

Sol–gel-fluorination synthesis of amorphous magnesium fluoride

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Dedicated to Professor Hans Georg von Schnering on occasion of his 75th birthday

Abstract

The sol–gel fluorination process is discussed for the reaction of magnesium alkoxides with HF in non-aqueous solvents to give X-ray amorphous nano-sized magnesium fluoride with high surface areas in the range of 150–350 m²/g (HS-MgF₂). The H2 type hysteresis of nitrogen adsorption–desorption BET-isotherms is indicative for mesoporous solids. A highly distorted structure causes quite high Lewis acidity, shown by NH₃ temperature-programmed desorption (NH₃-TPD) and catalytic test reactions. XPS data of amorphous and conventionally crystalline MgF₂ are compared, both show octahedral coordination at the metal site. Thermal analysis, F-MAS NMR- and IR-spectroscopy give information on composition and structure of the precursor intermediate as well as of the final metal fluoride. The preparation of complex fluorides, M⁺MgF₃⁻, by the sol–gel route is reported. From the magnesium fluoride gel of the above process thin films for optical application are obtained by, e.g., spin coating.

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1. Introduction

Sol–gel synthesis of metal fluorides is rarely reported in literature, describing a methodology combined of a first step comprising hydrous metal oxide synthesis and a second step comprising treatment with hydrogen fluoride or a hydrolysable covalent fluoride to convert the hydrous oxide to the fluoride [1a–c]. This arrangement of reactions is obviously non-typical to a sol–gel methodology and the designation as such is misleading. Other syntheses started from magnesium alkoxide in non-aqueous solvent, in alcohol, which was, however, reacted with aqueous hydrofluoric acid [1d,e]. According to our experiences, the presence of water results inevitably in formation of magnesium oxyfluoride or mixtures of oxide and fluoride leading to markedly higher surface area as reported in [1f].

Here, we report on a newly discovered genuine sol–gel fluorination reaction where metal fluoride gels are inherent particularities of the process and decisive for unexpected properties and structures [2]. The procedure is similar to the well-known sol–gel reaction of metal oxide preparation. Starting from metal organic derivatives as, e.g., metal alkoxides, and non-aqueous HF the reaction provides a viable and low-cost method for high surface area metal fluorides with high Lewis acidity as, for instance, in case of AlF₃ [3] as well as for thin film coating for optical materials as it is shown for MgF₂. Technological achievements are projected as the latter may result in a strong growth in the photonic market overcoming current technological barriers [1a]. The characteristics of the process consist in generating amorphous highly distorted metal fluorides with unusually high surface area caused by a mesoporous morphology and surface texture. The chemical inertness and weak to moderate Lewis acidity of MgF₂ make it useful as support and/or host in mixed metal fluoride catalyst systems [4]. Low refractive indices and wide ranges

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of light transmission make some of the metal fluorides preferred candidates in optical as well as protective coating forming fluoride glasses.

2. Experimental

2.1. Syntheses

HS-MgF₂: The synthesis procedure followed basically that given in [2]. Mg turnings (99.98%, Aldrich) were reacted with excessive, thoroughly dried CH₃OH under reflux conditions. The Mg(OMe)₂·2MeOH was not separated but after cooling reacted further under stirring with stoichiometric amounts of HF dissolved in MeOH or ether. A clear gel or a sol, the viscosity of which depends on concentration was formed. Low concentrated sols of low viscosity were used for coating experiments. The wet viscous gel was dried under vacuum at temperatures up to 70 °C yielding a white solid containing some organics, a result which corresponds to that observed in course of HS-AlF₃ synthesis [2a], although in the latter system the remaining organics measured as carbon content was substantially higher. By further fluorination with N₂ diluted gaseous HF or CCl₂F₂ or CHClF₂ at temperatures up to 250 °C in a tube-type flow reactor HS-MgF₂ was obtained as fine white powder.

Mg(OH,F)-materials: The preparation is a two-step process described in [5]. Magnesium hydroxofluorides with F/Mg molar ratios between 0 and 2 were synthesized from, e.g., 0.2 mol magnesium methoxide in dry methanol and then fluorinated with less than two equivalents of a HF/Et₂O solution. The remaining –OCH₃ groups (Eq. (1), product I) were hydrolysed by addition of the equivalent amount of water to give the magnesium hydroxofluoride of the general formula Mg(OH)_{2-x}F_x.

