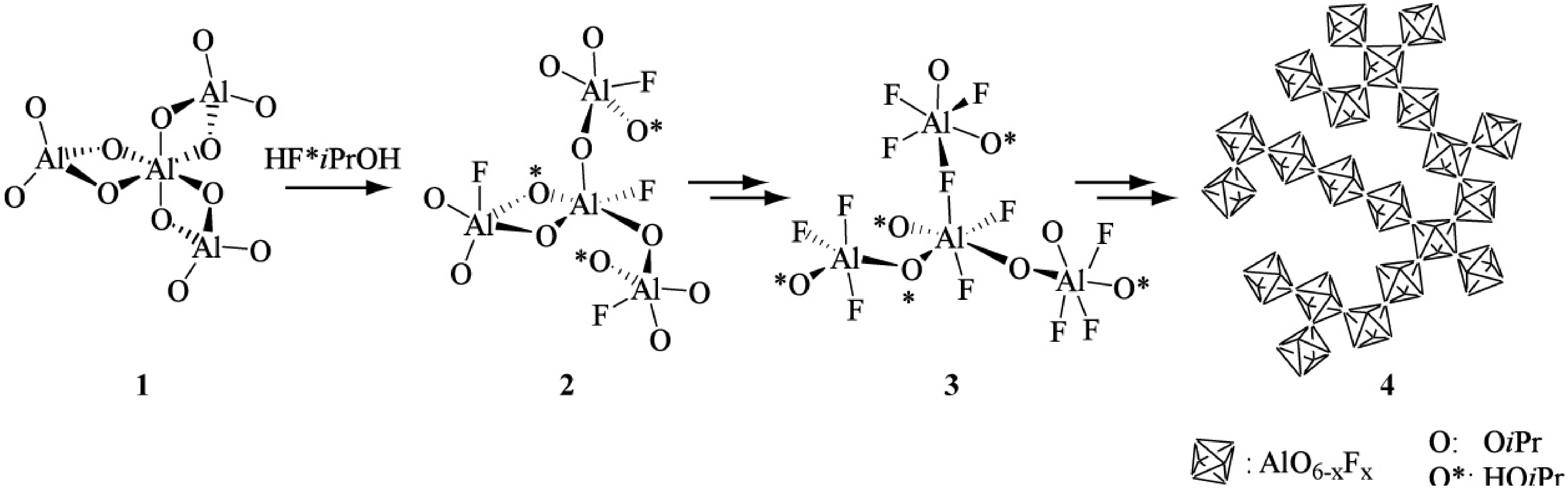
Chem. Mater., **2007**, 19, 2229-2237. *J. Phys. Chem., C*, **2009**, *113,* 16674–16680.
J. Phys. Chem., C, **2009**, 113, 155786-15585. *Dalton,* **2011**, 40, 8701-8 710.

Structures of aluminium alkoxide fluorides



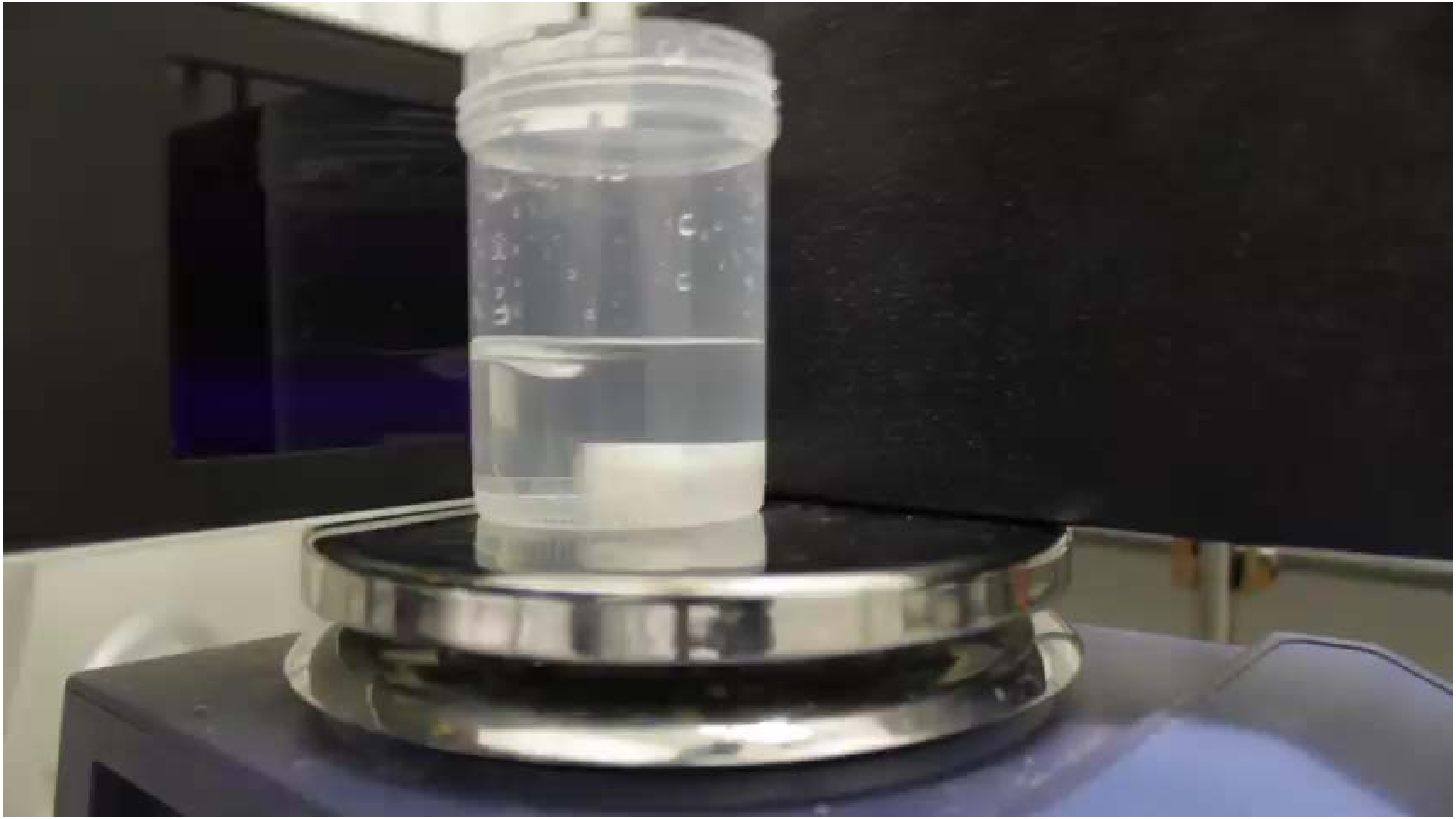
Structures of aluminium alkoxide fluorides obtained from sols of varying aluminium isopropoxide to HF ratios sorted according to their Al to F ratio within the structure.
1: $Al_4(O\mathit{i}Pr)_{12;}$ **2**: $Al_3F(O^iPr)_8$•D (D = Py, DMSO), Al:F = 3:1;
3: $Al_4F_4(\mu_4O)(O^iPr)_5(H(^iPrO)_2)$, Al:F = 1:1; **4**: $Al_5F_5(\mu_5O)(O^iPr)_8$, Al:F = 1:1;
5: $Al_7F_{10}(\mu_4O)(O^iPr)_9$•3Py, Al:F = 1:1.43, **6**: $Al_{10}F_{16}(\mu_4O)_2(O^iPr)_{10}$•4Py, Al:F = 1:1.6,
7: $Al_6F_{10}(O^iPr)_8$•4Py, Al:F = 1:1.67

Schematic representation of the formation of highly distorted nanosopic aluminium fluoride by reacting aluminium isopropoxide with anhydrous hydrogen fluoride in isopropanol as solvent.



Nanoparticle formation proceeds very fast

85% $Sr(OLac)_2$, 5% $Ce(OAc)_3$ and 10% $Tb(OAc)_3$ (0.2 mol/l) with 2.15 eq. HF/MeOH within 30 sec under illumination at 254 nm.



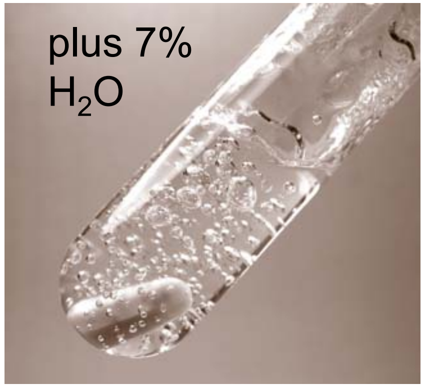
Impact of various synthesis parameters

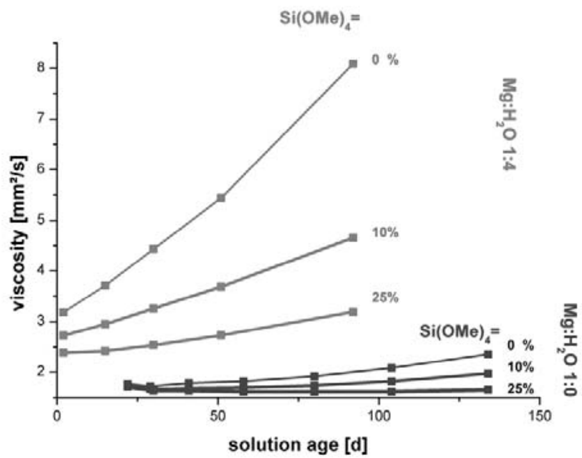
General rule: only soluble precursors yield transparent sols

Solvents and precursors

$Mg(OOCH_3)_2$ + 2HF → MgF_2 + $2CH_3COOH$

CH_3COOH + C_2H_5OH → $CH_3COOC_2H_5$ + H_2O





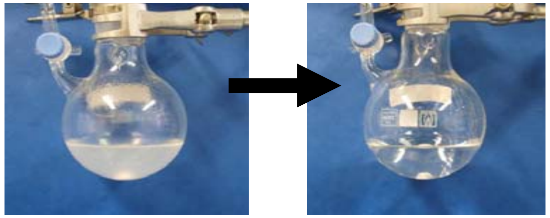
$Mg(CH_3COO)_2 \cdot 4H_2O$ → $(Mg_5(\mu_3\text{-}OH)_2(OAc)_8 \cdot 1.19H_2O)$ → $Mg(CH_3COO)_2$

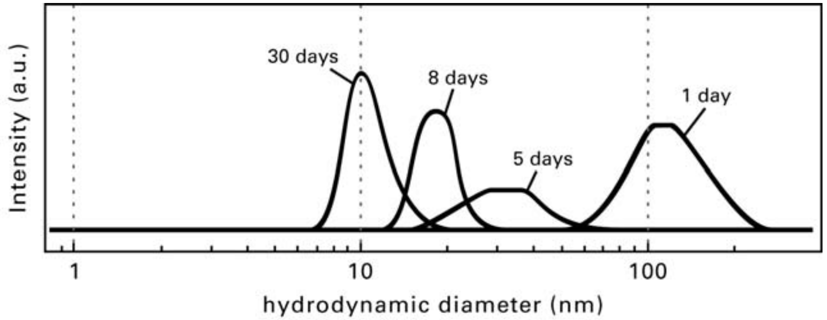
Caution: fast formation of insoluble alcohol-solvates

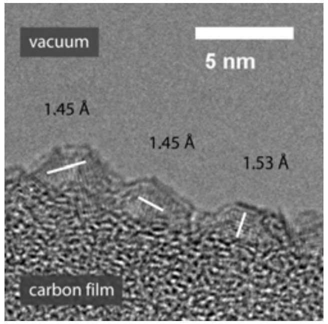
Metal alkoxide precursors

Availability and durability: Mg methoxide as precursor

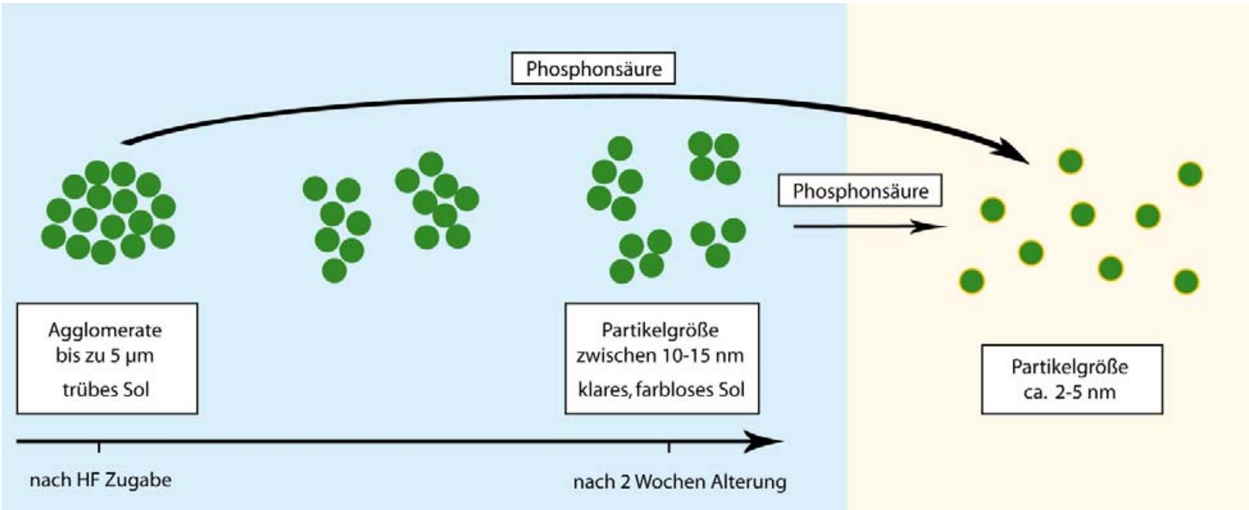
$Mg + 2CH_3OH \rightarrow Mg(OCH_3)_2 + H_2 \rightarrow + 2HF \rightarrow MgF_2 + 2CH_3OH$





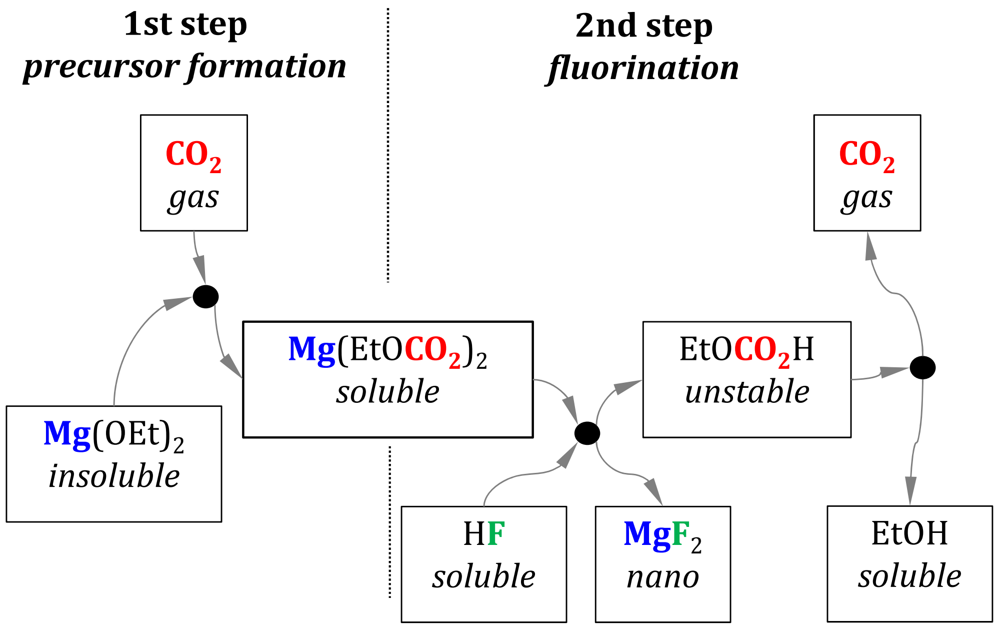


addition of complexing“ agents (ca. 2mol%)



Metal alkoxides: Mg-Ethoxide (it is insoluble!)

$$Mg(C_2H_5O)_2 + 2CO_2 \rightarrow EtOH + Mg(C_2H_5OCO_2)_2$$



1st: $Mg(OEt)_2 + 2\,CO_2 \rightarrow Mg(EtOCO_2)_2$

2nd: $Mg(EtOCO_2)_2 + 2\,HF \rightarrow MgF_2 + 2\,EtOH + 2\,CO_2$

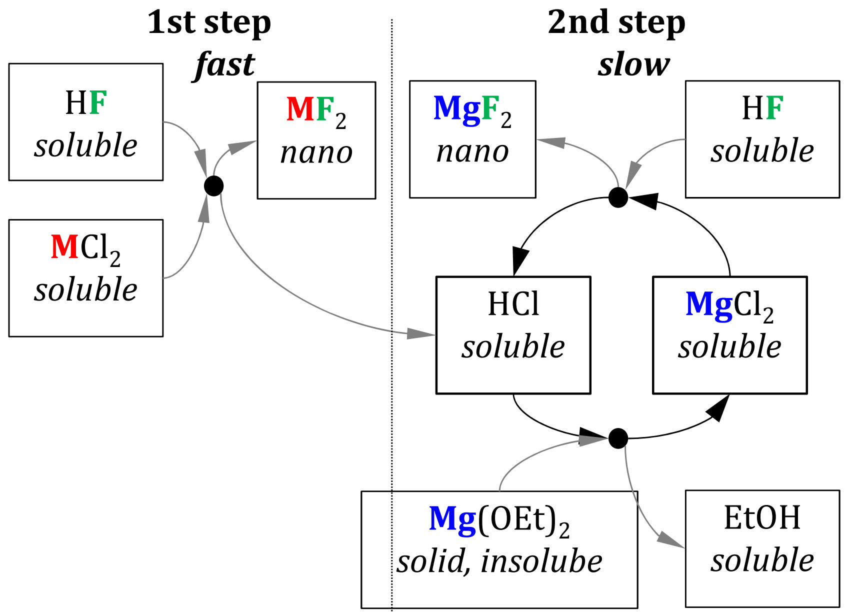
Brutto reaction

$$Mg(OEt)_2 + 2\,HF \rightarrow MgF_2 + 2\,EtOH$$

J. Mater. Chem. C, **2016**, 4, 1454-1466

The HCl-mediated route

$$xMg(OMe)_2 + yMgCl_2 + 2(x+y)HF \rightarrow (x+y)MgF_2 + xMeOH + yHCl$$



$MCl_2 + 2\,HF \rightarrow MF_2 + 2\,HCl$ | $Mg(OEt)_2 + 2\,HF \rightarrow MgF_2 + 2\,EtOH$

Brutto reaction

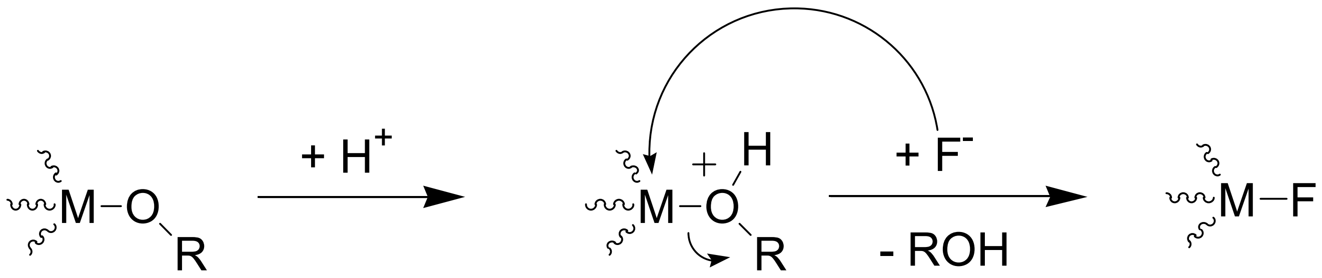
$$(1\text{-}x)\,Mg(OEt)_2 + x\,MCl_2 + 2\,HF$$
$$\downarrow$$
$$(1\text{-}x)\,MgF_2 + x\,MF_2 + 2x\,HCl + (2\text{-}2x)\,EtOH$$

J. Mater. Chem. C, **2016**, 4, 1454-1466

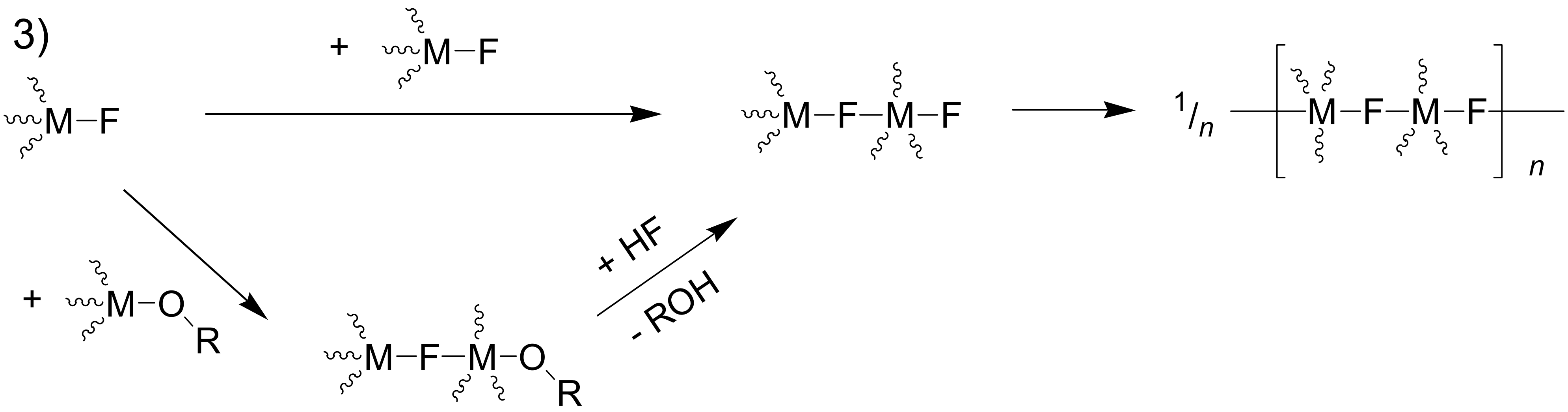
Rationalisation of the reaction mechanism

1) $(HF)_n \rightarrow H^+ + [F(HF)_{n-1}]^-$ and $H^+ + HO\textit{i}Pr \rightarrow H\cdots O(H)\textit{i}Pr$

2)



3)



Which horse to ride? It depends on the way you go...

