NMP3-CT-2004-505575

FUNFLUOS

Functionalised Metal Fluorides

Specific Targeted Research Project – STRP

PRIORITY 3 - NMP

Final Report

Total Activity Report

Period covered: from 2004-09-01 to 2008-01-30

Date of preparation: 2008-03-15

Start of Project: 2004-09-01

Duration: 41 months

Project coordinator name: Prof. Dr. Erhard Kemnitz

Project coordinator organisation name: Humboldt-Universität zu Berlin

Revision 1

Publishable executive summary

The scientific activities of FUNFLUOS were focussed on the development of fluorinated materials with tailored characteristics for specific applications. Hence, the major activities were attributed to the following fields:

- Development of new, highly innovative routes for the synthesis of inorganic fluorinated materials with outstanding and controllable surface characteristics.
- Key physico-chemical and structural characterisation of new samples synthesised with the aim to understand the underlying processes that are responsible for the enhancement of their characteristics.
- Screening and testing of selected functionalised fluorinated materials in processes of application relevance that open new development and innovation perspectives.

I. Syntheses

New synthesis routes to binary as well as complex metal fluorides and oxide fluorides with interesting, potentially very useful surface and/or optical properties were in the main focus of the preparative work. Three different synthesis strategies towards nanoscopic metal fluorides have been followed in detail which are

i) non-aqueous sol-gel synthesis,
ii) oxidative decomposition of suitable precursors and
iii) functionalization of fluorinated materials with well defined chemical compositions and crystalline networks

The non-aqueous sol-gel synthesis route comprises basically the reaction of a metal alkoxide or another suitable metal organic compound in an organic solvent like alcohol with an ethereal or alcoholic solution of hydrogen fluoride. This reaction can also be applied to mixtures of different metal compounds. Another route, which is not general applicable, is the direct dissolution of the respective metal in an alcoholic hydrogen fluoride solution. This route is preferentially applicable for aluminium and magnesium.

Both routes result in the formation of a non-aqueous metal fluoride sol or gel, which upon drying yields an X-ray amorphous metal fluoride precursor which – depending on the respective metal – may still contain some remaining organics.

Since for the properties of the final metal fluoride the sol-gel state and the subsequently formed precursor are of obvious importance, the process of sol-gel formation including all parameters which might have effect on the process and the nature of the precursor have been comprehensively investigated. The majority of these investigations were focussed on magnesium fluoride and especially on aluminium fluoride synthesis because of the very unusual, extremely high Lewis acidity of the final high surface area aluminium fluoride (HS-AlF_3). The precursor state of this material was comprehensively characterised by FT-IR, MAS-NMR, thermal analysis, BET, NH_3-TPD, CO-adsorption FT-IR, and XRD. The primary process of sol-gel formation has also been subject of detailed investigations employing multinuclear liquid as well as MAS-NMR using ^{27}Al, ^{19}F, ^{13}C and ^{1}H as spin probes, backend by calculations. All these investigations showed the sol-gel fluorination being a very robust process not much influenced by parameter variations.

To get rid of the organic constituents of the precursor and thereby bring about the extremely high Lewis acidity of HS-AlF_3 an additional fluorination step of the solid precursor with a gaseous fluorinating agent is necessary. Promising and effective post fluorination agents are CCl_2F_2, $CHClF_2$ and HF. Also elemental fluorine could be used for the activation of a precursor, which was obtained after microwave treatment of the respective sol-gel, whereas plasma-fluorination failed to yield HS-AlF_3. For synthesis of HS-MgF_2, which exhibits much lower Lewis acidity than HS-AlF_3, HF is the post-fluorination agent of choice.