Complex magnesium fluorides: 30 mmol of each magnesium methoxide and potassium methoxide in 30 ml methanol were mixed and reacted with 0.1 mol of HF/MeOH at room temperature to give KMgF₃ after drying under vacuum. Similar reactions were carried out with varying the K:Mg ratio between 1 and 3. The amorphous or low crystalline material was calcined at 300 °C under inert carrier gas.

MgF₂ coatings: Thoroughly purified and dried small plates of SiO₂ or Si were placed on a spin-coater (KW-4A, Chemat), covered with low viscous sols of MgF₂ in MeOH, and spun for 40 s at 5000 rpm. After drying at 100 °C the coating was repeated or the layer was immediately calcined at 300 or 500 °C.

2.2. Characterisation

X-ray powder diffraction (XRD) characterisation was carried out on a XRD-7 Seiffert-FPM with Cu-K α radiation.

Surface area of the catalysts was determined using N₂ adsorption by means of a Micromeritics ASAP 2000

instrument at 77 K. Before each measurement, the samples were degassed at 4×10^{-3} Torr and 150 °C for 10 h. The surface area was calculated according to the BET method.

Temperature-programmed desorption of ammonia (NH₃-TPD) was employed to determine the strength of acid sites and its distribution. The sample (about 0.2 g) was first heated under nitrogen up to 300 °C, then at 120 °C exposed to NH₃. After flushing the excess NH₃ at 120 °C with N₂ for 1 h and cooling to 80 °C the TPD programme was started (10°/min up to 500 °C, keeping for 30 min). Desorbed NH₃ was monitored continuously via IR spectroscopy (FT-IR System 2000, Perkin-Elmer).

Highly resolved X-ray photoelectron spectra (XPS) and X-ray excited Auger electron spectra (XAES) were acquired using a VG Scientific ESCALAB 200X electron spectrometer as described in [6] with non-monochromatized Al K α excitation ($h\nu = 1486.6$ eV) operated at 15 kV and 20 mA and in CAE 10 mode. Before recording the spectra the samples were stored overnight in the VG Extended PrepLock chamber of the ESCALAB in a vacuum better than 10^{-6} mbar in order to degas. During analysis the vacuum in the spectrometer was better than 10^{-8} mbar. Binding or kinetic energy data were referenced to the aliphatic C 1s peak at 284.8 eV.

Thermal analysis was done with a NETZSCH thermoanalyser STA 409 C Skimmer[®] system equipped with a quadrupole mass spectrometer BALZERS QMG 421 as described in [2a] recording the thermoanalytical curves (T, TG, DTA) together with the ionic current (IC) curves in the multiple ion detection (MID) mode.

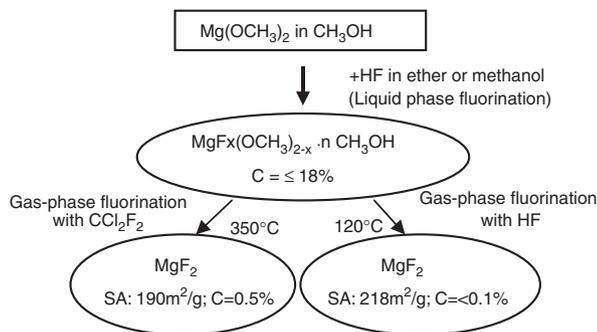
Solid-state F MAS NMR experiments were done on a Bruker AVANCE 400 spectrometer using a 2.5 mm magic angle spinning probe. Spectra were measured at 376.5 MHz with ultrafast spinning of 30–36 kHz. Chemical shifts were referenced to CFCl₃.

FT-IR measurements were done of wafers of KBr and CsI. Spectra were recorded between 200 and 4000 cm⁻¹ on a Perkin-Elmer 2000 spectrometer.