Horse or maule horse: fluorine or oxygen, fluorides or oxides?

Many fluorides are accessible via sol-gel

- MF: M = Li, Na, K, Ag, …
- MF_2: M = Be, Mg, Ca, Sr, Ba, Zn, Fe, Cu,…
- MF_3: M = Al, In, Ga, Cr, Fe, V
- $MF_2/M`F_X$: M = Mg, Zn; M`= Cr, Fe, V, Ti, Zr, Sb, Ta, Nb, …

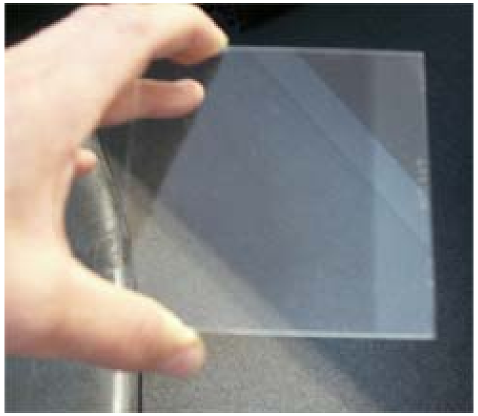
- $A_2^IB^IM^{III}F_6$ A = K, Rb, Cs; B = Li, Na, K, Rb M = Al (G, In, Fe)
- $A_3^IM^{III}F_6$ A= Na, Rb, Cs; M = Al (G, In, Fe…)
- $A^IB^IC^IM^{III}F_6$ A = Li; B = K; C = Na, Rb, Cs; M= Al….
- AMF_4 A = K, Rb; M= Al ….
- AMF_3 A = Li, Na M = Zn .....

J. Fluorine Chem. **2007**, 128, 353-368,
Handbook „Sol-Gel Sciences, Chapter 28, 2016 in press

Novel applications due to homodispersed nanoscaled metal fluorides

Up- & down-coversion

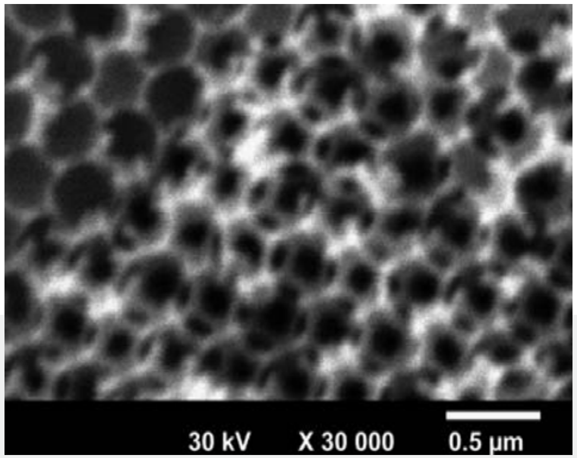
Antireflective coating



New ceramics

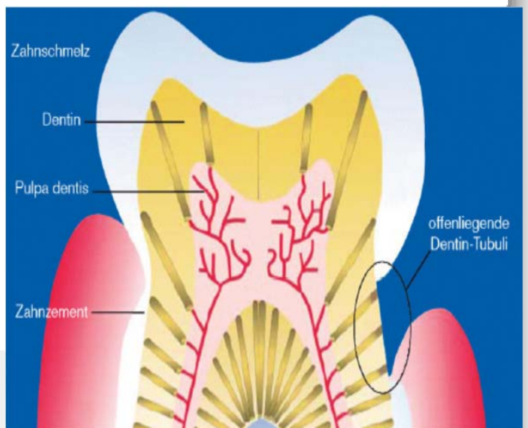
MF_n sols

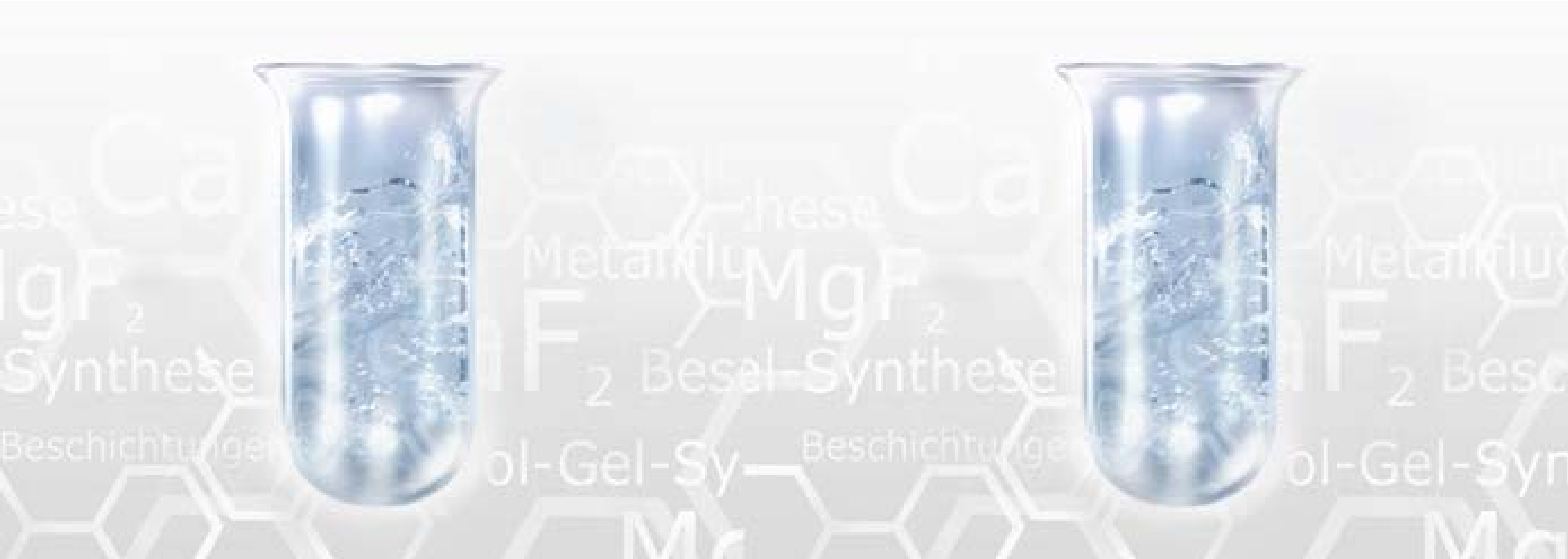
Meso structured materials
Heterogeneous catalysis



MF_n based composites

Dentistry





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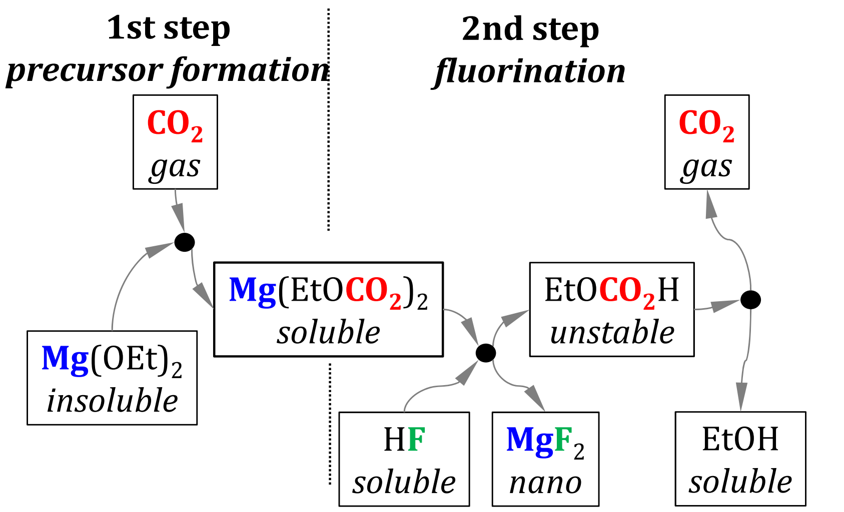
   - the principle of the *fluorolytic* Sol-Gel-synthesis
2. Mechanism/reaction path
   - chemical aspects – AlF_3
   - topological aspects – MgF_2
3. Applications: **up- and down conversion**
4. Summary

Magnesium ethoxide precursor

...is insoluble in methanol, ethanol, isopropanol,.....

$$Mg(C_2H_5O)_2 + 2CO_2 \xrightarrow{EtOH} Mg(C_2H_5OCO_2)_2$$



1st: $Mg(OEt)_2 + 2\ CO_2 \rightarrow Mg(EtOCO_2)_2$

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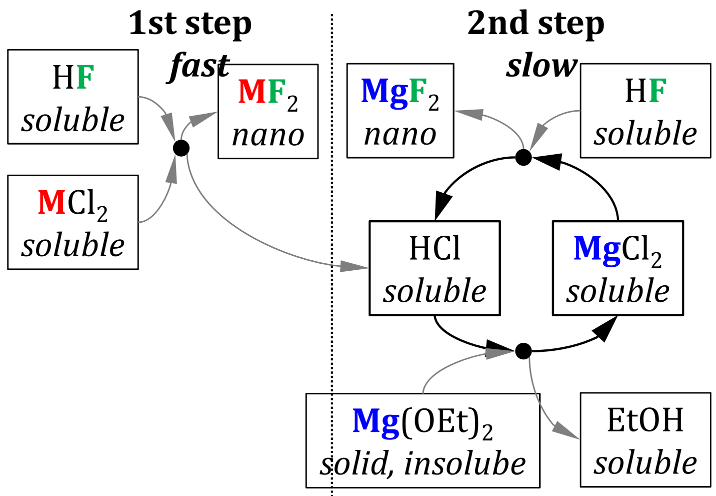
Brutto reaction

$Mg(OEt)_2 + 2\ HF \rightarrow MgF_2 + 2\ EtOH$



$MCl_2 + 2\ HF \rightarrow MF_2 + 2\ HCl$ | $Mg(OEt)_2 + 2\ HF \rightarrow MgF_2 + 2\ EtOH$

Brutto reaction

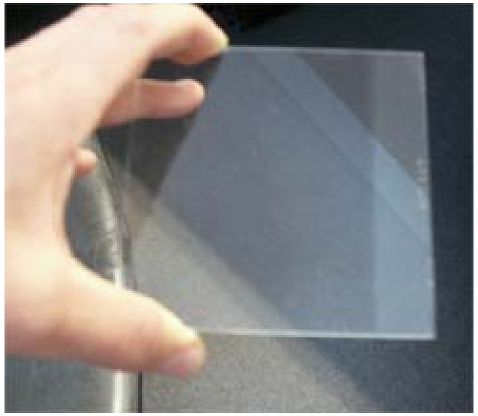
$(1\text{-}x)\ Mg(OEt)_2 + x\ MCl_2 + 2\ HF$

$\downarrow$

$(1\text{-}x)\ MgF_2 + x\ MF_2 + 2x\ HCl + (2\text{-}2x)\ EtOH$

Novel applications due to homodispersed nanoscaled metal fluorides

Antireflective coating

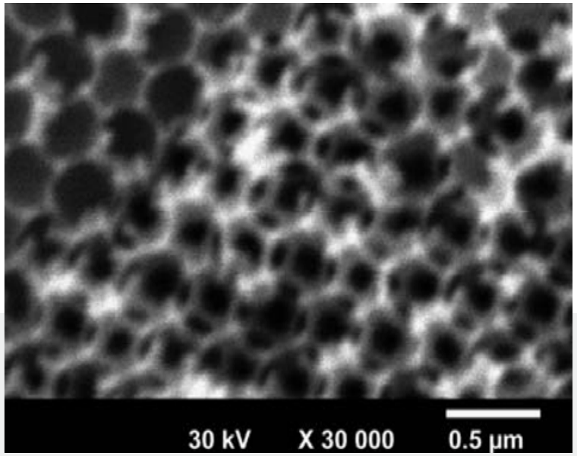


Up- & down-coversion

New ceramics

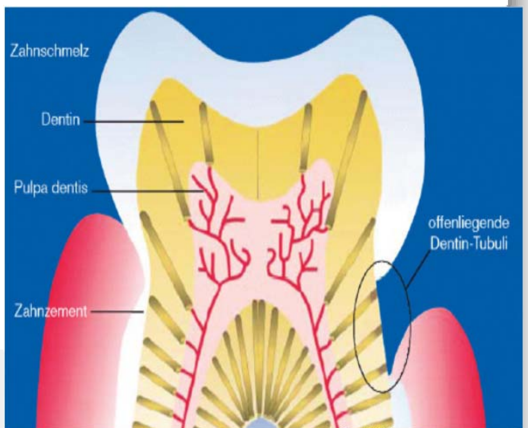
MF_n sols

Meso structured materials
Heterogeneous catalysis



MF_n based composites

Dentistry



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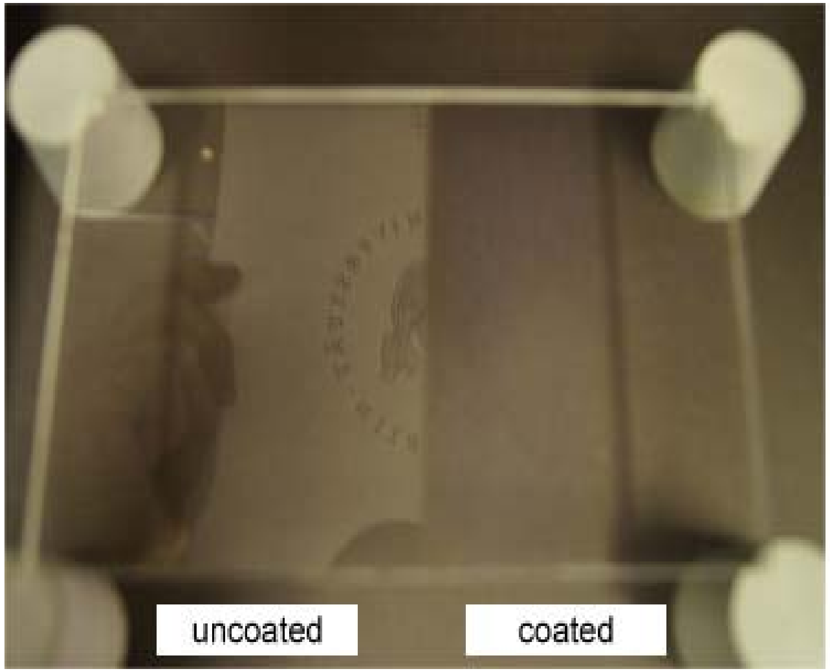
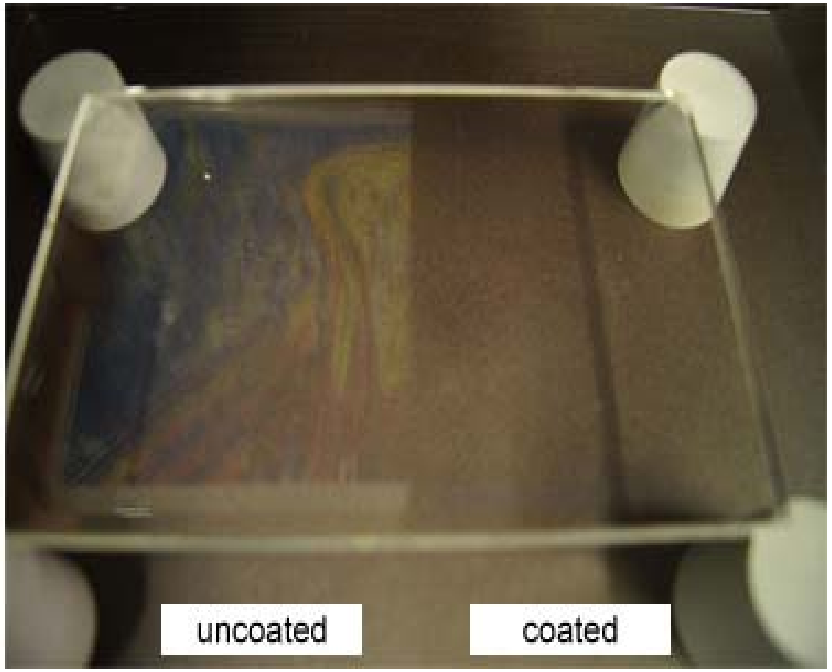
3. Applications: **antireflective coatings**
4. Summary

Selected physical data of different materials

Formula	Structure	F_p	opt. range	n	solubility
BeF_2		555° C			good in H_20 EtOH
MgF_2	rutil	1256° C	120nm - 8µm	1,38	0,13 g/L
CaF_2	cubic	1423° C	130nm - 8µm	1,40	0,016 g/L
SrF_2	cubic	1477° C	130nm - 11µm	1,44	0,11 g/L
BaF_2	cubic	1368° C	150nm - 12µm	1,48	1,60 g/L
SiO_2	diamond	1713° C	150nm - 4µm 50µm - 1000µm	1,54 (thin film)	0,01 g/L quarz 0,12 g/L am. SiO_2

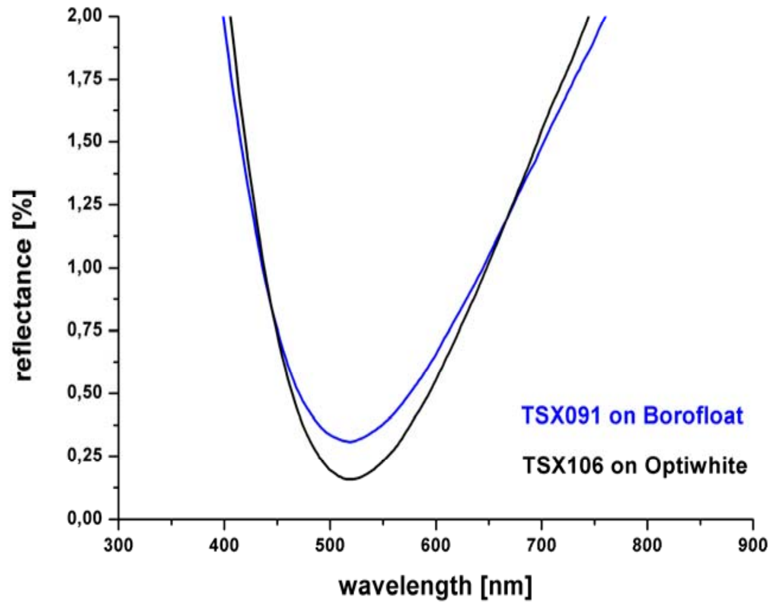
AR – Layers based on MgF_2





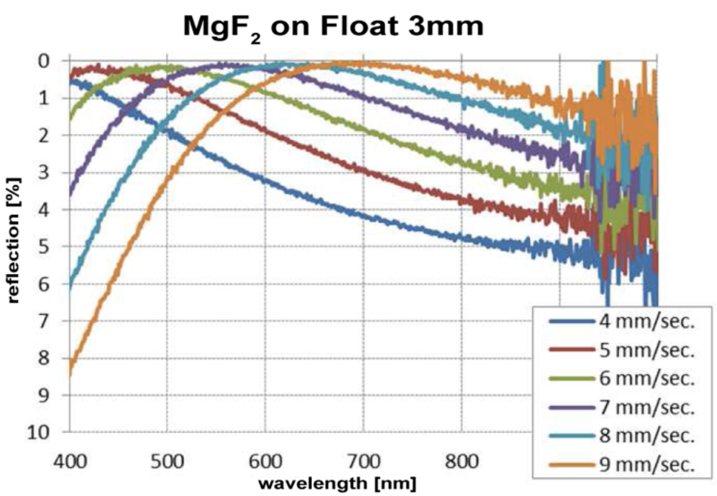
Layer	n_{sub}	n_{film}	d_{film}
Borofloat	1,47	1,261	103 nm
Optiwhite	1,52	1,268	103 nm