An alternative route towards highly distorted metal fluorides was investigated, which proceeds via **oxidative decomposition** and direct preparation of metal fluoride aerogels. In the first case, activities were focused on the preparation of aluminium and chromium fluorides. Some work was done also on iron and gallium fluorides. The general path consists of the reaction between hydrazinium fluorometalates and fluorine. Reaction between the fluoroaluminates and fluorine is strongly exothermic and difficult to control, especially under gas-solid (heterogeneous) conditions. By performing the reaction in liquid aHF medium a much better control over the decomposition was achieved. The AlF_3 products obtained in this way are X-ray amorphous with high surface areas (250-300 m^2g^{-1}). The procedure can be regarded as an inorganic alternative for the sol-gel route to HS-AlF_3. This HS-AlF_3 is strongly Lewis acidic; its catalytic activity is only slightly lower than that of sol-gel derived HS-AlF_3. For CrF_3, the oxidative decomposition of the starting compound $N_2H_6CrF_5 \cdot H_2O$ proceeds in several steps. Formation of volatile $Cr^{>3+}$ is the key factor to achieve HS-CrF_3 with 200-300 m^2g^{-1}. The level of impurities in HS-CrF_3 is much lower than in HS-AlF_3. Attempts to prepare HS-FeF_3 or HS-GaF_3 were much less successful indicating that the oxidative decomposition route to HS-MFs can not be generalised and must be treated on the case-by-case basis.

Developments of direct preparation of metal fluoride aerogels were less successful, mainly due to the technical limitations anticipated in the work programme. Equipment for high temperature supercritical drying can not be used for simultaneous fluorination due to severe corrosion problems.

Functionalization of fluorinated materials with well defined chemical compositions and crystalline networks in connection with their chemical properties such as reactivity, acidic, hydrophobic character, and optical absorption properties has been performed in order to find and develop new applications. Four key-points were identified:

- The development of new routes to prepare diversive inorganic fluorinated materials exhibiting specific or outstanding chemical and electronic properties.
- The correct control of the chemical composition using an adapted synthesis route, for obtaining fluorinated compounds with defined F/OH atomic ratios.
- The accurate determination of the type of crystalline network, local environments and surface features which can be related to the chemical and physical properties of defined compounds.
- The evaluation and analysis of the chemical properties, surface reactivity (nature and strength of acidic sites) and UV-visible absorption properties, as well as the reduction of the refractive index as a function of the chemical composition and structural features.

Three cations have been considered: Al^{3+}, Si^{4+} and Ti^{4+} in which relevant properties can be identified in fluorinated compounds. The presence of either OH^-, F^- or O^{2-} in the vicinity of these cations allows to tune the chemical bonding and therefore the properties. Hydrothermal routes have been developed to prepare well defined compositions. The crystalline networks have been analyzed, as well as the morphology, thermal stability and crystallinity of these materials. Local environments have been confirmed by ^{27}Al, ^{19}F MAS-NMR and FTIR investigations. Acidic properties have been measured for Al^{3+}-based compounds and UV shielding with low refractive index have been evaluated in the case of Ti^{4+}-based materials. In the case of fluorinated silicas which are amorphous, the F content has been determined as well as thermal stability, water affinity and Si-F/Si-OH chemical bonding have been investigated using ^{29}Si, ^{19}F, ^{1}H MAS-NMR and FTIR spectroscopy.

In aluminium-based fluorinated materials the occurrence of hydroxyl and fluorine groups into the vicinity of Al^{3+} cations is of great importance to create both Lewis and Brønsted acidic/basic character. In order to better understand the behaviour of these inorganic compositions, the chemical properties (acidity and reactivity) have been investigated, considering the respective compositions, the structural features and surface areas, as well as the character of the crystallized particles.