3. Results and discussion

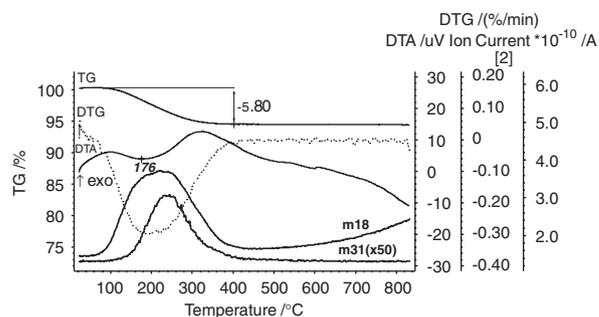
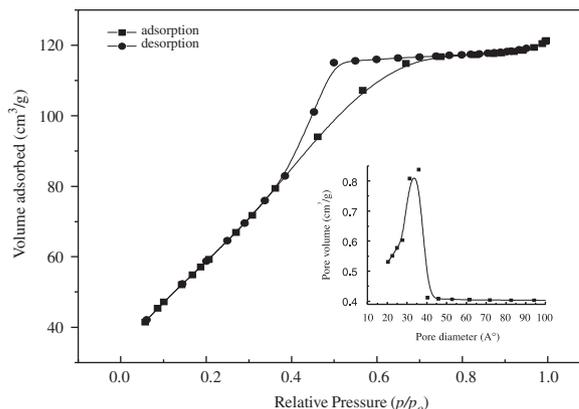
3.1. Synthesis and reaction mechanism

The sol-gel fluorination reaction results in complex development of a polymer-like network of gel structures, essentially determined by the strength of formed H-bonding and of van der Waals interaction forces, causing also formation of solvates by Mg...O-bonding. The latter depends on the partial charge at the metal. Therefore, in this respect sol-gel reactions and gel stability are very sensitive to solvent properties such as dielectric constant DK, ability to hydrogen bonding, polarity and geometric size of the molecule. Generally, the state of the gel is irreversible and permanent. The fresh wet gel morphology is weak and cannot survive harsh drying treatments at elevated temperatures leading to a

Scheme 2. HS-MgF₂ syntheses procedures.

because of incomplete fluorination. Although the nucleophilic substitution reaction is thermodynamically favoured, the reaction is kinetically controlled because of the gel viscosity (see also [2a]). Obviously, this does not hold for very diluted systems of low viscosity as used for thin film preparation. The presence of alkoxy groups or solvent solvates is indicated by the carbon content in elemental analysis and by thermal analysis as well as by spectroscopic methods. The carbon content of the “precursor” compound, i.e. the dried gel, is in the range of 5–15% depending on reaction conditions and the alcohol used. However, MgF₂ obtained from very diluted sol, as used for thin films, by evaporation the solvent had a carbon content corresponding to the limit of determination, i.e., ≤0.5% C. Mild post-fluorination of the product in reaction (1) with CCl₂F₂ replaces the methoxy groups by fluorine preserving the distorted structure. Alternatively, post-fluorination of the precursor compound with HF at lower temperatures preserves a high surface area of the fluoride of, e.g., 218 m²/g and a strongly reduced carbon content of <0.1% (Scheme 2). After post-fluorination HS-MgF₂ is not longer a gel and can not be transformed into a gel.

The principal reaction route to magnesium fluoride according to Eq. (1) and Schemes 1 and 2 is also confirmed by DTG/MS. The major weight loss to be found in the TG curve (not shown) of a precursor of HS-MgF₂ is 18.8% caused by the liberated methanol. At elevated temperatures remaining methoxy groups are decomposed releasing ethylene (*m/z* 27; C₂H₃⁺) according to the well-known thermal decomposition pathway [8]. At 392 °C the exothermic crystallisation point occurs revealing the transition of amorphous to crystalline material. Post-fluorination of the precursor results in HS-MgF₂, the thermal analysis of which is shown in Fig. 1. The weight loss is only 5.8% mainly due to loss of adsorbed water identified in MS by its mass number of 18. The DTG peak of the water loss expectedly corresponds with an endothermic peak in the DTA curve. The loss of methanol is minor as shown by the mass number *m/z* 31(CH₃O⁺) in correspondence with the carbon content of <0.1%. Besides magnesium methoxide as starting material, also the ethoxide and *n*-butoxide were used with principally similar results.

Fig. 1. TA/MS curves of HS-MgF₂ with the IC curves for *m/z* 18 (H₂O⁺) and *m/z* 31 (CH₃O⁺).Fig. 2. BET-N₂ adsorption–desorption isotherms and pore size distribution (insert) of a HS-MgF₂ of 218 m²/g surface area.