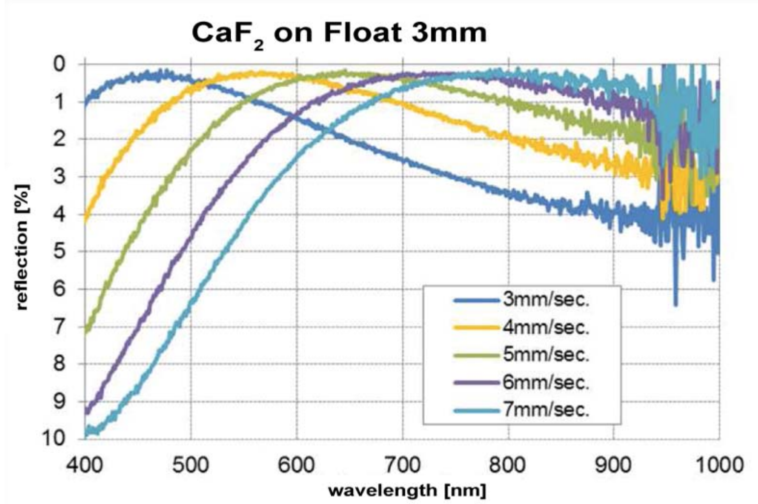
Thin Solid Films **2008**, 516, 4175
Phys. Stat. Sol. **2008**, 205, 821



Antireflective (AR) and interference layers optical data

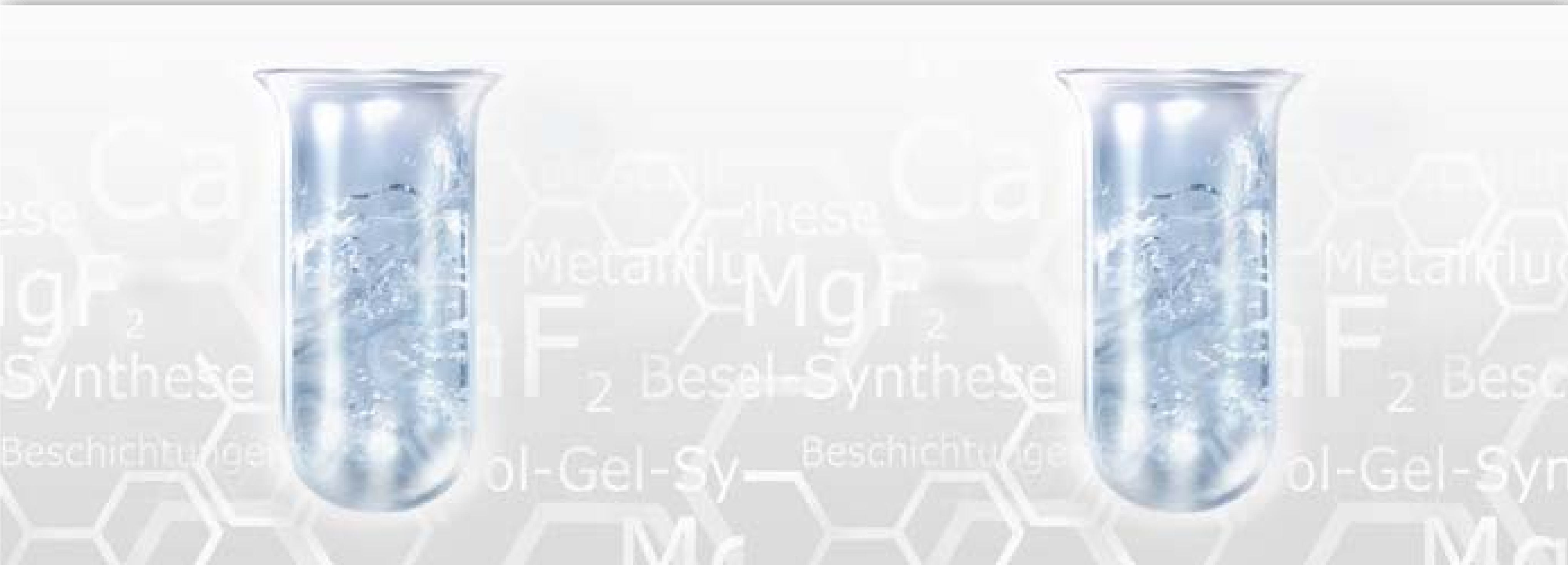
B. Lintner: Prinz Optics





- **Optical data** for MgF_2 (left) and CaF_2 (right) layers of different thickness.
- In both cases, the optical transmission is nearly 100% over a wide range of wave lengths

Benefits: (i) No light loss, (ii) gain of efficiency compared to „state of the art“-SiO_2-coatings of at least 4 to 5% resulting in higher energy yield



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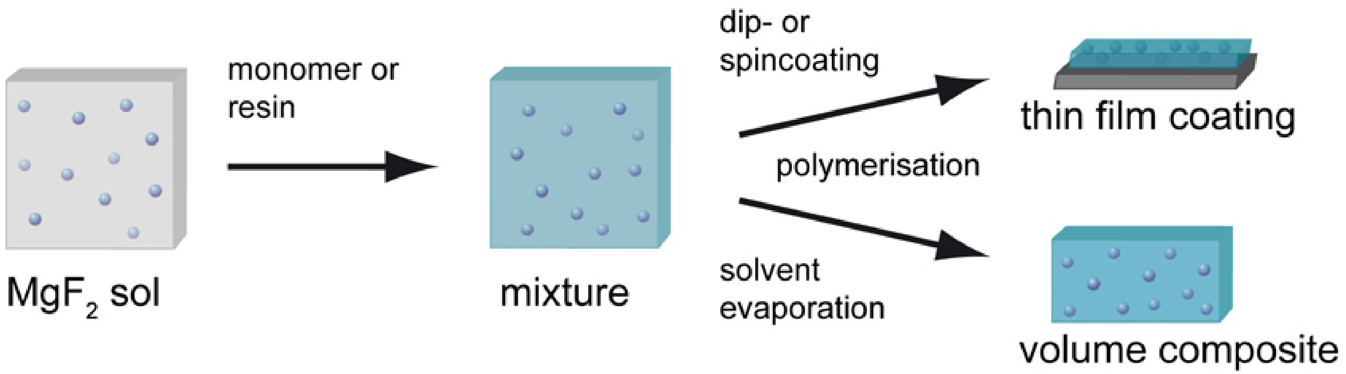
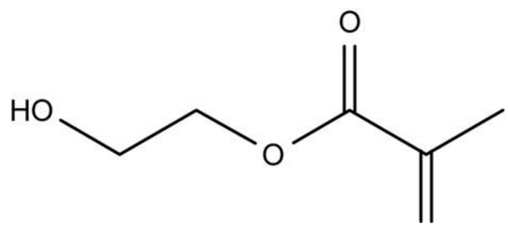
Manufactering of nano composites

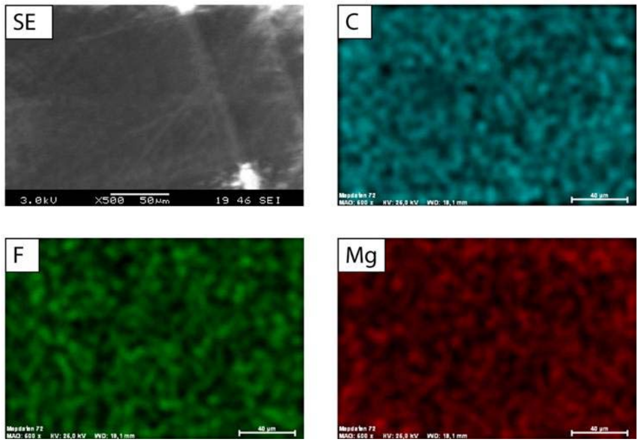


Composite of 10% PA-stabilized MgF_2 in PolyHEMA
Radical induced polymerisation with benzoylperoxide at 60-90°C



2-Hydroxyethylmethacrylat

Characterization of nano composites



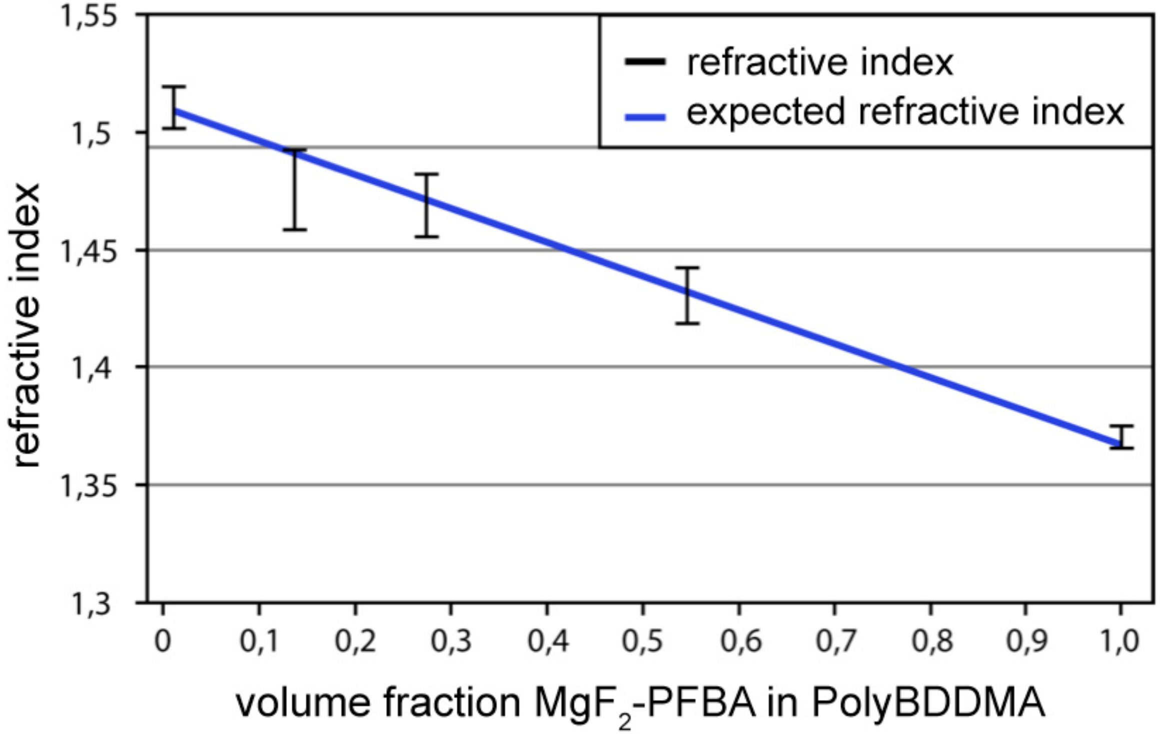
Optical transparancy:
No agglomeration or phase separation

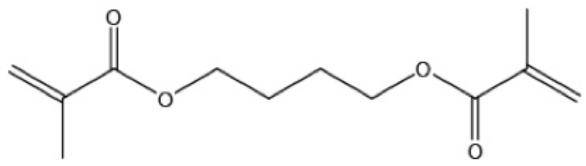
EDX:
Homogeneous distribution of magnesium and fluorine in the polymer

Nanoscale 2011, 3, 4774-4779

Characterization of nano composites

Ellipsometric determination of the refractive index of the composites





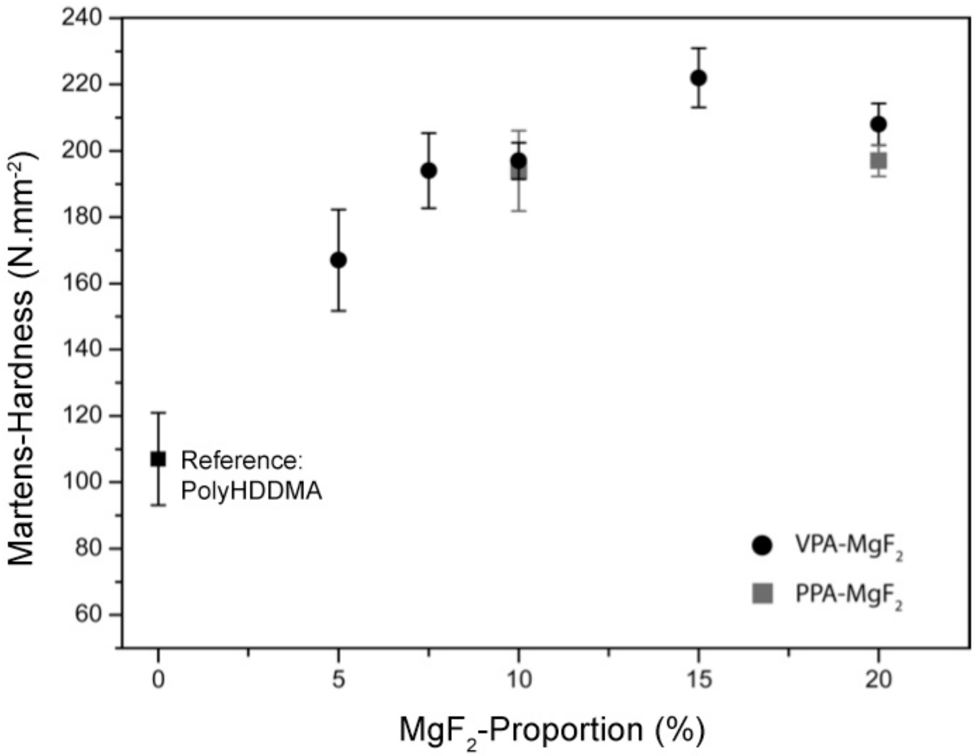
$$n_{Komposit} = \sum_i n_i \cdot \phi_i$$

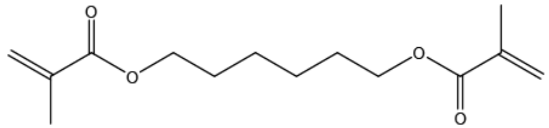
- Decrease of refractive index of polymer materials is possible
- fine tuning by addition of nano-MgF_2 successful

Nanoscale **2011**, 3, 4774-4779

Mechanical properties of composites

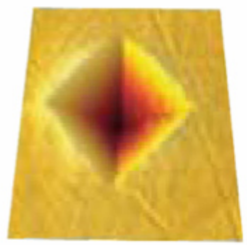
Indentation investigations at composites with PA-stabilised MgF_2





1,6-Hexandioldimethacrylat

$$H = \frac{F}{A_c}$$



- adding nano-MgF_2 causes drastic increase of the Martens-hardness of the composite
- cratch resistance raises

Nanoscale **2011**, 3, 4774-4779

Polymerisation of bulk-composites

Stabilised MgF_2-Sol in HEMA:
- *Radical induced polymerisation with benzoylperoxid @ 60-90ºC*

Glass transition temperature by DMA:

sample	0%	2,5%	5,0%	10%	20%
T_g in ºC	102	108	118	118	126

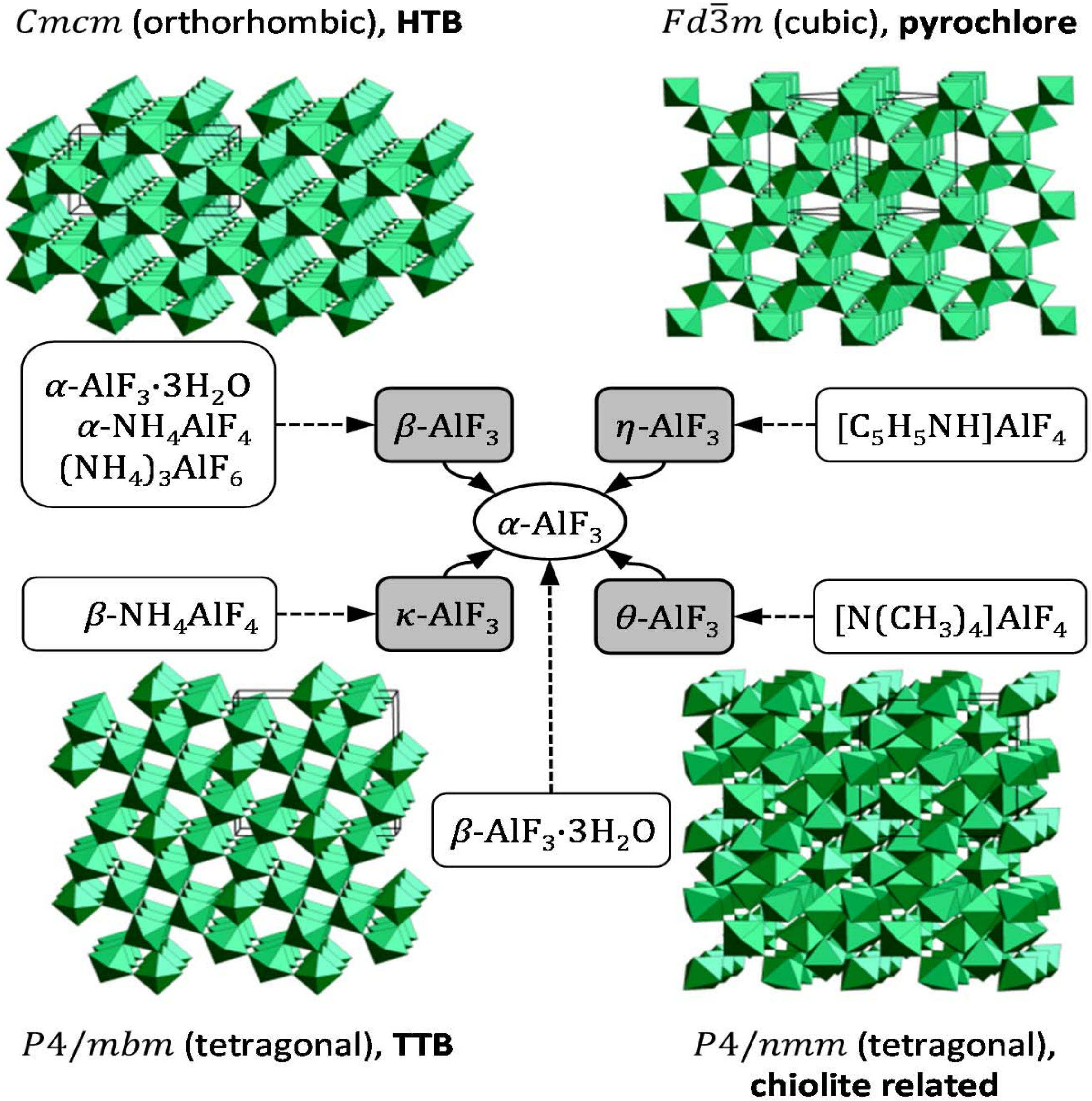
→ **High Transparency**
→ **Increasing T_g with increasing MgF_2 content**
→ **Decreasing refractive index with increasing MgF_2-content**
→ **Increasing Hardness with increasing MgF_2 content**

Nanoscale **2011**, 3, 4774-4779

1. The *fluorolytic* sol-gel-synthesis of metal fluorides
   - the principle of the *fluorolytic* Sol-Gel-synthesis
2. Mechanism/reaction path
   - chemical aspects – AlF_3
   - synthesis parameter
3. Applications: **Catalysis**
4. Summary

AlF_3 an exciting solid Lewis acid

Aluminium fluoride phases – structures and synthesis



Fluoride Ion Affinity (FIA) – the pF Scale

$L_a + :F^- \longrightarrow [L_a–F]^-$ FIA = $-\Delta_r H$ (L_a ~ Lewis acid)

Molecule	FIA [a] meas	pF [b] meas	FIA [a] calc	pF [b] calc
$BF_{3(g)}$			351	8.38
$BCl_{3(g)}$			405	9.67
$AlF_{3(g)}$	488	11.66	484	11.56
$AlClF_{2(g)}$	491	11.73	494	11.80
$AlCl_2F_{(g)}$	499	11.92	501	11.97
$AlCl_{3(g)}$	506	12.09	506	12.09
$AlBr_{3(g)}$			512	12.23
$Al(O^tC_4F_9)_{3(g)}$			537	12.83
$GaF_{3(g)}$	461	11.01	453	10.82
$GaCl_{3(g)}$			445	10.63
$AsF_{5(g)}$			426	10.17
$SbF_{5(g)}$ [c]			489	11.68

[a] in kJ mol^{-1}
[b] pF = FIA/(41.868 kJ mol^{-1})
[c] 490 kJ mol^{-1} is a good average value for liquid SbF_5 containing oligomers Sb_nF_{5n} (n = 1, 2, 3, 4)
Measured values from [59, 60]; Calculated values from [52, 53, 57]

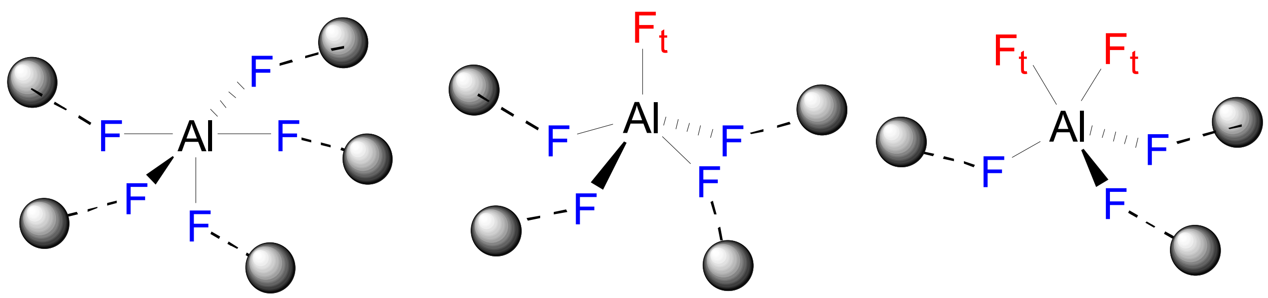
Fluoride ion affinities (FIA) and pF values of selected molecules (meas ~ measured, calc ~ calculated).