In the case of fluorinated mesoporous silica, the stabilization of fluorine in the vicinity of Si^{4+} cations leads to new functionalized silicas exhibiting modulated reactivity as well as controlled hydrophilic /hydrophobic balance. The direct F_2-gas fluorination of silica gel has been shown to be a unique method leading to very high levels of fluorination (up to 13 %wt F in the bulk). The final powders are homogeneous with a controlled amount of grafted fluorine. Elemental analyses and FTIR data yield the bulk composition $SiO_{2-x-y}(OH)_{2x}F_{2y}$. An F/OH substitution occurs during the fluorination process and the grafted F-amount depends on the F_2 concentration in the fluorinating gas and also on the concentration of surface hydroxyl groups and physisorbed water trapped on starting silica. For low fluorine contents the elimination of silanol groups follows the grafting of fluorine, whereas for higher fluorine contents, a reaction path takes place involving Si-O-Si opening. Redox processes involving O_2/OH^- and F_2/F^- couples allow to explain the high level of attained F/OH substitution rates without formation of SiF_4 or SiF_6^{2-} species, which are generally observed in classical routes using aqueous fluorinating agents. The materials are stable up to T=250°C for high F contents and up to T=400°C for the lower ones.

II. Physico-chemical characterization and modelling

Because of the very high Lewis acidity of HS-AlF_3, which proved to be the second strongest solid Lewis acid at all, topped only by aluminium chlorofluoride (ACF), all physical and chemical characterisation methods available to the FUNFLUOS consortium have been applied. As catalyst for reactions depending on Lewis acidic catalysts HS-AlF_3 proved superior not only to □-AlF_3 and $AlCl_3$ but even to SbF_5. Analysing the IR absorption spectra of adsorbed CO as measure for the surface acidity of the X-ray amorphous HS-AlF_3 a strong blue-shift of the IR frequency was detected which had never been observed before. The extremely high Lewis acidity limits the use of HS-AlF_3 as catalyst as the strongest acid sites might become blocked by adsorbed molecules from the reaction mixture. Radiotracer investigations confirmed the extraordinary properties of HS-AlF_3. Thus, the dehydrochlorination of *tert*-butyl chloride proceeds at room temperature and HCl behaves towards HS-AlF_3 as a base which becomes strongly adsorbed. Exciting results originate from

XPS, XANES, and EXAFS measurements, which provide beneficial information on the near range arrangement of the AlF_x-polyhedra in these X-ray amorphous phases.

The experimental characterisation of sol-gel derived HS-AlF_3 phases showed that residual alkoxide and water content have a strong influence on molecular-level bulk and surface properties. The complex surface composition changes due to the influence of the various oxygen-containing functional groups (alkoxide, water, OH-groups) and the presence of undercoordinated (dangling) fluoride species at the surface could be resolved by XPS and XAS by comparison with predictions of the systematic computational studies. The previous 'static' view of the stoichiometric AlF_3 phases as having sterically hindered Al^{3+} Lewis acid centres has been challenged and superseded.

XAS revealed for catalytically active materials that the local coordination and electronic structure of Al centres appears to be similar to those found in hydroxofluoride and oxofluoride phases. The mentioned dangling surface groups appear to be the prerequisite for the emergence of catalytic activity, because they are associated with mobile, 'dynamic' electron density at the surface.

In course of the theoretical investigations, candidate Lewis active sites have been identified on the surface of aluminium fluoride providing the first atomic scale model of the working catalyst. Thus, thermodynamics calculations based on hybrid-exchange density functional theory were employed to predict the composition and structure of the basal plane surface of α-AlF_3 for the first time. The structure of a range of possible terminations (Al, 3F, 2F and F surfaces) has been computed and the relative stability of these surfaces has been evaluated as a function of external F chemical potential.

Calculations of the phase stability of the β–AlF_3(100) surface led to the identification of two possible low energy surfaces denoted T1 and T6. Each surface provides a different Lewis acid site. The T1 surface has a higher surface energy than the T6 surface so it may only occur on high surface area AlF_3. This observation provides a possible explanation for the high reactivity displayed by high surface area AlF_3.

In addition, the same procedure has been used to investigate the surface structure of the layered $AlCl_3$ system.

The work on clean surfaces has been extended to include hydroxylated surfaces. This work has led to the prediction of a surface phase diagram for the F/OH α-AlF_3 (0001) surface.