3.2. Morphology, structural and surface properties

Morphology and texture as well as physico-chemical properties including surface behaviour of crystalline MgF₂ are strikingly different from that of amorphous HS-MgF₂ obtained from the sol–gel fluorination. SEM micrographs of the amorphous material present a porous material with a high total pore volume, while conventionally prepared fluoride shows a clear-cut morphology of well-sized crystallites [6]. The porous structure results in unusually high surface area ranging from 150 to 350 m²/g, compared with expected surface areas of crystalline MgF₂ in the range of 1–44 m²/g [10]. The commercially available crystalline magnesium fluoride (Aldrich) has a surface area of 0.4 m²/g. Nitrogen adsorption–desorption in Fig. 2 exhibit a broad hysteresis typical of adsorbents possessing mesopores. The shape of the hysteresis loop and the steep desorption branch classify it as of the H2 type, associated with a more complex bottle neck pore structure in which network effects are of importance [11]. The relative uniformity of pores is shown with the distribution curve inserted in Fig. 2.

The octahedral coordination of magnesium by fluorine as known from X-ray structure determination of crystalline MgF₂ holds also for the X-ray amorphous sol–gel fluoride. From XPS data presented as chemical

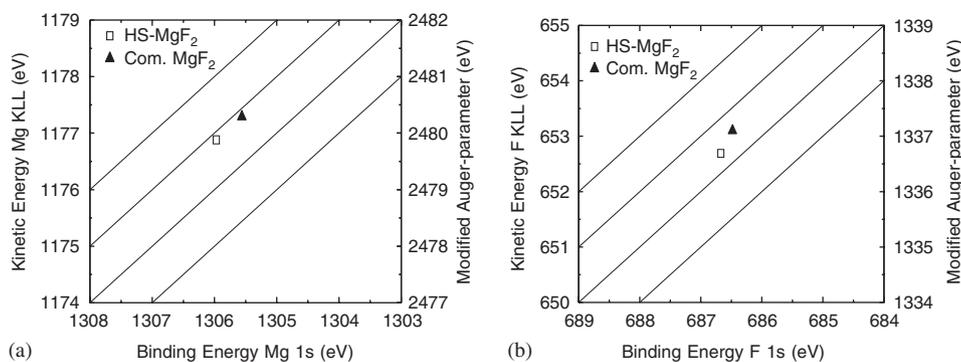


Fig. 3. (a) Chemical state plot for Mg of MgF_2 . (b) Chemical state plot for F of MgF_2 .

state plots in Figs. 3a and b the structural similarity of the two is evident, because crystalline and amorphous HS- MgF_2 are positioned in the same grid of the graph. Nevertheless, the binding energies (BE) and modified Auger parameters (MAP = BE + KE = BE of core levels + kinetic energies of Auger electrons) of the Mg 1s and F 1s are different for the two fluorides. The BE of the Mg 1s orbital of 1306.0 eV of the amorphous sample is shifted to little higher values, indicative for a higher positive charge, i.e., increased Lewis acidity, at the magnesium.

3.2.1. F MAS NMR spectra

Solid-state MAS NMR is the preferred analytical tool for amorphous material, of which X-ray data are mostly not available for structural elucidation. The amorphous HS- MgF_2 provides in F MAS spectra a symmetric unresolved peak of Lorentzian line shape with a chemical shift of 198.7 ppm. The samples were rotated at 30–36 kHz resulting in strong line narrowing. Considering the chemical shift parameter there is no remarkable difference to that of crystalline MgF_2 with 198.5 ppm, but indication for identical coordination numbers. Otherwise, the line width of the two peaks is different. Full-width at half-height is 2210 kHz for HS- MgF_2 and 1830 kHz for MgF_2 *cryst.* The larger line width results from structural distortion and the related anisotropy of shielding. Quite differently, the substitution of fluorine by other ligands, e.g., OH groups in magnesium hydroxofluorides of the Section 3.5, shifts the resonance to the lower field [5].

3.2.2. IR spectra

Because of the octahedral coordination of magnesium by fluorine one has to expect O_h symmetry for an ordered structure with two infrared active modes. In HS- MgF_2 the Mg–F stretch ν_1 is at 450 cm^{-1} and the bending vibration δ at 260 cm^{-1} . An additional, weaker band occurs at 400 cm^{-1} . For the amorphous HS- MgF_2 the bands are significantly broader than those of the crystalline MgF_2 . The structural disorder of the compound corresponds with the broadness of absorption bands. These result from the superimposition of all the existing structural deviations.