K. O. Christe et al., *J. Fluorine Chem.*, 2000, **101**, 151-153

Modelling the Lewis Acidity of AlF_3 Surfaces

Al^{V} type 1 | **Al^{V} type 2** | **Al^{V} type 3**

T6 (Al^{V} type 2),
T1 (Al^{V} type 1).



F ~ bridging fluoride | F_t ~ terminal fluoride

$[AlF_{5/2}]$ — *high to very high Lewis acidity*

$[AlF_{4/2}F_{1/1}]$ — *medium Lewis acidity*

$[AlF_{3/2}F_{2/1}]$ — *low to medium Lewis acidity*

Schematic pictures five-fold coordinated aluminium on the surface of AlF_3.

Spheres ~ AlF_3 bulk network.

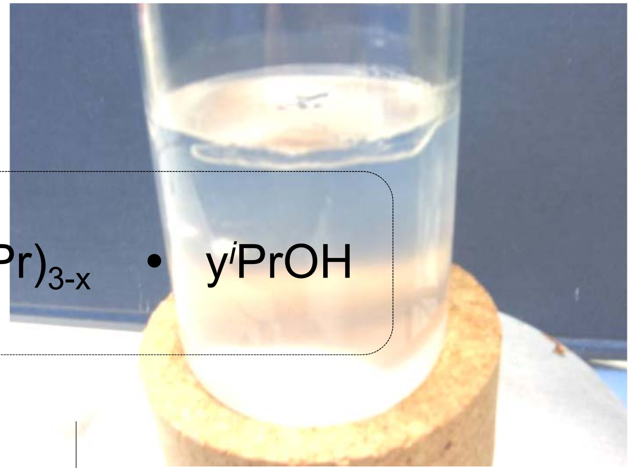
Calculated reaction enthalpy of ammonia with different aluminium halides. The highest binding energy at *β*-AlF_3 is bold marked. T1 and T6 are two different accessible sites at the (100) surface of *β*-AlF_3. Molecular compounds are given for comparison.

Species	Centre Type [a]	$\Delta H(NH_3)$ kJ mol^{-1}		Comment [b]		
α-$AlF_{3(s)}$	Al^V type 2	129		, largest surface, stable termination		
	Al^V type 2	133		, small surfaces at edges of crystallites		
	Al^V type 3	141		, small surfaces at corners of crystallites		
	Al^V type 1	173		, possible metastable termination		
β-$AlF_{3(s)}$	Al^V type 1	179…189 169…179 151…166		surface [c] minor sites T1		NH_3 coverage
	Al^V type 2	149…154 128…135 117…119		surface [c] major sites T6		NH_3 coverage
	Al^V type 2	≈132		(010) surface	low	NH_3 coverage
$AlF_{3(g)}$	Molecular	168.0	169.9	484		
$AlCl_{3(g)}$ [d]	Molecular	160.3		506		
$AlBr_{3(g)}$ [e]	Molecular	158.9	158.3	512	For comparison: FIA in kJ mol^{-1}	
$Al(O^tC_4F_9)_{3(g)}$	Molecular	158.7		537		
$SbF_{5(g)}$	Molecular	160.8	166.5	489		

Nanoscopic high surface (HS) aluminium fluoride

Gel

$Al(O^iPr)_3$ + x HF →(^{i}PrOH) $AlF_x(O^iPr)_{3-x}$ • y^iPrOH

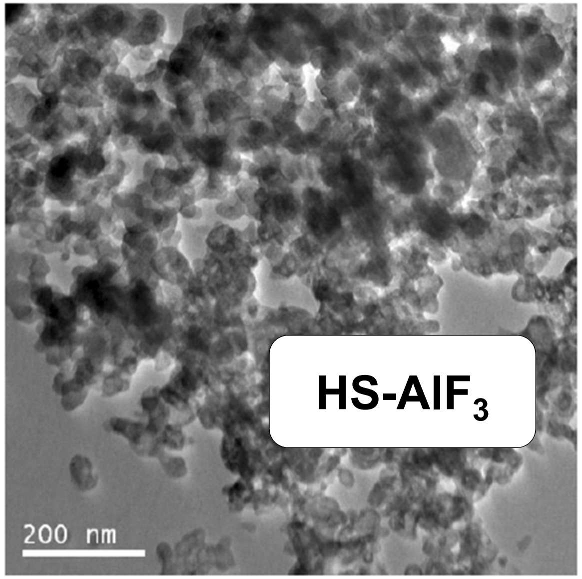


↓ solvent removal

xerogel „precursor“

$AlF_{2.3}(O^iPr)_{0.7}$ ← y^iPrOH

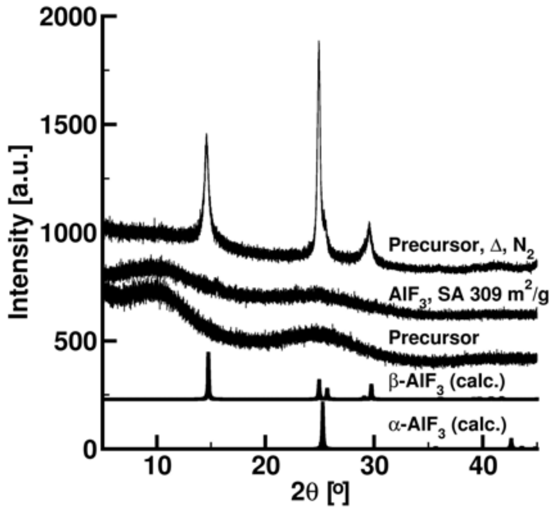
←($CHClF_2$, 240° C) „post fluorination“

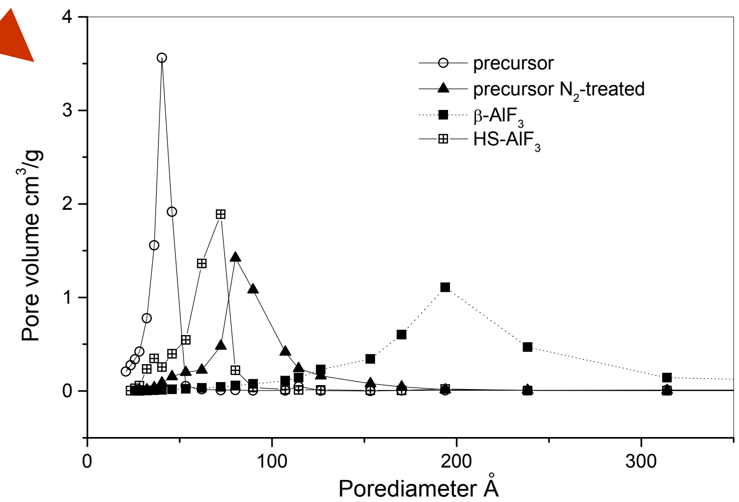


Angew. Chem. Int. Edit. **2003**, 42, 4251, *Chem. Mater.* **2008,** *20*, 5687

HS-AlF_3: Some physical properties

- X-ray → amorphous
- TEM → nano crystalline
- BET-S_g → 200-450 m^2/g
  (meso-porous, narrow pore size distribution)
- XPS → pure AlF_3 (BE~77,5 eV)
- EDX → phase pure (traces O, ads. H_2O)
- IR and NMR → high degree of disorder
- Al K-edge XAS → disordered structure of dried fluoride alkoxide precursor is preserved during fluorination

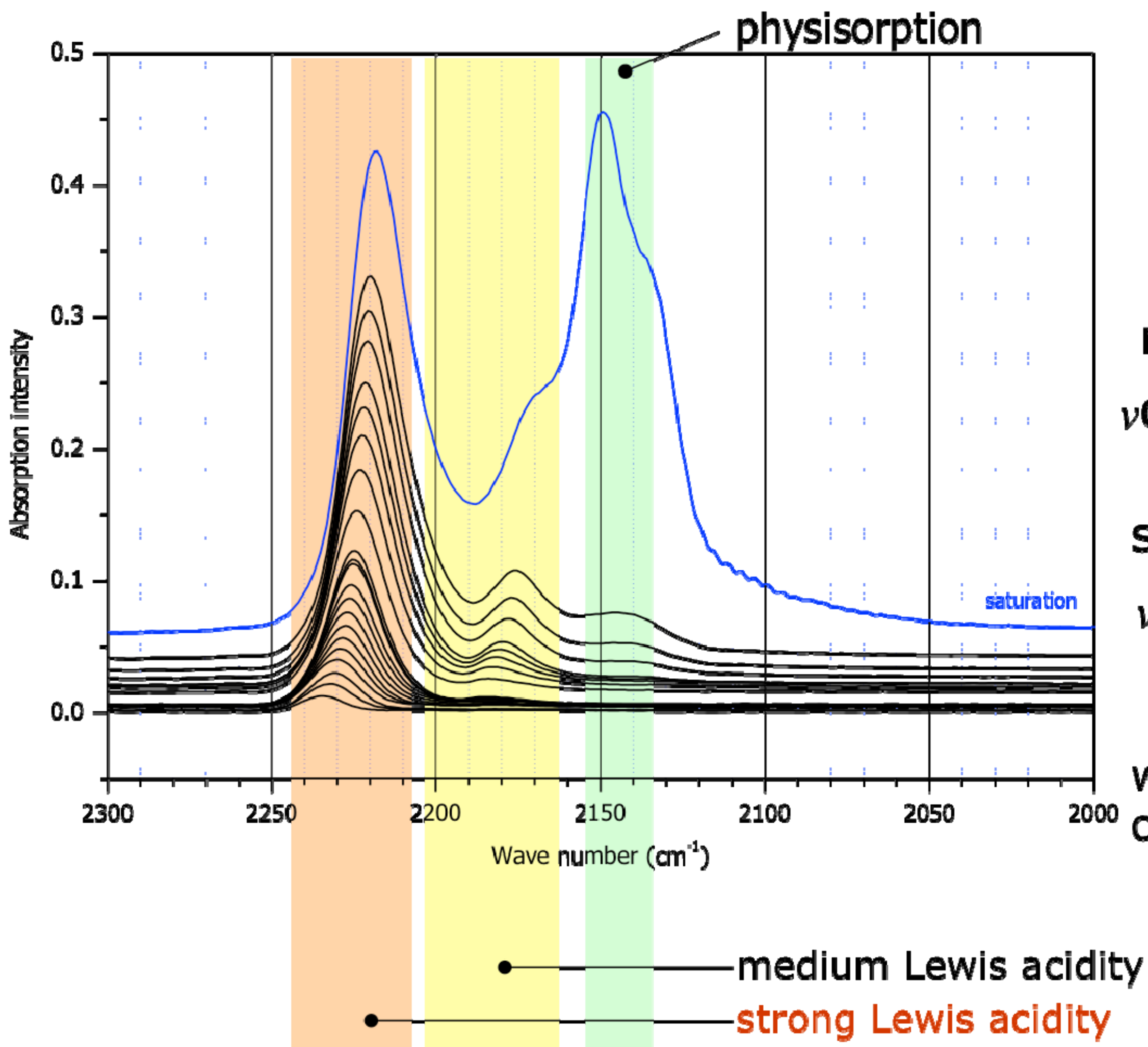


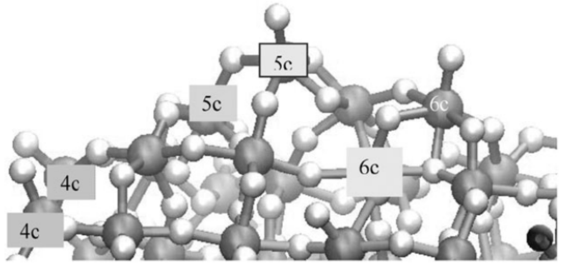


- Al-surface sites CN < 6 Lewis acidity

J. Phys. Chem. C **2009**, *113*, 15576–15585

Acidity HS–AlF_3 CO-adsorption





medium strong sites

$\nu CO_{(g)}$ 2175 cm^{-1}

strong sites

$\nu CO_{(g)}$ 2240-2220 cm^{-1}

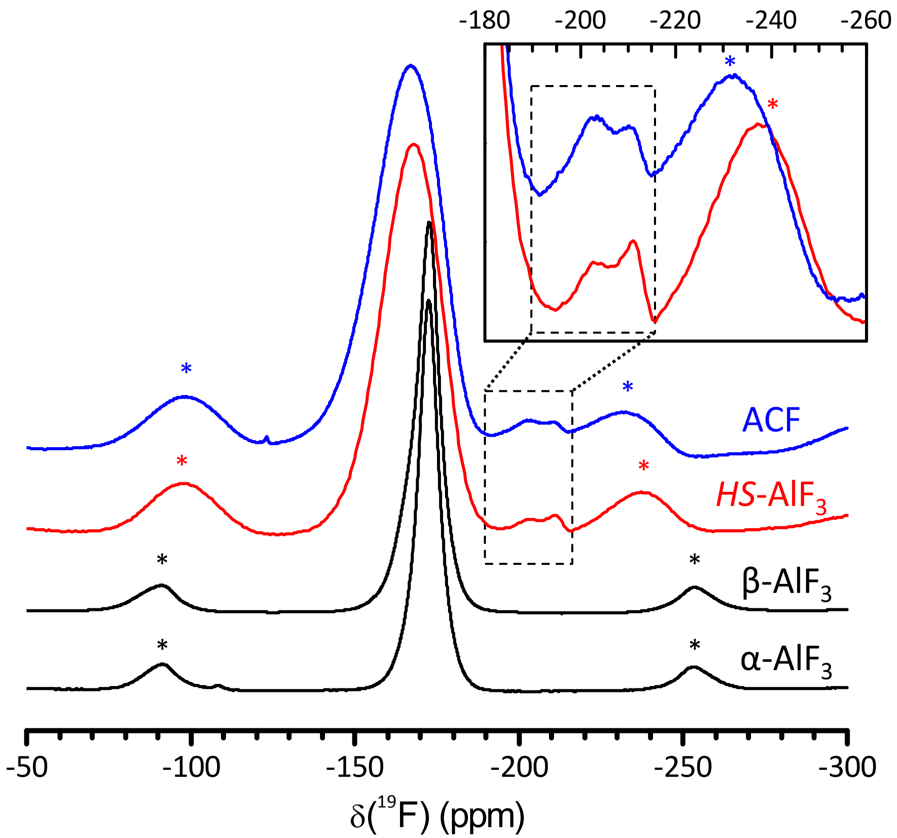
wave number depends on the coverage rate

J. Phys. Chem. C **2009**, *113* , 15576, *J. Phys. Chem. C* **2007**, 111, 18317

Aluminium chlorofluoride (ACF)

$$AlCl_3 + (3-x)\ CCl_3F \longrightarrow AlCl_xF_{3-x} + (3-x)\ CCl_4$$

$x \approx 0.05 \ldots 0.3$



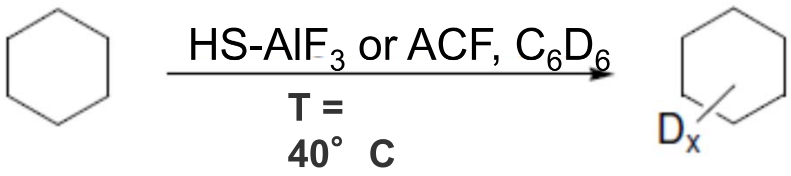
[19]F MAS NMR spectra (376 MHz) of α-AlF_3 and β-AlF_3 (v_{rot} = 30 kHz) compared to *HS*-AlF_3 and ACF (v_{rot} = 25 kHz). Inset: Magnification of terminal fluoride signals at –190 … –215 ppm. (*) Spinning side bands.

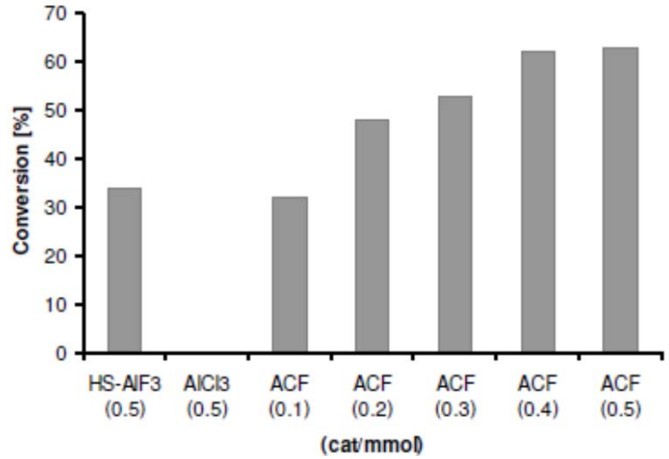
C. G. Krespan and V. A. Petrov, *Chem. Rev.*, 1996, **96**, 3269-3302,
T. Krahl and E. Kemnitz, *Angew. Chem. Int. Ed.*, 2004, **43**, 6653-6656.

Some examples proofing the catalytic potential of AlF_3

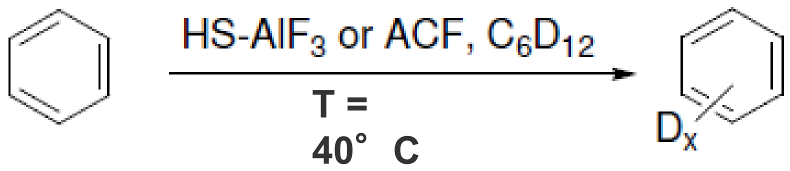
Heterogeneous C-H-activation at room temperature without precious metals

H/D-exchange between C_6D_6 and C_6H_{12}



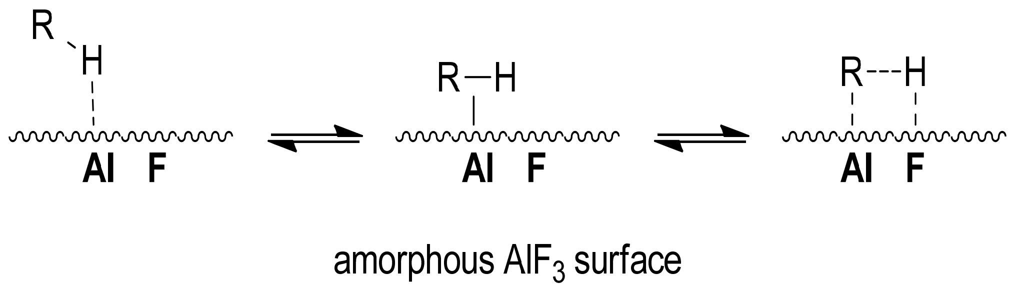


H/D-exchange between C_6D_{12} and C_6H_6



X = 65-90%

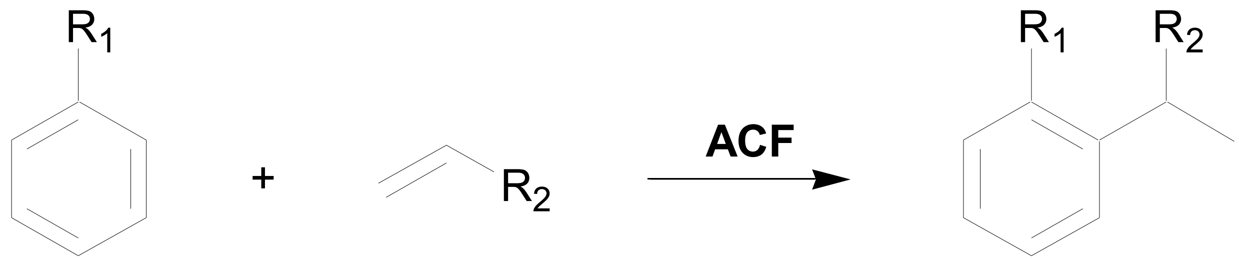
C–H activation of bifunctional Lewis acidic *HS*-AlF_3 or ACF surface sites. R = alkyl, aryl.