Work on the adsorption of small molecules onto the catalytically active β–AlF_3(100) surface including characterisation of the strength of the Lewis acid sites via determination of the binding energy of NH_3 molecules and an investigation of poisoning of active sites via HF adsorption has been modelled too.

III. Applications

To improve the industrial applicability of HS-AlF_3 it was supported on Al_2O_3. The catalytic activity of the supported HS-AlF_3 was found to be effective for $CHClF_2$ dismutation as well as for $CBrF_2CBrFCF_3$ isomerization, whereby HS-AlF_3/γ-Al_2O_3 exhibited superior activity, which was about 10–30 times higher than that of HS-AlF_3/α-Al_2O_3, in terms of isomerization activity.

Binary and guest/host metal fluorides have been tested for several catalytic reactions and showed in several cases very promising activities. Among these reactions just one will be highlighted here: the hydrodefluorination of CF_3CHCF_3 since this involves an activation of a CF_3-group, a very complicated process but which is possible in case of HS-AlF_3 because of its very high Lewis acidity.

Modifying the sol-gel method, highly dispersed noble metals or other catalytically interesting metal species have been successfully incorporated as guests into the lattices of different *High Surface* metal fluorides, and the developed new synthetic approach was used for the preparations of heterogeneous VO_x-, Pd- and Pt- catalysts. With catalyst systems consisting of VO_x-species supported on *HS*-AlF_3 very promising results have been obtained for the oxidative dehydrogenation of propane as well as for the conversion of methanol into formaldehyde.

Additionally, we developed and investigated catalyst systems for some important industrial processes using the noble metal catalysts (Pd, Pt) supported on *HS*-(AlF_3, MgF_2, ZrF_4 or K_3AlF_6). Further experiments were successfully conducted for the dehydrohalogenation of fluoroalkanes to the respective fluoroethylens as well as for the Suzuki coupling reaction.

A catalytically very interesting modification of high surface metal fluorides can be obtained by introducing defined small amounts of water into the synthesis process. This way Brønsted acidity, or after calcination Brønsted basicity can be introduced in addition to the basic Lewis acidity. This way magnesium fluoride based catalysts with exciting properties for Michael addition reactions and others for vitamin E synthesis, which are superior to all nowadays used catalysts were obtained.

$HS\text{-}AlF_3$ used as adsorbent agent proved to be suitable for purifying PFCL. Isomerisation of 1,2-dibromohexafluoropropane to 2,2-dibromohexafluoropropane was performed to produce samples for medical related application tests. Mixtures with silicone oil have the potential for the use as endotamponade in eye surgery from a physico-chemical point of view, but the compound shows cytotoxic reaction also in the purified form. The cytotoxicity can be masked by silicon oil shielding but the risk for human use still remains. On the other hand, synthesis of R_FR_H compounds, typically a radicalic reaction, as well as the reaction of diamines with fluoroalcylated propenoxides did not proceed under the catalytic action of $HS\text{-}AlF_3$. An alternative application of solid Lewis acids as absorbents for medical gases could be demonstrated.

For the liquid anhydrous sol state of metal fluorides obtainable by sol-gel fluorination a very promising new field of potential use, besides synthesis of high surface area fluorides, could be successfully tested namely thin film coating of varied solid surfaces. The functionalisation of solid surfaces by coating with fluorides can be used for surface protection as well as an alternative to silicone lubrication.

As far as optical absorption properties are concerned, the evolution of optical band gap as well as refractive indices are of crucial importance for applications in UV-Vis range. UV absorbers for solar protection represent the main field of applications for these inorganic compositions containing Ti^{4+} cations for instance. Finally, the presence of fluorine in these materials allows to tune parameters such as the optical band gap and to limit the refractive index in order to get higher transparency in visible range. This drastic decrease of refractive index in these fluorinated series compared to TiO_2 with rutile or anatase networks leads us to consider these materials to improve the transparency of such UV absorbers in the visible range. Moreover, considering the diffuse reflectance spectra, the band gaps appear around 3.2 eV with a promising UV shielding.