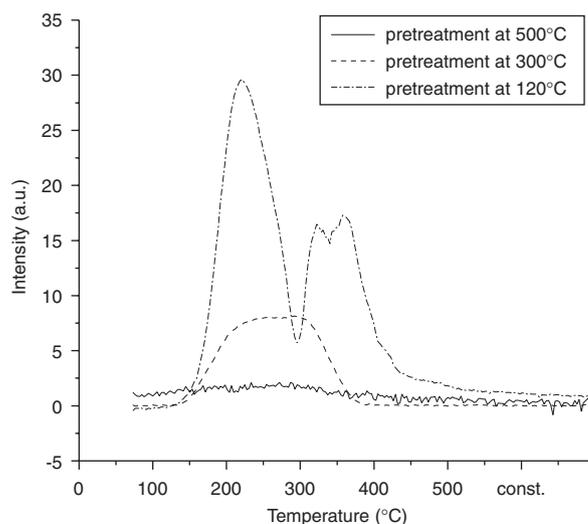


Fig. 4. NH_3 -TPD of HS- MgF_2 .

In the precursor state of HS- MgF_2 characteristic bands of the remaining organic alkoxy groups were found. These are in the wave number range at $1050\text{--}1130\text{ cm}^{-1}$ assigned to the C–O stretching mode and for C–H stretching at $2750\text{--}3100\text{ cm}^{-1}$.

3.2.3. Lewis acidity

According to Pearsons HSAB concept of hard and soft acids and bases, Mg^{2+} ion is defined as a hard, i.e., strong Lewis acid, possessing unoccupied orbitals that can accept an electron pair from a donor molecule. Actually, highly ordered crystalline MgF_2 exhibits only little Lewis acidity because of the complete shielding of the acidic metal site by fluorine ligands in an octahedral lattice. Such weak surface acidity is reported because of pyridine adsorption and of moderate catalytic activity in dehydration reaction of *i*-propanol at $320\text{ }^\circ\text{C}$ [12].

If the magnesium fluoride becomes X-ray amorphous, that is, lattice distortions occur with deviating –Mg–F–Mg– angle from 180° and probably metal coordination numbers lower than 6 due to structure defects, then the acidic metal site may be accessible for basic reactants. This agrees well with the fact we have observed in the aluminium fluoride system [2,13].

To provide evidence for Lewis acidity a catalytic test reaction and NH_3 -TPD were performed, the results of which are shown in Fig. 4. The desorption peaks give information on the strength and number of acidic sites of the solid. The desorption behaviour of HS- MgF_2 depends strongly on the temperature of its pre-treatment. The 500°C pre-treated sample did not show any NH_3 desorption because at this temperature the sample became crystalline and the ordered MgF_2 structure is practically not Lewis acidic. In full contrast, the dotted line curves, pre-treatment at 120 and 300°C , show desorption of NH_3 because at these temperatures the structural disorder of the amorphous MgF_2 remains and the metal site is accessible for the base as discussed for HS- AlF_3 [13]. As expected, strongest sites were found at 120°C , i.e., the lowest temperature of pre-treatment. The bimodal curve with two maxima points to Lewis acidic sites of different strengths. In going from 120 to 300°C pre-treatment, the structure of HS- MgF_2 is partly affected, and especially the strongest sites disappeared, because the temperature is already near the phase transition temperature, which is according to our thermal analysis investigations at 392°C .

As catalytic test the dismutation of CHClF_2 , a reaction known to depend on Lewis acidic catalyst was monitored with increasing temperature. At 300°C 3%, at 350°C a 60% conversion of CHClF_2 over HS- MgF_2 could be observed, which is indicative for weak to moderate Lewis acidity. For comparison, the strong Lewis acidic solid catalyst HS- AlF_3 yields a 96% conversion at only 250°C . However, the test reaction needs rather high temperatures at which HS- MgF_2 becomes already partially deactivated. Reactions proceeding at distinctly lower temperatures should be much more efficiently catalysed by HS- MgF_2 . The Lewis acidity of HS- MgF_2 is further evidenced by the observed formation of $[\text{MgF}_3]^-$ entities, i.e., of complex magnesium fluorides, acting as a weak F^- ion acceptor according to Eq. (3):