Chem. Eur. J. **2011**, 17, 14385-14388

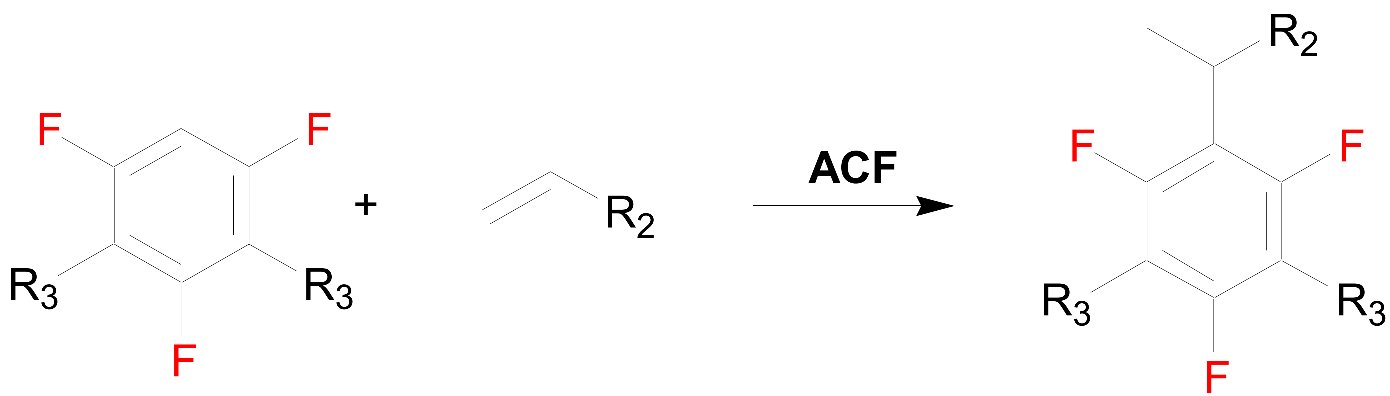
Heterogeneously catalysed hydroarylation of olefins

(rt & 70° C and at low pressure < 2 bar)



R_1 = H, CH_3; R_2 = H, CH_3

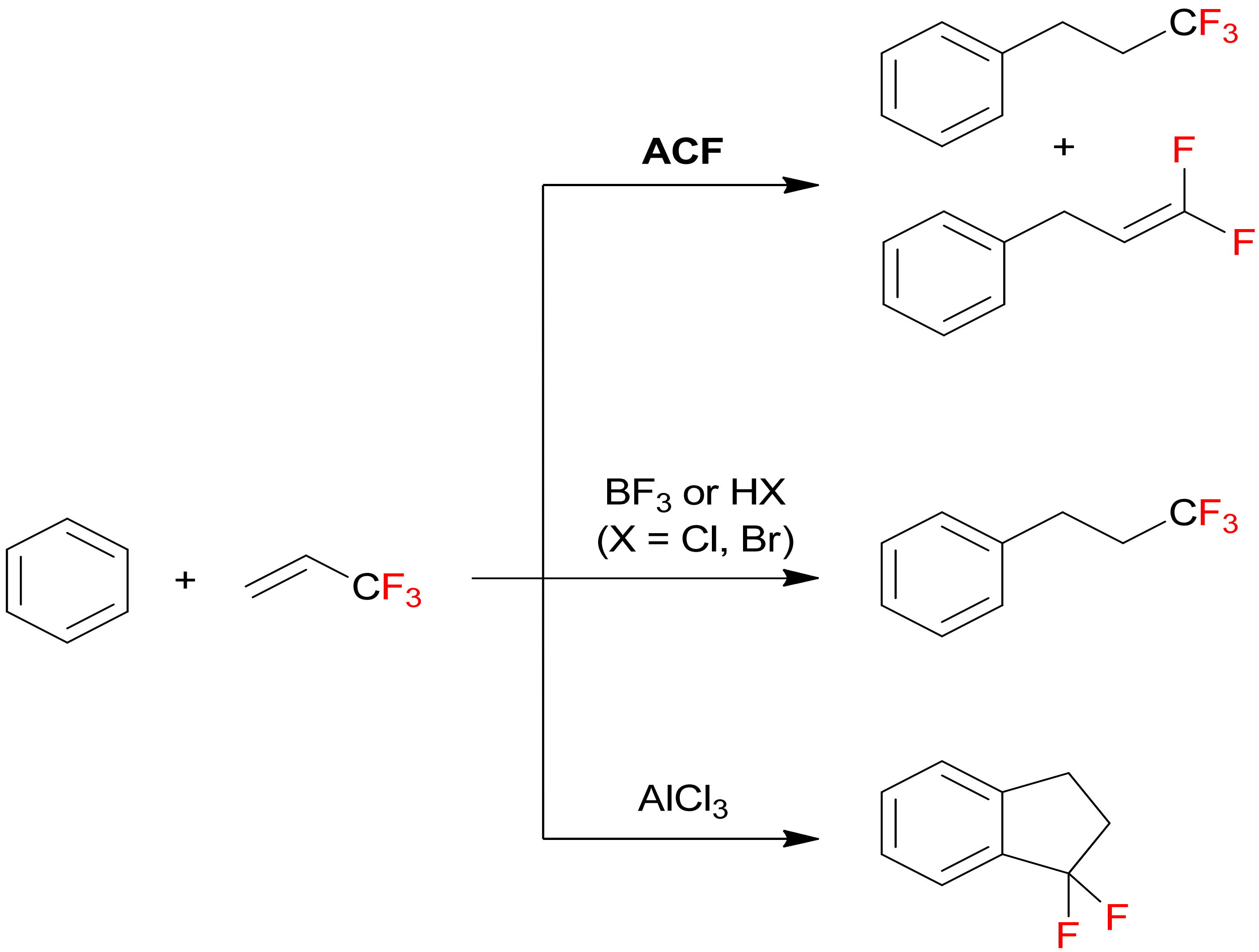
R_1 = H; R_2 = *n*-C_4H_9



R_2 = H, CH_3; R_3 = H, F

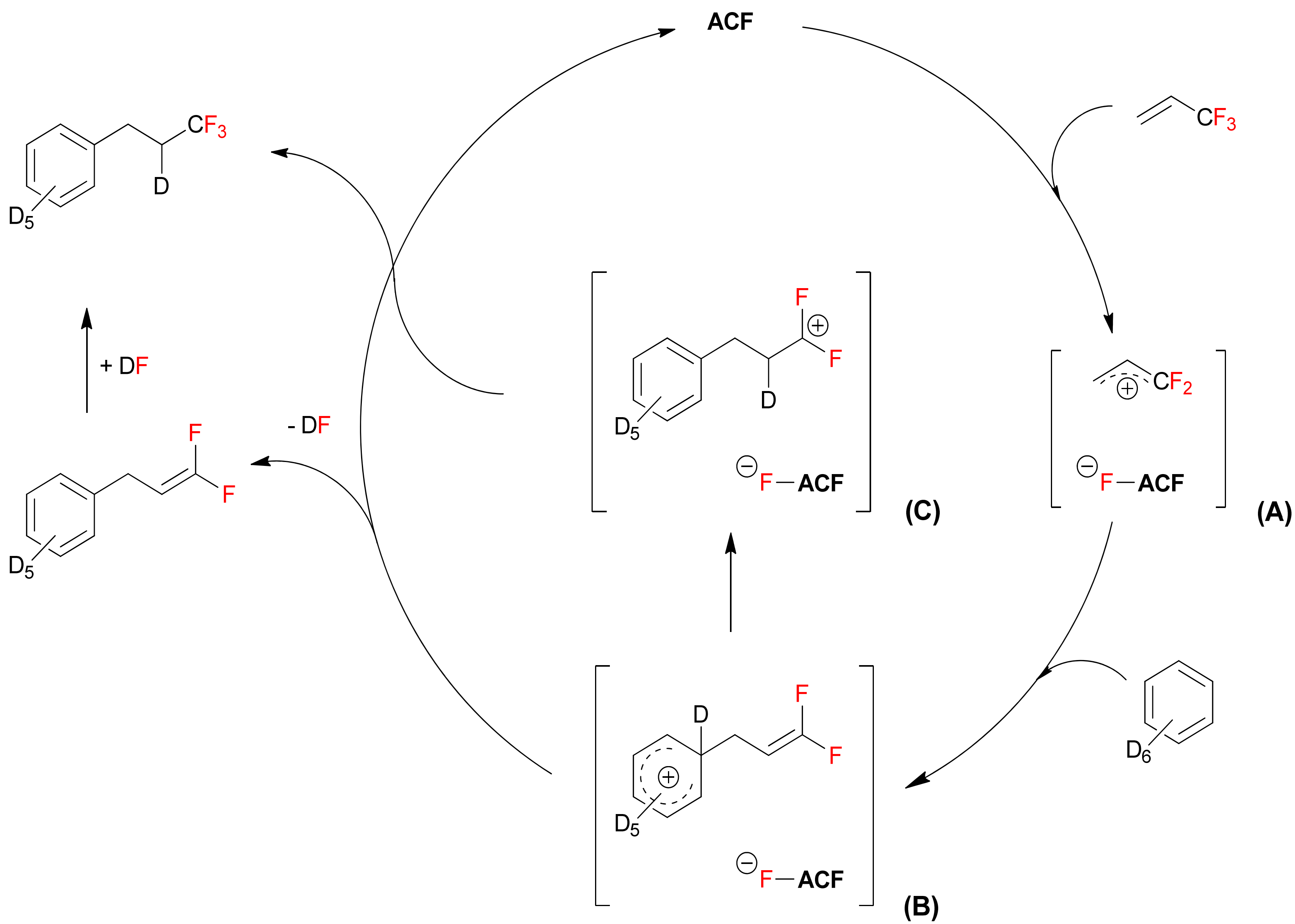
ChemCatChem, 2016, **8**, 1945-1950

Reactivity of 3,3,3-trifluoropropene towards different Lewis acids

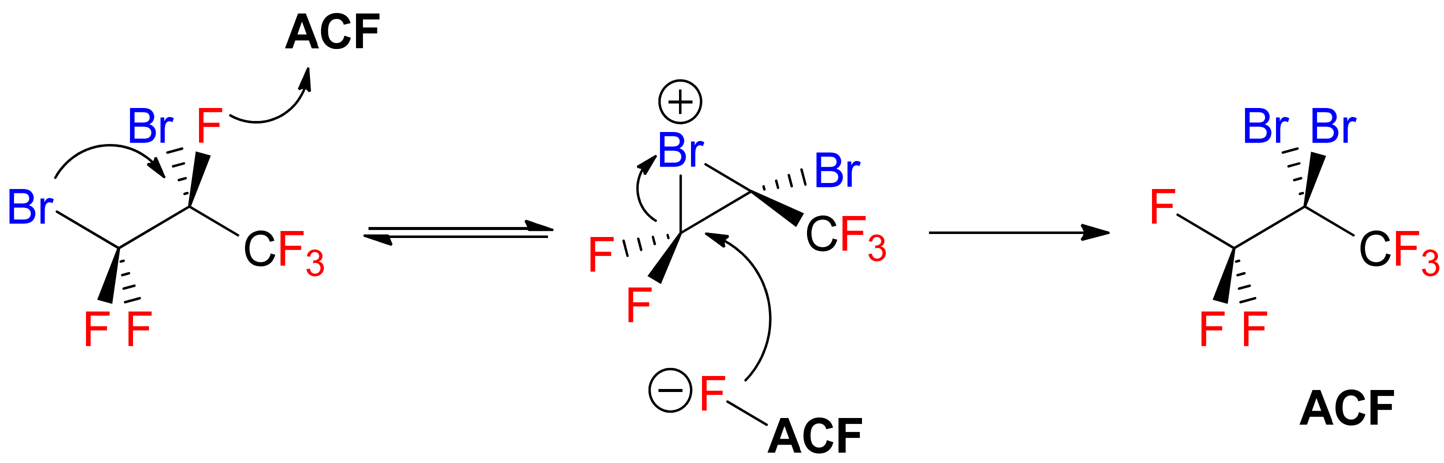


Note the change in chemoselectivity in case of ACF

Proposed mechanism for the formation of $C_6D_5–CH_2–CH=CF_2$ and $C_6D_5–CH_2–CHD–CF_3$ by C–F and C–H bond activation reactions.



C–F activation reactions



Catalyst	X[%]
$AlCl_3$	< 0.1
ACF	> 90
HS-AlF_3	> 90
β-AlF_3	0

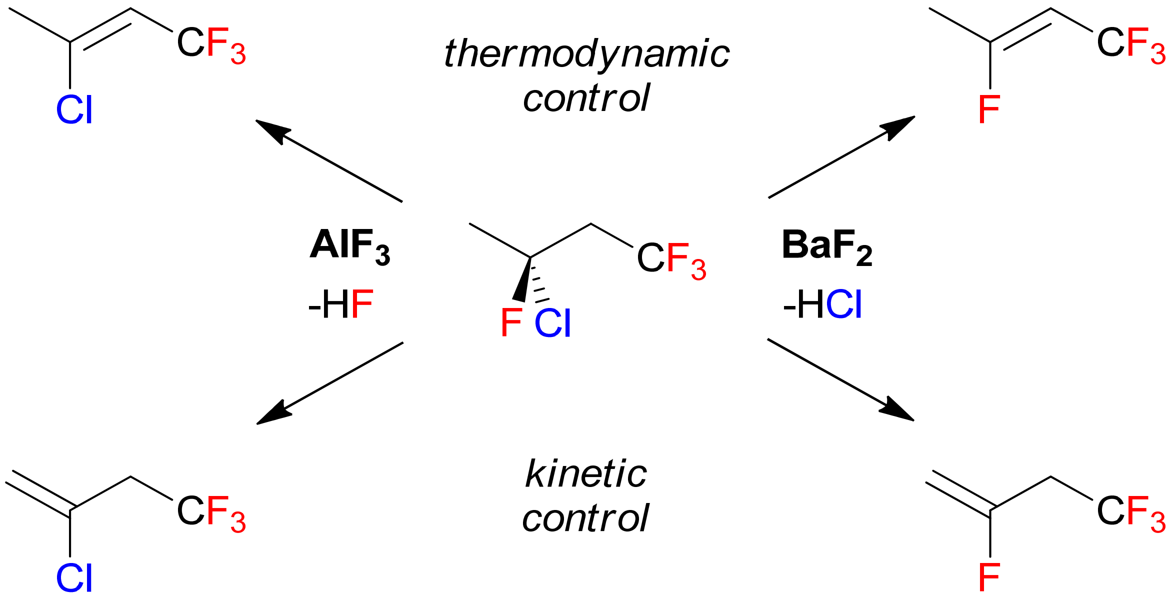
ACF – aluminium chloride fluoride
($AlCl_xF_{3-x}$ – 0.3<x>0.1)

Liquid phase:
room temperature, 10µl/mg.cat

SbF_5: X>90% at ca. 80° C!

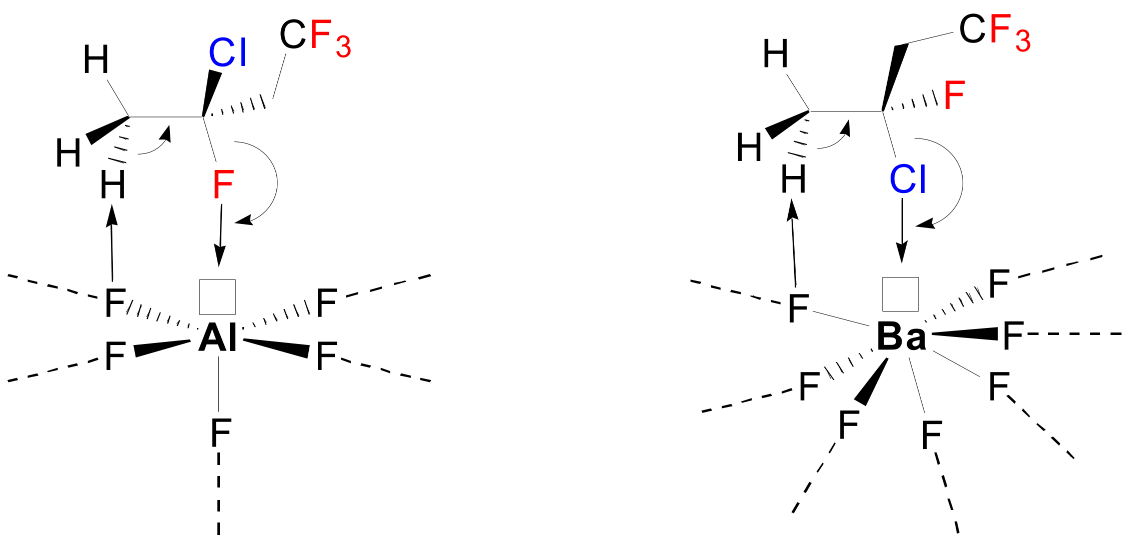
Inorg. Chem., 2003, 42, 6474 & *Angew. Chem. Int. Ed*. 2003, 42, 4251
Review: *J. Fluorine Chem*. 127 (2006) 663-678

C–F activation reactions



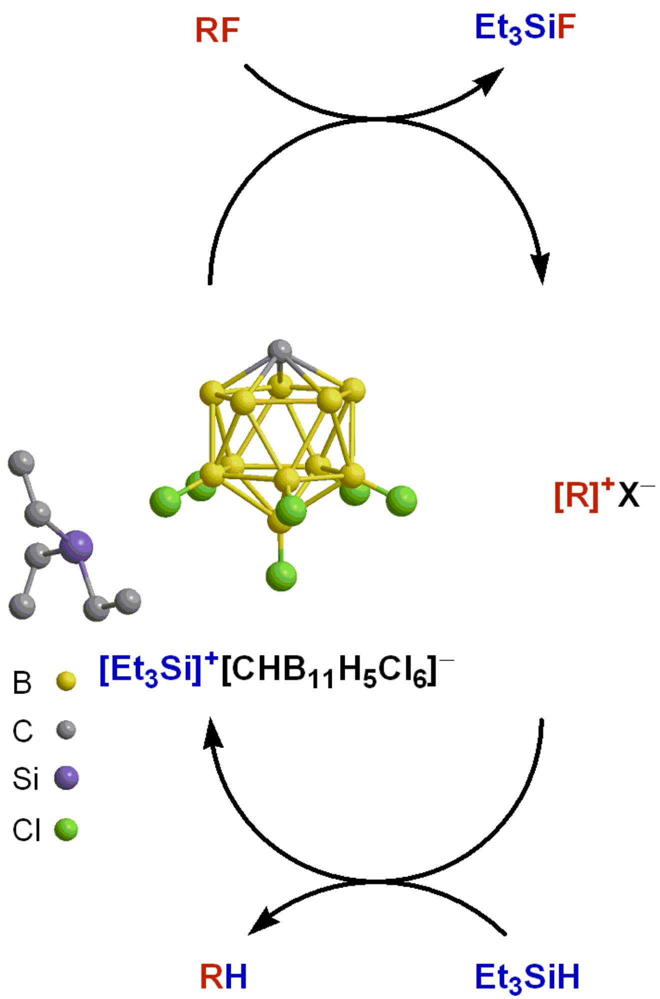
Catalytic dehydrohalogenation of 3-chloro-1,1,1,3-tetrafluorobutane. Thermodynamic or kinetic control is achieved by different contact times.

Proposed mechanism for the dehydrohalogenation of 3-chloro-1,1,1,3-tetrafluorobutane. The square indicates a free coordination site at the metal ion



J. Catal., 2011, **282**, 175-182.

Can ACF or HS-AlF_3 interact with Et_3SiH → silylium ion formation?

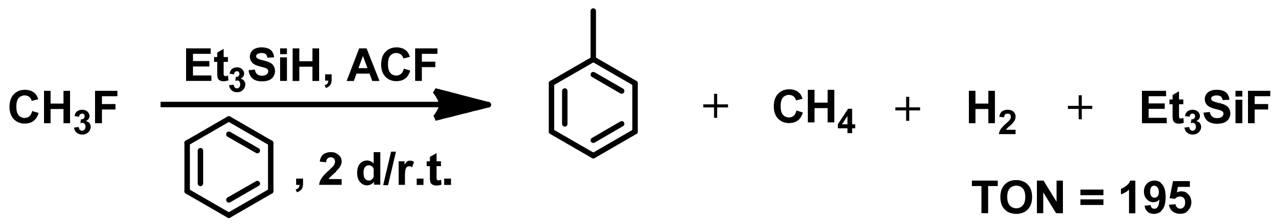


R = fluorinated alkanes, but no methanes or perfluorinated alkanes

- new heterogeneous approach for the cleavage of C-X bonds
- based on silylium-ion chemistry from homogeneous catalysis
- in the presence of Benzene -> Friedel-Crafts-products
- heterogeneous concept:
  - strong Lewis-acids like $AlCl_xF_{3-x}$ (x=0.05-0.3) (ACF) and *HS*-AlF_3
  - surface-bond silylium-like species
  - substrate (RF): fluorinated and chlorinated compounds

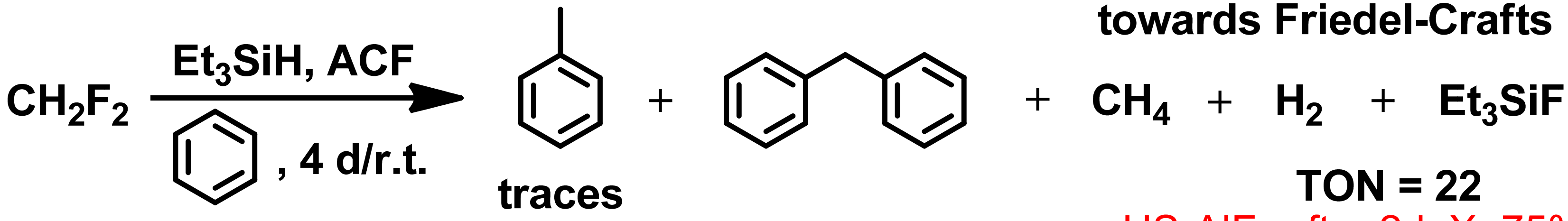
C. Douvris, O.V. Ozerov, *Science* **2008**, *321*, 1188.

Yes it does!



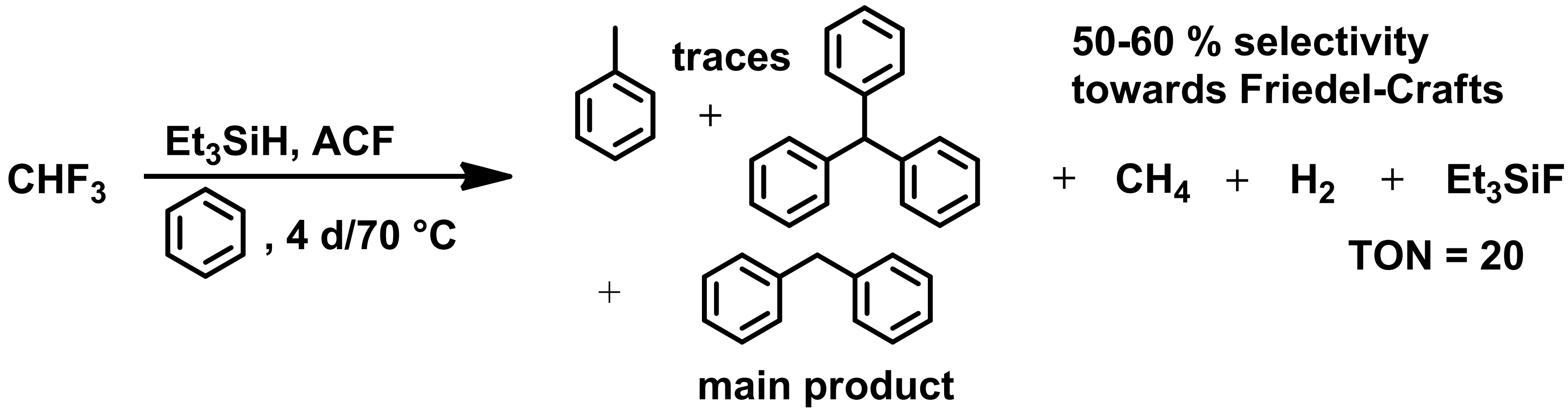
60-85 % selectivity towards Friedel-Crafts

60-70 % selectivity towards Friedel-Crafts



HS-AlF_3 after 2d: X=75%, TON 47

50-60 % selectivity towards Friedel-Crafts

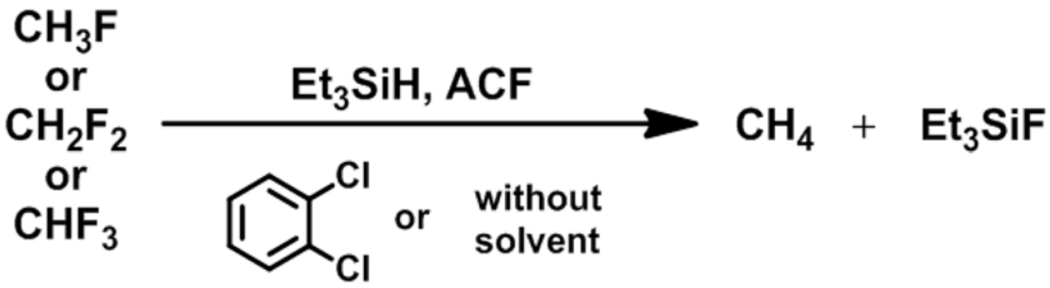


No partly fluorinated products can be detected

Angew. Chem. **2013**, *125*, 5436

Fluoromethanes

Avoiding Friedel-Crafts reactions:



absence of C_6D_6

TONs under different conditions

		benzene	*o*-$C_6H_4Cl_2$	neat
2 d / r.t.	**CH_3F**	195	190	400
4 d / r.t.	**CH_2F_2**	22	80	120
4 d / 70 ° C	**CHF_3**	20	5	5

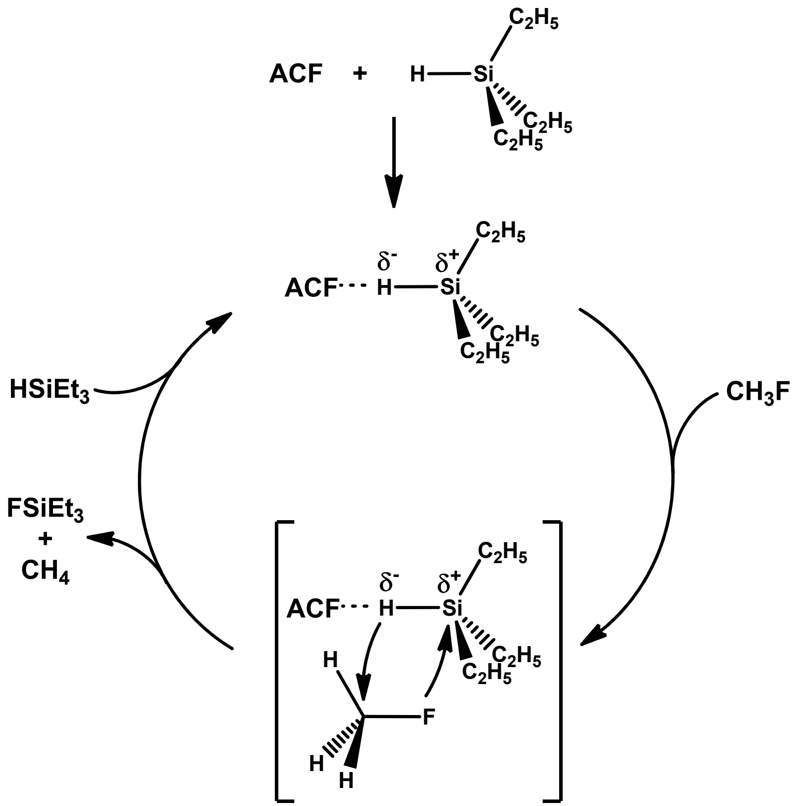
- still traces of Friedel-Crafts products in *o*-$C_6H_4Cl_2$
- CHF_3: first Friedel-Crafts reaction could be important

C-F-activation

How does it work?

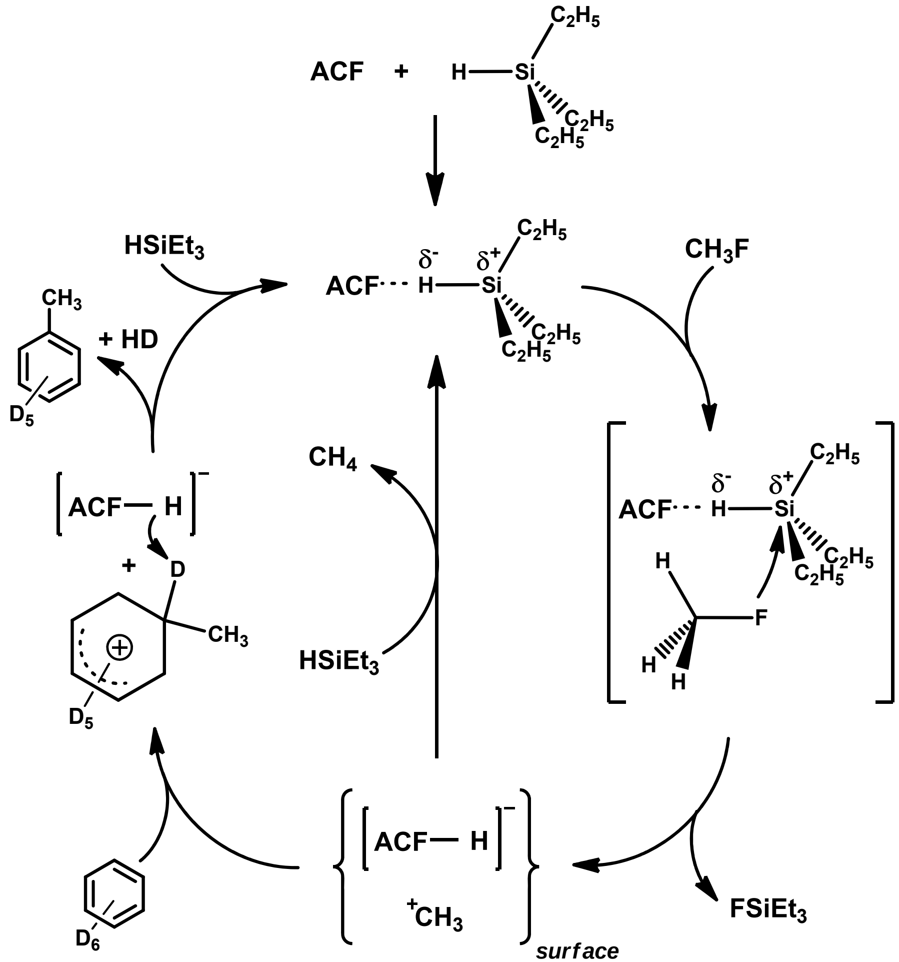
cycle **A** *(HDF)*

"Si–H/C–F metathesis" concerted



cycle **B** *(Friedel-Crafts)*

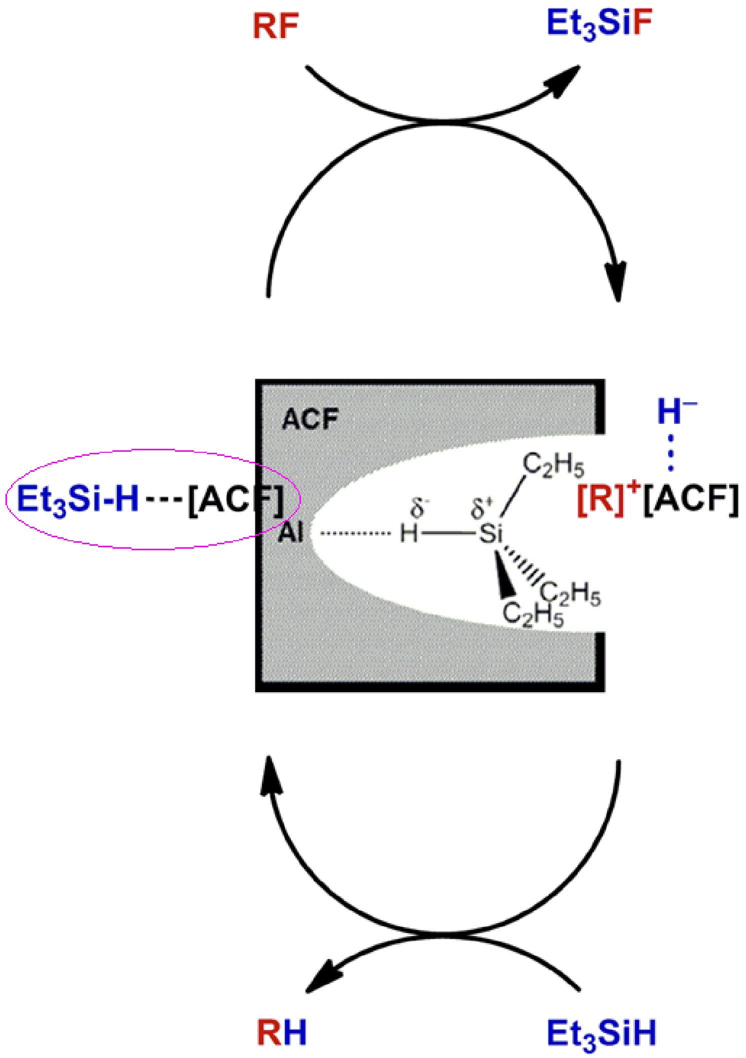
A non-concerted carbocation



ACF generates silylium ions and acts as a WCA

Angew. Chem. **2013**, *125*, 5436

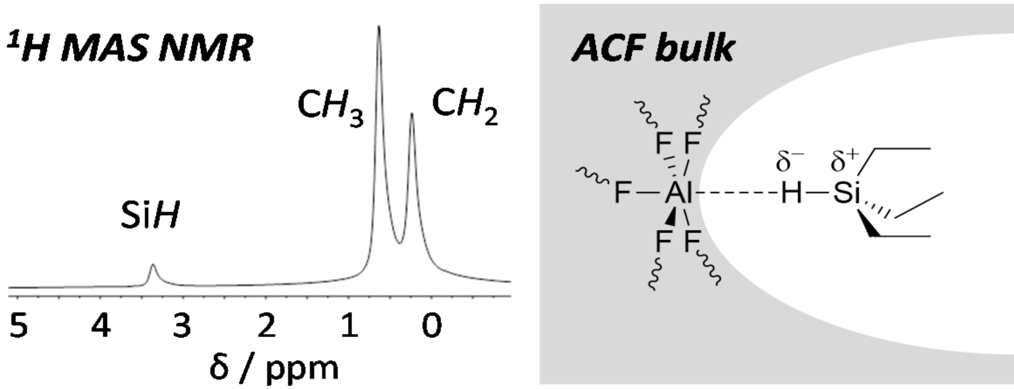
Conclusion and Outlook



R = CF_2H, CFH_2, CH_3

R = fluorinated alkanes, but no methanes or perfluorinated alkanes

- heterogeneous concept:
  - strong Lewis-acids like $AlCl_xF_{3-x}$ (x=0.05-0.3) (ACF) and *HS*-AlF_3
  - surface-bond silylium-like species
  - substrate (RF): fluorinated and chlorinated compounds



^{1}H MAS NMR of surface bound Et_3SiH with the Si–H resonance at δ = 3.45 ppm (ν_{rot} = 10 MHz). Et_3SiH in C_6D_6 solution: at δ = 3.85 ppm.

Angew. Chem. **2013**, *125*, 5436

Bifunctional, Lewis and Brønsted-acids?

Can we make use of the competitive hydrolysis reaction?

$$M(OR)_n \quad + \quad nHF \quad + \quad nH_2O \longrightarrow MF_n \textbf{ or } M(OH)_n \textbf{ or } MF_{n-x}(OH)_x?$$

Two possible scenario

1) $M(OR)_n \quad + \quad nHF \quad + \quad mH_2O \longrightarrow MF_{n-x}(OH)_x$

2) $M(OR)_n \quad + \quad yHF \quad + \quad xH_2O \longrightarrow MF_y(OH)_x \quad (x+y=n)$

Review: *J Fluorine Chem* **2007,** *128* (4), E. Kemnitz in *Functionalized Inorganic Fluorides*, Ed. Alain Tressaud, Publishers Wiley 2010, Chapter I: p.1-35; Review *Dalton Trans.*, **9** (2008) 1117 – 1127 , Review: *Catalysis Science & Technology* **2015,** *5*, 786-806;

Sol-gel-synthesis of hydroxylated magnesium fluorides

$$Mg(OCH_3)_2 + 2HF / water \longrightarrow ????$$

<u>HF-concentration:</u>
100% HF (solved in MeOH), 87% HF, 71% HF, 57% HF and 40% HF

$$-Mg\text{-}OR + H\text{-}OH \longrightarrow -Mg\text{-}OH + HOR$$

$$-Mg\text{-}OR + H\text{-}F \longrightarrow -Mg\text{-}F + HOR$$

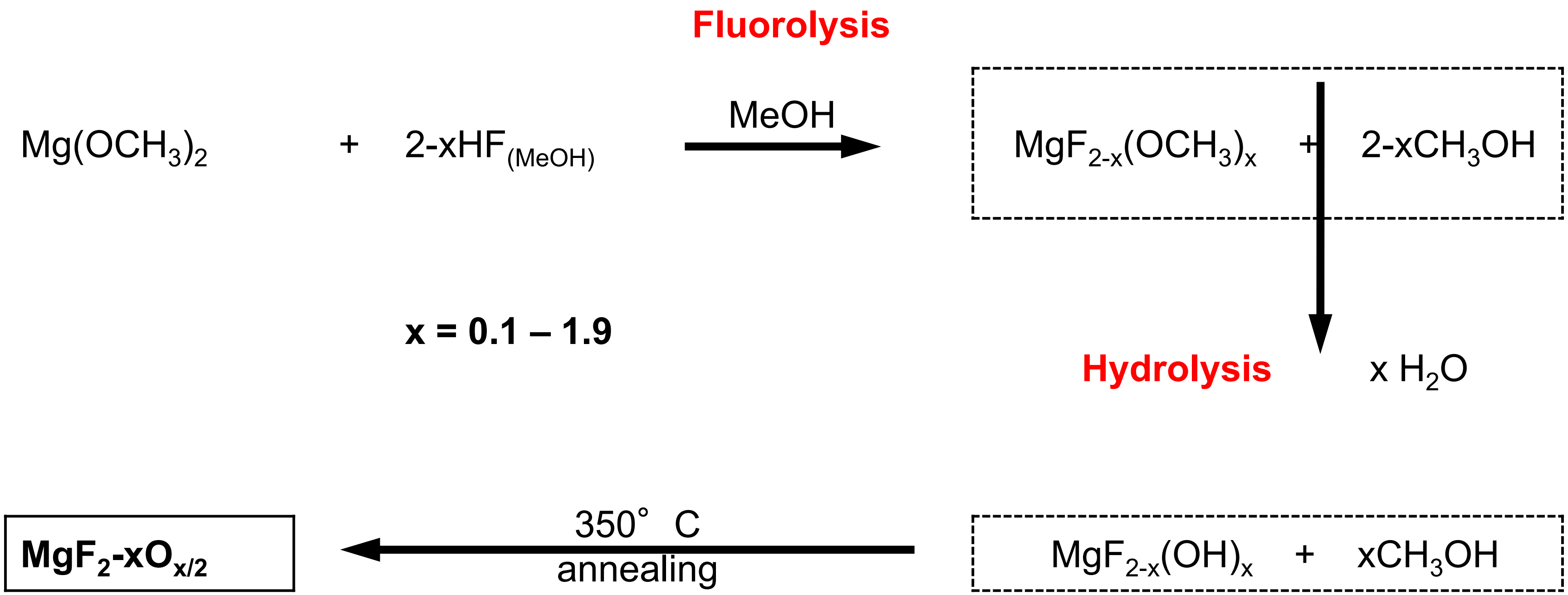
$$Mg(OCH_3)_2 + 2\,HF + (x+y)\,H_20$$

$$\downarrow$$

$$\mathbf{MgF_{2\text{-}x}(OH)_x} + 2\,CH_3OH + x\,HF + y\,H_2O$$

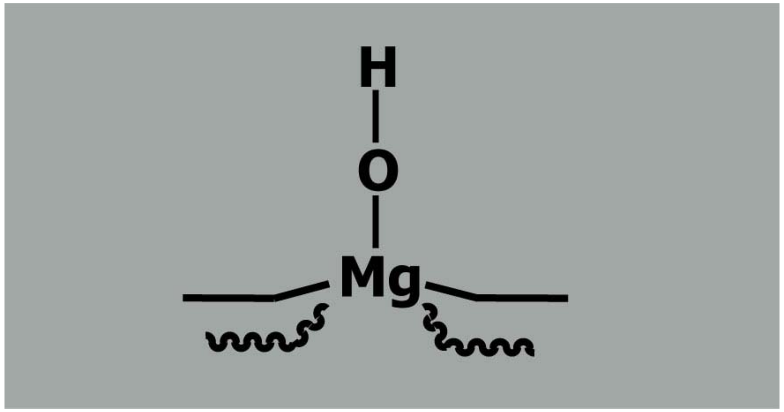
Review: *J Fluorine Chem* **2007,** *128* (4), E. Kemnitz in *Functionalized Inorganic Fluorides*, Ed. Alain Tressaud, Publishers Wiley 2010, Chapter I: p.1-35; Review *Dalton Trans.*, **9** (2008) 1117 – 1127 , Review: *Catalysis Science & Technology* **2015,** *5*, 786-806;

Sol-gel-synthesis of magnesium (hydr)oxo fluorides



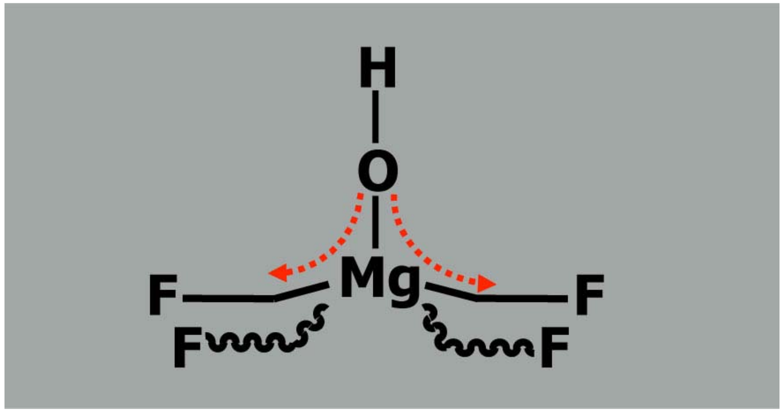
Review: *J Fluorine Chem* **2007,** *128* (4), E. Kemnitz in *Functionalized Inorganic Fluorides*, Ed. Alain Tressaud, Publishers Wiley 2010, Chapter I: p.1-35; Review *Dalton Trans.*, **9** (2008) 1117 – 1127 , Review: *Catalysis Science & Technology* **2015,** *5*, 786-806;

Brønsted-acidic Mg-OH-units



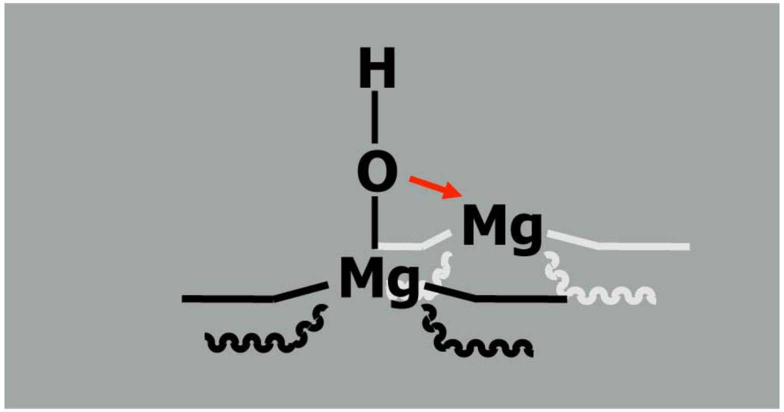
Can we rationalize Brønsted acidity of a Mg-OH group?