3.3. Mixed magnesium methoxide fluoride and magnesium hydroxofluoride

Magnesium hydroxide as well as its oxide are basic materials. Especially under the aspect of their use as catalyst [5] a tuning of the acidic–basic behaviour is of interest. This can be done by creating magnesium oxide/hydroxide fluorides of tailored Mg-to-F ratio for which the sol/gel synthesis route provides excellent preconditions. The only one structurally known magnesium hydroxofluoride, $\text{Mg}(\text{OH})\text{F}$, is obtained by hydrothermal synthesis, the structure of which was solved by powder methods from X-ray data [14]. It exists as intermediate brucite sellait phase between $\text{Mg}(\text{OH})_2$ and MgF_2 of $Pnma$ space group.

The sol–gel fluorination method opens a simple route to more differently substituted hydroxofluorides of the above type. Adding under-stoichiometric amounts of HF to

Table 1
XPS results of MgF_2 and different $\text{Mg}(\text{OH})_{2-x}\text{F}_x$

Sample	BE of Mg 1s (eV)
MgF_2 (sol–gel, amorphous)	1306.0
MgF_2 (comm., crystalline)	1305.6
$\text{Mg}(\text{OH})_{0.4}\text{F}_{1.6}$	1304.0
$\text{Mg}(\text{OH})_{0.8}\text{F}_{1.2}$	1303.0
$\text{Mg}(\text{OH})_{1.2}\text{F}_{0.8}$	1302.8
$\text{Mg}(\text{OH})_{1.6}\text{F}_{0.4}$	1302.6

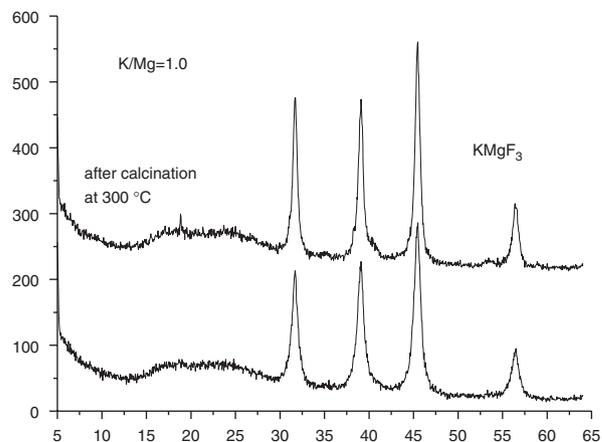


Fig. 5. XRD diffraction of sol–gel prepared KMgF_3 before and after calcinations.

methanolic $\text{Mg}(\text{OCH}_3)_2$ results in only partial substitution of the methoxy groups by fluoride, i.e., magnesium methoxide fluoride according to Eq. (1) is formed as an intermediate. The residual methoxy groups can then be removed either thermally or by subsequent hydrolysis adding a defined amount of water. This way followed by the steps of drying and calcinations magnesium oxide/hydroxide fluorides of varied composition were prepared, which showed surprisingly good catalytic properties [5].

The tendency of acidity/basicity changes with substitution of F by OH is demonstrated with the BE of the Mg 1s orbitals in Table 1.

Decreasing the fluorine content in the magnesium fluoride compounds shifts the BE of the Mg 1s orbital to lower values synonymously with a decrease in positive charge for Mg and the apparent Lewis acidity of the sample.

3.4. Complex magnesium fluorides

Complex magnesium fluorides of the general formula M^+MgF_3^- , isostructural with perovskite phases, have been synthesised by high-temperature melting process or as shown recently [15] by a hydrothermal reaction at 120 – 240°C . Under the soft sol–gel conditions KMgF_3 is obtained from a 1:1 molar mixture of magnesium methoxide and potassium methoxide in methanol solvent fluorinated with 3 equivalents of HF/MeOH. The KMgF_3

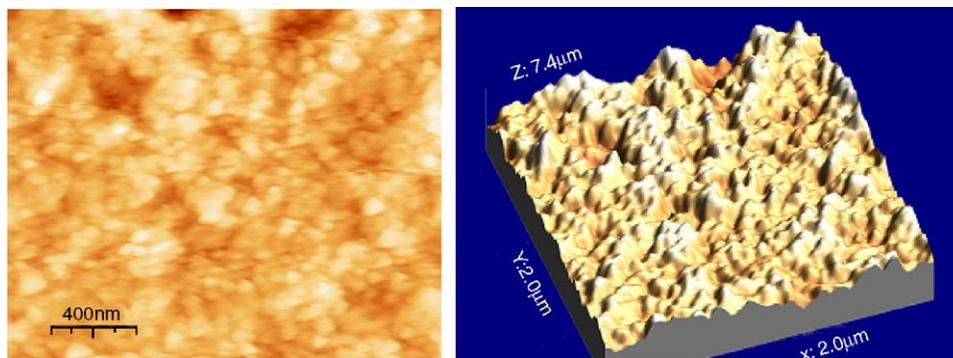
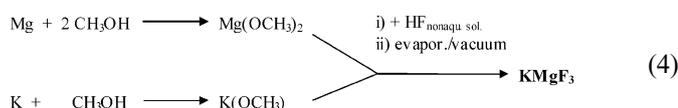


Fig. 6. AFM micrograph of a spin-coated MgF_2 layer on SiO_2 calcined at 300°C .

obtained this way



is in the crystalline state according to XRD analysis, calcinations at 300°C did not alter the diffraction pattern (Fig. 5). The BET surface area of the calcined material was $85 \text{ m}^2/\text{g}$. With a K/Mg ratio of 2, the expected K_2MgF_4 was not formed. Besides an unidentified amorphous solid broad XRD reflexes indicate low crystalline KMgF_3 . Further increase of the K/Mg ratio resulted in additional KHF_2 formation.

3.5. Magnesium fluoride as host or support for catalyst preparations

The high surface area of HS-MgF_2 and its easy preparation makes it a promising host for doping with higher valent metal ions such as, e.g., Cr^{3+} [4], Fe^{3+} [16], Ga^{3+} and others [6] to be used as catalysts as already reported by us. HS-MgF_2 can further be an interesting support for catalytically active materials such as, e.g., Pd or Pt, as preliminary successful hydrodechlorination experiments indicate.

3.6. Thin film magnesium fluoride

The reaction of magnesium methoxide in methanol with stoichiometric amounts of a non-aqueous solution of HF in, e.g., methanol results in a clear gel or a clear sol of low viscosity, depending on the magnesium concentration used. Thus, in terms of stoichiometry, a non-aqueous stable “solution” of MgF_2 is obtained, which should be ideal for depositing MgF_2 layers on solids by established techniques. To prove this Si as well as SiO_2 plates were tentatively coated with methanolic MgF_2 sol by dip- or spin-coating. This way after drying and subsequent calcination at 300 or 500°C a clear transparent layer was formed. Thickness and refraction index of these layers were determined by ellipsometry. The thickness of these tentative layers ranged

from 19 to 222 nm and correlated well with the MgF_2 concentration of the sol and of the number of coatings applied. The refractive index agreed very well with literature data over the experimental wavelength range from 300 to 1000 nm . AFM micrographs showed a homogeneous layer formed of submicron particles as shown in Fig. 6 for a layer prepared by threefold coating and calcination at 300°C . The MgF_2 layers adhere strongly to their support and are mechanically rigid. Altogether, the new non-aqueous MgF_2 sol/gel easily accessible by our new route opens a broad field of applications as coating in, preferably, optical applications [17].

4. Conclusions

The newly developed anhydrous sol–gel methodology can be applied for the preparation of magnesium fluoride yielding an amorphous high surface area magnesium fluoride (HS-MgF_2) with outstanding properties. Thus, although the arrangement of the next neighbours of magnesium is in HS-MgF_2 the same as in crystalline MgF_2 , i.e., six F atoms octahedrally arranged, the former exhibits markedly higher Lewis acidity, obviously because of its high distortion in combination with coordinatively unsaturated Mg surface sites like in HS-AlF_3 and ACF [13]. In addition to HS-MgF_2 synthesis, the sol–gel route opens multiple possibilities for the preparation of, e.g., doped MgF_2 or MgF_2 -supported systems and magnesium oxide fluorides as high surface area catalysts, MgF_2 thin layers, and complex magnesium fluorides.

Acknowledgments

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