Brønsted-acidic Mg-OH-units



- elektronegative fluoro ligands → stronger Lewis-acidic Mg-sites

Brønsted-acidic Mg-OH-units



- elektronegative fluoro ligands → stronger Lewis-acidic Mg-sites
- flexible „dangling“ OH-groups

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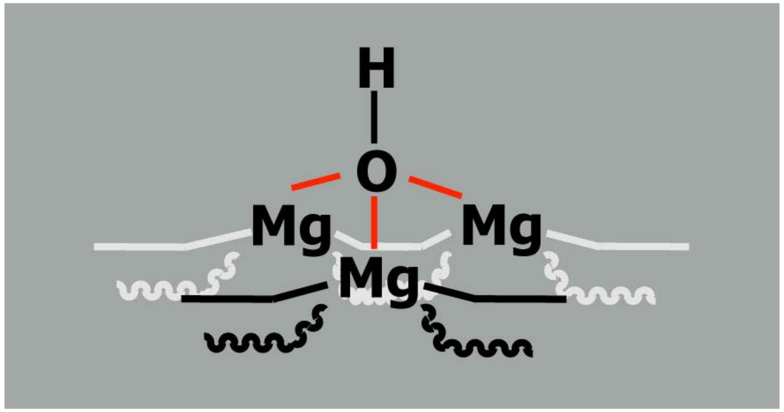
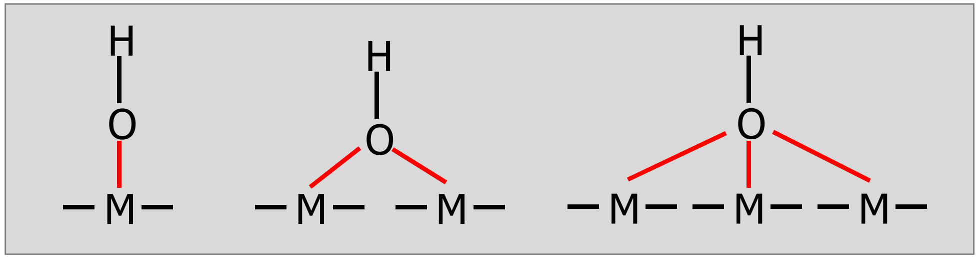
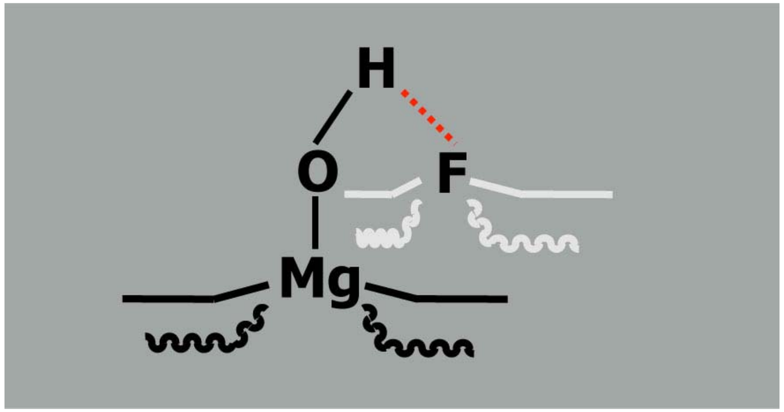


- elektronegative fluoro ligands → stronger Lewis-acidic Mg-sites
- flexible „dangling“ OH-groups
- bridging OH-groups

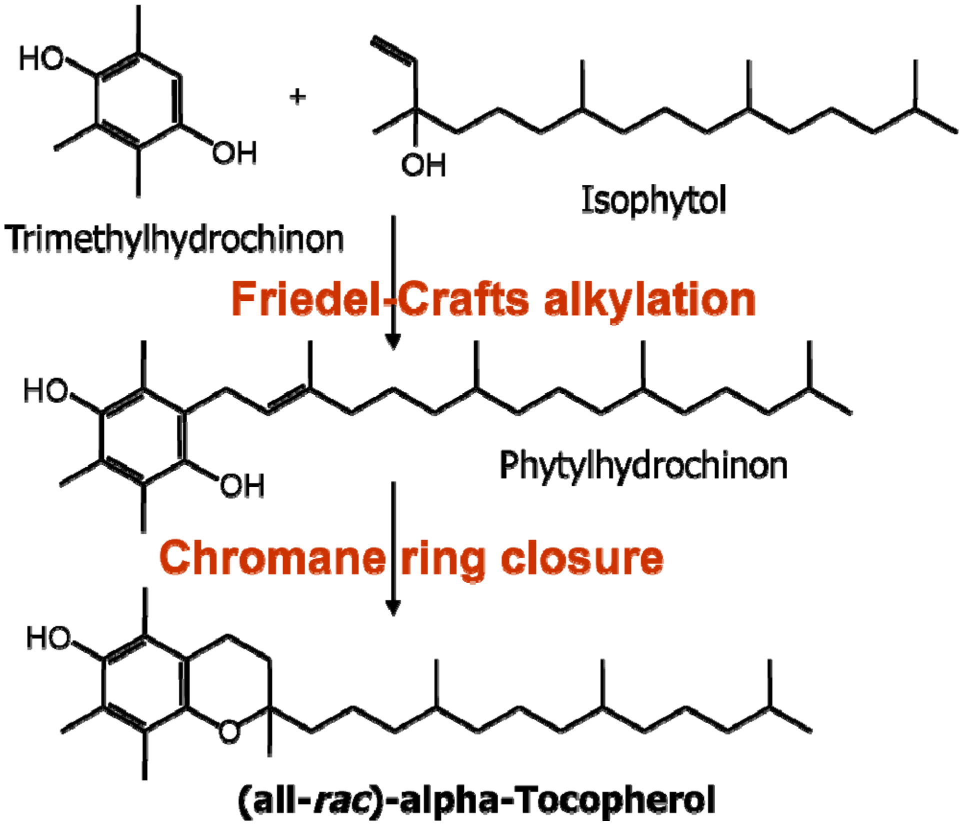


Brønsted-acidic Mg-OH-units



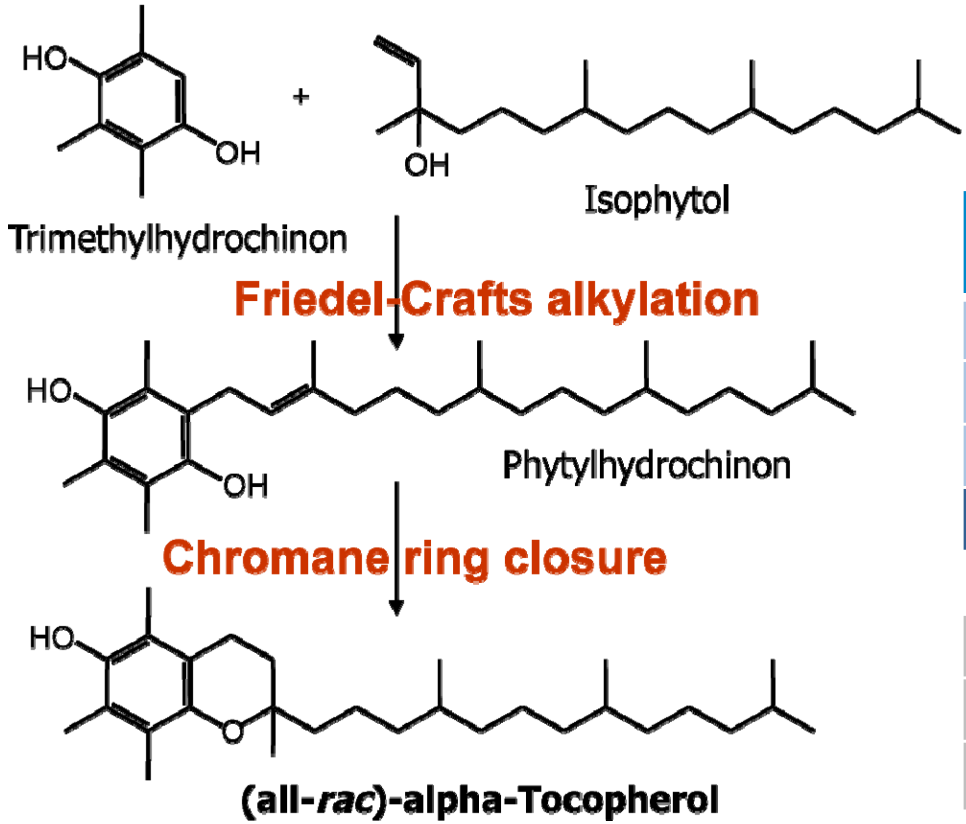
- elektronegative fluoro ligands → stronger Lewis-acidic Mg-sites
- flexible „dangling“ OH-groups
- bridging OH-groups
- formation of hydrogen bonds???

Vitamin E synthesis



Chem. Eur. J. **2008**, 14, 11488 & *Adv. Synth. Catal.* **2008**, 350, 2517

Vitamin E synthesis



catalyst	IP/cat. molar rat.*	time min	selectivity to Tocopherol
MgF_2-40	119	300	76,3
MgF_2-57	76	300	82,6
MgF_2-71	123	300	87,0
MgF_2-71	123	180	> 99,9
MgF_2-87	60	360	0
MgF_2-100	37	360	0
MgF_2-K	n.b.	1200	0

Conversion of IP (X = 100 %).
*ratio calculated based on NH_3-TPD-results.

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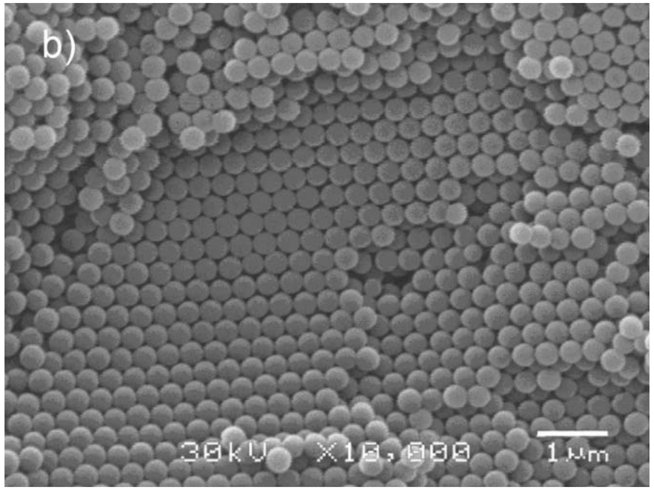
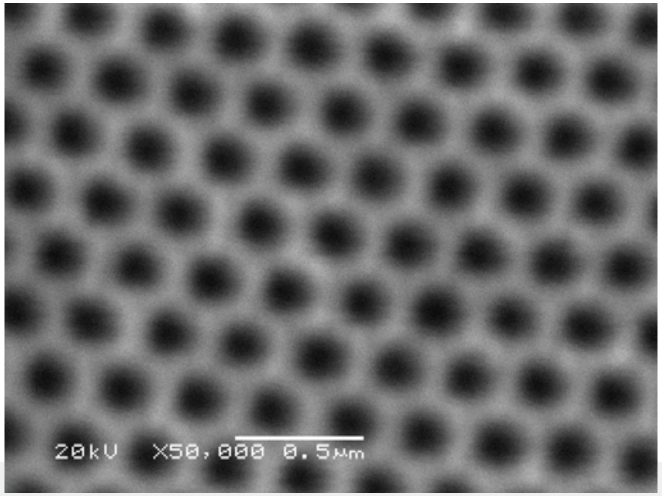
Inverse Opale für Photonic/ Katalyse

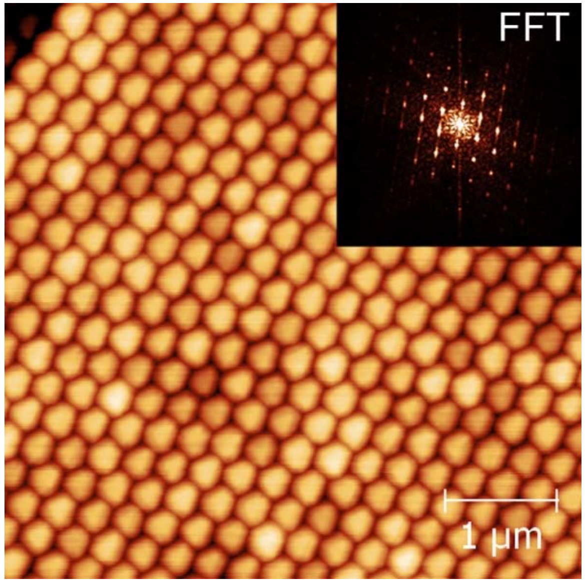
PMMA kolloidaler Kristall
Partikeldurchmesser ca.400 nm

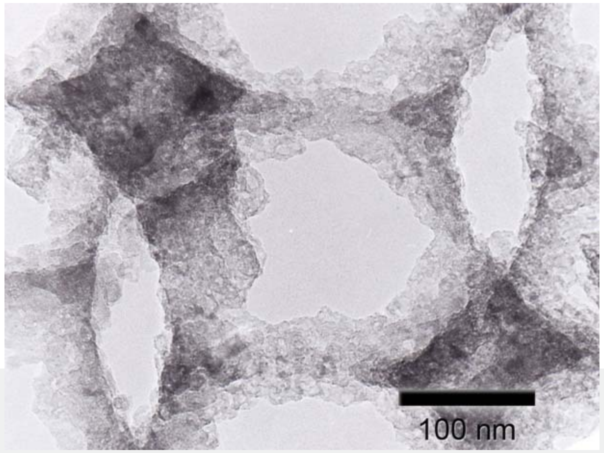




SEM image of an MgF_2 inverse opal film at 50.000× magnification

AFM-Bild eines kolloidalen Kristallfilms von PMMA-Kugeln auf Glass (Partikeldurch-messer 308 nm) und 2D FFT-Bild





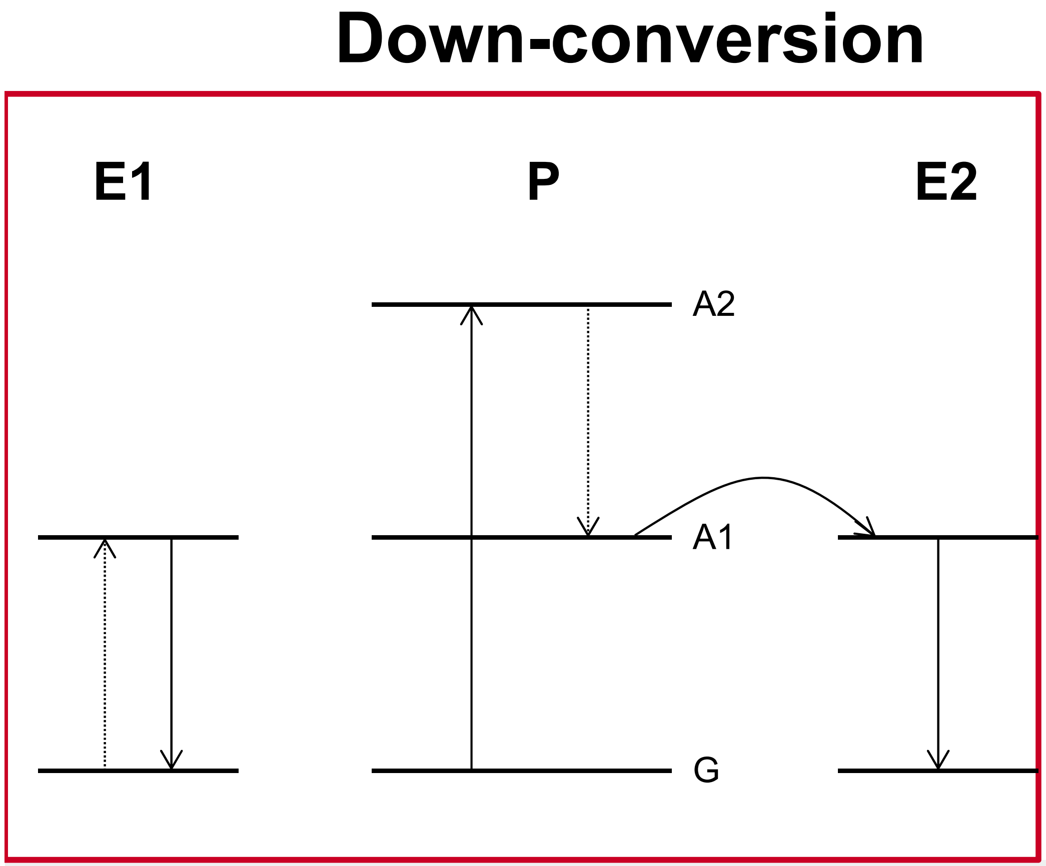
TEM image of an MgF_2 inverse opal.

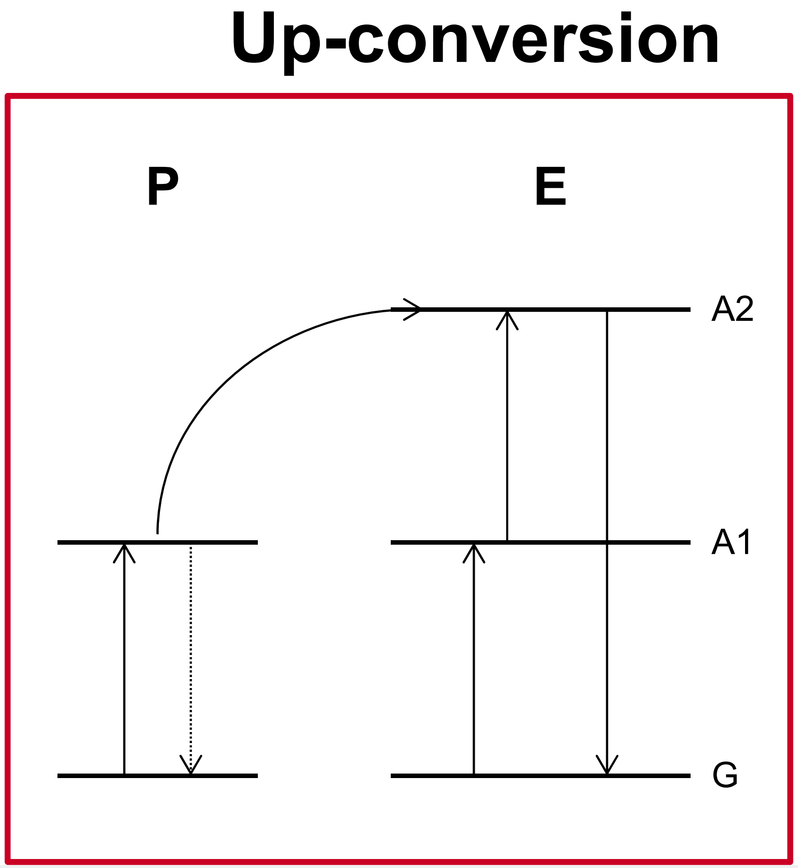
1. The *fluorolytic* sol-gel-synthesis of metal fluorides
   - the principle of the *fluorolytic* Sol-Gel-synthesis
2. Mechanism/reaction path
   - chemical aspects – AlF_3
   - synthesis parameter
3. **Applications: up- and down-conversion**
4. Summary

Up- and down conversion

Mechanism of Luminescence for rare earth metals

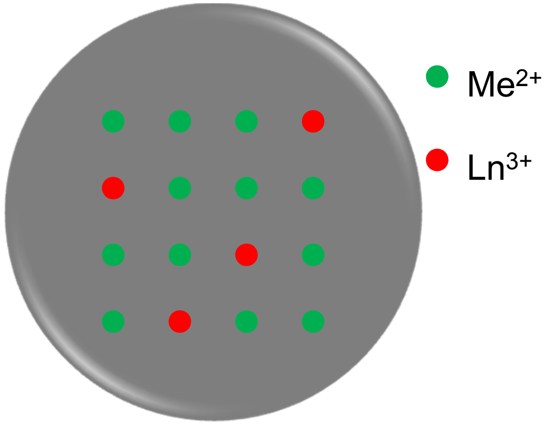
- Non-linear optical processes





Up- and down conversion

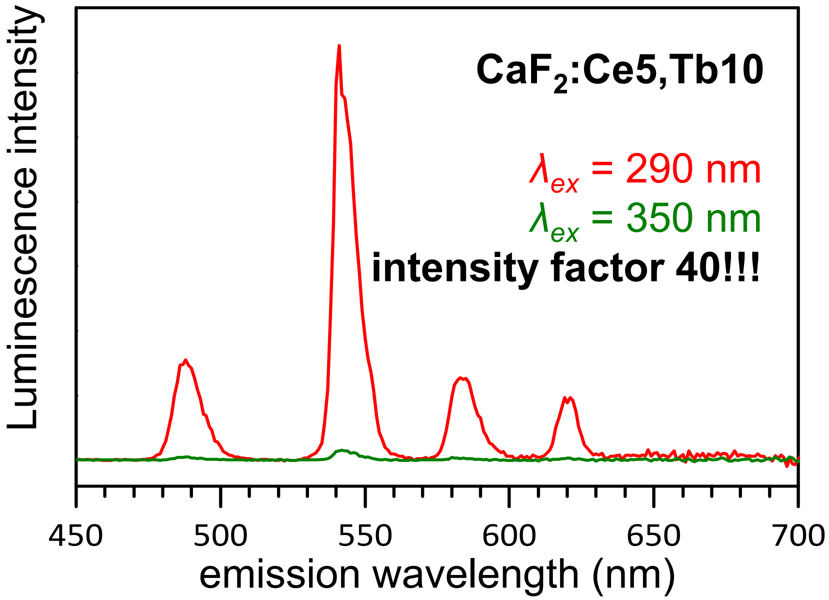
Why MF_2 (M=Ca, Sr, Ba) as matrix for REM-doping?

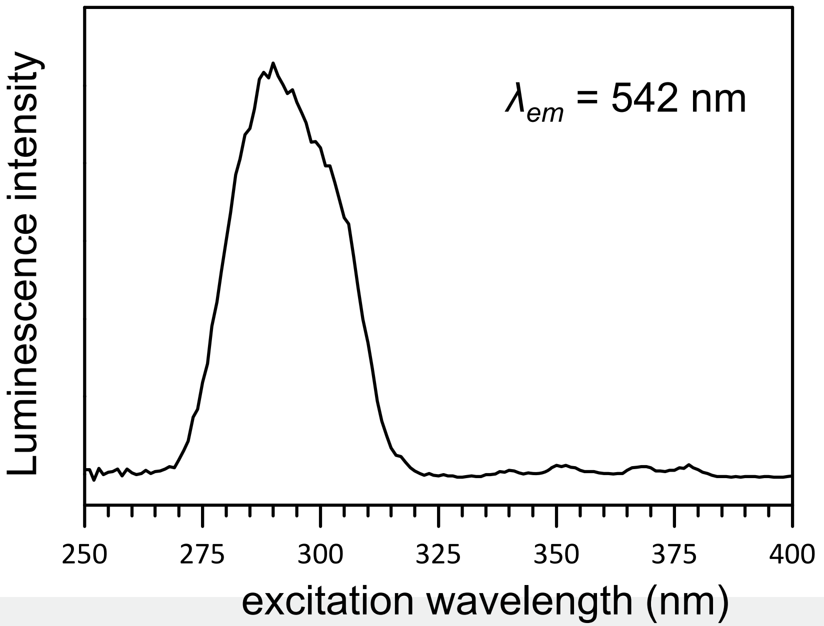


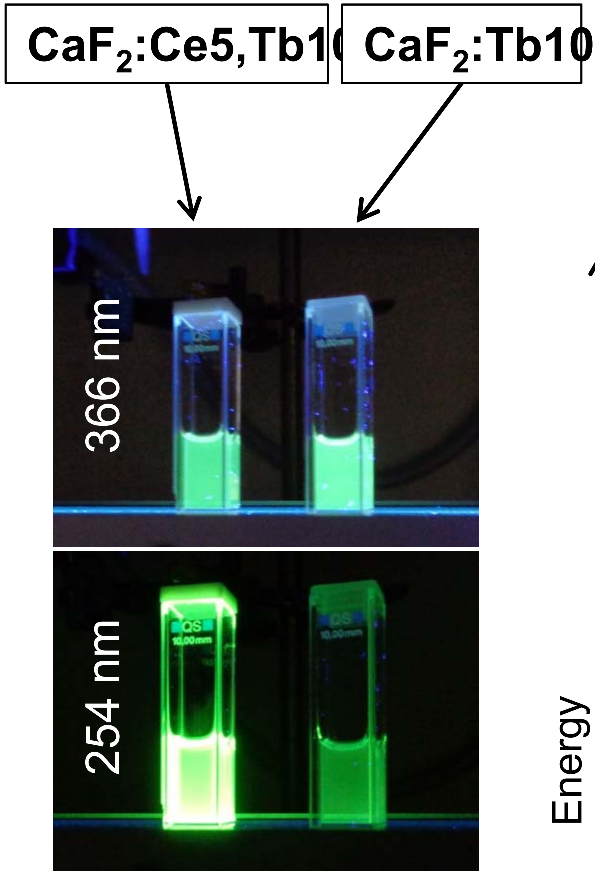
- Low phonon energy [1]
  1. CaF_2 456 cm^{-1}
  2. SrF_2 366 cm^{-1}
  3. BaF_2 319 cm^{-1}
- Long life times of exited states
- Doped CaF_2-phases exhibit high hardnes [2]
- Ionen conductivity increases with ionic radia
  1. $Ca^{2+} < Sr^{2+} < Ba^{2+}$ und $Lu^{3+} <\ldots< La^{3+}$
  2. Application in fluoride-ion-batteries [3]
  3. Application in fluor storage $Me_{1-x}Ln_x^{III}F_{2+x} + \frac{x}{2}F_2 \rightleftharpoons Me_{1-x}Ln_x^{IV}F_{2+2x}$

[1] M. Haase, H. Schäfer, *Angew Chem Int Edit* ***2011, 50, 5808-5829.;*** [2] M. Y. Gryaznov et al. *Crystallogr Rep* ***2012, 57, 144-150;*** [3] C. Rongeat et al. J. Phys.Chem. C **2013, 117, 4943-4950.**

Energy transfer – a simple example $Ce^{3+} \rightarrow Tb^{3+}$





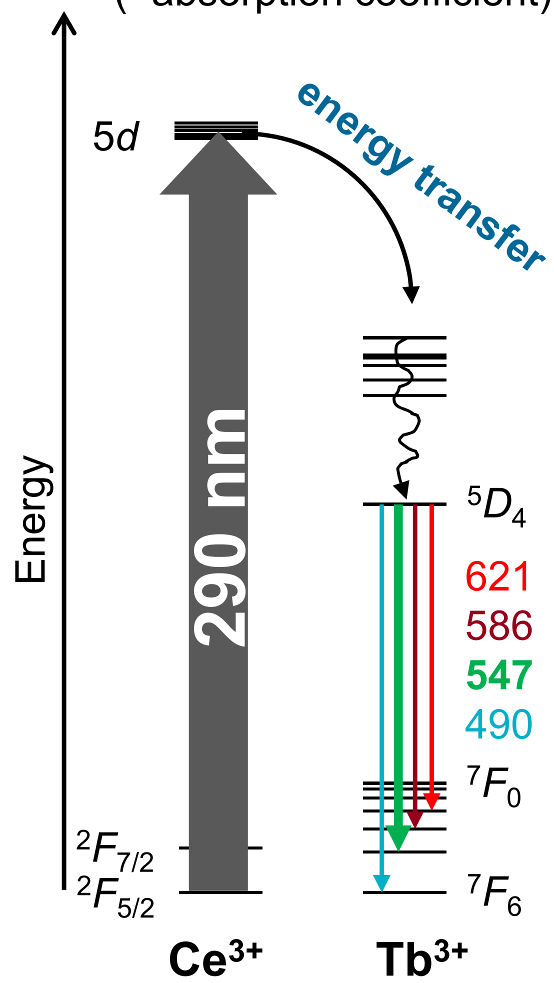


0.2 M nanoparticles in MeOH

d-f **transition is allowed**

↓

high oscillator strength (=absorption coefficient)

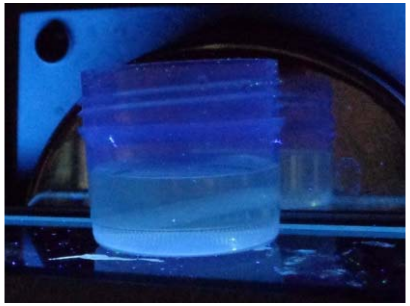


Energy transfer – influence of the matrix

λ_{ex} = 254 nm

0.16 M
Ca(OLac)$_2$
0.02 M Ce(OAc)$_3$
0.02 M Tb(OAc)$_3$

solution



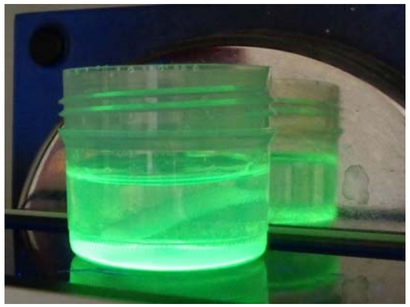
d(Ce^{3+}-Tb^{3+}) ≈ 20 Å → no energy transfer

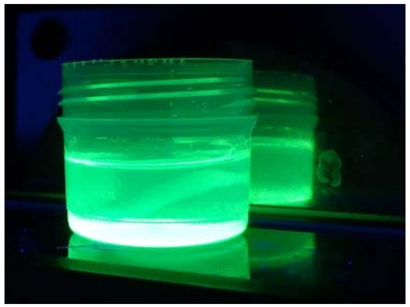
+2.2 eq HF

λ_{ex} = 254 nm

0.2 M
$Ca_{0.8}Ce_{0.1}Tb_{0.1}F_{2.2}$

nanoparticles





d(Ce^{3+}-Tb^{3+}) ≈ 4 Å → effective energy transfer

Energy transfer between lanthanoides

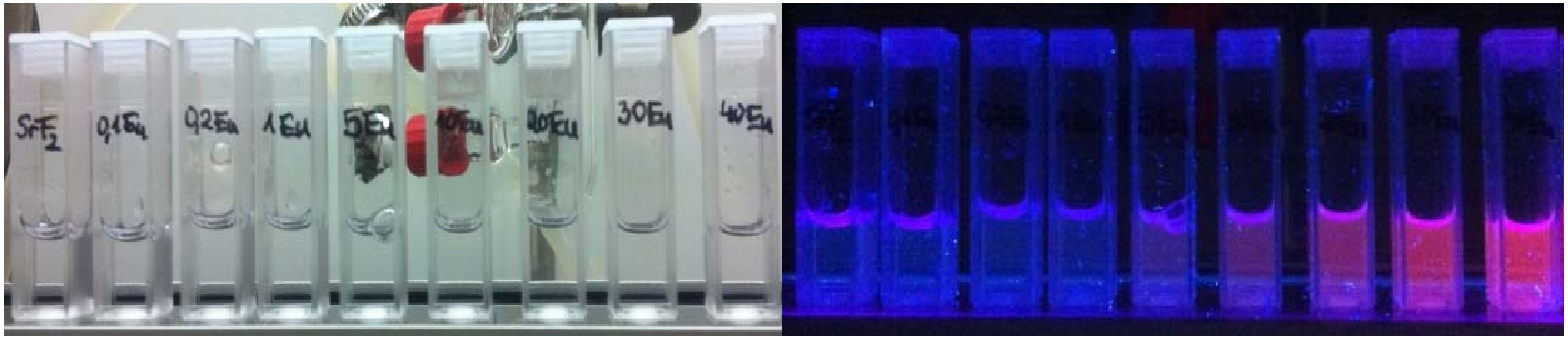
- ions must be in close proximity
- works only in a host matrix
- very effective in a fluoride matrix
- in liquid state only with nanoparticles

Effect of doping rate

Doping series from SrF_2 till SrF_2:Eu40

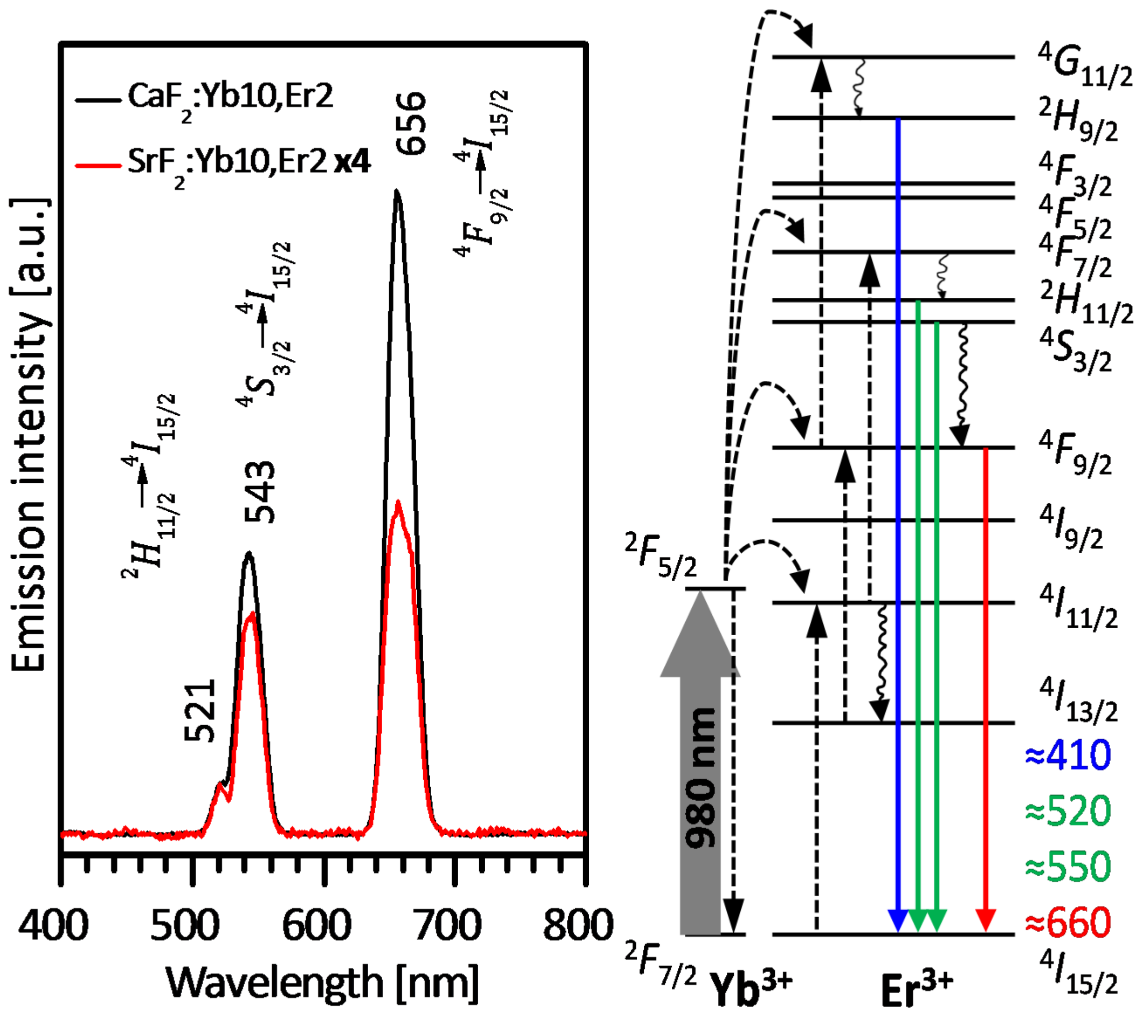
Ex.: visible light

Ex.: 393 nm

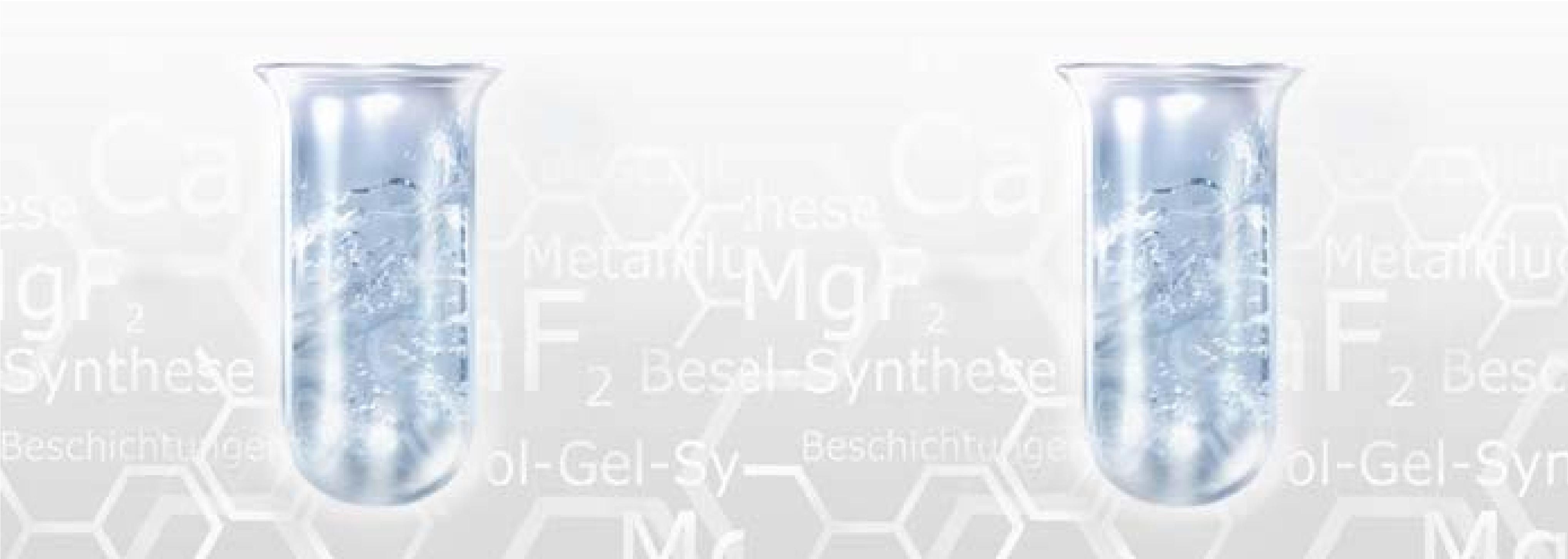


- Transparent colloidal solutions till 40 mol% of Eu^{3+} doping
- Linear increase of intensity till 10 mol% Eu^{3+}
- No quenching of luminescence increase till 40 mol% Eu^{3+}

Photon up-conversion Yb^{3+}-Er^{3+}



Excitation with continuous 980 nm laser (1 W). Right: schematic representation of the energy transfer between Yb^{3+} and Er^{3+}.



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